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**Registry No.** 2a, 65009-00-9; 2b, 85630-17-7; 2c, 85630-18-8; 2d, 85630-19-9; 2e, 85630-20-2; 3a, 85630-42-8; 3b (3-OMe), 85630-43-9; 3b (5-OMe), 85630-44-0; 3c, 85630-45-1; 3d, 85630-46-2; 3e, 85630-47-3; 4a (E = CHO), 85630-21-3; 4a (E = CO<sub>2</sub>H), 85630-22-4; 4a (E = CONEt<sub>2</sub>), 82819-70-3; 4a (E = SiMe<sub>3</sub>), 85630-23-5; 4b (E = CO<sub>2</sub>H), 85630-24-6; 4c (E = CO<sub>2</sub>H), 85630-25-7; 4d (E = Me), 85630-26-8; 4d (E = CHO), 85630-27-9; 4d (E = CO<sub>2</sub>H), 85650-28-8; 4d (E = SiMe<sub>3</sub>), 85630-28-0; 5a (E = Me), 95-48-7; 5a (E = CHO), 90-02-8; 5a (E = CO<sub>2</sub>H), 69-72-7; 5a (E = CONEt<sub>2</sub>), 19311-91-2; 5a (E = SiMe<sub>3</sub>), 15288-53-6; 5b (E = CO<sub>2</sub>H), 3147-64-6; 5c (E = CO<sub>2</sub>H), 2237-36-7; 5d (E = Me), 5307-05-1; 5d (E = CHO), 672-13-9; 5d (E = CO<sub>2</sub>H), 2612-02-4; 5d (E = SiMe<sub>3</sub>), 85630-29-1; 6a, 19311-91-2; 6b, 85630-30-4; 6c, 85630-31-5; 6d, 85630-32-6; 6e, 19351-20-3; 6f, 85630-33-7; 6g, 85630-34-8; 7, 85630-35-9; 8, 85630-36-0; 9a, 85630-37-1; 9b, 85630-38-2; 10a, 85630-39-3; 10b, 85630-40-6; 10c, 85630-41-7; 2-methyl-1-naphthol, 7469-77-4.

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### Novel Diterpenes with a Cyclobutenone Moiety from the Brown Alga *Pachydictyon coriaceum*

**Summary:** The structures of acetylcoriacenone and isoacetylcoriacenone, new diterpenes possessing a cyclobutenone moiety, have been elucidated as 4a and 4b, respectively, by spectral and chemical means.

**Sir:** Brown algae of Dictyotaceae have attracted recent interest because of their variety of unique components that are not found in terrestrial plants. *Pachydictyon coriaceum* of this family, which grows along the California coast, has been reported to produce the unusual diterpenes acetoxycrenulatin<sup>1</sup> and pachydictyol A.<sup>2</sup> The same species, collected on the Japanese coast, has been shown to contain a different diterpene, sanadaol.<sup>3</sup> This communication reports that two new compounds isolated from the same alga have the novel structures 4a and 4b, possessing a cyclobutenone moiety.

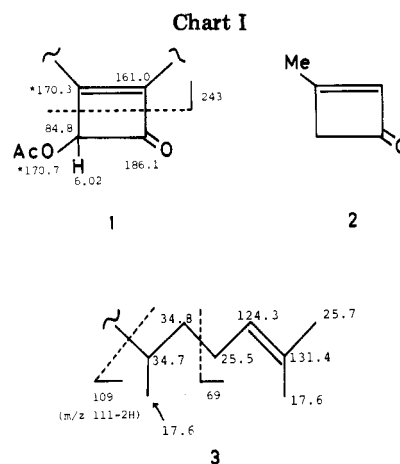
The methanol extract of *P. coriaceum* (collected at Izu-Shimoda beach, Japan, in July 1981) was fractionated chromatographically, giving a fraction containing a pair of isomers. These isomers were separated by preparative TLC (Merck, Kieselgel 60 F-254, hexane-ethyl acetate, 95:5, 11 developments) as viscous oils, which were designated as acetylcoriacenone (0.09% of the methanol extract) and isoacetylcoriacenone (0.07%).

High-resolution mass spectral analysis of acetylcoriacenone<sup>4</sup> showed a molecular ion at  $m/e$  344.233 corresponding to C<sub>22</sub>H<sub>32</sub>O<sub>3</sub>. An intense IR absorption at 1770 cm<sup>-1</sup> and a weak but sharp signal at 1610 cm<sup>-1</sup> suggested

Table I. Nuclear Magnetic Resonance Data for Acetylcoriacenone (4a) and the Epoxide 6a

position no.	carbon-13 chemical shift <sup>a</sup> of 4a	proton chemical shift <sup>b</sup>	
		4a	6a
1	161.0		
2	170.3 <sup>c</sup>		
3	28.5	2.79 (dt, 12, 3) 2.3 <sup>d</sup>	2.67 (ddd, 14, 13, 4) 2.88 (br d, 14)
4	25.2	1.98 <sup>d</sup>  2.28 <sup>d</sup>	1.18 (ddd, 15, 13, 10)  2.28 (br dd, 15, 4)
5	122.8	5.13 (dd, 11, 3)	2.88 (br d, 10)
6	140.4		
7	40.2	1.9 <sup>d</sup> 2.25 <sup>d</sup>	2.22 <sup>d</sup>
8	31.6	<i>e</i> <i>e</i> <i>e</i>	1.85 <sup>d</sup> <i>e</i> <i>e</i>
9	43.4		
10	34.7	1.7 <sup>d</sup>	1.7 <sup>d</sup>
11	34.8	1.3 <sup>d</sup>	<i>e</i>
12	25.5	1.85 <sup>d</sup>	1.85 <sup>d</sup>
13	124.3	5.01 (br t, 7)	5.01 (br t, 7)
14	131.4		
15	25.7	1.67 (br s)	1.67 (br s)
16	17.6	1.57 (br s)	1.57 (br s)
17	17.6	0.91 (d, 7)	0.93 (d, 7)
18	186.1		
19	84.8	6.02 (s)	6.07 (s)
20	16.3	1.41 (br s)	1.07 (s)
AcO	20.8	2.11 s	2.08 (s)
	170.7 <sup>c</sup>		

<sup>a</sup> Determined by off-resonance and selective decoupling experiments at 22.5 MHz. <sup>b</sup> Based on double and triple resonance experiments at 400 MHz. <sup>c</sup> Assignments may be reversed. <sup>d</sup> These chemical shifts were deduced on the basis of double resonance experiments. However, coupling patterns were not clarified, because of overlapping on other signals. <sup>e</sup> Undetermined.



the existence of a highly strained enone system, which was assumed to be included in a cyclobutane ring because these IR absorptions were reasonably close to those reported for 3-methylcyclobutenone (2).<sup>5</sup> A short-wavelength absorption maximum (229 nm) with a small molar absorptivity ( $\epsilon$  6500) in the UV spectrum was also compatible with the reported value (219 nm,  $\epsilon$  6300) of 2.<sup>5</sup> The unusual downfield chemical shifts of the olefinic carbons, 170.3 (or 170.7) and 161.0 ppm, together with the upfield chemical shift of the carbonyl carbon (186.1 ppm) in the <sup>13</sup>C NMR spectrum (Table I) were characteristic of a cyclobutenone moiety.<sup>6</sup>

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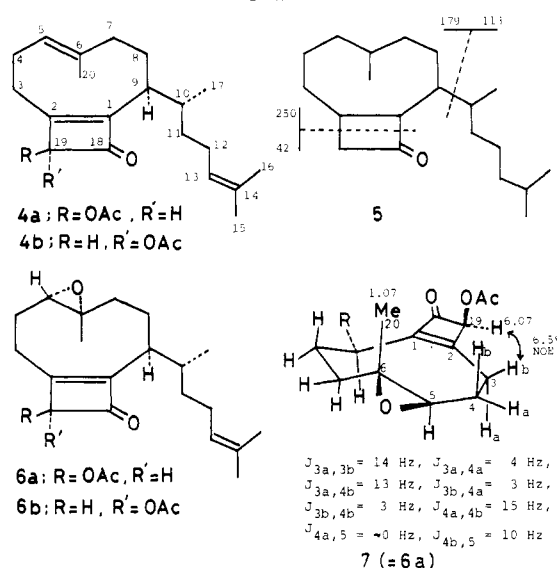
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(4) 4a: mass spectrum (relative intensity, %),  $m/z$  344 (M<sup>+</sup>, 1), 302 (5), 274 (14), 243 (100), 163 (48), 147 (60), 109 (60), 69 (24).

Chart II



The presence of an acetoxy group in acetylcoriacenone was easily recognized from the IR bands at 1740 and 1220  $\text{cm}^{-1}$  and also the sharp singlet at 2.10 ppm in the  $^1\text{H}$  NMR spectrum (Table I). The position of the acetoxy group was assumed to be adjacent to the carbonyl group of the cyclobutenone system on the basis of a downfield singlet at 6.02 ppm (1 H) in the  $^1\text{H}$  NMR spectrum and a doublet at 84.8 ppm in the  $^{13}\text{C}$  NMR spectrum. These properties allowed us to deduce partial structure 1 (Chart I). A fragment at  $m/z$  243 (base peak) in the mass spectrum supported this partial structure.

Further analysis of the spectra of acetylcoriacenone revealed the presence of a side chain 3 ( $^{13}\text{C}$  NMR<sup>7</sup> and mass spectra) and a trisubstituted olefin having a methyl group. The configuration of the olefin was deduced to be *E* from the  $^{13}\text{C}$  chemical shift (16.3 ppm) of the methyl group. In the  $^1\text{H}$  NMR spectrum, the signal due to this methyl appeared relatively upfield (1.41 ppm). Such shielded olefinic methyls are frequently encountered in the  $^1\text{H}$  NMR spectra of sesqui- and diterpenes that consist of medium-sized rings.<sup>8</sup>

Catalytic hydrogenation of acetylcoriacenone brought about removal of the allylic acetoxy, yielding the hexahydro derivative 5<sup>9</sup> (Chart II). An attempted Baeyer-Villiger reaction (MCPBA,  $\text{CDCl}_3$ , room temperature, 72 h) resulted in recovery of 5. This inertness is reasonable only if the carbonyl group of 5 is located close to a bulky group, the side chain. From these facts as well as biogenetic considerations, structure 4a (except the configurations of the substituents) was assumed for acetylcoriacenone. Since hydrogenation of isoacetylcoriacenone

under the same conditions also afforded 5, the structure of this isomer was assumed to be 4b.<sup>10</sup>

Structures 4a and 4b were confirmed by the following experiments, carried out on the epoxides 6a<sup>11</sup> and 6b,<sup>12</sup> which were easily obtained by autoxidation<sup>13</sup> of 4a and 4b. By triple resonance experiments, the protons on C-3, C-4, and C-5 of 6a could be assigned in perspective structure 7. Observation of a 6.5% NOE on 19-H (6.07 ppm) upon irradiation of 3-H<sub>b</sub> (2.88 ppm) lead to confirmation of the location of the acetoxy at C-19. Although no NOE between 19-H and 20-methyl (1.07 ppm) was found for 6a, a 10% NOE was detected between the corresponding proton (5.93 ppm) and methyl (1.00 ppm) for the isomer 6b. On the basis of these findings, the configurations of the acetoxy groups relative to 20-methyls of 6a and 6b were assigned as depicted in the respective structures. The chiroptical properties of 4a and 4b supported these assignments; the CD curves of 4a [226 nm ( $\Delta\epsilon$  -7.8), 316 nm ( $\Delta\epsilon$  1.2)] and 4b [234 nm ( $\Delta\epsilon$  11.6), 317 nm ( $\Delta\epsilon$  -2.2)] are almost antisymmetric, showing that the Cotton effect is primarily affected by the acetoxy adjacent to the carbonyl group and that the acetoxy-cyclobutenone moieties of these two isomers are in an enantiomeric relationship.

Of the possible conformations of epoxide 6a, the conformer 7 (or its enantiomer) is the only one that fulfills the  $^1\text{H}$  NMR properties, that is, coupling patterns, shielding of the methyl at C-6, and NOE.<sup>14</sup>

Compounds 4a and 4b are the first representatives of a novel class of diterpenes that incorporate a cyclobutenone fused to a nine-membered ring system.

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**Registry No.** 4a, 85612-73-3; 4b, 85648-01-7; 6a, 85612-74-4; 6b, 85648-02-8.

(10) 4b: mass and IR spectra are almost identical with those of 4a; UV (EtOH)  $\lambda_{\text{max}}$  229 nm ( $\epsilon$  6100);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  0.96 (d, 3 H,  $J = 6.5$  Hz, 17-H), 1.35 (br s, 3 H, 20-H), 1.58 (br s, 3 H, 16-H), 1.68 (br s, 3 H, 15-H), 2.10 (s, 3 H, Ac), 2.67 (dd, 1 H,  $J = 12, 3$  Hz, 3-H), 5.07 (br t, 1 H,  $J = 7$  Hz, 13-H), 5.19 (dd, 1 H,  $J = 10, 4$  Hz, 5-H), 5.92 (s, 1 H, 19-H);  $^{13}\text{C}$  NMR  $\delta$  16.2 (q), 17.8 (q), 17.8 (q), 20.9 (q), 23.8 (t), 25.4 (t), 25.7 (q), 28.1 (t), 32.7 (t), 34.5 (d), 34.9 (t), 40.4 (t), 43.6 (d), 84.5 (d), 123.6 (d), 124.7 (d), 131.4 (s), 140.3 (s), 163.7 (s), 170.6 (s), 172.9 (s), 187.0 (s).

(11) 6a: mass spectrum,  $m/z$  360 ( $M^+$ , 3), 332 (8), 318 (13), 300 (30), 243 (47), 161 (87), 109 (100), 69 (55), 43 (76); IR ( $\text{CCl}_4$ ) 1765 (s), 1740 (s), 1620 (w), 1220 (s)  $\text{cm}^{-1}$ .

(12) 6b: mass and IR spectra are almost identical with those of 6a;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  0.96 (d, 3 H, 17-H), 1.00 (s, 3 H, 20-H), 1.58 (br s, 3 H, 16-H), 1.68 (br s, 3 H, 15-H), 2.11 (s, 3 H, Ac), 2.62 (td, 1 H,  $J = 13, 4$  Hz, 3-H<sub>a</sub>), 2.75 (dt, 1 H,  $J = 13, 4$  Hz, 3-H<sub>b</sub>), 2.88 (br d, 1 H,  $J = 11$  Hz, 5-H), 5.07 (br t, 1 H,  $J = 7$  Hz, 13-H), 5.93 (s, 1 H, 19-H).

(13) A solution of acetylcoriacenone (17 mg) in  $\text{CDCl}_3$  (0.3 mL) was allowed to stand in a refrigerator for 48 h. Separation of the product by flash chromatography yielded unchanged acetylcoriacenone (14 mg) and the epoxide 6a (2 mg).

(14) If the side chain at C-9 had  $\alpha$  configuration in this conformer, the bulky alkyl chain would come inside the ring, which would make the conformation unfavorable.

(6) Carbon-13 NMR data for cyclobutenones are not well documented. We thank Professor E. A. Shapiro for providing the  $^{13}\text{C}$  NMR spectrum of 4-ethoxy-2,3-dimethylcyclobutenone. The spectrum exhibits signals at  $\delta$  175.0 (C-3), 149.2 (C-2), and 92.3 (C-4). Signals assignable to carbonyl carbon were not recorded, possibly due to the long  $T_1$  of the carbon atom. H<sub>a</sub> appears at  $\delta$  4.62 in the  $^1\text{H}$  NMR spectrum. See; Nefedov, O. M.; Dolgii, I. E.; Shapiro, E. A. *Izv. Akad. Nauk SSSR, Ser. Khim.* 1978, 1209.

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(9) 5: IR ( $\text{CCl}_4$ ) 1770  $\text{cm}^{-1}$ ; mass spectrum,  $m/z$  292 ( $M^+$ , 2), 250 (25), 179 (25), 137 (33), 109 (32), 95 (100), 81 (78), 69 (43). This product is a mixture of stereoisomers, because it shows two intense spots, the  $R_f$  values of which are very close, on TLC.

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