

CHEMISTRY OF SPONGES, IX.¹ NEW DITERPENES FROM THE
MARINE SPONGE *DICTYODENDRILLA CAVERNOSA*

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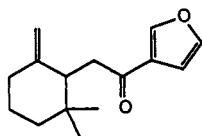
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ABSTRACT.—Spongian-16-one [2] and spongia-15,16-dione [3], two new diterpenes with the spongiane skeleton, have been isolated from the dendroceratid sponge *Dictyodendrilla cavernosa*.

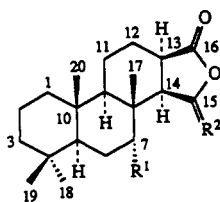
Recently, we described the structure elucidation of a new furanosesquiterpenoid, pallescensone [1], which was obtained from the New Zealand marine sponge *Dictyodendrilla cavernosa* Lendenfeld (Order Dendroceratida, Family Dictyodendrillidae) (1). Further collections from two locations in New Zealand have revealed that there are two chemically distinct types of *D. cavernosa*; one contains pallescensone, and a second lacks pallescensone but contains the two new diterpenes 2 and 3.

Spongian-16-one [2] was obtained (0.058%) from *D. cavernosa*, after chromatography of a hexane extract on Si gel, as a crystalline solid, mp 155–159°, [α]_D +53° (c = 0.0011, CHCl₃). A

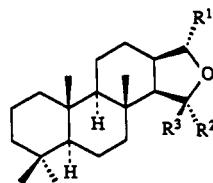
molecular formula of C₂₀H₃₂O₂ was established from the hrms. The ir spectrum showed an absorption at 1765 cm⁻¹ corresponding to a saturated γ -lactone, and the presence of this group was confirmed from the ¹³C-nmr spectrum which contained signals at δ 179.0 (s) and 67.6 (t). The five double bond equivalents required by the molecular formula could be accommodated by a tetracyclic skeleton, one of the rings being that of the γ -lactone. The ¹³C-nmr spectrum (Table 1) suggested that 2 possessed the unrearranged spongiane skeleton found in the diacetate 5 (2), with oxidation at C-16 only. Further support for the spongiane skeleton was provided from the ms: ions at m/z = 205,



1



- 2 R¹=H, R²=H₂
3 R¹=H, R²=O
4 R¹=OAc, R²=H₂



- 5 R¹=R²=OAc, R³=H
6 R¹=H, R²=R³=O

¹For Part VIII, see M.R. Kernan, R.C. Cambie, and P.R. Bergquist, *J. Nat. Prod.*, **53**, 720 (1990).

191, and 123 were attributed to fragmentation of rings B and C as shown in Scheme 1.

TABLE 1. ^{13}C -nmr Chemical Shifts of Spongian-16-one [2], Spongia-15, 16-dione [3], Diacetate 5, and Lactone 6 (CDCl_3).

Carbon	Compound			
	2	3	5 ^a	6 ^b
C-1	40.0 (t) ^c	40.0 (t) ^c	40.1 (t)	39.5 (t)
C-2	18.5 (t) ^d	18.5 (t) ^d	18.5	18.2 (t)
C-3	41.9 (t) ^c	41.8 (t) ^c	42.0 (t)	41.6 (t)
C-4	33.3 (s)	33.3 (s)	33.3 (s)	32.9 (s)
C-5	56.7 (d) ^e	56.4 (d) ^e	56.7 (d)	56.2 (t)
C-6	17.9 (t) ^d	18.1 (t) ^d	18.2	17.6 (t)
C-7	42.1 (t) ^c	42.3 (t) ^c	42.9 (t)	42.7 (t)
C-8	35.7 (s)	37.2 (s)	34.8 (s)	36.0 (s)
C-9	56.4 (d) ^e	56.5 (d) ^e	56.7 (d)	56.2 (d)
C-10	37.3 (s)	37.8 (s)	37.5 (s)	37.7 (s)
C-11	17.2 (t) ^d	17.1 (t) ^d	17.1	16.2 (t)
C-12	22.4 (t)	21.2 (t)	22.5 (t)	23.9 (t)
C-13	37.4 (d)	39.4 (d)	39.2 (d)	33.8 (d)
C-14	50.5 (d)	55.3 (d) ^e	59.1 (d)	54.1 (d)
C-15	67.6 (t)	173.7 (s) ^f	101.7 (d)	178.2 (s)
C-16	179.0 (s)	171.2 (s) ^f	99.7 (d)	70.7 (t)
C-17	15.5 (q)	17.2 (q)	17.1	16.0 (q)
C-18	33.3 (q)	33.3 (q)	33.3 (q)	33.0 (q)
C-19	21.5 (q)	21.6 (q)	21.5	21.2 (q)
C-20	16.3 (q)	16.5 (q)	16.4 (q)	17.7 (q)

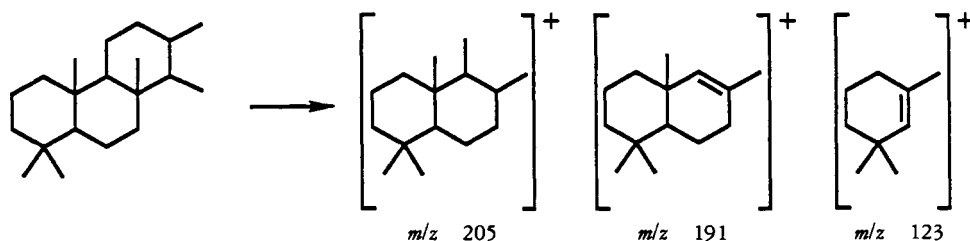
^aData in this column are from Cimino *et al.* (2).

^bData in this column are from Sierra *et al.* (6)

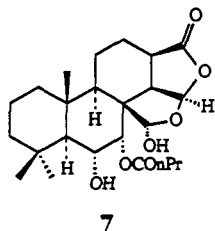
^{c-f}Values in the same column with the same superscript are interchangeable.

Analysis of the ^1H -nmr spectrum of **2** and ^1H - ^1H connectivities observed in a COSY spectrum suggested that **2** was the 7-deacetoxy derivative of the lactone **4** (3). The ^1H -nmr signal assigned to H-15 α [δ 4.09 (dd, $J = 10, 5$ Hz)] was correlated to signals at δ 4.20 (d, $J = 10$ Hz, H-15 β) and δ 2.07 (dd, $J = 8, 5$ Hz, H-14 α). The signal at δ 2.07 also showed a correlation to a signal at δ 2.52 (br dd, $J = 8, 6$ Hz, H-13) that in turn had correlations to signals at δ 1.60 (br ddd, $J = 14, 13, 6$ Hz, H-12 α) and 2.29 (br ddd, $J = 14, 5, 3$ Hz, H-

12 β). The small coupling ($J = 6$ Hz) between H-12 α and H-13 α was consistent with that of an equatorial H-13 α proton and was similar to the H-12 α -H-13 α coupling ($J = 7$ Hz) observed in the spectrum of the lactone **7** (4). The coupling between H-13 α and H-14 α ($J = 8$ Hz) is similar to the coupling observed for other cis lactones such as **4** ($J_{13\alpha, 14\alpha} = 8$ Hz) and **7** ($J_{13\alpha, 14\alpha} = 7$ Hz). A molecular model showed that **2** has an H-14 α -H-15 β dihedral angle of approximately 90° and an H-12 β -H-13 α dihedral angle of approximately



SCHEME 1. Ms fragmentation of the spongiane skeleton.



90°, consistent with the very small coupling observed between these protons ($J_{14\alpha, 15\beta} < 1$ Hz, $J_{12\beta, 13\alpha} < 1$ Hz).

The anhydride spongia-15, 16-dione [3] was obtained (0.041%) as a crystalline compound, mp 152–154°, $[\alpha]_D + 21^\circ$ ($c = 0.0014$, CHCl_3) for which the molecular formula $\text{C}_{20}\text{H}_{30}\text{O}_3$ was established from the hrms. The ir spectrum showed absorptions at 1850, 1785, and 1780 cm^{-1} that were indicative of an asymmetric anhydride group. The ^{13}C -nmr spectrum of 3 (Table 1) indicated that the H-15 protons in 2 were replaced by an oxygen in 3. Peaks at m/z 205, 191, 123 in the mass spectrum provided further support for the presence of an unrearranged spongian skeleton with no oxygen atoms in rings A or B (Scheme 1). The ^1H -nmr and COSY spectra of 3 also suggested that the H-15 protons in 2 were replaced by an oxygen in 3. The signal assigned to H-14 α [δ 2.73 (d, $J = 9$ Hz)] had a correlation to a signal at δ 3.07 (br dd, $J = 9, 7$ Hz) that was assigned to H-13. The signal at δ 3.07 had correlations to signals at δ 2.43 (br dd, $J = 14, 8$ Hz) and δ 1.59 (m) that were assigned to H-12 α and H-12 β , respectively. Most of the remaining signals in the ^1H -nmr spectrum were assigned from analysis of the COSY spectrum. The observed couplings ($J_{12\alpha, 13\alpha} = 7$ Hz, $J_{13\alpha, 14\alpha} = 9$ Hz) for H-13 α suggested that this proton was equatorial and that 3 was a cis lactone, allowing assignment of the relative stereochemistry as shown. Both the ^{13}C - and ^1H -nmr spectra of 3 were consistent with the proposed structure.

Spongian-16-one is the least substituted of the spongian diterpenes that have been isolated as secondary metabo-

lites from sponges of the order Dendroceratida. Although lactones and esters are common natural products, 3 is the first anhydride to be isolated from a marine sponge. The presence of diterpenes in some specimens of *D. cavernosa* and sesquiterpenes in other specimens is unexpected and may indicate that the morphology of the species is more complex than previously supposed.

The racemate of spongian-15-one [6], misnamed as spongian-16-one (5), has been prepared during a synthesis of (\pm)-spongia-13(16), 14-diene (6). Its ^{13}C -nmr spectrum (Table 1) is distinctly different from that of 2.

EXPERIMENTAL

ISOLATION OF NATURAL PRODUCTS.—Individual specimens of freeze-dried *D. cavernosa* (IV Station 134 Terra Nova, British Museum of Natural History; P.R.B.L.R. 7/29/72) collected from Little Barrier Island, New Zealand (April 1988) and the Alderman Islands (May 1988) were extracted with CH_2Cl_2 . Each extract was filtered and screened by tlc (25% EtOAc/hexane) for the presence of diterpenes ($R_f = 0.35$) or pallescensone ($R_f = 0.75$). The extracts that contained diterpenes (2.43 g) were combined and evaporated to give a yellow oil (133 mg) that was separated on a Chromatotron (Si gel, 25–50% EtOAc/hexane) followed by hplc on μ -Porasil (40% Et₂O/hexane) to obtain the lactone 2 (1.4 mg, 0.058%) and the anhydride 3 (1.0 mg, 0.041%).

SPONGIAN-16-ONE [2].—The compound was obtained as colorless needles, mp 155–159°. Found $[\text{M}]^+ 304.2389$, $\text{C}_{20}\text{H}_{32}\text{O}_2$ requires $[\text{M}]^+ 304.2404$. $[\alpha]_D + 52.8^\circ$ ($c = 0.0011$, CHCl_3); ir ν max (CHCl_3) 1765 cm^{-1} (γ -lactone); ^1H nmr (CDCl_3) δ 4.40 (br d, $J = 10$ Hz, H-15 β), 4.09 (dd, $J = 10, 5$ Hz, H-15 α), 2.52 (br dd, $J = 8, 6$ Hz, H-13 α), 2.29 (br ddd, $J = 14, 5, 3$ Hz, H-12 β), 2.07 (dd, $J = 8, 5$ Hz, H-14 α), 1.81 (dt, $J = 13, 3$ Hz, H-1 α), 1.72 (br d, $J = 13$ Hz, H-6 α), 1.60 (brt ddd, $J = 14, 13, 6$ Hz, H-12 α), 1.55 (m, 1H), 1.53 (m, H-11 α), 1.43 (m, 1H), 1.35 (m, 1H), 1.32 (m, 1H), 1.26 (dddd, $J = 15, 13, 12, 3$ Hz, H-11 β), 1.12 (ddd, 1H, $J = 14, 14, 5$ Hz), 1.02 (ddd, 1H, $J = 13, 12, 3$ Hz), 0.95 (ddd, 1H, $J = 17, 12, 7$ Hz), 0.88 (m, 1H), 0.85 (s, 3H), 0.84 (s, 3H), 0.81 (s, 3H), 0.79 (s, 3H), 0.77 (m, H-5), 0.75 (m, H-9); ^{13}C nmr (CDCl_3) see Table 1; ms m/z 304 (3.7% base peak), 289 (23), 285 (12), 248 (15), 205 (20), 191 (100), 123 (60), 95 (60), 69 (70), 55 (50), 41 (60).

SPONGIA-15, 16-DIONE [3].—The com-

pound was obtained as colorless plates, mp 152–154°. Found $[M]^+$ 318.2192, $C_{20}H_{30}O_3$ requires $[M]^+$ 318.2195. $[\alpha]_D^{25} +21.4^\circ$ ($c=0.0014$, $CHCl_3$); ir ν max ($CHCl_3$) 1850, 1785, 1780 cm^{-1} (anhydride); 1H -nmr ($CDCl_3$) δ 3.07 (br dd, $J=9, 7$ Hz, H-13 α), 2.73 (d, $J=9$ Hz, H-14 α), 2.43 (br dd, $J=14, 7$ Hz, H-12 β), 2.19 (br ddd, $J=13, 11, 4$ Hz, H-11 α), 1.73 (dt, $J=13, 3$ Hz, H-1 β), 1.63 (m, H-1 α), 1.59 (m, H-12 α), 1.44 (m, 1H), 1.39 (br dd, $J=15, 3$ Hz, H-6 α), 1.32 (m, H-11 β), 1.2–1.35 (m, 3H), 1.17 (ddd, $J=15, 14, 5$ Hz, H-6 β), 0.94 (s, 3H), 0.87 (s, 3H), 0.87 (m, H-9 α), 0.84 (s, 3H), 0.84 (s, 3H), 0.79 (dd, $J=14, 3$ Hz, H-5); ^{13}C nmr ($CDCl_3$) see Table 1; ms m/z 318 (25% base peak), 303 (61), 285 (8), 275 (17), 262 (15), 233 (11), 215 (9), 205 (9), 191 (13), 161 (10), 138 (40), 123 (100), 109 (50), 95 (65), 82 (45), 81 (50), 69 (80), 55 (60), 41 (70).

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