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CHEMISTRY OF SPONGES, V.[1] DICTYODENDRILLOLIDE, A NEW PRENYLATED BUTENOLIDE FROM A SPONGE

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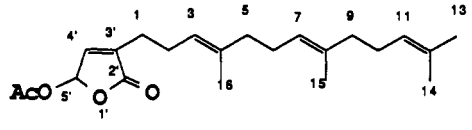
A rare jet-black sponge of the genus *Dictyodendrilla*[2] from the Great Barrier Reef has yielded a new prenylated γ-acetoxy butenolide, dictyodendrillolide [**1**], which was obtained (0.18%) from a hexane extract as an optically active oil after purification by cc and hplc. A molecular formula for **1** of $C_{22}H_{32}O_4$ was established by hrms. The 60-MHz ^{1}H-nmr spectrum showed signals consistent with the presence of an acetate group (δ 2.11, 3H), three *cis*-vinylic methyl groups (δ 1.60, s, 9H), and one *trans*-methyl group (δ 1.67, s, 3H). Comparison of the 15-MHz ^{13}C-nmr spectrum with those of ambliofuran [**2**] (1,2) and thorectolide monoacetate [**3**] (3) suggested the presence of an all *trans*-C_{15} prenyl chain (Table 1). The remaining signals could be accounted for by an acetate group (δ 170.6, s; 20.7, q) and a butenolide group (δ 92.4, d; 138.4, s; 141.3, d; 169.0, s). The ^{1}H- and ^{13}C-chemical shifts ascribed to the butenolide group suggest two possible partial structures (**A** or **B**) for this portion of the molecule. Partial structure **A**, and, thus, the structure of **1**, was chosen on the basis that the ^{13}C-nmr signals for the butenolide moiety of compounds **3** and **5** (4) did not agree with those of **1**, whereas those of compound **4** gave a close match (Table 2). The assignment was supported by the ^{1}H-nmr spectrum of **1**, wherein a broad two-proton singlet at δ 6.78 corresponded with a two-pro-



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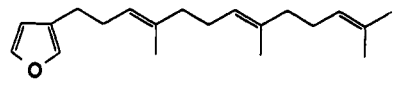

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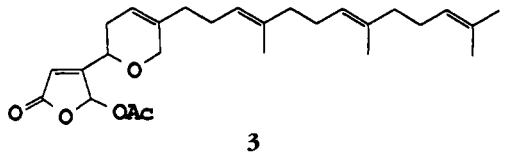

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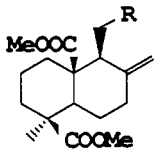
[1]For Part IV see R.C. Cambie, P.A. Craw, M.J. Stone, and P.R. Bergquist, *J. Nat. Prod.*, **51**, 293 (1988).

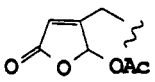
[2]*Dictyodendrilla* n.sp. is a jet-black ramose sponge with conulose surface; it extends 30.0 cm from attachment base, and individual branches are up to 1.5 cm in diameter. The skeletal pattern is regular and rectangular which is typical for the genus. There are seven known species of *Dictyodendrilla* [P.R. Bergquist, *N.Z. J. Zool.*, **7**, 443 (1980)]. Body form and tissue pigmentation are stable taxonomic characteristics in the Dictyodendrillidae, and the new species dicussed here is distinctive in both of these features. Full description of the species must await collection of additional material.

TABLE 1. Comparison of ^{13}C-nmr Chemical Shifts of All *trans*-C_{15} Prenyl Chains.

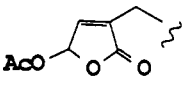
Carbon	Compounds			Multiplicities
	1	**2**	**3**	
1	25.4	28.7	28.3	t
2	25.5	25.3	25.8	t
3	122.0	124.7	123.3	d
4	137.2	134.8	134.8	s
5	39.6	39.9	39.6	t
6	26.6	27.0	26.5	t
7	123.9	124.0	124.0	d
8	135.1	135.5	135.6	s
9	39.7	39.9	39.6	t
10	26.8	26.8	26.6	t
11	124.2	124.3	124.2	d
12	131.2	130.8	131.0	s
13	25.7	25.7	25.7	q
14	17.7	17.7	17.6	q
15	16.0	16.0	15.9	q
16	16.2	16.0	15.9	q



4 R=**A**
5 R=**B**



A



B

ton singlet at δ 6.84 recorded (4) for H-4′ and H-5′ of **4** but not with the presence of two multiplets at δ 5.93 and 6.77 corresponding to H-3′ and H-5′ of **5**. The uv and ir spectral data, λ max 196 nm, ϵ 41900 (αβ-unsaturated ester), ν max 1774 cm^{-1} (γ-lactone), 1661 cm^{-1} (isolated *trans*-olefin), are also consistent with the proposed structure.

No evidence was found for the presence of ambliofuran [**2**] in the sponge.

EXPERIMENTAL

General experimental details are given in Karuso *et al.* (2).

ISOLATION OF DICTYODENDRILLOLIDE [**1**].—A freeze-dried sample (14.6 g) of the *Dictyodendrilla* sp. (Ref. No. P.R.B. P.A. 1. 27/5/84) collected from Pandora Cay, Great Barrier Reef,

TABLE 2. Comparison of ^{13}C-nmr Chemical Shifts of the 5-Acetoxy-(2,5-dihydro)-furan-2-ones and 2-Acetoxy-(2,5-dihydro)-furan-5-ones.

Carbon	Compounds			
	1	**3**	**4**	**5**
2′	169.0	92.8	169.0	94.6
3′	138.4	165.9	138.8	167.1
4′	141.3	118.5	141.1	118.4
5′	92.4	169.1	92.5	169.0

Australia at a depth of 10–12 m, was extracted (Soxhlet) with hexane to give a green gum (0.43 g). This was chromatographed on Si gel to give crude dictyodendrillolide in fractions eluted with 15% EtOAc/hexane. Reversed-phase hplc (90% MeOH/H_2O) yielded pure **1** (26 mg, 0.18% of sponge dry weight) as an unstable (the compound decomposed after storage for one week) colorless oil, $[\alpha]^{23}$ +21.9° (c = 0.43, $CHCl_3$) (found $[M]^+$ 360.2302, $C_{22}H_{32}O_4$ requires 360.2300); ir ν max (CCl_4) 2940, 1788 (OAc), 1774 (γ-lactone), 1661 (*trans* C=C), 1440, 1365, 1327, 1200, 1185, 1010, 980, 962 cm^{-1}; uv λ max (hexane) 196 (ε 41900), 317 nm (ε 80); ^1H nmr δ_H (60 MHz) (CCl_4) 1.60 (br s, 9H, 4,8,12-Me), 1.67 (s, 12-Me), 1.99 (br s, 6H, CH_2), 2.11 (s, 3H, OAc), 2.15 (br m, 2H, CH_2), 5.00 (br t, 3H, H-3, H-7, H-11), 6.78 (br s, 2H, H-4′, H-5′); ^{13}C nmr ($CDCl_3$) see Tables 1 and 2; ms *m/z* $[M]^+$ 360 (5%), $[M-Me]^+$ 345 (2), $[M-Ac]^+$ 317 (7), $[M-HOAc]^+$ 300 (4), 287 (5), 275 (6), 257 (8), 231 (12), 203 (10), 189 (18), 163 (22), 137 (47), 136 (61), 135 (46), 121 (69), 107 (64), 43 (100).

ACKNOWLEDGMENT

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