(12 H, m), 1.22 (19 H, m), 2.25 (2 H, m), 3.46 (3 H, s), 4.44 (2 H, s), 5.77 (1 H, m), 5.95 (1 H, m); MS, m/z (relative intensity) 324 (M^+, 3), 279 (6), 138 (20), 112 (100). Anal. Calcd for $C_{21}H_{40}O_2$: 324.3028. Found: 324.3030.

2-Hydroxy-3-methylidene-7,11,15-trimethylhexadecanyl methyl ether (9c): IR (neat) 3450, 2920, 2860, 1460, 1115 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.8–0.9 (12 H, m), 1.22 (19 H, m), 2.0 (2 H, m), 2.55 (1 H, br s), 3.40 (3 H, s), 3.4 (2 H, m), 4.25 (1 H, m), 4.95 (1 H, m), 5.22 (1 H, m); MS, m/z (relative intensity) 326 (M^+, 10), 294 (7), 115 (71), 111 (50), 83 (100). Anal. Calcd for $C_{21}H_{42}O_2$: 326.3184. Found: 326.3177.

MB-Sensitized Photooxygenation of 1d. Ethyl phytyl ether (**1d**) was photooxygenated and analyzed by GLC as above, and subsequent preparative TLC (eluting with 1:4 ethyl acetate–hexane) of the product (0.3 g) gave trans-epoxy acetal *trans*-**7d** (R_f 0.73, 73 mg), ketone **8** (R_f 0.70, 6 mg), cis-epoxy acetal *cis*-**7d** (R_f 0.63, 40 mg), and β-hydroxyhomoallyl alcohol monoethyl ether **9d** (R_f 0.43, 71 mg).

***trans*-3,7,11,15-Tetramethyl-2,3-epoxyhexadecanal diethyl acetal (*trans*-7d)**: IR (neat) 2925, 1055 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.8–0.9 (12 H, m), 1.1–1.6 (28 H, m), 2.87 (1 H, d, J = 6.8 Hz), 3.71 (4 H, m), 4.34 (1 H, d, J = 6.8 Hz) [the cis and trans dispositions of the acetal groups were further confirmed by using a shift reagent]; MS, m/z (relative intensity) 339 (M^+ - 45, 0.1), 311 (7), 310 (38), 103 (100). Anal. (determined for M^+ - 45 peak) Calcd for $C_{22}H_{43}O_2$: 339.3262. Found: 339.3267.

***cis*-3,7,11,15-Tetramethyl-2,3-epoxyhexadecanal diethyl acetal (*cis*-7d)**: IR (neat) 2925, 1055 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.8–0.9 (12 H, m), 1.1–1.6 (28 H, m), 2.86 (1 H, d, J = 6.7 Hz), 3.70 (4 H, m), 4.32 (1 H, d, J = 6.7 Hz); MS, m/z (relative intensity) 339 (M^+ - 45, 0.1), 311 (7), 310 (26), 103 (100). Anal. (determined for M^+ - 45 peak) Calcd for $C_{22}H_{43}O_2$: 339.3262. Found: 339.3269.

Ethyl 2-hydroxy-3-methylidene-7,11,15-trimethylhexadecanyl ether (9d): IR (neat) 3450, 2925, 1465, 1105 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.8–0.9 (12 H, m), 1.22 (22 H, m), 1.98 (2 H, m), 2.68 (1 H, br s), 3.46 (2 H, m), 3.55 (2 H, q, J = 7 Hz), 4.25 (1 H, m), 4.94 (1 H, m), 5.15 (1 H, m); MS, m/z (relative intensity) 340 (M^+, 6), 294 (13), 129 (47), 111 (43), 83 (100). Anal. Calcd for $C_{22}H_{44}O_2$: 340.3341. Found: 340.3336.

Reduction of Hydroperoxides 2b and 3b by Trimethyl Phosphite ($(CH_3O)_3P$). Phytyl acetate (**1b**) was photooxygenated as previously described. The obtained hydroperoxides (**2b** and **3b**) were reduced by adding 1 mL of $(CH_3O)_3P$ at 0 °C with stirring for 12 h. The resulting mixtures were analyzed directly by GLC (see Table I).

Reactions of Hydroperoxides 2b and 3b with Ac_2O/Pyr. Phytyl acetate (**1b**) was photooxygenated as previously described. The obtained hydroperoxides (**2b** and **3b**) were treated with 1 mL of acetic anhydride in 0.8 mL of pyridine (Ac_2O/Pyr) at room temperature and allowed to stand for 2 h. The resulting mixture were analyzed directly by GLC. Subsequent preparative TLC (eluting with 3:7 ethyl acetate–hexane; R_f 0.58~0.70) and preparative HPLC of product (0.23 g) gave two acylals, *trans*-**7b** (54 mg) and *cis*-**7b** (27 mg), in addition to 11 (130 mg).

***trans*-3,7,11,15-Tetramethyl-2,3-epoxyhexadecylidene diacetate (*trans*-7b)**: IR (neat) 2925, 1765, 1240, 1205 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.8–0.9 (12 H, m), 1.39 (24 H, m), 2.11 (6 H, s), 2.99 (1 H, d, J = 8 Hz), 6.64 (1 H, d, J = 8 Hz) [the cis and trans dispositions of the acylal group were further confirmed by using a shift reagent]; MS, m/z (relative intensity) 353 (M^+ - 59, 1), 293 (1), 269 (2), 144 (38), 102 (52), 43 (100). Anal. (determined for M^+ - 59 peak) Calcd for $C_{22}H_{41}O_3$: 353.3055. Found: 353.3046.

***cis*-3,7,11,15-Tetramethyl-2,3-epoxyhexadecylidene diacetate (*cis*-7b)**: IR (neat) 2925, 1765, 1240, 1200 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.8–0.9 (12 H, m), 1.33 (24 H, m), 2.11 (6 H, s), 3.01 (1 H, d, J = 8 Hz), 6.68 (1 H, d, J = 8 Hz); MS, m/z (relative intensity) 353 (M^+ - 59, 0.5), 293 (0.5), 269 (2), 144 (19), 102 (28), 43 (100). Anal. (determined for M^+ - 59 peak) Calcd for $C_{22}H_{41}O_3$: 353.3055. Found: 353.3064.

Registry No. **1a**, 150-86-7; **1b**, 10236-16-5; **1c**, 66432-64-2; **1d**, 66432-65-3; **2a**, 100605-80-9; **2b**, 100605-82-1; **2c**, 100605-84-3; **2d**, 100605-86-5; **3a**, 100605-81-0; **3b**, 100605-83-2; **3c**, 100605-85-4; **3d**, 100605-87-6; **4**, 100759-12-4; **5**, 100605-88-7; (*E*)-**6**, 100605-89-8; (*Z*)-**6**, 100605-90-1; **7b** (R_3 = CH_3CO), 100605-91-2; **7c** (R_3 = C_2H_5), 100605-92-3; **7d** (R_3 = C_2H_5), 100605-93-4; **8**, 16825-16-4; **9a**, 100605-94-5; **9b**, 100605-95-6; **9c**, 100605-96-7; **9d**, 100605-97-8; **10**, 100605-98-9; **11b**, 100655-22-9; **11c**, 100605-99-0; **12**, 100606-00-6.

6α,7α,17β-Trihydroxy-15β,17-oxidospongian-16-one 7-Butyrate: A New Diterpene Lactone from an Australian *Aplysilla* Species

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A growing number of diterpenes of the spongian-type have been isolated[1,2] from sponges of the orders Dendroceratida and Dictyoceratida. In addition, the isolation of norrisolide[3] and other rearranged spongian metabolites[4] from spongivorous nudibranchs of the genus *Chromodoris* implies additional but as yet undiscovered sponge sources of these diterpenes. The recent X-ray structural elucidation[2] of lactone **1** from the Caribbean sponge *Igernella notabilis* prompts us to report the isolation of the corresponding 6α-hydroxy derivative **2** (see Chart I) from an Australian *Aplysilla sp.*

A pink, thinly encrusting sponge of the genus *Aplysilla* was collected in Port Phillip Bay, Australia. Flash chromatography of the dichloromethane-soluble portion of the methanol extract with hexanes gave a small amount of ambliofuran (**3**), identified by comparison of the spectral data with the literature values.[5] Further elution with ether/hexane mixtures afforded the crystalline lactone **2**, mp 212–213 °C. More polar fractions yielded, after high-performance LC, the minor methyl ester **8**.

The lactone **2** had a molecular formula of $C_{24}H_{36}O_7$ that was inferred from ^{13}C NMR and mass spectral data. The ^1H NMR spectrum indicated that lactone **2** was a butyrate ester of a diterpene, and hydrolysis of **2** with potassium carbonate in methanol gave the expected triol **4**. The differences observed between the ^{13}C NMR spectra of **1** and **2** (Table I) could be rationalized by proposing that lactone **2** was the 6α-hydroxy derivative of lactone **1**. This proposal was supported by the following ^1H NMR data. Irradiation of the equatorial H-7 proton signal at δ 4.93 collapsed the axial H-6 proton signal at δ 4.18 to a doublet of doublets (J = 11.5, 6.0 Hz). Irradiation of the H-6 signal in turn sharpened the H-7 signal to a singlet and collapsed the axial H-5 signal at δ 1.47 (d, 1 H, J = 11.5 Hz) to a singlet (observed by difference decoupling).

Selected nuclear Overhauser effect difference spectroscopy (NOEDS) experiments (Table II) confirmed the regio- and stereochemical relationships of all functional groups. Irradiation of the H-17α signal enhanced the signals of

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0022-3263/86/1951-1144$01.50/0

Chart I

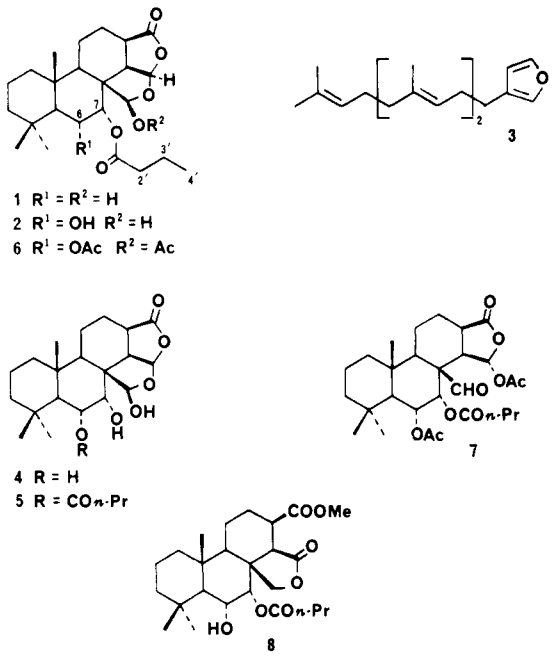

Table I. ^{13}C NMR Data for Lactones 1 and 2

C	chem shift, ppm (mult) 1[a]	2[b]
1	38.9 (t)	39.0 (t)
2	18.7 (t)	18.6 (t)
3	41.9 (t)	43.3 (t)
4	32.8 (s)	33.1 (s)
5	49.6 (d)[c]	52.4 (d)
6	24.6 (t)	69.5 (d)
7	72.7 (d)	77.2 (d)
8	50.8 (s)	51.2 (s)
9	48.5 (d)[c]	48.8 (d)
10	39.3 (s)	39.0 (s)
11	16.2 (t)	16.3 (t)
12	23.3 (t)[c]	23.0 (t)
13	37.7 (d)	37.5 (d)
14	42.2 (d)	42.7 (d)
15	104.4 (d)	104.1 (d)
16	177.3 (s)	177.6 (s)
17	103.6 (d)	103.3 (d)
18	33.0 (q)	36.2 (q)
19	21.2 (q)	21.6 (q)
20	15.3 (q)	16.7 (q)
1′	173.0 (s)	174.7 (s)
2′	36.7 (t)	36.6 (t)
3′	18.7 (t)[c]	18.6 (t)
4′	13.8 (q)	13.7 (q)

[a] $CDCl_3$, 75 MHz. [b] $CDCl_3$, 50 MHz. [c] Signals reassigned on the basis of a 2D ^1H–^{13}C correlation experiment on **2**.

H-6β and H-7β and the signal at δ 0.99 (s, 3 H) assigned to the methyl group at C-10. Enhancements were also observed for the H-15α, H-13α/H-14α, H-6β, and H-17 signals upon irradiation of the H-7β signal. The observed dipolar coupling between the H-17 and H-7β signals specifically excluded a possible structure with the lactone carboxylate at C-17 and hemiacetal at C-16 and suggested that the hemiacetal hydroxyl adopts an endo configuration to ring C. This was also intimated by the failure of the C-17 hydroxyl to react with trichloroacetyl isocyanate[7] which smoothly added to the C-6 hydroxyl to afford the corresponding monourethane in quantitative yield.

In the course of the structural elucidation, several unusual reactions of lactone **2** were observed. During the hydrolysis of lactone **2** to triol **4**, the butyrate group first underwent a 1,2-acyl migration to obtain 6α,7α,17β-trihydroxy-15β,17-oxidospongian-16-one 6-butyrate (**5**). In the ^1H NMR spectrum of the rearrangement product **5** the H-5 and H-14 signals were observed at δ 1.82 and 3.57, respectively, both shifted downfield with respect to the values of lactone **2** due to their 1,3-diaxial relationship[8] with the hydroxyl group at C-7.

Although there was no ^1H NMR evidence for equilibrium between a hemiacetal and a ring-opened aldehyde form, acetylation of lactone **2** gave a 1:1 ratio of two isomeric diacetates **6** and **7** in quantitative yield. The ^1H NMR spectrum of diacetate **6** showed downfield shifts for the H-17 signal at δ 6.28 (s, 1 H) and the H-6β signal at 5.62 (dd, 1 H, J = 12.3, 2.7 Hz) and the appearance of two acetate methyl signals at δ 1.98 (s, 3 H) and 2.32 (s, 3 H). The downfield methyl group at δ 2.32 was correlated with the endo acetoxyl group at C–17 which lies in the vicinity of the C-16 carbonyl deshielding cone.[9] Diacetate **7** is an isomer of diacetate **6** that has undergone hemiacetal ring opening and inversion of configuration at C-15 prior to acetylation. The ^1H NMR spectrum of **7** contained an aldehyde proton signal at δ 9.96 (s, 1 H), an acetal proton signal at δ 6.17 (s, 1 H), a deshielded H-6 signal at δ 5.29 (dd, 1 H, J = 12.2, 2.5 Hz), and two acetate methyl signals at δ 2.01 (s, 3 H) and 1.99 (s, 3 H). The ^{13}C NMR spectrum confirmed the presence of a single acetal carbon. The stereochemistry was elucidated from NOE measurements. Irradiation of the H-17 proton caused the expected enhancements of the H-7β, H-6β, and CH_3-20 signals. The enhancement of the H-17 and H-7β signals caused by irradiation of the H-15β signal defined the stereochemistry at C-15. A molecular model of **7** has an H-14α, H-15β dihedral angle of approximately 90° as required by the observed lack of coupling between these protons ($J_{14,15} \simeq$ 0 Hz).

Compound **8** gave a molecular ion at m/z 450 in the mass spectrum. Comparison of the ^1H and ^{13}C NMR spectra of **8** with those of **2** showed that the ABC ring

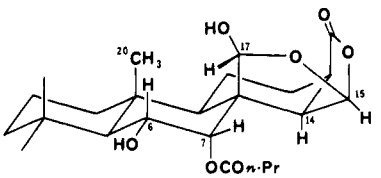

Figure 1. Representation of lactone **2** showing the proximity of selected hydrogen atoms.

Table II. Selected Nuclear Overhauser Enhancement Data

irradiated proton	obsd NOE's (%[a]) 2	7
6β	H-17 (11) H-7β (11)	
7β	H-15α (5), H-17 (7) H-13α/14α (5)	
15β		H-17 (1.7), 7β (14) H-14α (3)
17	H-6β (11), H-7β (5) 17-OH (8), H_3-20 (3)	H-15β (4), H-7β (2) H-6β (5), H_3-20 (1.8)

[a] These reported steady state NOE's are less than maximum since subsaturating decoupler rf power levels were employed on undegassed sample solutions.[6]

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(8) Bhacca, N. S.; Williams, D. H. "Applications of NMR Spectroscopy in Organic Chemistry: Illustrations from the Steroid Field"; Holden-Day: San Francisco, 1964; p 30.

(9) Bhacca, N. S.; Williams, D. H. "Applications of NMR Spectroscopy in Organic Chemistry: Illustrations from the Steroid Field"; Holden-Day: San Francisco, 1964; pp 69–73.

systems were identical. The acetal proton signals of **2** were absent, but new signals were observed at δ 4.13 (d, 1 H, J = 10.2 Hz), 4.35 (d, 1 H, J = 10.2 Hz), and 3.72 (s, 3 H) corresponding to oxymethylene and methoxyl groups, respectively. The ^{13}C NMR spectrum of **8** showed three carboxyl groups (δ 172.7, 174.4, and 175.6), while a band in the infrared spectrum at 1770 cm^{-1} confirmed the presence of a γ-lactone. On the basis of this evidence a tetracyclic *ent*-isocopalane[10] structure is proposed for methyl ester **8**. Ester **8** can be formally derived from **2** by methoxide-initiated lactone ring opening followed by hydride transfer from C-15 to C-17. Since compounds **2** and **8** were obtained from methanol extracts of the sponge, ester **8** may in fact be an artifact of the isolation procedure.

Experimental Section[11]

Extraction of *Aplysilla* sp. Samples of a pink, thinly encrusting sponge (*Aplysilla sp.*) were carefully scraped from substrata (−3 to −10 m) in Port Phillip Bay, Australia (December 1984) and immediately frozen. The sponge (22.3 g, dry weight) was soaked in methanol at 4 °C for 1 week and the methanol extract concentrated in vacuo and partitioned between dichloromethane and water. The organic layer was dried (Na_2SO_4) and evaporated to obtain a yellow oil (1.07 g). A portion of this extract (563 mg) was separated by chromatography over TLC grade silica using hexane, mixtures of ether/hexane, and finally ether/ethyl acetate. Ambliofuran (**3**, 5 mg, 0.04% dry weight) was eluted with hexanes. Further elution with ether/hexane gave a yellow solid (267 mg), which, when triturated with ether/hexane, afforded the crystalline lactone **2** (164 mg). Later fractions were combined with the mother liquors from crystallization of **2** and separated by high-performance LC (Partisil, 9:13 ethyl acetate–hexanes) to obtain more lactone **2** (18 mg, combined weight 182 mg, 1.6% of dry weight) and the ester **8** (13 mg, 0.1% of dry weight).

6α,7α,17β-Trihydroxy-15β,17-oxidospongian-16-one 7-butyrate (2): plates from ether, mp 212–213 °C dec; $[\alpha]_{365}$ +4.9° (c 1.4, $CHCl_3$); CD (MeOH) 215 nm ($\Delta\epsilon$ −3.1); IR ($CHCl_3$) 3600–3200, 1780, 1725 cm^{-1}; 360–MHz ^1H NMR ($CDCl_3$) δ 0.99 (s, 3 H, 20), 1.01 (s, 3 H, 19), 1.02 (t, 3 H, J = 7 Hz, 4′), 1.09 (s, 3 H, 18), 1.47 (d, 1 H, J = 11.5 Hz, 5α), 1.55 (d, 1 H, J = 6 Hz, 5-OH), 1.73 (m, 2 H, 3′), 1.98 (qd, 1 H, J = 12.7, 5 Hz, 11β), 2.37 (br dd, 1 H, J = 13, 5 Hz, 12β), 2.43 (dt, 1 H, J = 16, 7.6 Hz, 2′), 2.47 (dt, 1 H, J = 16, 7.6 Hz, 2′), 2.73 (m, 2 H, $W_{1/2}$ = 8.5 Hz, 13α, 14α), 3.41 (d, 1 H, J = 2 Hz, 17-OH), 4.18 (ddd, 1 H, J = 11.5, 6, 2.7 Hz, 6β), 4.93 (d, 1 H, J = 2.7 Hz, 7β), 5.57 (d, 1 H, J = 2 Hz, 17), 6.06 (m, 1 H, $W_{1/2}$ = 7 Hz, 15); ^{13}C NMR ($CDCl_3$), see Table I; EIMS, m/z (relative intensity) 418 ($M^+ - H_2O$, 1.7), 400 (5.5), 348 (6), 330 (31), 315 (11), 312 (10), 302 (100), 301 (27), 274 (39), 256 (24), 245 (49), 179 (56), 153 (44), 123 (57), 109 (45), 71 (54); high-resolution mass spectrum, obsd m/z 418.2345, $C_{24}H_{34}O_6$ ($M^+ - H_2O$) requires m/z 418.2355, obsd m/z 330.1845, $C_{20}H_{26}O_4$ requires m/z 330.1830.

Methyl ester 8: oil; IR ($CHCl_3$) 3600–3300, 1770, 1730 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.84 (s, 3 H), 1.00 (s, 3 H), 1.03 (t, 3 H, J = 7.3 Hz), 1.09 (s, 3 H), 1.75 (m 2 H), 1.93 (m, 2 H), 2.45 (t, 2 H, J = 7.3 Hz), 2.78 (m, 2 H), 2.87 (d, 1 H, J = 5.6 Hz), 3.72 (s, 3 H), 4.13 (d, 1 H, J = 10.2 Hz), 4.16 (ddd, 1 H, J = 11.4, 7, 2.6 Hz), 4.35 (d, 1 H, J = 10.2 Hz), 5.08 (d, 1 H, J = 2.6 Hz); ^{13}C NMR ($CDCl_3$) 13.7, 15.7, 18.2, 18.7, 20.4, 20.9, 21.8, 33.1, 36.4, 36.5, 38.6, 38.7, 38.9, 43.4, 44.1, 45.7, 46.8, 52.0, 52.7, 69.5, 71.4, 78,2, 172.7, 174.4, 175.6 ppm; EIMS, m/z (relative intensity 450 (M^+, 12), 435 (9, $M^+ - CH_3$), 419 (5, $M^+ - OCH_3$), 362 (100), 316 (72), 71 (59); high-resolution mass spectrum, obsd m/z 362.2096, $C_{21}H_{30}O_5$ ($M^+ - C_3H_7COOH$) requires m/z 362.2092.

Treatment of Lactone 2 with Trichloroacetyl Isocyanate. A solution of lactone **2** (ca. 2 mg) in $CDCl_3$ (ca 0.4 mL) was shaken with trichloroacetyl isocyanate (1 drop). After 5 min the ^1H NMR spectrum showed complete conversion to the corresponding 6-*O*-urethane. No further change was observed (TLC, ^1H NMR) after 3 h: ^1H NMR ($CDCl_3$), partial data, δ 0.94 (s, 3 H), 0.97 (s, 3 H), 1.02 (t, 3 H, J = 7.4 Hz), 1.08 (s, 3 H), 5.06 (d, 1 H, J = 2.3 Hz), 5.46 (dd, 1 H, J = 12.2, 2.4 Hz), 5.63 (d, 1 H, J = 1.6 Hz), 6.03 (m, 1 H, $W_{1/2}$ = 7 Hz), 8.20 (s, 1 H).

Treatment of Lactone 2 with Potassium Carbonate in Methanol. Potassium carbonate (44 mg) was added to a stirred solution of lactone **2** (13.5 mg, 0.031 mmol) in methanol (1.5 mL) at 0 °C. The reaction mixture was allowed to warm to room temperature and after 40 min was concentrated under reduced pressure, diluted with water (10 mL), and extracted with ethyl acetate (2 × 10 mL). The combined organic extracts were washed once with water and evaporated to give a pale yellow solid (5.9 mg) that was separated by LC on Partisil using hexanes–ethyl acetate–2-propanol (99:99:2) as eluant to obtain **5** (2.3 mg) and **4** (0.5 mg). The hydrolysis of **2** to **4** was essentially complete after 72 h.

6α,7α,17β-Trihydroxy-15β,17-oxidospongian-16-one 6-butyrate (5): needles from methanol/water, mp 215–218 °C dec; $[\alpha]_{365}$ −25° (c 0.26, $CHCl_3$); IR ($CHCl_3$) 3580, 1785, 1730 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.87 (s, 3 H), 0.97 (t, 3 H, J = 7.4 Hz), 0.98 (s, 3 H), 1.03 (s, 3 H), 1.82 (d, 1 H, J = 12 Hz), 1.96 (qd, 1 H, J = 13, 4 Hz), 2.09 (br s, 1 H, OH), 2.31 (m, 2 H), 2.78 (dd, 1 H, J = 11.5, 8 Hz), 3.05 (br s, 1 H, OH), 3.42 (br d, 1 H, J = 2 Hz), 3.57 (dd, 1 H, J = 11.5, 6 Hz), 5.39 (dd, 1 H, J = 12, 2 Hz), 5.57 (br s, 1 H), 6.05 (d, 1 H, J = 6 Hz); EIMS, m/z (relative intensity) 418 ($M^+ - H_2O$, 0.7), 389 (28), 330 (25), 302 (10).

6α,7α,17β-Trihydroxy-15β,17-oxidospongian-16-one (4): colorless crystals, mp 233–235 °C dec; IR ($CHCl_3$) 3600–3200, 1780, 1760 (sh) cm^{-1}; ^1H NMR (1% $CD_3OD/CDCl_3$) δ 0.95 (s, 3 H), 1.02 (s, 3 H), 1.13 (s, 3 H), 1.45 (d, 1 H, J = 11.5 Hz), 1.98 (qd, 1 H, J = 13, 4 Hz), 2.31 (br d, 1 H, J = 14 Hz), 2.81 (dd, 1 H, J = 11.4, 7.4 Hz), 3.36 (d, 1 H, J = 2.6 Hz), 3.53 (dd, 1 H, J = 11.4, 6.2 Hz), 3.98 (dd, 1 H, J = 11.5, 2.6 Hz), 5.40 (s, 1 H), 6.06 (d, 1 H, J = 6.2 Hz); EIMS m/z (relative intensity) 349 ($M^+ - H_2O$, 38), 330 (54), 245 (100), 179 (99); high-resolution mass spectrum, obsd m/z 348.1935, $C_{20}H_{28}O_5$ ($M^+ - H_2O$) requires m/z 348.1936.

Acetylation of Lactone 2. A stirred solution of lactone **2** (15.9 mg, 0.036 mmol) in dry pyridine (1.0 mL) was treated with acetic anhydride (1.0 mL) and the mixture was stirred at 25 °C for 20 h then at 70 °C for 5 h. The volatile solvents were removed under high vacuum and the residue triturated with toluene and re-evaporated. Filtration of the residue through silica followed by LC on Partisil (1:1 ethyl acetate–hexane) gave the isomeric diacetates **6** (9.5 mg) and **7** (11.1 mg).

6α,17β-Diacetoxy-7α-hydroxy-15β,17-oxidospongian-16-one 7-butyrate (6): plates from ether, mp 223–224 °C; IR ($CHCl_3$) 1795–1760, 1735 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.83 (s, 3 H), 0.84 (s, 3 H), 0.97 (s, 3 H), 1.05 (t, 3 H, J = 7.4 Hz), 1.73 (d, 1 H, J = 12 Hz), 1.98 (s, 3 H), 2.32 (s, 3 H), 2.59 (dt, 1 H, J = 10.3, 8.3 Hz), 2.97 (dd, 1 H, J = 10.3, 5.3 Hz), 5.44 (d, 1 H, J = 2.7 Hz), 5.62 (dd, 1 H, J = 12, 2.7 Hz), 5.93 (d, 1 H, J = 5.3 Hz), 6.28 (s, 1 H); EIMS, m/z (relative intensity) 505 ($M^+ - CH_3$, 0.6), 302 (100).

6α,15α-Diacetoxy-7α-(butanoyloxy)-16-oxospongian-17-al (7): plates from ether, mp 176–178 °C; IR ($CHCl_3$) 1793, 1762, 1740 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.81 (s, 3 H), 0.83 (s, 3 H), 0.98 (s, 3 H), 1.02 (t, 3 H, J = 7.4 Hz), 1.99 (s, 3 H), 2.01 (s, 3 H), 2.52 (d, 1 H, J = 8.3 Hz), 3.01 (br t, 1 H, J = 8.3 Hz), 5.29 (dd, 1 H, J = 12, 2.5 Hz), 5.72 (d, 1 H, J = 2.5 Hz), 6.17 (s, 1 H), 9.96 (s, 1 H); ^{13}C NMR ($CDCl_3$) 13.8, 16.2, 16.5, 18.3, 18.7, 20.5, 21.3, 21.7, 21.8, 32.8, 35.0, 36.0, 36.3, 38.8, 39.6, 43.1, 45.2, 50.1, 50.6 52.3, 69.5, 69.7, 92.6, 167.7, 169.4, 172.4, 176.1, 201.3; EIMS, m/z (relative intensity) 505 ($M^+ - CH_3$, 0.6), 302 (100).

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