Total Synthesis of Three Eudesman-12,8-olides, (±)-Isoalantolactone, (±)-Dihydrocallitrisin and (±)-Septuplinolide; Structure Revision of Septuplinolide

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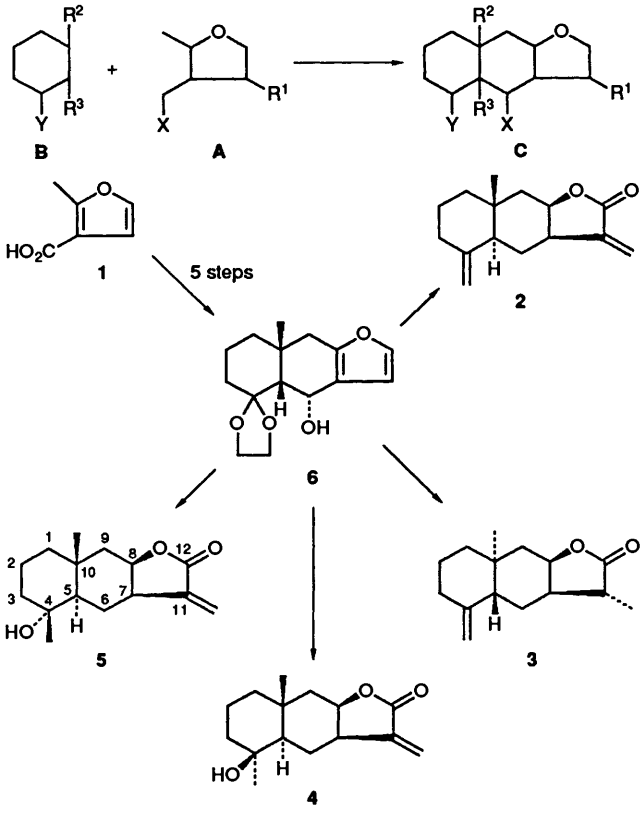
Four eudesman-12,8-olides, (±)-isoalantolactone, (±)-dihydrocallitrisin, (±)-septuplinolide and its epimeric eudesmanolide at C-4 were synthesized stereoselectively *via* the route involving alkylation annulation of 2-methyl-3-furoic acid and oxidation of the furan ring. It was found that the structure of septuplinolide is the C-4 epimer of the reported structure.

Recently, manifoldly oxygenated eudesmanolides have been isolated from different plant sources, and have been shown a wide range of biological activity, such as allergenic agent, plant-growth inhibitor, antibacterial agent and antitumour agent activity.[1-7] Previously, we reported syntheses of several furanoeremophilanes which are natural perhydronaphthofurans, *via* the coupling of two fragments **A** and **B** by alkylation of 2,4-dimethyl-3-furoic acid.[8] Eudesmanolides are also popular natural perhydronaphthofuran derivatives whose common carbon skeleton has methyl groups at different positions from those in the furanoeremophilanes. We intended to synthesize various eudesmanolides by a similar synthetic route which includes alkylation–annulation of 2-methyl-3-furoic acid **1**[9] and oxidation of a furan ring to a γ-lactone ring.[10] The relative stereochemistry of the γ-lactone ring with the 10-Me group of isoalantolactone **2**[11] is opposite to that of dihydrocallitrisin **3**.[12,13] Septuplinolide was isolated by Ober and Fischer in 1987 and the structure was proposed to be a eudesmanolide with structure **4**.[14] In our survey of eudesmanolides, the oxygen function of C-4 of eudesmanolides is bonded on the 4α side,[2-7,15-19] except for a few compounds.[20,21] The spectral data of the synthesized compound **4**, which has the proposed structure for septuplinolide, were apparently different from the reported data of septuplinolide.[22] The difference in the ^{1}H NMR spectra between the two compounds suggested that the correct structure of septuplinolide is the C-4 epimer **5** of the reported structure **4** for septuplinolide. We report here the stereoselective syntheses of four eudesman-12,8-olides, (±)-isoalantolactone **2**,[11] (±)-dihydrocallitrisin **3**,[12,13] (±)-septuplinolide[14] **5** and the C-4 epimeric (±)-eudesmanolide **4** of **5**, and the spectroscopic structural elucidation of septuplinolide (Scheme 1).



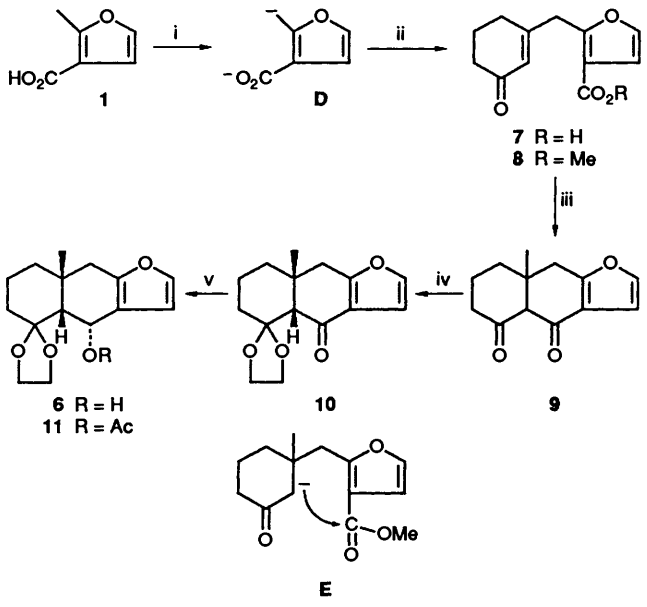
Scheme 1 Synthetic route to eudesmanolides

Results and Discussion

The concept of our synthetic plan was to construct the skeleton of eudesmanolides by coupling two fragments **A** and **B** to construct system **C**. The γ-lactone ring should be prepared by the oxidation of the furan ring. Variously oxygenated eudesmanolides may be produced by this synthetic plan.

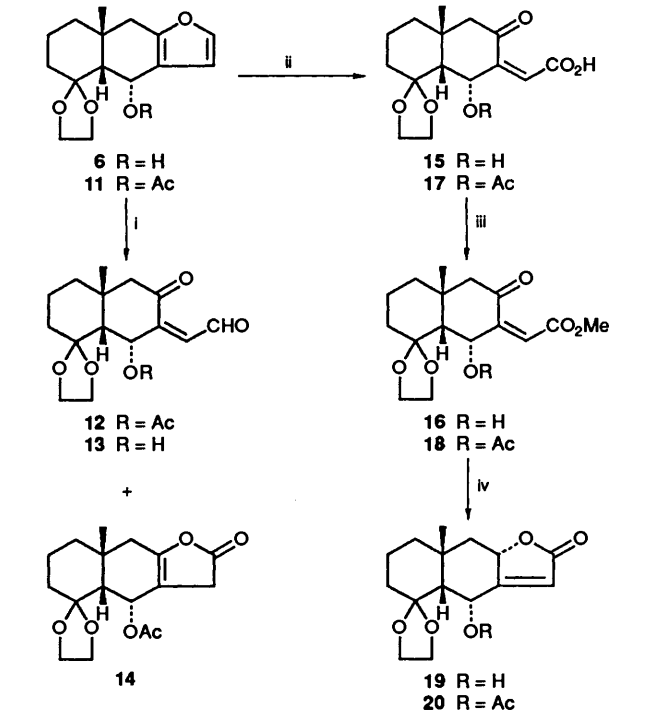
A dianion **D** which corresponds to the synthon **A** in our synthetic investigation was generated from 2-methyl-3-furoic acid **1** with lithium diisopropylamide (LDA) (Scheme 2). The dianion **D** was trapped with 3-methoxycyclohex-2-enone, which corresponds to synthon **B**, to afford a keto acid **7**. The keto acid **7** was methylated with diazomethane to give ester **8** (yield 74% from **1**). The ester **8** was converted into tricyclic dione **9** directly by treatment with $LiMe_2Cu$ at 0 °C for 44 h (yield 93%). An intermediate anion **E** could easily be cyclized by intramolecular acylation with the methyl ester. A carbonyl group at C-4 (eudesmane numbering) of compound **9** was protected as its ethylene ketal to give an A/B *cis*-ketone **10** whose stereochemistry was deduced from a nuclear Overhauser enhancement (NOE) between 10-Me and 5-H (88%). The *cis*-ketone **10** was reduced with $NaBH_4$ in diglyme–water–NaOH at 105 °C stereoselectively to obtain an important intermediate alcohol **6** (95.5%) in our synthetic investigation.

(±)-*Isoalantolactone* **2**.—Acetylation of the alcohol **6** in Ac_2O–pyridine at ambient temperature gave the acetate **11** (99.8%). The stereochemistry of compounds **6** and **11** was assigned by their ^{1}H NMR spectra. The ^{1}H NMR spectrum of the acetate **11** showed the C-6 proton as a broad doublet at δ 5.97 (*J* 6.0 Hz). The chemical shift of the C-10 methyl group of acetate **11** appears at δ 1.15 (s) which is near to that of the alcohol **6** at δ 1.07 (s). These indicate that the only possible stereochemistry of the alcohol **6** and the acetate **11** should be that shown in the formulae.



Scheme 2 *Reagents and conditions:* i, LDA; ii, 3-methoxycyclohex-2-enone; then CH_2N_2; iii, $LiMe_2Cu$ in Et_2O; iv, PTSA, $HOCH_2CH_2OH$, reflux in PhH; v, $NaBH_4$–NaOH in aq. diglyme; then Ac_2O–pyridine

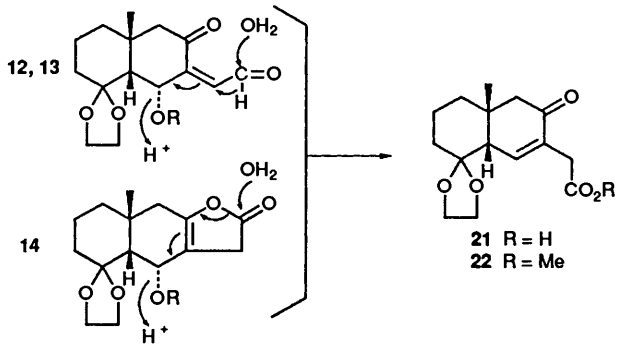
Oxidative conversion of the furan ring into a γ-lactone ring was then examined by using *m*-chloroperbenzoic acid (MCPBA).[23] The acetate **11** was oxidized by 1.2 mole equivalents of MCPBA in CH_2Cl_2 to give a mixture of unstable compounds, a keto aldehyde **12** and a lactone **14** (**12**:**14** 95:5, 92%), whereas the alcohol **6** afforded only the keto aldehyde **13** by similar treatment (1.06 mole equiv. of MCPBA) (90%). The ratio of products **12** and **14** was changeable depending upon the reaction time. This should mean that complicated mixtures of oxidation products would be formed upon oxidation of furan derivatives. Oxidation of the alcohol **6** and the acetate **11** with ~2 mole equivalents of MCPBA proceeded selectively to give acids **15** (94%) and **17** (87%), respectively. The stereochemistry



Scheme 3 *Reagents:* i, MCPBA (1.2 mol equiv.); ii, MCPBA (2 mol equiv.); iii, CH_2N_2 in Et_2O; iv, $NaBH_4$ in MeOH

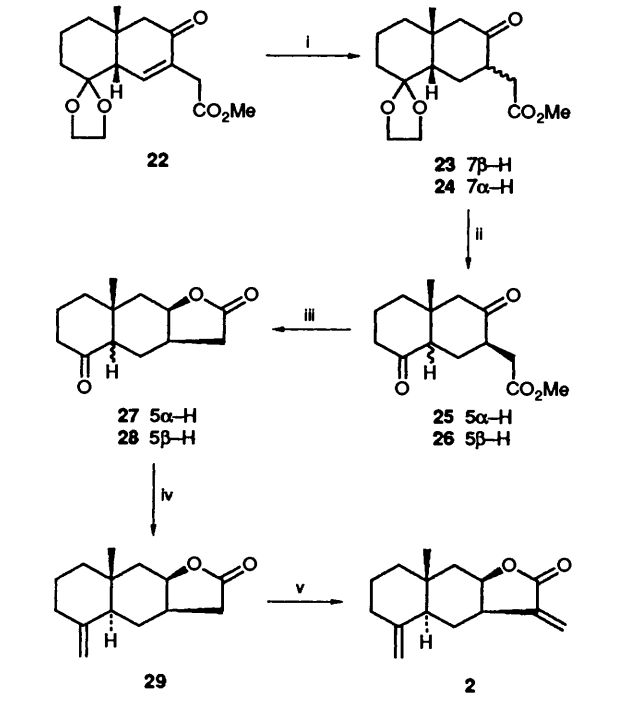
of the double bond in acids **15** and **17** was deduced from the conversion of acids **15** and **17** into lactones **19** (62%) and **20** (78%) by a two-step reaction (CH_2N_2 in Et_2O; $NaBH_4$ in MeOH), respectively (Scheme 3).

Treatment of the mixture **12** + **14** with toluene-*p*-sulfonic acid (PTSA) in tetrahydrofuran (THF) at ambient temperature for 44 h, followed by esterification with diazomethane, afforded the ester **22** (55% from **6**). The mechanism of transformation of keto aldehyde and β,γ-unsaturated lactone into the acid **21** could be as shown in Scheme 4. The ester **22** was converted into two eudesmanolides, **2** and **3**, stereoselectively.



Scheme 4 Reaction mechanism to give unsaturated acid **21**

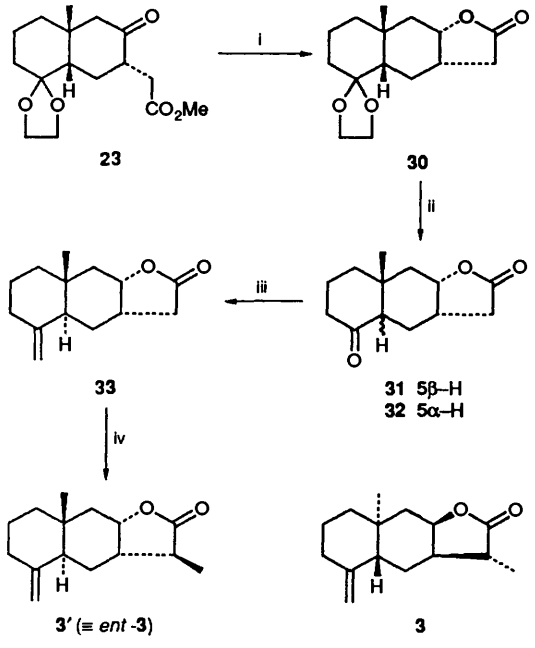
Catalytic hydrogenation of the ester **22** with 5% Pd/C in AcOEt yielded esters **23** (7β-H) and **24** (7α-H) (8:1) (99%) (Scheme 5). The stereochemistry of the major ester **23** was assumed from the coupling constants ($J_{5,6}$ 12.8 and 4.4; $J_{6,7}$ 5.8 Hz) in the ^1H NMR spectrum. The mixture of the esters **23** + **24** was successively submitted to deketalization with acetone–PTSA, equilibration in MeOH–KOH, and methylation with diazomethane to give diketo esters **25** and **26** (3:1, 85% from a mixture of ketals **23** and **24**). Both of these diketo esters, **25** and **26**, have a 7β-side chain, which was confirmed by conversion of



Scheme 5 *Reagents:* i, H_2, 5% Pd/C in EtOAc; ii, PTSA in acetone; then KOH in aq. MeOH; then CH_2N_2 in Et_2O; iii, $NaBH_4$ in MeOH; then PDC in CH_2Cl_2; iv, $Ph_3P{=}CH_2$ in THF–HMPA; v, NaH–EtO_2CH; then $NaBH_4$ in MeOH; then *p*-TsCl in pyridine

both esters **25** and **26** into isoalantolactone **2**. The mixture of **25** + **26** was reduced by $NaBH_4$ in MeOH, without separation. The product was oxidized with pyridinium dichromate (PDC) to give keto lactones **27** and **28** (3:1, quantitative from the mixture of esters **25** and **26**). After separation by HPLC, the A/B *cis* keto lactone **28** was equilibrated in 1% KOH–MeOH to give a similar mixture of epimers **27** and **28**. Wittig reaction of the A/B *trans*-compound **27** [$Ph_3P{=}CH_2$ in THF–hexamethylphosphoric triamide (HMPA)] produced the lactone **29** (93.6%), which was elaborated to isoalantolactone **2** according to the procedure described in the literature.[24] The synthesized compound **2** was identical (IR and ^1H NMR spectra) with natural isoalantolactone.[25]

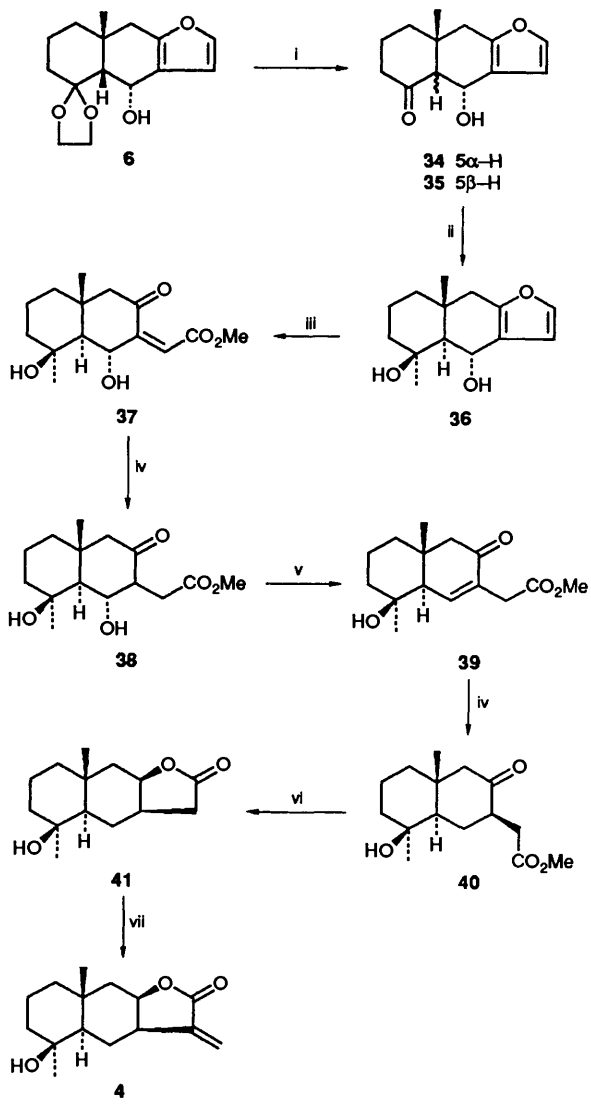
(±)-*Dihydrocallitrisin* **3**.—The stereochemistry of the decalin ring system of dihydrocallitrisin is opposite to that of isoalantolactone **2**. The keto ester **23**, which has a 7β-H, was elaborated to dihydrocallitrisin as follows. Reduction of the ester **23** with $NaBH_4$ in MeOH gave lactone **30** quantitatively (Scheme 6). Treatment of compound **30** in acetone–PTSA gave



Scheme 6 *Reagents:* i, $NaBH_4$ in MeOH; ii, PTSA in acetone; then KOH in aq. MeOH; iii, $Ph_3P{=}CH_2$ in THF–HMPA; iv, LDA in THF; then MeI

an A/B *cis*-compound **31**, which was equilibrated in MeOH–KOH to afford a mixture of A/B *trans* and *cis* compounds **31** and **32** (1:10, 89% from **30**). The A/B *trans* compound **32**, which was crystallized selectively from a solution of epimers **31** and **32** in Et_2O–hexane, was methylenated by Wittig reaction with $Ph_3P{=}CH_2$ in THF–HMPA to produce compound **33** (95.4%). Stereoselective methylation of compound **33** with LDA–methyl iodide gave dihydrocallitrisin 3′ (≡*ent*-**3**) which was identical (IR and ^1H NMR spectra) with the natural product **3**. The structure of synthesized dihydrocallitrisin 3′ is written in the mirror image of natural dihydrocallitrisin **3** for consistency with the stereochemistry of its precursors **23** and **30**–**33**.

(±)-*Septuplinolide and its* 4-*Epimer* **4**.—A eudesmanolide **4** which has the proposed structure for septuplinolide was synthesized first from the alcohol **6** as follows. The ketal group at C-4 of the alcohol **6** ($J_{5,6}$ 5.8 Hz) was deprotected by acetal-exchange in acetone containing PTSA monohydrate to form an A/B *cis*-keto alcohol **34**, which was epimerized solely to the A/B *trans*-isomer **35** with KOH–MeOH (yield 70.5% from the

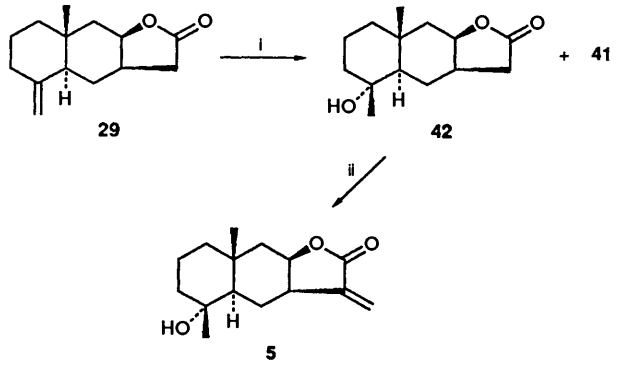


Scheme 7 *Reagents and conditions:* i, PTSA in acetone; then KOH in aq. MeOH; ii, MeLi in Et_2O; iii MCPBA (2 mol equiv.); then CH_2N_2 in Et_2O; iv, H_2, 5% Pd/C in EtOAc; v, PTSA, reflux in PhH; vi, $NaBH_4$ in MeOH; vii, NaH, EtO_2CH–Et_2O; then $NaBH_4$ in MeOH; then *p*-TsCl in pyridine

alcohol **6** (Scheme 7). The stereochemistry at C-5, -6 and -10 (eudesmane numbering) of compound **35** was deduced from NOE peaks between 10-Me and 6-H in the NOESY spectrum and from the coupling constant $J_{5,6}$ 8.5 Hz). Stereoselective methylation of ketone **35** with 5.4 mole equivalents of methyllithium in diethyl ether gave a diol **36** whose stereochemistry was confirmed by the observation of NOEs between 10-Me and 6-H and between 4-Me and 5-H in the NOESY spectrum and by the coupling constant $J_{5,6}$ 8.5 Hz (81%). Oxidation of the furan ring[10,23] of diol **36** with 2 mole equivalents of MCPBA in CH_2Cl_2 afforded a carboxylic acid (quantitative yield), which was converted into its methyl ester **37** with CH_2N_2. Hydrogenation of the unsaturated ester **37** with H_2 and 5% Pd/C produced an ester **38** [δ 4.07 (t, J 10.0 Hz, 6-H)] (95.5%) selectively. Selective dehydration of the 6-OH group (eudesmane numbering) which is located β to the C-8 carbonyl group was accomplished by reflux in benzene-PTSA for 3 h to give an enone **39** [ν_{max} 1670 cm^{-1}; δ_C 146.7 and 134.4; δ_H 7.00 (1 H, br s)], which was not successfully obtained by treatment of the ester **38** under basic conditions (MeONa–MeOH under Ar at room temperature for 2 h). The observation of NOEs between 4-Me and 5-H and between 4-Me and 6-H of

enone **39** showed its stereochemistry clearly. The double bond of enone **39** was reduced selectively with H_2 and 5% Pd/C to give the keto ester **40** in quantitative yield. Reduction of γ-keto ester **40** with $NaBH_4$ in MeOH formed lactone **41** directly (92%). The stereochemistry of compound **41** was deduced from the observation of NOEs between 5-H and 7-H and between 7-H and 8-H. Finally, an α-methylene group was introduced onto the γ-lactone ring of compound **41** by similar consecutive reactions to those used in the synthesis of isoalantolactone **2** (i, NaH–HCO_2Et; ii, $NaBH_4$ in MeOH; iii, *p*-TsCl–pyridine) to give the desired compound **4** (24%).[24] The spectral data of compound **4** were entirely different from the reported data of septuplinolide.[14] The structure of synthesized compound **4** is quite definite from the NMR experiment on the intermediates as described above. The difference in chemical shifts of 10-Me (δ 1.13; lit., 0.94) and 5-H (δ 1.08; lit., 1.45–1.56) in the ^1H NMR spectrum suggest that the stereochemistry of septuplinolide at C-4 is the reverse of that originally proposed.

The lactone **29**, which was synthesized in our total synthesis of isoalantolactone **2**, seemed to be a useful intermediate for the stereoselective synthesis of authentic septuplinolide **5**. Oxymercuriation of ene lactone **29** was examined with mercury(II) acetate in THF–water (1:1), followed by reduction with sodium borohydride to give hydroxy lactones **41** and **42** in the ratio of 7:1 (67%). (Scheme 8). The minor product **41** was identical with



Scheme 8 *Reagents:* i, aq. $Hg(OAc)_2$; then $NaBH_4$–NaOH; then HCl; ii, NaH, EtO_2CH–Et_2O; then $NaBH_4$ in MeOH; then *p*-TsCl in pyridine

the previously synthesized compound. The structural proof of the major hydroxy lactone **42**, which has a C-4 α-hydroxy group, was obtained from COSY spectroscopy, a differential NOE experiment, and coupling constants in the ^1H NMR spectrum. The NOEs between 10-Me and 4-Me, between 10-Me and 6β-H, and between 7-H and 8-H confirmed the stereochemistry of compound **42** as that shown in Scheme 8. This showed that the hydroxylation of the double bond at C(4)–C(14) of the lactone **29** occurred from the less hindered side in the three-step reaction (mercuriation, substitution with water and reduction with $NaBH_4$). The *exo*-methylene group at C-11 on the lactone ring was introduced by the above mentioned consecutive reactions as in the case of 4-*epi*-septuplinolide **4** to produce the desired lactone **5** in 42% yield. The structure of compound **5** was confirmed by the NOEs between 10-Me and 4-Me and between 7-H and 8-H. The ^1H and ^{13}C NMR spectra of synthesized product **5** were completely in agreement with those of natural septuplinolide.* These results indicate that the structure of septuplinolide should be revised to **5**.

* We found an error in the reported ^{13}C NMR spectral data upon a detailed 2D-NMR investigation and comparison of the spectrum with that of natural septuplinolide.

Experimental

NMR spectra were measured on a JEOL GX-270 spectrometer at 270 (^1H) and 67.89 MHz (^{13}C) for samples in $CDCl_3$ or CD_3OD (mentioned) containing tetramethylsilane as internal standard. *J*-Values in Hz. IR and UV spectra were measured on a JASCO IR-810 infrared spectrometer and a JASCO UVDEC-460 spectrophotometer, respectively. Mass spectra were recorded on a JEOL JMS-DX-300 spectrometer. M.p.s were measured on a MEL-TEMP (Laboratory Device) and are uncorrected; TLC was carried out on Kiesel-gel GF_{254} (0.25 mm thickness). Wakogel C-200 was used for column chromatography. HPLC was performed on a Jasco BIP-1 instrument (RI detector) with a column (10 × 250 mm) of LiChroprep Si 60 (Merck) (hexane–EtOAc).

Methyl 2-(3-*oxocyclohex*-1-*enylmethyl*)*furan*-3-*carboxylate* **8**.—Butyllithium solution (1.63 mol dm^{-3}) in hexane (67.5 cm^3) was added to a solution of diisopropylamine (15.5 cm^3) in dry THF (150 cm^3) cooled in an ice-bath. After being stirred at ambient temperature for 20 min, the solution was cooled to −78 °C and then treated with a solution of 2-methyl-3-furoic acid **1** (6.3 g) in THF (30 cm^3) for 30 min. The solution turned orange in colour due to the formation of the dianion **D**. A solution of 3-methoxycyclohex-2-one (6.3 g) in THF (30 cm^3) was added to the solution of the dianion **D** at 0 °C. After being stirred for 1 h at ambient temperature, the reaction mixture was treated with water, acidified with hydrochloric acid, and extracted with diethyl ether. The ethereal solution was washed with brine, dried ($MgSO_4$), and evaporated. The residue was chromatographed on a silica gel column to give crude acid **7** as an oil.

The acid **7** was dissolved in methanol and methylated with diazomethane in diethyl ether, and the product was purified by column chromatography on silica gel to afford the title methyl ester **8** (8.7 g, 74% from **1**) as a yellow liquid (Found: M^+, 234.092. $C_{13}H_{14}O_4$ requires *M*, 234.089); ν_{max}(neat)/cm^{-1} 3128, 2954, 1719, 1670, 1602, 1516, 1439 and 1311; δ_H 7.33 (1 H, d, *J* 1.8), 6.69 (1 H, d, *J* 1.8), 5.78 (1 H, s), 3.94 (2 H, s), 3.83 (3 H, s), 2.35 (4 H, m) and 2.01 (2 H, m); δ_C 199.2, 163.6, 160.6, 156.9, 141.5, 126.7, 114.8, 110.5, 51.2, 36.9, 35.2, 29.1 and 22.2; *m*/*z* 234 (M^+, 100%), 174 (11), 160 (16), 147 (43), 133 (30), 95 (65) and 53 (36).

7,8,8a,9-*Tetrahydro*-8a-*methylnaphtho*[2,3-b]*furan*-4,5(4aH,6H)-*dione* **9**.—A 1 mol dm^{-3} solution of methyllithium in diethyl ether (630 cm^3) was added to a mixture of CuI (60 g) and dry diethyl ether (100 cm^3) at 0 °C under Ar. To this mixture was added a solution of the keto ester **8** (33 g) in diethyl ether (300 cm^3) and the mixture was stirred at 0 °C for 44 h. The reaction was stopped by addition of wet diethyl ether and the mixture was acidified by conc. HCl. The precipitates were filtered off and the ethereal solution was washed successively with 10% aq. Na_2SO_4 and brine, and dried over anhydrous $MgSO_4$. After removal of the solvent, the residue was subjected to column chromatography (SiO_2; hexane–ethyl acetete 10:1) to give dione **9** (23 g, 93%), m.p. 84.5–85.5 °C (Found: M^+, 218.095. $C_{13}H_{14}O_3$ requires *M*, 218.094); ν_{max}(KBr)/cm^{-1} 3146, 2950, 2700, 1610 and 1570; δ_H 15.09 (1 H, s), 7.34 (1 H, d, *J* 1.8), 6.70 (1 H, d, *J* 1.8), 2.76 (2 H, s), 2.2–2.6 (2 H, m), 1.6–2.0 (4 H, m) and 1.19 (3 H, s); δ_C 187.0, 175.7, 163.8, 142.8, 119.0, 110.6, 106.7, 38.2, 37.6, 35.4, 29.4, 27.7 and 17.2; λ_{max}(EtOH)/nm 218 (ε 15 000 dm^3 mol^{-1} cm^{-1}), 272 (6250) and 325 (11 500); *m*/*z* 218 (M^+, 20%), 203 (100), 175 (20), 147 (24), 86 (20) and 53 (21).

(4aβ,8aβ)-5-*Ethylenedioxy*-5,6,7,8,8a,9-*hexahydro*-8a-*methylnaphtho*[2,3-b]*furan*-4-(4aH)-*one* **10**.—A mixture of the dione **9** (6.5 g), benzene (150 cm^3), ethylene glycol (20 cm^3) and PTSA (700 mg) was refluxed for 17 h with a Dean–Stark water-trap (3

Å molecular sieves) under Ar. To the reaction mixture were added 5% aq. NaOh and diethyl ether. The organic layer was washed with brine, dried over anhydrous $MgSO_4$, and evaporated. Crystallization of the residue from diethyl ether–hexane gave the title ketal **10** (6.9 g, 88%), m.p. 145.5–146.0 °C (Found: M^+, 262.115. $C_{15}H_{18}O_4$ requires *M*, 262.121); ν_{max}(KBr)/cm^{-1} 3140, 3118, 2922, 1666, 1599 and 1513; δ_H 7.24 (1 H, d, *J* 2.0), 6.58 (1 H, d, *J* 2.0), 3.65–3.75 (3 H, m), 3.26–3.39 (2 H, m), 2.32 (1 H, s), 2.19 (1 H, d, *J* 17), 1.30–1.85 (6 H, m) and 0.97 (3 H, s); δ_C 193.5, 167.5, 142.4, 120.2, 109.8, 106.2, 65.6, 64.3, 62.5, 38.9, 38.0, 35.8, 32.1, 29.9 and 19.3; λ_{max}(EtOH)/nm 204 (ε 60 500) and 268 (25 700); *m*/*z* 262 (M^+, 24%), 99 (25) and 86 (100).

4aβ,8aβ)-5-*Ethylenedioxy*-4,4a,5,6,7,8,8a,9-*octahydro*-8a-*methylnaphtho*[2,3-b]*furan*-4α-*ol* **6**.—A mixture of the ketone **10** (9.0 g) diglyme (160 cm^3), NaOH (3 g), water (40 cm^3) and sodium borohydride (3.0 g) was heated at 105 °C. Further sodium borohydride (4.0 g) was added by portions to the mixture. After being heated for 13 h, the mixture was cooled, and extracted with diethyl ether. The extract was washed by brine, dried over anhydrous $MgSO_4$, and evaporated. The residue was crystallized from hexane to give the title alcohol **6** (8.5 g, 95.5%), m.p. 116 °C (Found: M^+, 264.144. $C_{15}H_{20}O_4$ requires *M*, 264.136); ν_{max}(KBr)/cm^{-1} 3442, 3108, 1634 and 1501; δ_H 7.22 (1 H, d, *J* 1.8), 6.44 (1 H, d, *J* 1.8), 5.04 (1 H, m), 4.87 (1 H, m), 3.92 (1 H, m), 3.77 (2 H, m), 3.60 (1 H, m), 2.99 (1 H, d, *J* 16.0), 2.13 (1 H, d *J* 6.0), 1.98 (1 H, d *J* 16.0), 1.35–1.83 (6 H, m) and 1.07 (3 H, s); δ_C 149.4, 140.1, 117.8, 112.2, 108.1, 66.3, 64.7, 62.5, 49.1, 38.8, 37.6, 36.3, 31.3, 29.4 and 19.0; *m*/*z* 264 (M^+, 12%), 262 (14), 133 (31), 114 (13), 99 (27), 86 (100) and 53 (15).

(4aβ,8aβ)-4α-*Acetoxy*-5-*ethylenedioxy*-4,4a,5,6,7,8,8a,9-*octahydro*-8a-*methylnaphtho*[2,3-b]*furan* **11**.—A solution of the alcohol **6** (1.46 g) in a mixture of pyridine (15 cm^3) and acetic anhydride (15 cm^3) was stirred for 12 h at 30–40 °C. The solution was cooled to 0 °C and extracted with diethyl ether and water. The ethereal layer was washed successively with 2 mol dm^{-3} HCl and brine, dried over $MgSO_4$, and evaporated to give the title acetate **11** (1.69 g, 99.8%) as a yellow liquid (Found: M^+, 306.148. $C_{17}H_{22}O_5$ requires *M*, 306.147); ν_{max}(neat)/cm^{-1} 3120, 1740, 1650 and 1505; δ_H 7.26 (1 H, d, *J* 1.8), 6.30 (1 H, d, *J* 1.8). 5.97 (1 H, br d, *J* 6.0), 3.4–3.8 (4 H, m), 3.02 (1 H, d, *J* 16.0), 2.41 (1 H, d, *J* 6.0), 2.09 (3 H, s), 2.06 (1 H, m), 1.41–1.78 (6 H, m) and 1.15 (3 H, s); δ_C 171.0, 151.8, 140.8, 114.3, 110.8, 108.4, 68.5, 65.2, 63.6, 47.6, 38.5, 37.9, 37.0, 32.4, 29.6, 21.4 and 19.4; *m*/*z* 306 (M^+, 36%), 263 (41), 246 (55), 231 (39), 219 (29), 201 (71), 185 (20), 133 (25), 114 (29), 99 (22), 86 (100), 71 (40), 60 (30) and 54 (40).

Oxidation of the Alcohol **6**.—(*a*) A solution of the alcohol **6** (500 mg) and 70% MCPBA (500 mg, 1.06 mol equiv.) in CH_2Cl_2 (150 cm^3) was refluxed under Ar for 7 h. The solution was cooled, and washed successively with 10% aq. Na_2CO_3 and brine, dried over anhydrous $MgSO_4$, and evaporated to give the keto aldehyde **13** (477 mg, 90%), m.p. 127–130 °C (Found: M^+, 280.129. $C_{15}H_{20}O_5$ requires *M*, 280.131); ν_{max}($CDCl_3$)/cm^{-1} 3430 and 1673; δ_H 9.77 (1 H, d, *J* 8.0), 6.34 (1 H, dd, *J* 3.0 and 8.0), 4.85 (1 H, dd, *J* 3.0 and 6.0), 3.5–4.2 (4 H, m), 3.24 (1 H, d, *J* 15.5), 2.45 (1 H, dd, *J* 2.0 and 6.0), 2.05 (1 H, dd, *J* 2.0 and 15.5), 1.2–1.9 (6 H, m) and 1.13 (3 H, s); δ_C 202.3, 192.8, 160.0, 127.5, 112.7, 70.8, 63.9. 62.5, 51.6, 49.3, 39.6, 35.6, 34.3, 29.9 and 18.8; *m*/*z* 296 (M^+, 10%), 99 (100), 86 (35) and 53 (14).

(*b*) The alcohol **6** (2.0 g) was treated with a solution of 70% MCPBA (4 g, 2.12 mol equiv.) in CH_2Cl_2 (100 cm^3) for 16 h at room temperature. The products were separated by column chromatography (SiO_2; CH_2Cl_2, then EtOAc) and recrystallized from MeOH to give 2.1 g of crude acid **15** (2.1 g, 94%), m.p. 195–198 °C (Found: M^+, 296.129. $C_{15}H_{20}O_6$ requires *M*, 196.126); ν_{max}(KBr)/cm^{-1} 3270, 1759, 1121 and 915; δ_H(CD_3OD) 5.93 (1 H, s), 5.04 (1 H, d, *J* 5.9), 4.08 (1 H, m), 3.49 (2 H, m), 3.08 (1 H, m), 2.40 (1 H, d, *J* 5.9), 1.82 (1 H, d, *J* 13.0), 1.7–1.4 (6 H, m) and 1.36 (3 H, s); δ_C(CD_3OD) 175.2, 173.4, 113.6, 111.3, 107.1, 68.8, 64.7, 63.5, 54.9, 42.7, 41.4, 37.6, 35.9, 30.4 and 19.9; *m*/*z* 296 (M^+, 10%), 99 (100), 86 (35) and 53 (14).

To a methanolic (15 cm^3) solution of the acid **15** was added a solution of CH_2N_2 in diethyl ether carefully at 0 °C with monitoring by TLC to avoid 1,3-dipole addition. After evaporation of the solvent, the residue was chromatographed over SiO_2 (eluted with hexane–EtOAc 3:1) to give the ester **16** (1.80 g, 76.3%) as crystals, m.p. 136.6–138.0 °C (Found: M^+, 310.139. $C_{16}H_{22}O_6$ requires *M*, 310.142); ν_{max}(KBr)/cm^{-1} 3515, 1727, 1683, 1628, 1430, 1304 and 1233; λ_{max}(EtOH)/nm 204 (ε 6380) and 243 (4860); δ_H 6.24 (1 H, d, *J* 2.8), 4.88 (1 H, d, *J* 7.3), 4.79 (1 H, ddd, *J* 2.8, 5.1 and 7.3), 4.06–3.78 (4 H, m), 3.75 (3 H, s), 3.26 (1 H, d, *J* 15.7), 2.36 (1 H, dd, *J* 1.5 and 5.1), 1.95 (1 H, dd, *J* 1.5 and 15.7), 1.85–1.33 (6 H, m) and 1.09 (1 H, s); δ_C 201.4, 168.1, 152.1, 118.0, 112.7, 70.5, 64.0, 62.7, 51.8, 51.4, 48.2, 38.8, 35.6, 34.6, 29.9 and 18.9; *m*/*z* 310 (M^+, 22%), 278 (22), 99 (60), 83 (51), 71 (100) and 54 (72).

Oxidation of the Acetate **11**.—To a solution of the acetate **11** (240 mg) in CH_2Cl_2 (40 cm^3) was added 95% MCPBA (168 mg). The reaction mixture was placed at room temperature for 40 h, after which the solution was washed successively with 10% aq. Na_2CO_3 and brine, dried over anhydrous $MgSO_4$, and evaporated to give a crude mixture of compounds **12** and **14** (232 mg, 92%) in the ratio 95:5 (estimated by ^{1}H NMR spectroscopy). The mixture was chromatographed on a SiO_2 column (eluted with hexane–diethyl ether 2:1) and was then crystallized from hexane–diethyl ether to give compounds **12** and **14**.

Compound **12**, m.p. 133–134 °C (Found: M^+, 322.137. $C_{17}H_{22}O_6$ requires *M*, 322.142); ν_{max}(Nujol)/cm^{-1} 1795, 1744, 1693, 1618, 1255 and 1152; δ_H 9.90 (1 H, d, *J* 7.5), 6.23 (1 H, dd, *J* 7.5 and 2.8), 5.93 (1 H, dd, *J* 5.9 and 2.8), 3.96–3.75 (4 H, m), 3.31 (1 H, d, *J* 15.2), 2.66 (1 H, d, *J* 5.9), 2.15 (3 H, s), 2.10 (1 H, d, *J* 15.2), 1.75 (1 H, br d, *J* 14.0), 1.61 (2 H, m), 1.47 (3 H, m) and 1.19 (3 H, s); δ_C 200.5, 192.2, 169.2, 153.7, 127.4, 110.0, 70.1, 64.3, 63.0, 49.8, 49.1, 38.5, 35.6, 21.91, 20.6 and 18.6; *m*/*z* 322 (M^+, 8%), 280 (27), 263 (37), 99 (40), 86 (100) and 53 (19).

Compound **14**, m.p. 145–146 °C (Found: M^+, 322.139); ν_{max}($CDCl_3$)/cm^{-1} 1803, 1730 and 1238; δ_H 5.68 (1 H, br s), 3.84 (4 H, m), 3.19 (2 H, m), 2.46 (1 H, m), 2.06 (3 H, s), 1.8–1.3 (8 H, m) and 1.18 (3 H, s); δ_C 175.9, 170.7, 152.2, 110.3, 107.0, 68.1, 65.6, 63.3, 51.2, 49.9, 46.9, 36.1, 33.7, 29.7, 29.6, 21.1 and 19.1; *m*/*z* 322 (M^+, 1%), 279 (4), 236 (8), 114 (17), 99 (21) and 86 (100).

[(4aβ,8aβ)-1α-*Acetoxy*-8-*ethylenedioxy*-1,2,3,4,4a,5,6,7,8,8a-*decahydro*-4a-*methyl*-3-*oxo*-2-*naphthylidene*]*acetic Acid* **17**.—The crude acetate **11**, which was prepared from the alcohol **6** (2 g) by the above method, was treated with a solution of 70% MCPBA (3 g) in methylene dichloride (100 cm^3) for 43 h. The reaction mixture was extracted with 10% aq. Na_2CO_3. The aqueous layer was acidified with 2 mol dm^{-3} HCl and the mixture was extracted with $CHCl_3$. The extract was dried ($MgSO_4$) and evaporated. The residue was chromatographed on a SiO_2 column (eluted with diethyl ether–hexane 1:3) and was then crystallized from $CHCl_3$–hexane to give the acid **17** (2.1 g, 87% from **6**) as crystals, m.p. > 140 °C (decomp.) (Found: M^+, 338.135. $C_{17}H_{22}O_7$ requires *M*, 338.137); ν_{max}(KBr)/cm^{-1} 3360, 1760, 1710, 1262 and 1148; δ_H(CD_3OD) 6.01 (2 H, m), 4.0 (4 H, m), 2.62 (1 H, d, *J* 5.7), 2.47 (1 H, d, *J* 13.5), 2.13 (3 H, s), 1.8–1.2 (7 H, m) and 1.40 (3 H, s); δ_C(CD_3OD) 172.8, 171.7, 169.4, 112.3, 111.9, 106.7, 69.8, 65.2, 64.2, 52.9, 42.9, 41.7, 37.6, 37.3, 30.3, 20.8 and 19.7; *m*/*z* 338 (M^+, 10%), 279 (52), 99 (100), 86 (42) and 53 (18).

(4aβ,8aβ,9aβ)-5-*Ethylenedioxy*-4a,5,6,7,8,8a,9,9a-*octahydro*-4α-*hydroxy*-8a-*methylnaphtho*[2,3-b]*furan*-2(4H)-*one* **19**.—Keto ester **16** (4.0 g, 0.0129 mol) was dissolved in methanol (100 cm^3) and the solution was stirred at 0 °C for 3 h after the addition of sodium borohydride (1 g). The reaction mixture was extracted with brine and ethyl acetate. The ethyl acetate layer was washed with brine, dried over anhydrous $MgSO_4$, and evaporated. The residue was crystallized from ethyl acetate–hexane to give lactone **19** (2.9 g, 81%), m.p. 175.3–178–8 °C (Found: M^+, 280.134. $C_{15}H_{20}O_5$ requires *M*, 280.131); ν_{max}(Nujol)/cm^{-1} 3415, 1778, 1742 and 1643; δ_H 5.95 (1 H, m), 5.19 (1 H, d, *J* 5.9), 5.02 (1 H, ddd, *J* 11.5, 7.2 and 1.8), 4.96 (1 H, ddd, *J* 6.5, 5.9 and 2.0), 4.07–3.78 (4 H, m), 2.36 (1 H, d, *J* 6.5), 2.25 (1 H, dd, *J* 11.5 and 11.5), 1.83–1.22 (6 H, m) and 1.20 (1 H, s); δ_C 175.0, 173.4, 112.4, 109.4, 78.7, 68.3, 63.5, 62.1, 51.6, 39.9, 37.4, 36.6, 34.7, 28.5 and 18.3; λ_{max}(EtOH)/nm 208 (ε 9520) and 222 (10 400); *m*/*z* 280 (M^+, 16%), 99 (100), 86 (36) and 53 (14).

(4aβ,8aβ,9aβ)-4α-*Acetoxy*-5-*ethylenedioxy*-4a,5,6,7,8,8a,9,9a-*octahydro*-8a-*methylnaphtho*[2,3-b]*furan*-2(4H)-*one* **20**.—To a solution of the acid **17** (330 mg) in MeOH (20 cm^3) was added carefully an ethereal solution of diazomethane with monitoring by TLC at 0 °C. After 8 h, the solvent was evaporated off and the residue was chromatographed to give methyl ester **18**, m.p. 130–132 °C (Found: M^+, 352.155. $C_{18}H_{24}O_7$ requires *M*, 352, 152); ν_{max}(KBr)/cm^{-1} 1740sh, 1752, 1687, 1614, 1313 and 1245; δ_H 6.04 (1 H, d, *J* 2.9), 5.82 (1 H, dd, *J* 5.5 and 2.9), 3.89 (4 H, m), 3.76 (3 H, s), 3.23 (1 H, d, *J* 15.3), 2.53 (1 H, d, *J* 5.5), 2.10 (3 H, s), 2.03 (1 H, d, *J* 15.5), 1.8–1.3 (6 H, m) and 1.16 (3 H, s); δ_C 200.1, 169.6, 167.5, 146.1 118.9, 110.3, 70.9, 64.7, 63.5, 52.1, 49.9, 48.9, 38.7, 36.1, 35.8, 29.6, 21.0 and 19.0; *m*/*z* 352 (M^+, 22%), 324 (20), 293 (64), 275 (33), 261 (159), 189 (20), 147 (15), 139 (24), 113 (20), 99 (100), 86 (97) and 53 (34).

A solution of the methyl ester and sodium borohydride (82 mg) in MeOH (10 cm^3) was stirred at 0 °C for 1.5 h. The reaction mixture was extracted with brine and chloroform. The chloroform layer was washed with brine, dried with anhydrous $MgSO_4$, and evaporated. The residue was recrystallized from diethyl ether to give lactone **20** (245 mg, 78% from **17**), m.p. 160–162 °C (Found: M^+, 322.137. $C_{17}H_{22}O_6$ requires *M*, 322.141); ν_{max}($CDCl_3$)/cm^{-1} 1783sh, 1755sh, 1740, 1657, 1240 and 1138; δ_H 5.88 (2 H, m), 5.10 (1 H, dd, *J* 11.0 and 7.0), 3.88 (4 H, m), 2.61 (1 H, d, *J* 6.4), 2.28 (1 H, t, *J* 12.0), 2.12 (3 H, s), 1.8–1.2 (7 H, m) and 1.26 (3 H, s); δ_C 172.9, 169.9, 169.2, 110.4, 110.2, 78.9, 68.8, 64.2, 63.0, 50.4, 40.3, 37.9, 36.6, 36.2, 28.5, 20.8 and 18.5; *m*/*z* 322 (M^+, 8%), 263 (22), 113 (15), 99 (100), 86 (60) and 53 (23).

Methyl [(4aβ,8aβ)-8-*Ethylenedioxy*-3,4,4a,5,6,7,8,8a-*octahydro*-4a-*methyl*-3-*oxo*-2-*naphthyl*]*acetate* **22**.—The crude acetate which was prepared from the alcohol **6** (1 g) by the above method was treated with a solution of MCPBA (900 mg) in CH_2Cl_2 (50 cm^3) for 40 h at room temperature. The reaction mixture was washed with 10% aq. Na_2CO_3, dried ($MgSO_4$), and evaporated. The residue was treated with PTSA (400 mg) in wet THF (20 cm^3) for 44 h. To the mixture was added an excess of diazomethane in diethyl ether. The mixture was evaporated and the residue was chromatographed over SiO_2 (eluted with diethyl ether–hexane 1:1) to give the title ester **22** (610 mg, 55% from **6**) as an oil (Found: M^+, 294.149. $C_{16}H_{22}O_5$ requires *M*, 294,147); ν_{max}(neat)/cm^{-1} 1740, 1675, 1380, 1340, 1265, 1250 and 1170; δ_H 6.8 (1 H, d, *J* 5.0), 3.88 (4 H, m), 3.68 (3 H, s), 3.24 (2 H, s), 2.88 (1 H, d, *J* 16.5), 2.50 (1 H, d, *J* 5.0), 2.00 (1 H, d, *J* 16.5), 1.61–1.77 (3 H, m), 1.5 (2 H, m), 1.30 (1 H, m) and 1.10 (3 H, s); δ_C 199.2, 171.8, 145.5, 134.2, 110.1, 65.5, 64.4, 51.8, 51.3, 46.9, 37.6, 36.4, 35.1, 34.7, 29.0 and 19.4; *m*/*z* 294 (M^+, 9%), 114 (24), 99 (14), 86 (100) and 71 (19).

Methyl [(4aβ,8aβ)-5-*Ethylenedioxy*-1,2,3,4,4a,5,6,7,8,8a-*decahydro*-4a-*methyl*-3-*oxo*-2-*naphthyl*]*acetate* **23** *and* **24**.—A mixture of enone **22** (490 mg) and 5% Pd/C (100 mg) in ethyl acetate (20 cm^3) was stirred under H_2 at ambient temperature for 20 h. The reaction mixture was filtered through Celite and the filtrate was evaporated to give a mixture of title compounds **23** and **24** (493 mg, 99%) in the ratio of 8:1. The keto ester **23** was purified by HPLC (silica gel; hexane–ethyl acetate 2:1), m.p. 64–66 °C (Found: M^+, 296.156. $C_{16}H_{24}O_5$ requires *M*, 296.162; ν_{max}(Nujol)/cm^{-1} 1732, 1705, 1159 and 1088; δ_H 3.70–4.03 (4 H, m), 3.67 (3 H, s), 2.91 (1 H, m), 2.74 (1 H, dd, *J* 16.8 and 7.4), 2.38 (1 H, dd, *J* 13.5 and 1.1), 2.27 (1 H, ddd, *J* 12.8, 5.8 and 4.4), 2.15 (1 H, dd, *J* 16.8 and 5.8), 2.08 (1H, d, *J* 13.5), 1.96 (1 H, dd, *J* 12.8 and 4.5), 1.30–1.77 (6 H, m), 1.24 (3 H, s) and 1.11 (1 H, m); δ_C 210.3, 172.9, 110.7, 64.4, 63.4, 55.5, 51.7, 48.0, 45.3, 41.0, 33.7, 32.9, 30.8, 29.8, 28.3 and 19.6; *m*/*z* 296 (M^+, 8%), 99 (100), 86 (63) and 53 (28); compound **24** had m.p. 83–85 °C (Found: M^+, 296.155); ν_{max}($CDCl_3$)/cm^{-1} 1732, 1705, 1162 and 1097; δ_H 4.1–3.7 (4 H, m), 3.67 (3 H, s), 3.34 (1 H, m), 3.18 (1 H, d, *J* 12.6), 2.79 (1 H, dd, *J* 17.5 and 5.3), 2.35 (1 H, ddd, *J* 12.6, 7.5 and 1.0), 2.15 (1 H, dd, *J* 16.5 and 7.5), 1.85 (1 H, d, *J* 12.5), 1.7–1.1 (8 H, m) and 0.93 (3 H, m); δ_C 212.9, 173.4, 111.0, 64.9, 64.1, 51.5, 48.4, 47.0, 42.90, 40.2, 39.5, 35.1, 34.4, 29.4, 27.8 and 19.3; *m*/*z* 296 (M^+, 4%), 232 (25), 217 (13), 161 (23), 145 (15), 133 (16), 121 (19), 105 (30), 99 (42), 91 (74), 88 (40), 81 (55), 69 (52), 56 (67) and 53 (100).

Methyl [(4,8aβ)-1,2,3,4,4a,5,6,7,8,8a-*Decahydro*-4a-*methyl*-3,8-*dioxo*-2β-*naphthyl*]*acetate* **25** *and* **26**.—The keto ester mixture (**23** and **24**) (520 mg) was dissolved in acetone (30 cm^3) containing PTSA (60 mg) and the solution was stirred for 65 h at room temperature. After evaporation of the solvent, the residue was extracted with 10% aq. Na_2CO_3 and chloroform. The chloroform layer was dried ($MgSO_4$) and evaporated to give a product mixture (410 mg), which was dissolved in methanol (20 cm^3) containing 10% aq. KOH (2 cm^3) and the mixture was stirred for 24 h at room temperature before being acidified with conc. HCl and extracted with chloroform. The extract was dried ($MgSO_4$) and evaporated. The residue was dissolved in ethyl acetate and an excess of diazomethane in diethyl ether was added to the solution. After evaporation of the solvent, the products were separated by silica gel column chromatography (hexane–ethyl acetate 2:1) to give a 3:1 mixture of diketo esters **25** and **26** (377 mg, 85%). Compound **25** was obtained as an oil (Found: M^+, 252.129. $C_{14}H_{20}O_3$ requires *M*, 252.136); ν_{max}($CDCl_3$)/cm^{-1} 1736, 1710, 1434, 1375, 1302, 1245 and 1170; δ_H 3.68 (3 H, s), 2.73–2.94 (2 H, m), 2.50 (1 H, d, *J* 13.5), 2.4 (2 H, m), 2.28 (1 H, d, *J* 13.5), 1.60–2.25 (8 H, m) and 0.76 (3 H, s); δ_C 210.0, 208.4, 172.7, 55.9, 55.1, 51.7, 45.8, 43.7, 41.1, 39.8, 33.7, 28.3, 22.4 and 18.2; *m*/*z* 252 (M^+, 58%), 220 (100), 205 (12), 192 (30), 177 (25), 149 (16), 121 (16), 111 (79), 95 (23) and 53 (40). Compound **26** was an oil (Found: M^+, 252.131); ν_{max}($CDCl_3$)/cm^{-1} 1736, 1709, 1436, 1363, 1299, 1258 and 1175; δ_H 3.68 (3 H, s), 3.05 (1 H, m), 2.58 (1 H, dd, *J* 16.0 and 7.0), 1.56–2.55 (12 H, m) and 1.12 (3 H, s); δ_C 210.7, 210.2, 172.5, 54.1, 51.6, 48.5, 44.5, 42.4, 41.2, 38.6, 33.8, 28.3, 27.3 and 22.3; *m*/*z* 252 (M^+, 46%), 220 (91), 202 (14), 192 (41), 177 (35), 149 (26), 121 (27), 111 (100), 99 (27), 95 (35), 86 (29), 79 (38), 67 (41) and 53 (83).

(3aα,8aβ,9aα)-3,3a,4,4a,6,7,8,8a,9,9a-*Decahydro*-8a-*methylnaphtho*[2,3-b]*furan*-2,5-*dione* **27** *and* **28**.—To a solution of the mixture of diketo esters **25** and **26** (345 mg) in methanol (20 cm^3) was added sodium borohydride (180 mg) and the solution was stirred for 4 h at room temperature. After evaporation of the solvent, the residue was extracted with brine–ethyl acetate. The ethyl acetate layer was dried ($MgSO_4$) and evaporated. The product was dissolved in methylene dichloride (25 cm^3) and PDC (1 g) was added to the solution. After being

stirred for 16 h at room temperature, the reaction mixture was chromatographed over silica gel (eluted with diethyl ether) to give a 3:1 mixture of keto lactones **27** and **28** (318 mg, quantitative yield). Crystallization of the mixture **27** and **28** from ethyl acetate–hexane gave pure compound **27** (142 mg). The residue from the filtrate of the crystallization process was equilibrated in 1% aq. KOH–MeOH to give a similar mixture of epimers **27** and **28** (3:1). Compound **27** had m.p. 153–155 °C (Found: M^+, 222.125. $C_{13}H_{18}O_3$ requires *M*, 222.126); ν_{max}(KBr)/cm^{-1} 1753, 1711, 1444, 1426, 1385, 1320, 1221 and 1162; δ_H 4.56 (1 H, ddd, *J* 5.0, 5.0 and 2.0), 2.73 (1 H, dd, *J* 16.0 and 7.0), 2.18–2.44 (6 H, m), 1.79–1.98 (3 H, m), 1.55–1.75 (3 H, m), 1.33 (1 H, ddd, *J* 15.0 and 12.0 and 12.0) and 0.9 (3 H, s). δ_C 210.7, 176, 4, 78.7, 54.4, 41.3, 41.1, 40.6, 37.9, 37.8, 35.1, 22.3, 21.7 and 18.6; *m/z* 222 (M^+, 28%) and 111 (100). Compound **28** had m.p. 119–121 °C (Found: M^+, 222.127); ν_{max}($CDCl_3$)/cm^{-1} 1770, 1700, 1440, 1426, 1340, 1280, 1202, 1181 and 1163; δ_H 4.58 (1 H, dd, *J* 7.5 and 4.2), 2.74 (1 H, m), 2.68 (1 H, dd, *J* 16.5 and 7.0), 2.26–2.37 (3 H, m), 2.26 (1 H, d, *J* 16.5), 2.12 (1 H, ddd, *J* 13.5, 6.0 and 3.0), 1.6–2.0 (6 H, m), 1.41 (1 H, ddd, *J* 14.5, 11.0 and 4.5) and 1.22 (3 H, s); δ_C 212.1, 176.9, 79.3, 53.1, 40.9, 38.6, 37.7, 37.3, 33.3, 30.8, 29.3, 22.8 and 21.9; *m/z* 222 (M^+, 93%), 207 (24), 179 (100), 163 (19), 153 (30), 135 (24), 119 (25), 111 (85), 93 (64), 86 (29), 79 (40), 67 (50) and 53 (94).

(3aα,4aα,8aβ,9aα)-3a,4,4a,5,6,7,8,8a,9,9a-*Decahydro*-8a-*methyl*-5-*methylenenaphtho*[2,3-b]*furan*-2(3H)-*one* **29**.—To a mixture of methyltriphenylphosphonium iodide (505 mg), THF (10 cm^3) and HMPA (2 cm^3) was added a 1.7 mol dm^{-3} solution of butyllithium in hexane (0.7 cm^3). After the mixture had been stirred for 2 h at room temperature, keto lactone **27** (111 mg) was added to the mixture, which was then stirred for a further 20 h at room temperature. After addition of wet diethyl ether, the mixture was stirred for 2 h at room temperature and then was passed through a short column of silica gel. The crude product was purified by HPLC (silica gel; hexane–ethyl acetate) to give the title compound **29** (103 mg, 93.6%), m.p. 133–134 °C (Found: M^+, 220.148. $C_{14}H_{20}O_2$ requires *M*, 220.146); ν_{max}($CDCl_3$)/cm^{-1} 1768, 1742, 1440 and 1417; δ_H 4.78 (1 H, d, *J* 1.7), 4.57 (1 H, ddd, *J* 5.0, 2.0 and 2.0), 4.46 (1 H, d, *J* 1.7), 2.73 (1 H, dd, *J* 16.5 and 7.0), 2.30–2.48 (2 H, m), 2.31 (1 H, d, *J* 16.5), 2.18 (1 H, br d, *J* 16.0), 2.0 (1 H, m), 1.81 (1 H, br d, *J* 12.0), 1.50–1.70 (4 H, m), 1.46 (1 H, dd, *J* 16.0 and 5.0), 1.19–1.37 (2 H, m) and 0.82 (3 H, s); δ_C 177.0, 149.1, 106.4, 79.6, 46.7, 42.1, 41.6, 38.2, 36.6, 35.7, 34.5, 26.0, 22.6 and 17.7; *m/z* 220 (M^+, 18%), 207 (31), 191 (26), 179 (20), 164 (12), 147 (33), 133 (18), 121 (19), 111 (29), 105 (40), 99 (100), 93 (37), 86 (78), 79 (39), 67 (59) and 53 (95).

(3aβ,4aβ,8aβ,9aβ)-5-*Ethylenedioxy*-3a,4,4a,5,6,7,8,8a,9,9a-*decahydro*-8a-*methylnaphtho*[2,3-b]*furan*-2(3H)-*one* **30**.—To a stirred solution of the keto ester **23** (100 mg) in methanol (10 cm^3) was added sodium borohydride (35 mg) at room temperature. After being stirred for 4 h at room temperature, the mixture was evaporated and the residue was extracted with brine–ethyl acetate. The ethyl acetate layer was dried ($MgSO_4$) and evaporated to give the lactone **30** (96 mg, quantitative yield) as a hygroscopic oil (Found: M^+, 266.156. $C_{15}H_{22}O_4$ requires *M*, 266.152); ν_{max}(neat)/cm^{-1} 1768, 1345, 1170, 1145 and 1088; δ_H 4.52 (1 H, q, *J* 3.9), 3.95 (2 H, m), 3.87 (2 H, m), 2.67 (1 H, dd, *J* 6.6 and 16.0), 2.32 (1 H, d, *J* 16.0), 2.02 (1 H, dd, *J* 15.5 and 3.3), 1.91 (1 H, m), 1.8–1.0 (10 H, m) and 1.12 (3 H, s); δ_C 177.3, 111.0, 79.6, 64.3, 63.4, 46.6, 41.2, 38.0, 34.8, 33.5, 29.9, 28.8, 26.0 and 19.3; *m/z* 266 (M^+, 19%), 139 (10), 113 (19), 99 (100) and 86 (44).

(3aβ,8aβ,9aβ)-3,3a,4,4a,6,7,8,8a,9,9a-*Decahydro*-8a-*methylnaphtho*[2,3-b]*furan*-2,5-*dione* **31** *and* **32**.—A solution of ketal **30** (70 mg) and PTSA (40 mg) in acetone (20 cm^3) was stirred for 17 h at room temperature. The reaction mixture was washed with 10% aq. Na_2CO_3 and extracted with brine and diethyl ether. The ethereal layer was washed with brine, dried ($MgSO_4$), and evaporated. The residue was dissolved in methanol (20 cm^3) containing 10% aq. KOH (2 cm^3). After being stirred for 20 h at 0 °C under Ar, the reaction mixture was acidified with 2 mol dm^{-3} HCl and extracted with diethyl ether. The extract was washed with brine, dried ($MgSO_4$), and evaporated to give a mixture of compounds **31** and **32** (10:1, ^{1}H NMR) (52 mg, 89%). Crystallization from diethyl ether–hexane gave pure compound **31**, m.p. 150–151 °C (Found: M^+, 222.129. $C_{13}H_{18}O_3$ requires *M*, 222.126); ν_{max}(Nujol)/cm^{-1} 1762, 1699, 1169, 1002 and 991; δ_H 4.71 (1 H, dd, *J* 9.6 and 4.8), 2.77 (1 H, dd, *J* 17.0 and 7.0), 2.55 (2 H, m), 2.40 (1 H, dd, *J* 17.0 and 3.5), 2.3–1.8 (7 H, m), 1.71 (1 H, ddd, *J* 13.9m, 6.5 and 4.5), 1.58 (1 H, dd, *J* 15.0 and 4.9), 1.44 (1 H, dt, *J* 13.9 and 4.5) and 1.04 (3 H, s); δ_C 216.6, 179.6, 80.6, 56.9, 39.4, 38.4, 37.5, 37.2, 35.1, 33.6, 25.6, 26.6 and 22.5; *m/z* 222 (M^+, 32%), 207 (30), 179 (40), 147 (50), 111 (35), 105 (37), 99 (100), 86 (92), 81 (40), 67 (40) and 53 (86). Compound **32** was an oil (Found: M^+, 222.130); ν_{max}(Nujol)/cm^{-1} 1766, 1698, 1169, 967 and 955; δ_H 4.03 (1 H, m), 2.7–2.4 (4 H, m), 2.25 (2 H, m), 1.98 (2 H, m), 1.81 (1 H, m), 1.7–1.5 (5 H, m) and 0.86 (3 H, s); δ_C 215.3, 178.1, 67.7, 51.6, 44.3, 42.0, 41.7, 41.0, 37.7, 31.3, 24.5, 23.4 and 18.0; *m/z* 222 (M^+, 47%), 207 (42), 179 (65), 147 (52), 111 (55), 99 (96), 91 (59), 86 (86), 81 (50), 67 (59) and 53 (100).

(3aβ,4aα,8aβ,9aβ)-3a,4,4a,5,6,7,8,8a,9,9a-*Decahydro*-8a-*methyl*-5-*methylenenaphtho*[2,3-b]*furan*-2(3H)-*one* **33**.—To an ice-cooled mixture of methyltriphenylphosphonium iodide (505 mg), THF (10 cm^3) and HMPA (2 cm^3) was added a 1.7 mol dm^{-3} solution of butyllithium in hexane (0.7 cm^3). After the mixture had been stirred for 2 h at 20 °C, the lactone **31** (111 mg) was added. The mixture was stirred for a further 16 h at room temperature and then wet diethyl ether was added to the reaction mixture. After being stirred for 2 h, the reaction mixture was passed through a short column of silica gel (eluted with diethyl ether). The crude product was purified by HPLC (silica gel; hexane–ethyl acetate 3:1) and recrystallization from diethyl ether–hexane to give the title compound **33** (105 mg, 95.4%), m.p. 103–105 °C (Found: M^+, 220.140. $C_{14}H_{20}O_2$ requires *M*, 220.146); ν_{max}(Nujol)/cm^{-1} 1761, 1641, 1177 and 1003; δ_H 4.79 (1 H, br s), 4.72 (1 H, dt, *J* 12.0 and 7.0), 4.49 (1 H, s), 2.90 (1 H, m), 2.6–2.3 (3 H, m), 2.1–1.9 (3 H, m), 1.77 (2 H, m), 1.60 (2 H, m), 1.49 (1 H, br d, *J* 15.5), 1.36 (1 H, dt, *J* 7.7 and 5.5), 1.24 (1 H, t, *J* 11.5) and 0.76 (3 H, s); δ_C 176.9, 148.7, 106.7, 77.3, 43.1, 42.3, 41.6, 37.0, 36.1, 34.9, 34.4, 24.2, 22.8 and 15.8; *m/z* 220 (M^+, 28%), 205 (17), 192 (20), 179 (28), 145 (35), 133 (21), 111 (35), 105 (41), 99 (100), 93 (67), 86 (77), 79 (44), 68 (32) and 53 (78).

Dihydrocallitrisin **3**.—A THF solution (5 cm^3) of compound **33** (110 mg) was added to a solution of THF (10 cm^3), HMPA (1 cm^3), diisopropylamine (70 mm^3, 56 mg) and butyllithium–hexane solution (1.7 mol dm^{-3}; 0.3 cm^3) at −78 °C and the mixture was stirred for 30 min. Methyl iodide (71 mg, 31 mm^3) was added to the mixture at 0 °C and the solution was stirred at 0 °C for 1 h. Water and diethyl ether were added and then the mixture was acidified with 2 mol dm^{-3} HCl. The ethereal layer was washed with aq. Na_2SO_3, dried ($MgSO_4$), and evaporated. Separation of the residue by HPLC gave dihydrocallitrisin **3** (72 mg) and starting material **33** (44 mg recovery).

(4aα,8aβ)-4,6,7,8,8a,9-*Hexahydro*-4α-*hydroxy*-8a-*methyl*-*naphtho*[2,3-b]*furan*-5(4aH)-*one* **35**.—To a solution of ketal **6** (5.87 g) in acetone (240 cm^3) at 0 °C was added PTSA (800 mg) and the solution was stirred for 1 h. Brine and 10% aq Na_2CO_3 were added to the reaction mixture, which was then extracted with diethyl ether. The extract was washed with brine,

dried ($MgSO_4$), and evaporated. The crude product was dissolved in methanol (180 cm^3) and 10% aq. KOH (18 cm^3) was added to the solution at 0 °C. After being stirred at 0 °C for 1 h, the reaction mixture was acidified with 2 mol dm^{-3} HCl and extracted with brine and diethyl ether. The ethereal layer was washed with brine, dried ($MgSO_4$), and evaporated. The product was chromatographed on a silica gel column (hexane–ethyl acetate 2:1) and crystallized from diethyl ether–hexane to give the title compound **35** (3.45 g, 70.5%), m.p. 89.5–90.5 °C (Found: M^+, 220.112. $C_{13}H_{16}O_3$ requires *M*, 220.110); ν_{max}(KBr)/cm^{-1} 3234br, 1711, 1629 and 1502; δ_H 7.28 (1 H, br), 6.47 (1 H, d, *J* 1.5), 4.97 (1 H, d, *J* 8.5), 3.10–3.40 (1 H, br), 2.71 (1 H, d, *J* 16), 2.25–2.54 (4 H, m), 1.65–2.08 (4 H, m) and 0.85 (3 H, s); δ_C 212.3, 148.50, 141.4, 117.9, 108.7, 62.7, 62.1, 41.6, 41.1, 39.6, 38.3, 22.0 and 19.2; *m/z* 220 (M^+, 15%), 202 (57), 187 (70), 131 (54), 111 (43), 99 (56), 91 (70), 86 (57), 81 (48), 77 (42), 69 (64), 56 (64) and 53 (100).

(4aα,8aβ)-4,4a,5,6,7,8,8a,9-*Octahydro*-5α,8a-*dimethylnaphtho*[2,3-b]*furan*-4α,5β-*diol* **36**.—To an ice-cooled solution of ketone **35** (151 mg) in dry diethyl ether (20 cm^3) was added a methyllithium–diethyl ether solution (1.03 mol dm^{-3}; 3.6 cm^3) under Ar. The mixture was stirred at ambient temperature for 15 h and then water was added. The mixture was extracted with diethyl ether and the extract was washed successively with 10% aq. Na_2SO_3 and brine, dried ($MgSO_4$), and evaporated. The residue was chromatographed over silica gel (hexane–ethyl acetate 2:1) to give crystals of compound **36** (131 mg, 81%), m.p. 148.5–151 °C (Found: M^+, 236.135. $C_{14}H_{20}O_3$ requires *M*, 236.141); ν_{max}(KBr)/cm^{-1} 3334br, 1641 and 1507; δ_H 7.25 (1 H, br), 6.43 (1 H, d, *J* 1.8), 4.87 (1 H, d, *J* 8.5), 2.45 (1 H, d, *J* 16), 2.25 (1 H, d, *J* 16), 1.51 (3 H, s), 1.35 (1 H, d, *J* 8.5), 1.40–1.90 (6 H, m) and 1.04 (3 H, s); δ_C 150.6, 141.2, 120.2, 108.8, 71.9, 65.6, 56.6, 43.0, 41.9, 41.4, 38.2, 33.7, 20.2 and 18.0; *m/z* 234 (M − 2, 4%), 200 (98), 185 (100), 157 (31), 91 (29), 77 (24) and 53 (26).

Methyl [(4aβ,8aα)-1,2,3,4,4a,5,6,7,8,8a-*Decahydro*-1α,8β-*dihydroxy*-4a,8α-*dimethyl*-3-*oxo*-3-*naphthylidene*]*acetate* **37**.—A solution of the diol **36** (1.2 g) and MCPBA (70%; 2.7 g) in CH_2Cl_2 (100 cm^3) was kept at ambient temperature for 17 h. The reaction mixture was chromatographed directly over silica gel and eluted with CH_2Cl_2 and then with ethyl acetate. The product was dissolved in methanol (10 cm^3) and methylated with diazomethane in diethyl ether by the above method. After evaporation of the solvent, crude keto ester **37** was obtained quantitatively (1.43 g) as an oil (Found: $M^+ - H_2O$, 264.135. $C_{15}H_{20}O_4$ requires *m/z* 264.136); ν_{max}(neat)/cm^{-1} 3420br and 1713; δ_H 6.25 (1 H, d, *J* 2), 4.74 (1 H, br d, *J* 10), 3.73 (3 H, s), 3.38 (1 H, m), 2.38 (1 H, d, *J* 15), 2.23 (1 H, d, *J* 15), 1.18–1.95 (6 H, br), 1.58 (1 H, d, *J* 10), 1.50 (3 H, s) and 1.08 (3 H, s); δ_C 201.2, 167.8, 153.8, 122.2, 71.9, 70.7, 57.8, 56.5, 52.2, 42.6, 41.6, 34.7, 33.4, 20.5 and 17.4; *m/z* 282 (M^+, 4%), 264 (13), 263 (21), 161 (40), 109 (100), 71 (72) and 53 (95).

Methyl [(4aβ,8aα)-1,2,3,4,4a,5,6,7,8,8a-*Decahydro*-1α,8β-*dihydroxy*-4a,8α-*dimethyl*-3-*oxo*-2-*naphthyl*]*acetate* **38**.—A mixture of unsaturated ester **37** (52 mg) and 5% Pd/C (5.2 mg) in ethyl acetate (10 cm^3) was stirred under H_2 at ambient temperature for 20 h. Filtration of the mixture with Celite and evaporation of the solvent gave the title compound **38** (50 mg, 95.5%) as an oil (Found: $M^+ - 2$, 282.148. $C_{15}H_{22}O_5$ requires *m/z* 282.147); ν_{max}(neat)/cm^{-1} 3460, 1710 and 1171; δ_H 4.07 (1 H, br t, *J* 10), 3.70 (3 H, s), 2.98 (1 H, dd, *J* 5.5 and 16.5), 2.84 (1 H, br ddd, *J* 5, 5 and 10), 2.59 (1 H, dd, *J* 5.0 and 16.5), 2.28 (1 H, d, *J* 13.5), 2.23 (1 H, br), 2.08 (1 H, d, *J* 13.5), 1.62 (1 H, d, *J* 12), 1.54 (3 H, s), 1.25–1.75 (5 H, m) and 0.96 (3 H, s); δ_C 206.9, 174.4, 73.1, 57.1, 56.4, 51.8, 43.2, 41.6, 35.6, 34.2, 30.9. 20.1 and 17.4; *m/z* 284 (M^+, 3%), 282 (48), 181 (30), 163 (26), 149 (41), 139 (100), 121 (32), 109 (40), 95 (27) and 53 (33).

Methyl [(4aβ,8aα)-3,4,4a,5,6,7,8,8a-*Octahydro*-8β-*hydroxy*-4aβ,8α-*dimethyl*-3-*oxo*-2-*naphthyl*]*acetate* **39**.—A solution of compound **38** (240 mg) and PTSA (12 mg) in benzene (20 cm^3) was refluxed under Ar for 3 h. The product was separated by column chromatography (silica gel; hexane–ethyl acetate 3:1) to give unsaturated ester **39** (146 mg, 65%) as an oil (Found: M^+, 266.146. $C_{15}H_{22}O_4$ requires *M*, 266.152); ν_{max}(neat)/cm^{-1} 3450, 1736 and 1670; δ_H 7.00 (1 H, br s), 3.68 (3 H, s), 3.26 (2 H, br s), 2.36 (1 H, d, *J* 2.0), 2.28 (1 H, d, *J* 16.2), 2.24 (1 H, d, *J* 16.2), 1.37 (3 H, s), 1.30–1.95 (6 H, m) and 1.16 (3 H, s); δ_C 1.98.1, 171.8, 146.7, 134.4, 70.7, 56.1, 52.8, 51.9, 40.8, 39.8, 39.7, 35.1, 30.0, 18.6 and 17.6; *m/z* 266 (M^+, 10%), 248 (25), 235 (14), 216 (26), 161 (42), 149 (100), 121 (86), 79 (24) and 53 (28).

Methyl [(4aβ,8aα)-1,2,3,4,4a,5,6,7,8,8a-*Decahydro*-8β-*hydroxy*-4aβ,8α-*dimethyl*-3-*oxo*-2-*naphthyl*]*acetate* **40**.—A mixture of unsaturated ester **39** (15 mg) and 5% Pd/C (2 mg) in ethyl acetate (6 cm^3) was stirred under H_2 for 15 h. The mixture was filtered and evaporated to give compound **40** (15 mg, quantatitive yield), m.p. 47–49 °C (Found: M^+, 268.173. $C_{15}H_{24}O_4$ requires *M*, 268.168); ν_{max}(neat)/cm^{-1} 3525, 1734 and 1700; δ_H 3.69 (1 H, s), 2.75–2.92 (2 H, br), 2.14–2.30 (3 H, br), 2.06 (1 H, d, *J* 15.0), 1.27 (3 H, s), 1.25–1.90 (10 H, m) and 0.99 (3 H, s); δ_C 209.7, 173.1, 71.4, 57.8, 51.6, 50.7, 46.8, 41.3, 41.2, 38.8, 34.1, 30.7, 28.9, 19.2 and 18.0; *m/z* 268 (M^+, 10%), 250 (28), 218 (29), 151 (50), 139 (75), 121 (72), 109 (73), 91 (52), 86 (41), 79 (57), 67 (57) and 53 (100).

(3aα,4aα,8aβ,9aα)-3a,4,4a,5,6,7,8,8a,9,9a-*Decahydro*-5β-*hydroxy*-5α,8a-*dimethylnaphtho*[2,3-b]*furan*-2(3H)-*one* **41**.—To a solution of keto ester **40** (103 mg) in methanol (10 cm^3) was added sodium borohydride (20 mg) and the solution was stirred at ambient temperature for 40 min before being evaporated, and the residue was extracted with brine and ethyl acetate. The ethyl acetate layer was washed with brine, dried ($MgSO_4$), and evaporated to give the lactone **41** (84 mg, 92%), m.p. 67–69 °C (Found: $M^+ - H_2O$, 220.145. $C_{14}H_{20}O_2$ requires *m/z* 220.146); ν_{max}(neat)/cm^{-1} 3494 and 1763; δ_H 4.53 (1 H, ddd, *J* 1.8, 4.5 and 4.5), 2.72 (1 H, dd, *J* 7 and 17), 2.43 (1 H, m), 2.29 (1 H, d, *J* 17), 2.04 (1 H, dd, *J* 1.8 and 15), 1.19 (3 H, s), 1.14 (3 H, s) and 1.10–1.70 (10 H, m); δ_C 177.0, 79.6, 71.3, 49.3, 44.6, 42.0, 41.3, 38.1, 36.7, 32.8, 30.3, 23.4, 20.1 and 17.3; *m/z* 238 (M^+, 10%), 220 (20), 151 (100), 93 (30), 71 (56) and 53 (41).

4β-*Hydroxyeudesm*-11(13)-*en*-12,8β-*olide*:(3aα,4aα,8aβ,-9aα)-3a,4,4a,5,6,7,8,8a,9,9a-*Decahydro*-5β-*hydroxy*-5α,8a-*dimethyl*-3-*methylenenaphtho*[2,3-b]*furan*-2(3H)-*one* **4**.—To sodium hydride (60% in oil; 50 mg), which was washed with dry hexane, were added an ethereal solution (6 cm^3) of lactone **41** (20 mg) and then ethyl formate (0.25 mg). After being stirred at ambient temperature for 17 h, the mixture was treated with water and 2 mol dm^{-3} HCl. The mixture was extracted with diethyl ether. The extract was washed with brine, dried ($MgSO_4$), and evaporated. The residue was dissolved in methanol (5 cm^3) and the solution was stirred with sodium borohydride (4 mg) at ambient temperature for 5 h. The solution was evaporated and the residue was extracted with brine and ethyl acetate. The organic layer was washed with brine, dried ($MgSO_4$), and evaporated. The residue was chromatographed over silica gel (eluted with hexane–ethyl acetate 2:1) to give a solid (15 mg). The solid (15 mg) and toluene-*p*-sulfonyl chloride (*p*-TsCl) (33 mg) were dissolved in dry pyridine (2 cm^3) and the mixture was stirred for 65 h. After reflux for 2 h, the mixture was dissolved in diethyl ether and washed successively with 2 mol dm^{-3} HCl, 10% aq. Na_2CO_3, and brine, dried ($MgSO_4$), and evaporated. The residue was chromatographed over silica gel (hexane–ethyl acetate 3:1) to give the title compound **4** (5 mg, 24% from **41**), m.p. 157–159 °C

(Found: M^+, 250.161. $C_{15}H_{22}O_3$ requires M, 250.157); ν_{max}(KBr)/cm^{-1} 3480, 1746 and 1665; δ_H 6.13 (1 H, d, J 1.2), 5.59 (1 H, br d, J 1.2), 4.47 (1 H, ddd, J 1.7, 5.0 and 5.0), 2.98 (1 H, m), 2.06 (1 H, dd, J 1.5 and 15.5), 1.35–1.94 (9 H, m), 1.21 (3 H, s), 1.13 (3 H, s) and 1.08 (1 H, dd, J 2.5 and 13.0); δ_C 170.6, 142.2, 120.0, 77.0, 71.2, 48.8, 44.4, 42.0, 41.5, 41.1, 32.5, 30.4, 24.9, 20.0 and 17.3; m/z 250 (M^+, 17%), 232 (42), 163 (71), 147 (25), 133 (28), 121 (47), 111 (35), 99 (51), 91 (76), 86 (58), 71 (76), 67 (58) and 53 (100).

Oxymercuriation of compound **29**.—To a solution of the olefinic compound **29** (9.1 mg) were added water (0.5 cm^3) and $Hg(OAc)_2$ (18 mg), and the mixture was stirred under Ar at ambient temperature for 5 h. The solution was made basic with 2.5 mol dm^{-3} NaOH (0.25 cm^3) and was stirred with a solution (1.3 g dm^{-3}) of $NaBH_4$ in 2.5 mol dm^{-3} NaOH (1 cm^3) for 30 min. The mixture was acidified with 2 mol dm^{-3} HCl and extracted with diethyl ether. The extract was washed with brine, dried ($MgSO_4$), and evaporated. The residue was dissolved in benzene (2 cm^3) and the solution was refluxed for 2 h. After evaporation of the solvent, the residue was chromatographed over silica gel to give compound **41** (0.8 mg, 8.1%) and compound **42** (5.8 mg, 59%); the latter compound had m.p. 66–68 °C (Found: M^+, 238.155. $C_{14}H_{22}O_3$ requires M, 238.157); ν_{max}(KBr)/cm^{-1} 3470, 1770 and 1165; δ_H 4.54 (1 H, ddd, J 2.0, 5.0 and 5.0), 2.70 (1 H, dd, J 6.5 and 16.0), 2.42 (1 H, m), 2.30 (1 H, d, J 16.0), 2.11 (1 H, br d, J 16), 1.96 (1 H, dd, J 6.0 and 12.0), 1.12 (3 H, s), 1.00–1.75 (9 H, m) and 0.98 (3 H, s); δ_C 177.2, 79.6, 71.8, 52.0, 45.3, 43.4, 41.4, 38.1, 36.7, 33.5, 23.2, 22.8, 19.9 and 19.5; m/z 238 (M^+, 3%), 220 (26), 205 (25), 151 (100), 145 (30), 93 (24) and 71 (27).

Septuplinolide **5**.—To sodium hydride (60% in oil; 80 mg), which was washed with dry hexane, were added an ethereal solution (6 cm^3) of lactone **42** (26 mg) and then ethyl formate (0.4 cm^3). After the mixture had been stirred at ambient temperature for 15 h, water and 2 mol dm^{-3} were added. The mixture was extracted with diethyl ether. The extract was washed with brine, dried ($MgSO_4$), and evaporated. The residue was dissolved in methanol (10 cm^3) and the solution was stirred with sodium borohydride (15 mg) at ambient temperature for 2 h before being evaporated, and the residue was extracted with brine and ethyl acetate. The organic layer was washed with brine, dried ($MgSO_4$), and evaporated. The residue was chromatographed over silica gel (eluted with hexane–ethyl acetate 3:1). The residue and *p*-TsCl (50 mg) were dissolved in dry pyridine (6 cm^3) and the solution was stirred for 48 h. After reflux for 2 h, the mixture was dissolved in diethyl ether and washed successively with 2 mol dm^{-3} HCl, 10% aq. Na_2CO_3, and brine, dried ($MgSO_4$), and evaporated. The residue was chromatographed over silica gel (hexane–ethyl acetate 3:1) to give septuplinolide **5** (11.5 mg, 42% from **42**), m.p. 118–120 °C (Found: M^+, 250.148. $C_{15}H_{22}O_3$ requires M, 250.157); ν_{max}(KBr)/cm^{-1} 3550, 3320, 1765, 1750, 1665, 1265 and 1150; δ_H 6.12 (1 H, d, J 1.2), 5.58 (1 H, d, J 1.2), 4.47 (1 H, ddd, J 2.0, 5.0 and 5.0), 2.96 (1 H, m), 2.12 (1 H, dd, J 2.0 and 15.5), 2.03 (1 H, m), 1.81 (1 H, m), 1.18–1.59 (9 H, m) 1.11 (3 H, s) and 0.98 (3 H, s); δ_C 170.7 (s), 142.1 (s), 120.2 (t), 76.8 (d), 71.8 (s), 51.4 (d), 45.0 (t), 43.5 (t), 41.5 (t), 41.3 (d), 33.3 (s), 24.8 (t), 22.7 (q), 19.8 (q) and 19.5 (t); m/z 250 (M^+, 8%), 235 (7), 233 (11), 232 (65), 217 (10), 204 (12), 189 (9), 163 (100), 119 (20), 91 (20), 81 (25), 71 (43) and 53 (23).

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