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BICYCLIC DITERPENES FROM TWO SPECIES OF BROWN ALGAE OF THE DICTYOTACEAE

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Key Word Index—*Dictyota dichotoma*; *Pachydictyon coriaceum*; Dictyotaceae; brown algae; structure determination; absolute configuration; diterpene; dictyotin.

Abstract—New diterpenes which possess a decalin skeleton have been isolated from the brown algae, *Dictyota dichotoma* and *Pachydictyon coriaceum* and thier structures including absolute stereochemistry have been determined by NMR spectroscopic and chemical means.

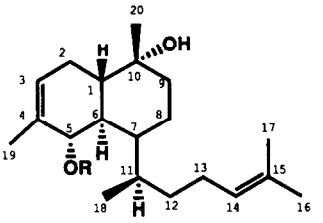
INTRODUCTION

Marine organisms are known to produce unique secondary metabolites, some of which have important biological and pharamaceutical activities [1]. In the course of our investigation on the biologically active components of the Dictyotaceae algae [2], we isolated several cytotoxic diterpenoids having a decalin skeleton. We describe their structures and chemical reactions to show that the carbon framework of the diterpenes is antipodal to that of biflora-4,10(19),15-triene (**12**) [3, 4] which has been isolated from the frontal gland secretion of termite soldiers.

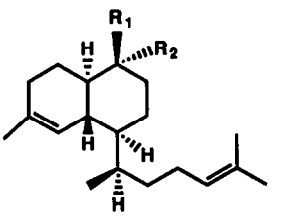
RESULTS AND DISCUSSION

Chromatographic separation of a methanol extract of *Dictyota dichotoma* furnished three cytotoxic diterpenoids, designated dictyotin A (**1**), B (**3**), and C (**4**), and separation of the extract of *Pachydictyon coriaceum* afforded two diterpenes, methyl ether **5** [=methoxydictydiene] [15] and dictyotin D methyl ether (**6**).

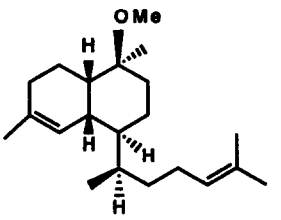
Dictyotin A (**1**), $C_{20}H_{34}O_2$, $[\alpha]_D^{20}$ −4.6° ($CHCl_3$; *c* 0.13), shows an intense IR absorption at 3500–3100 cm^{-1} which is ascribable to a hydroxy band. The ^{13}C NMR spectrum (125 MHz; Table 1) and the fragments at *m/z* 288 $[M-H_2O]^+$ and 270 $[M-2H_2O]^+$ in the mass spectrum revealed that two hydroxy groups were present in dictyotin A. The ^1H NMR spectrum (500 MHz; Table 1) taken in pyridine-d_5 gave well-defined signals, and by the decoupling difference, COSY-45, and C,H-COSY spectra, partial structures **A**–**D** were established (Fig. 1). Structure **D** was reinforced by the fragments at *m/z* 109 and 69 in the mass spectrum [5]. The multiplet at δ2.18 in **D** and the one at δ2.45 of **C** were overlapped with other signals; these two structures, however, could be combined into a larger



1 R = H
2 R = Bz



3 R_1=Me, R_2=OH
4 R_1=OH, R_2=Me
5 R_1=Me, R_2=OMe



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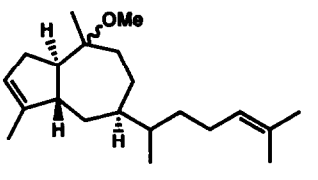

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*Author to whom correspondence should be addressed.

Table 1. ^1H and ^{13}C NMR spectral data for dictyotin A (1)

C	^1H δ*	^{13}C δ†
1	1.80 *ddd* (12, 11, 6)	41.0 *d*
2a	2.56 *ddq* (18, 11, 3)	24.5 *t*
2b	2.13 *m*	
3	5.48 *br s*	121.0 *d*
4		136.2 *s*
5	4.39 *br d*, (9)	68.8 *d*
6	2.46 *m*	43.2 *d*
7	2.45 *m*	34.1 *d*
8a	2.15 *tt* (13, 1.5)	20.3 *t*
8b	1.76 *dtd* (13, 3.5, 1.5)	
9	1.65 *m*	37.2 *t*
10		67.9 *s*
11	2.18 *m*	31.0 *d*
12	1.63 *m*	37.2 *t*
	1.33 *m*	
13	2.05 *m*	25.6 *t*
	1.97 *m*	
14	5.16 *br t* (7)	124.4 *d*
15		129.3 *s*
16	1.54 *br s*	24.4 *q*
17	1.48 *br s*	16.3 *q*
18	1.03 *d*, (7)	18.2 *q*
19	1.92 *br s*	19.0 *q*
20	1.23 *s*	28.0 *q*

*500 MHz in pyridine-d_5, residual pyridine as internal reference. Coupling constants are given in Hertz in parentheses.

†125 MHz in pyridine-d_5, pyridine-d_5 as internal reference. Multiplicity and assignments of the carbon signals were determined by INEPT and ^{13}C–^1H COSY experiments.

substructure by analysing the COSY spectrum taken in chloroform-*d*, in which the corresponding signals in **D** and **C** appear as isolated multiplets at δ1.85 and 2.03, respectively. Furthermore, connection of this substructure to **A** and **B** led to structure **1** (plain). The NOEs between H-3/H-2 and H-19/H-5 supported this structure. The axial properties of H-1, H-5 and H-6 are apparant from their coupling patterns (Table 1). The diaxial relationship between H-1 and H-6 has established the *trans*-decalin skeleton of dictyotin A. Because H_3-20 shows NOE to H-1, the methyl must be *cis* to H-1. The coupling constant between H-6 and H-7 was undeterminable because of the proximity of their chemical shifts (δ2.46 and 2.45, respectively). We at first assumed the equatorial orientation of the bulky side chain, and, because the benzoate (**2**) of dictyotin A showed negative $\Delta\varepsilon$ (λ_{max} 233 nm; $\Delta\varepsilon - 7.9$) in the CD spectrum [6], structure **1'** with the equatorial side chain was proposed for dictyotin A. However, this structure, in which C-7 had the *R*-configuration, seemed to be unusual, because the majority of the diterpenes isolated from the Dictyotaceae have the *S*-configuration at that carbon [7–9]. Therefore, we reinvestigated the NMR spectral properties of **2** in more detail. The ^1H NMR spectrum of **2** (C_6D_6) showed the signals due to H-6 and H-7 at δ2.64 and 2.10. Astonishingly, the coupling constant between them was found to be 6 Hz, showing the side chain is oriented in an axial manner. This was also confirmed by observation of an NOE between H_3-18 and H-1. On the basis of this finding, in addition to the CD data, structure **1** including the absolute configuration was assigned to dictyotin A. The NOEs depicted in **1a** are consistent with the assigned structure. Determination of the configurations at C-11 of **1** and other compounds will be described later.

Dictyotin B (**3**), $C_{20}H_{24}O$, $[\alpha]_D^{20} - 30°$ ($CHCl_3$; *c* 0.19), and dictyotin C (**4**), $C_{20}H_{24}O$, $[\alpha]_D^{20} + 5°$ ($CHCl_3$; *c* 0.61), are isomers and showed similar ^1H and ^{13}C NMR spectra (Table 2). Their structures were determined in essentially the same manner as described above. The *trans* fusion of the decalin skeleton of **3** and **4** was deduced from the coupling constant between H-1 and H-6 (both 10 Hz in **3** and **4**) in the ^1H NMR spectra (pyridine-d_5). Also, the *trans* relationship between H-6 and H-7 of both compounds was established by their coupling patterns ($J_{6,7}$ = 12 Hz in **3** and **4**). Contrary to **1**, the side chains of both compounds are located in equatorial positions. In the phase-sensitive NOESY spectra, H-20 of **3** shows an NOE cross peak to H-6, revealing the axial orientation of the methyl, and H-20 of **4** exhibits an NOE to H-1, suggesting the equatorial orientation of the methyl.

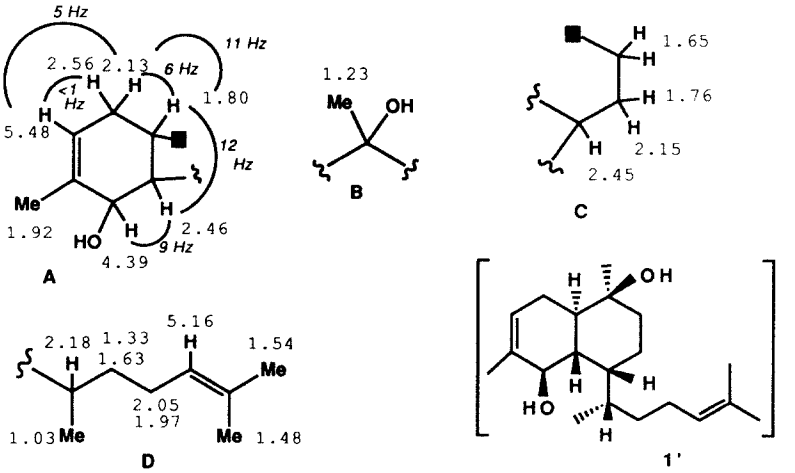
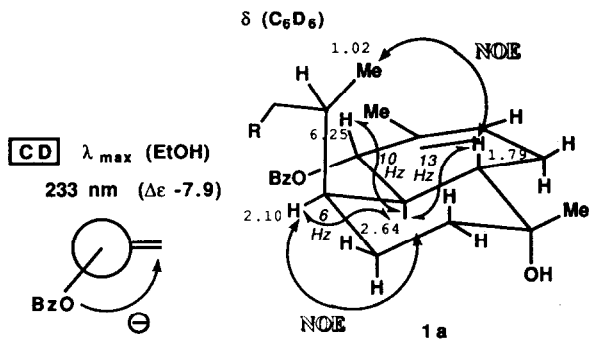


Fig. 1. Partial structures for compound **1**.



In order to determine the absolute configurations of **3** and **4**, the following chemical transformations involving a transannular cyclization were carried out using (−)-dilophol (**8**), the absolute configuration of which has been established by X-ray crystallography [10]. (−)-Dilophol was acetylated, and the acetate (**9**) allowed to stand with silica gel and dichloromethane, affording (−)-obscuronatin (**10**) [5, 11, 12]. Treatment of **10** with 1 mM sulphuric acid in aqueous acetone yielded a mixture of dehydrated products together with **3** and **4**. The $[\alpha]_D$ value of synthetic **3** [$-30°$ ($CHCl_3$; *c* 0.29)] was identical to that of natural **3**, which established the absolute configuration of dictyotin B as depicted in the structure. Synthetic **4** contained an inseparable impurity (^1H NMR spectrum) and showed an $[\alpha]_D$ value different from that of natural **4**. The transannular cyclization of obscuronatin (**10**) may have proceeded through the cationic intermediates **13** and **14** as previously proposed by Kodama *et al.* for the cyclization of a sesquiterpenoid [13, 14].

The structure and absolute configuration of **3** was further confirmed by converting it into **11** by dehydration with phosphorous oxytrichloride. The ^1H and ^{13}C NMR spectra of **11** were identical with those of (−)-biflora-4,10(19),15-triene (**12**), a termite soldier diterpene [4, 11]. However, $[\alpha]_D^{20}$ (+72°) of **11** was in an antipodal relation to that (−92°) of **12**.

Methyl ether **5**, $C_{21}H_{36}O$, $[\alpha]_D^{20}$ −48° ($CHCl_3$; *c* 0.59), showed ^1H and ^{13}C NMR spectra (Table 3) very similar to those of **3** and **4**, except that a methoxy signal was present in the spectra of **5**. Confusing was the fact that the NMR properties of **5** were identical to those of methoxydictydiene (**7**)* [15]. The structure **5** was verified by detailed analysis of the 1D and 2D ^1H NMR spectra (pyridine-d_5), which revealed the proton network illustrated below. Furthermore, NOEs were observed between H-6 and H-5, and H-11 and H-5 in the NOESY spectrum. The structure **7** is incompatible with these findings. Therefore, we concluded that structure **7** of methoxydictydiene should be altered to **5**.

*The ^{13}C NMR data reported in this reference are erroneous. Direct comparison of the spectrum of methoxydictydiene with that of **5** revealed that they coincide. The data described in the present paper are correct.

Table 2. ^1H and ^{13}C NMR spectral data for dictyotin B (**3**) and dictyotin C (**4**)

	3		**4**	
C	^1H δ*	^{13}C δ†	^1H δ*	^{13}C δ†
1	1.44 *ddd* (12, 10, 2)	50.9 *d*	1.08 *ddd* (12, 10, 2)	49.1 *d*
2a	2.37 *ddt* (12, 6, 2)	23.4 *t*	1.97 *ddd* (15, 6, 2)	23.6 *t*
2b	1.23 *dd* (12, 6)		1.69 *m*	
3a	1.93 *m*	31.6 *t*	1.97 *m*	31.5 *t*
3b	1.85 *br dd* (16, 6)		1.88 *br dd* (17, 6)	
4		134.9 *s*		134.2 *s*
5	5.55 *br s*	123.4 *d*	5.66 *br s*	123.9 *d*
6	1.78 *br dd* (12, 10)	40.0 *d*	2.42 *br dd* (12, 10)	37.9 *d*
7	1.15 *m*	45.6 *d*	1.16 *tt* (12, 3)	45.6 *d*
8a	1.44 *m*	22.8 *t*	1.37 *dq* (13, 3)	20.8 *t*
8b	1.11 *qd* (12.5, 3.5)		1.74 *qd* (13, 3)	
9a	1.68 *td* (12.5, 3.5)	43.3 *t*	1.40 *td* (13, 3)	41.6 *t*
9b	1.93 *dt* (12.5, 3.5)		1.85 *dt* (13, 3)	
10		71.1 *s*		69.6 *s*
11	1.93 *m*	31.4 *d*	2.01 *d sextet* (3, 7)	31.7 *d*
12	1.20 *q* (7)	36.3 *t*	1.24 *m*	36.2 *t*
13	1.93 *q* (7)	26.7 *t*	1.95 *m*	26.8 *t*
14	5.11 *br t* (7)	125.6 *d*	5.15 *br t* (7)	125.8 *d*
15		131.1 *s*		131.1 *s*
16	1.58 *br s*	25.9 *q*	1.59 *br s*	25.9 *q*
17	1.48 *br s*	17.9 *q*	1.51 *br s*	17.9 *q*
18	0.74 *d* (7)	13.8 *q*	0.78 *d* (7)	13.9 *q*
19	1.57 *br s*	24.2 *q*	1.61 *br s*	24.1 *q*
20	1.18 *s*	21.4 *q*	1.28 *s*	29.2 *q*

*500 MHz in pyridine-d_5, residual pyridine as internal reference. Coupling constants are given in Hertz in parentheses.

†125 MHz in pyridine-d_5, pyridine-d_5 as internal reference. Multiplicity and assignments of the carbon signals were determined by INEPT and ^{13}C–^1H COSY experiments.

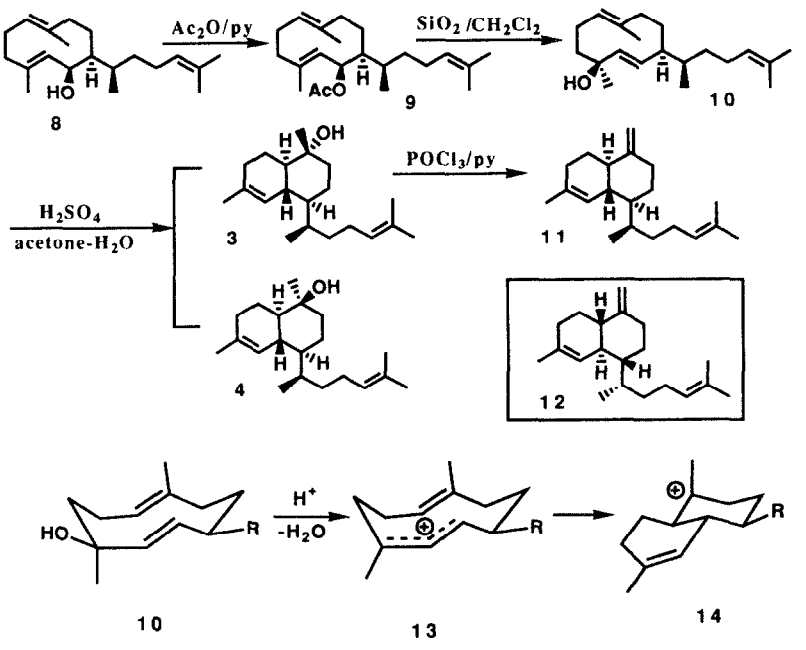


Table 3. ^{1}H and ^{13}C NMR spectral data for methoxydictydiene (**5**) and dictyotin D methyl ether (**6**)

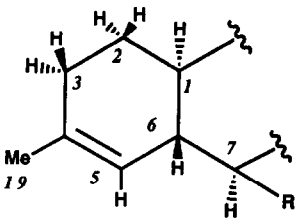
	5		**6**	
C	^{1}H δ*	^{13}C δ†	^{1}H δ*	^{13}C δ‡
1	1.34 *ddd* (12, 10.5, 2)	47.4 *d*	1.72 *br d* (13)	42.2 *d*
2a	2.00 *ddt* (12, 6, 2)	23.0 *t*	1.45 *m*	20.8 *t*[a]
2b	1.04 *qd* (12, 6)		1.36 *m*	
3a	1.86 *m*	31.3 *t*	1.85 *m*	31.6 *t*[b]
3b	1.77 *br dd* (17, 6)			
4		134.9 *s*		133.1 *s*
5	5.51 *br s*	123.2 *d*	5.56 *br d* (6)	125.4 *d*
6	1.74 *m*	39.6 *d*	2.38 *m* (10, 6)	34.0 *d*
7	1.02 *m*	45.2 *d*	1.35 *m*	42.2 *d*
8a	1.41 *dq* (12.5, 3.5)	22.2 *t*	1.12 *m*	19.6 *t*[a]
8b	0.96 *qd* (12.5, 3.5)		1.35 *m*	
9a	1.33 *td* (12.5, 3.5)	36.0 *t*	1.15 *m*	31.8 *t*[b]
9b	1.67 *dt* (12.5, 3.5)		1.59 *br d* (13)	
10		76.0 *s*		76.1 *s*
11	1.88 *m*	31.3 *d*	1.76 *d sextet* (3, 7)	31.7 *d*
12	1.18 *q* (7.5)	36.2 *t*	1.18 *m*	36.0 *t*
13	1.90 *m*	26.7 *t*	1.85 *m*	26.4 *t*
			1.93 *m*	
14	5.10 *br t* (7)	125.6 *d*	5.05 *br t* (7)	125.2 *d*
15		131.2 *s*		130.9 *s*
16	1.58 *br s*	25.9 *q*	1.55 *br s*	25.7 *q*
17	1.49 *br s*	17.9 *q*	1.45 *br s*	17.7 *q*
18	0.70 *d* (7)	13.7 *q*	0.78 *d* (7)	13.6 *q*
19	1.55 *br s*	24.1 *q*	1.53 *br s*	23.6 *q*
20	0.95 *s*	17.6 *q*	0.94 *s*	22.5 *q*
MeO	3.06 *s*	48.1 *q*	3.03 *s*	47.9 *q*

*500 MHz in pyridine-d_5, residual pyridine as internal reference. Coupling constants are given in Hertz in parentheses.

†125 MHz in pyridine-d_5, pyridine-d_5 as internal reference. Multiplicity and assignments of the carbon signals were determined by INEPT and ^{13}C–^{1}H COSY experiments.

‡22.5 MHz in $CDCl_3$, $CDCl_3$ as internal reference.

[a,b]Assignments are interchangeable.



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$J_{1,2\alpha}$=2 Hz, $J_{1,2\beta}$=12 Hz, $J_{1,6}$= 10.5 Hz, $J_{2\alpha,2\beta}$=12 Hz, $J_{2\alpha,3\alpha}$=6 Hz, $J_{2\alpha,3\beta}$=2 Hz, $J_{2\beta,3\alpha}$=12 Hz, $J_{2\beta,3\beta}$=6 Hz $J_{3\alpha,3\beta}$=17 Hz, $J_{5,6}$=0 Hz, $J_{6,19}$=2 Hz

Dictyotin D methyl ether (**6**), $C_{21}H_{36}O$, $[\alpha]_D^{20}$ −77° ($CHCl_3$; *c* 0.59), exhibits a ^1H NMR spectrum in which the signals are seriously overlapped in the aliphatic region. Although all the proton signals were not assignable, it was, fortunately, possible to pick up the key signals that were essential to deduce its carbon skeleton and stereochemistry. The *cis*-fusion of the decalin skeleton was indicated by the NOE from H-1 (δ1.72) to H-6 (δ2.38) as well as the coupling constant (6 Hz) between H-5 (δ5.56) and H-6. The large coupling constant (10 Hz) between H-6 and H-7 established the equatorial orientation of the side chain at C-7. The NOE from OMe-20 to H-6 indicated their *syn*-relation. Because compounds **5** and **6** contain methoxy functionalities, and the alga was stored in methanol, their synthesis via solvolysis is likely.

The side chain, 6-methyl-55-hepten-2-yl moiety, is included in a number of marine diterpenes, but, in many cases [16–18], the stereochemistry at the 2-position of the group has remained unsolved, plausibly because the side chain has been thought to be mobile and does not have a fixed conformation. (There are some examples of the determination of the stereochemistry at this position by chemical means [19]). However, with regard to the present diterpenes, the configurations at C-11 could be determined by detailed analyses of the ^1H NMR spectra including 2D NOESY spectra; the coupling constants between H-11 and H-7 of the diterpenes were all *ca* 3 Hz. These *J* values, together with the fact that NOEs were observed between H-11 and H-7 in all the compounds, suggest that the side chain of the each compound does not freely rotate around the C-7/C-11 axis and it exists in a certain fixed conformation so that H-11 and H-7 may form a dihedral angle of *ca* 60°. The configurations at C-11 of **1**–**6** were determinable from the *J*-values and the NOEs depicted in Fig. 2.

The present diterpenes [20–22] show the following cytotoxicity against murine B16 melanoma cells (IC_{50}); dictyotin A (**1**): 8 μg ml^{-1}, dictyotin B (**3**): 3 μg ml^{-1}, dictyotin C (**4**): 15 μg ml^{-1}, methoxydictyldiene (**5**): 10 μg ml^{-1}, dictyotin D methyl ether (**6**): 19 μg ml^{-1}.

EXPERIMENTAL

GC-MS spectra were measured using a glass column (1% OV-1; 0.5 × 100 cm). Optical rotations are recorded using a 10 cm microcell.

Extraction and isolation. Pachydictyon coriaceum (20 kg) was collected in June 1981 at the Izu-Shimoda beach, and *D. dichotoma* (18 kg) was obtained at Yagachi, Okinawa, in June 1983. Voucher specimens are preserved at the Experimental Fishery Station at Okinawa (Itoman). Identification of seaweeds was performed by Prof. M. Chihara (University of Tsukuba) to whom we are grateful. Seaweeds were soaked in MeOH immediately after collection and allowed to stand for 1 week. The respective MeOH extracts were concd and the residues successively washed with hexane, CH_2Cl_2 and EtOAc.

The hexane extract from *D. dichotoma* was concd to give a dark green residue (100 g) and this material was repeatedly sepd by CC on silica gel (Merck, Kieselgel 60 and Wako, Wakogel C-

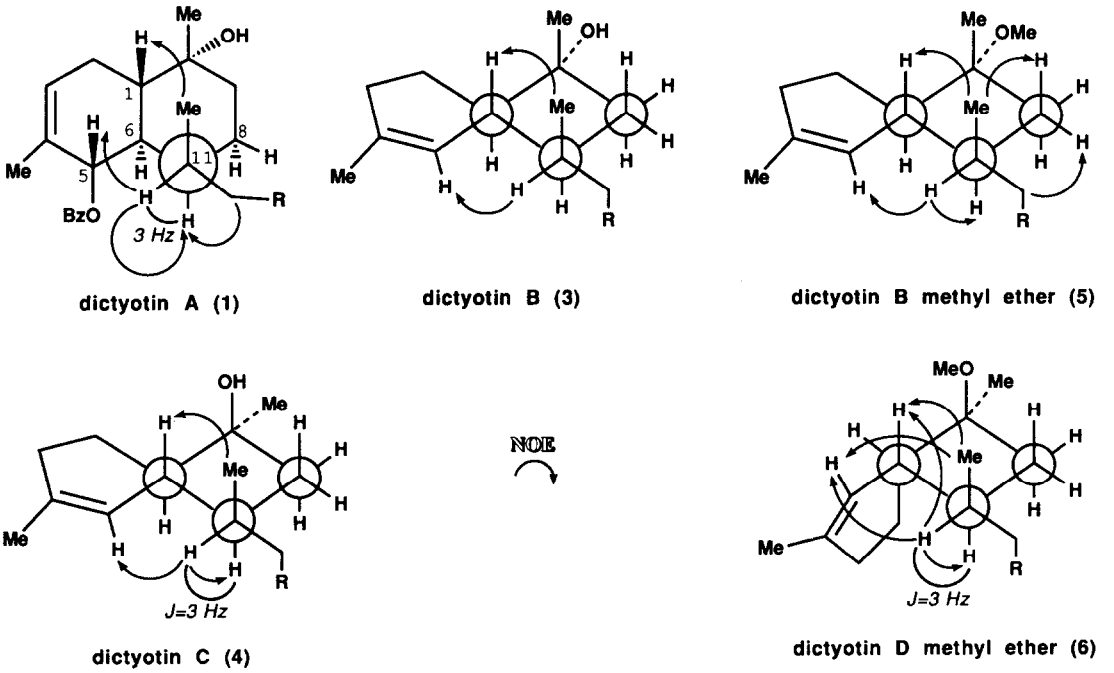

Fig. 2. NOEs used for determination of configurations at C-11 of compounds **1**, **3**–**6**.

300). Further purification by prep. TLC [Merck GF_{254}, 0.5 mm, hexane–EtOAc (7:3)] afforded dictyotin A (**1**; 4 mg), dictyotin C (**4**; 12 mg) and crude dictyotin B, which was further purified by HPLC [JAI GS-310; $CHCl_3$] to obtain pure dictyotin B (**3**; 30 mg). The hexane extract of *P. coriaceum* was concd to give a brown residue (93 g). Sepn by CC on silica gel and prep. TLC (0.5 mm, CH_2Cl_2) afforded pure methoxydictydiene (**5**; 8 mg) and dictyotin D Me ether (**6**; 8 mg).

Dictyotin A (**1**). HREIMS (probe) 20 eV, *m/z* 306.2561 ($C_{20}H_{34}O_2$, requires 306.2559), EIMS (probe) 20 eV, *m/z* (rel. int.): 306 $[M]^+$ (2), 288 $[M-18]^+$ (22), 270 (9), 177 (56), 175 (51), 159 (100), 109 (43), 69 (60). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3500–3200, 2910, 1440, 1370.

Dictyotin B (**3**). HREIMS (probe) 70 eV, *m/z* 290.2610 ($C_{20}H_{34}O$, requires 290.2610), EIMS (probe) 20 eV, *m/z* (rel. int.): 290 $[M]^+$ (36), 272 $[M-18]^+$ (76), 257 (19), 187 (59), 159 (100). IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3590, 2960, 2930, 2860, 1450, 1380, 1100, 930, 910.

Dictyotin C (**4**). HREIMS (probe) 70 eV, *m/z* 290.2587 ($C_{20}H_{34}O_2$, requires 290.2610), EIMS (probe) 20 eV, *m/z* (rel. int.): 290 $[M]^+$ (3), 272 $[M-18]^+$ (83), 257 (11), 187 (41), 161 (100). IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3610, 2960, 2930, 2860, 1450, 1375, 905, 880.

Methoxydictydiene (**5**). HREIMS (probe) 70 eV, 304.2793 ($C_{21}H_{36}O$, requires 304.2766), EIMS (probe) 20 eV, *m/z* (rel. int.): 304 $[M]^+$ (2), 272 $[M-MeOH]^+$ (90), 257 (7), 188 (46), 159 (62), 85 (100). IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1450, 1375, 1075, 865.

Dictyotin D methyl ether (**6**). HREIMS (probe) 70 eV, *m/z* 304.2756 ($C_{21}H_{36}O$, requires 304.2766), EIMS (probe) 20 eV, *m/z* (rel. int.): 304 $[M]^+$ (2), 272 $[M-MeOH]^+$ (100), 157 (8), 187 (54), 159 (64), 85 (71). IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1450, 1375, 1080, 885.

Benzoylation of dictyotin A (**1**). Benzoyl chloride (50 μl: 0.36 mmol) was added to a soln of dictyotin A (**1**; 1.3 mg, 4.2 μmol) in pyridine (0.1 ml) and the reaction mixt allowed to stand at room temp. for 18 hr. H_2O was added and the product taken up in CH_2Cl_2. The organic layer was washed with H_2O, brine, and dried (Na_2SO_4). Solvent was evapd to afford a crude product (9.0 mg). Purification by prep. TLC (0.5 mm, CH_2Cl_2) yielded pure benzoate (**2**; 1.3 mg, 75%); $C_{27}H_{38}O_3$; EIMS (probe) 20 eV, *m/z* (rel. int.): 410 $[M]^+$, 288, 270, 230, 186, 159 (base), 105. UV λ_{max}^{EtOH} nm (log ε): 228 (13 000); CD $\Delta\varepsilon_{233}$ – 7.9 (EtOH; *c* 0.0052); ^1H NMR (C_6D_6, 500 MHz): δ 0.98 (3H, *s*, H-20), 1.02 (3H, *d*, J = 7 Hz, H-18), 1.28 (1H, *ddd*, J = 14, 4, 3 Hz, H_a-9), 1.35 (2H, *m*, H-12), 1.48 (3H, *br s*, H_3-17), 1.56 (1H, *td*, J = 14, 4.4 Hz, H_b-9), 1.70 (3H, *br s*, H-16), 1.7–1.8 (3H, *m*, H-8, H-1, 1.84 (3H, *br s*, H-19), 2.0 (3H, *m*, H_b-2, H-13), 2.10 (1H, *m*, $W_{1/2}$ = 15 Hz, H-7), 2.25 (1H, *d sextet*, J = 3, 7 Hz, H-11), 2.32 (1H, *ddq*, J = 18, 10, 3 Hz, H_a-2), 2.64 (1H, *ddd*, J = 13, 10, 6 Hz, H-6), 5.19 (1H, *br t*, J = 7 Hz, H-14), 5.53 (1H, *br s*, H-3), 6.25 (1H, *dd*, J = 10, 1.5 Hz, H-5), 7.10 (3H, *m*, ArH), 8.25 (2H, *d*, J = 8 Hz, ArH).

Acetylation of (−)-dilophol (**8**). (−)-Dilophol [10] (74 mg, 0.2 mmol) was treated with Ac_2O (0.7 ml) and pyridine (0.6 ml) at room temp. for 18 hr. Excess reagents were evapd with an oil pump to give a yellow residue (**9** [5]; 79 mg, 92%). The ^1H NMR spectrum showed that the product was pure enough, and therefore, this material was used in the next reaction.

Conversion of (−)-dilophol acetate (**9**) *to obscuronatin* (**10**). A mixt. of dilophol acetate (**9**, 60 mg, 0.2 mmol) and silica gel (Merck, 2 g) in hexane–EtOAc (49:1, 10 ml) was allowed to stand at room temp. for 18 hr. Silica gel was removed by filtration and washed with 5 × 20 ml portions of EtOAc. The EtOAc extract was concd and the residue chromatographed on silica gel [hexane–EtOAc (49:1)], affording (−)-obscuronatin (**10** [11, 12]; 13.7 mg, 26%). The ^1H NMR spectrum of **10** was identical with that reported in the lit.

Conversion of obscuronatin (**10**) *to dictyotin B* (**3**) *and C* (**4**). A soln of obscuronatin (**10**; 13 mg, 0.04 mmol) in 1 mM H_2SO_4 in 10% aq. Me_2CO (1 ml) was stirred at 0° for 20 min. The soln was dild with H_2O and extracted with Et_2O. The Et_2O layer was washed with brine and dried (Na_2SO_4). Sepn of the crude product by flash chromatography [hexane–EtOAc (23:2)] yielded dictyotin B (**3**; 5.7 mg, 44%) and dictyotin C (**4**; 2.7 mg, 21%).

Dehydration of dictyotin B (**3**). To a soln of dictyotin B (**3**; 5.7 mg, 0.02 mmol) in pyridine (1.2 ml), was added a soln of $POCl_3$ (0.2 ml, 2 mmol) in pyridine (0.6 ml) at −15° for 35 min and at 15° for 150 min. The reaction soln was poured onto ice and the product taken up into Et_2O. The Et_2O extract was washed with H_2O and dried (Na_2SO_4). Removal of solvent afforded a crude oil (5 mg), from which the hydrocarbon [**11** [3]; 3 mg, 50%; HREIMS (probe) 20 eV *m/z* 272.2503 ($C_{20}H_{34}$, requires 272.2504)] was obtained by prep. TLC (0.5 mm, hexane).

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