Tetrahedron Vol 47, No. 8, pp. 1399-1410, 1991
Printed in Great Britain

0040-4020/91 $3.00+.00
Pergamon Press plc

NEW XENICANE AND HYDROAZULENOID DITERPENES FROM AN AUSTRALIAN COLLECTION OF *DICTYOTA DIVARICATA*

Gabriele M. König, Anthony D. Wright and Otto Sticher

Department of Pharmacy, Swiss Federal Institute of Technology
(ETH) Zurich, CH-8092, Zürich, Switzerland.

(*Received in Germany* 17 *October* 1990)

ABSTRACT-Seven new diterpenes and one already known diterpene have been isolated from the brown alga, *Dictyota divaricata*, collected from the Great Barrier Reef region of northern Australia. Of the novel diterpenes, five are xenicane derivatives (**1**-**5**) and two are hydroazulenoid diterpenes (**6** and **7**). The structures of **1**, [(2*R*, 3*R*, 4*S*, 6*E*, 9*E*, 10*R*)-17, 4-hydroxyxenic-6, 9, 13-trien-1-al-18-oic acid lactone], **2**, [(2*R*, 3*R*, 6*E*, 9*E*, 10*R*)-17-xenic-6, 9, 13-trien-1-al-18-oic acid lactone], **3**, [(2*R* 3*R*, 4*S*,, 6*R*, 7*R*, 9*E*, 10*R*)-17, 6, 7-epoxyxenic-4-hydroxy-9, 13-dien-1-al-18-oic acid lactone], **4**, [(2*R*, 3*R*, 4*S*,, 6*E*, 9*E*, 10*R*)-17-acetoxyxenic-4-hydroxy-6, 9, 13-trien-1, 2-dial], **5**, [17-acetoxy-4α-hydroxycrenulide], **6**, [deacetoxydictyol H], and **7**, [2-hydroxydictyoxide] were assigned by interpretation of their spectral parameters and by comparison with published data of selected known compounds.

INTRODUCTION

Algae of the genus *Dictyota* are known to be a rich source of many different structural classes of diterpenes. However, prior to the current investigation, samples of *D. divaricata* from Caribbean waters have yielded exclusively diterpenes of the dolabellane-type [1, 2]. In the present study a sample of *D. divaricata* collected from Australian waters was found to elaborate diterpenes of the xenicane (**1**-**5**) and hydroazulenoid (**6**-**8**) ('extended sesquiterpene') classes. The eight compounds reported herein comprise seven new natural products (**1**-**7**) and the known compound dictyol C (**8**) [3]. Compounds **1**-**3** are xeniolide derivatives with the carboxylic function at C-18 of the xenicane ring system. Examples of this structural variation are currently restricted to four compounds obtained from soft corals of the genus *Xenia* [4,5].

The alga, *D. divaricata*, was found growing at depths of 3-6 m over an area of approximately 50 sq m on the ocean floor of Geoffrey Bay, Magnetic Island, Australia. The solubles obtained after sequential extraction of the freeze-dried tissue with dichloromethane and methanol were chromatographed on silica gel, using hexane with increasing proportions of ethyl acetate as eluant. Further open column chromatography on silica gel and then either normal- or reversed-phase HPLC separations afforded compounds **1** - **8**.

DISCUSSION

Compound **1** was obtained as a clear oil of molecular formula $C_{20}H_{28}O_4$. Five of the degrees of unsaturation implied by the molecular formula were due to three carbon-carbon double bonds [123.4 (d), 132.4 (s), 136.9 (s), 125.4 (d), 148.6 (s), 157.1 (d)], an aldehyde carbonyl carbon [194.4 (d)], and an ester or lactone carbonyl carbon [173.2 (s)]. The molecule was thus considered bicyclic. Resonances at 71.6 (d) and 71.9 (t) in the ^{13}C NMR spectrum of **1** further suggested the presence of a secondary alcohol and a methylene adjacent to oxygen. The IR data further confirmed the presence of a hydroxy function (3450 cm^{-1}) and an unsaturated enal moiety (1690 cm^{-1}). The latter grouping was also indicated by the UV [λ_{max} (EtOH) 228 nm (ε 7750)] and ^1H NMR [δ 9.29 (s), 6.94 (dd, J 2.7, 8.6 Hz] spectroscopic data. At this point in the data analysis it was evident that **1** had many structural similarities with the known compounds, dictyodial (**10**) [6], its 4β-hydroxy derivative (**11**) [7] and xeniolide B (**12**) [4]. Detailed comparison of the ^{13}C NMR data for these three compounds with those for **1** (Table I) clearly pointed to **1** being a lactonic derivative of **11** with the lactone function occurring between C17 and C18 of **11**. Acetylation of **1** to give the monoacetate (**9**), was performed as a prelude to Horeau determination [8] of the absolute stereochemistry at C4 and hence for the complete molecule. From the Horeau determination the stereochemistry at C4 is *S* and so **1** is (2*R*, 3*R*, 4*S*, 6*E*, 9*E*, 10*R*)-17, 4-hydroxyxenic-6, 9, 13-trien-1-al-18-oic acid lactone.

Compound **2**, of the molecular formula $C_{20}H_{28}O_3$, was found to be spectroscopically very similar to **1**. Close examination of the IR spectrum of **2** clearly revealed the absence of a hydroxy function, as did the ^{13}C NMR data when compared with those for **1** (Table I). In its place was a methylene function [26.8 (t)]. All the remaining spectroscopic features of **2** were consistent with it being the 4β-dehydroxy derivative of **1**. Compound **2** is thus (2*R*, 3*R*, 6*E*, 9*E*, 10*R*)-17-xenic-6, 9, 13-trien-1-al-18-oic acid lactone.

Compound **3**, an analogue of **1**, was found to be of the molecular formula $C_{20}H_{28}O_5$. The major differences between **1** and **3** were again discerned from ^{13}C NMR spectroscopic comparisons (Table I). When the two sets of data for **3** and **1** were compared it was clear that the resonances for C6 and C7 in **3** were now those of sp^3 carbons [59.3 (s), 61.8 (d)] and not sp^2 carbons [136.9 (s), 125.4 (d)], as in the case of **1**. These observations together with the fact that the unsaturation in **3** is of the same order as in **1**, requires that there be an epoxy function between C6 and C7 in

Table I ^{13}C NMR data for compounds **1**-**7**, **9**-**13** and **15**-**16**

Carbon	1	9	3	2	4	12[a]	10[a]	7	16[a]	6	15[a]	5	13[a]	11[a]
1	148.6s	148.2s	148 9s	148.0s	148.1s	142.3s	148.5s	62 8d	[b]63.1d	46.0d	46 1d	128.6s	128.1s	147.9s
2	38 3d	39 0d	39 2d	44 6d	50.5d	57.3d	[c]56.5d	70 5d	29.8t	33.8t	34.0t	166.6s	168.5s	[d]52.0d
3	45.2d	44.3d	44 6d	41.9d	49.9d	37.1d	48 5d	134.0d	130 7d	124.1d	123.6d	45.0d	48.9d	50.5d
4	71 6d	73.5d	66.4d	26 8t	73 4d	37.5t	29.1t	146.9s	150.1s	141.5s	142.0s	70.1d	70.0d	73.6d
5	48 6t	44.5t	47.4t	39.6t	48.1t	39.8t	40.7t	57.0d	[b]61.3d	59.9d	59.5d	47.9t	48.6t	47.9t
6	136.9s	135.3s	59.3s	136 8s	137.7s	134 3s	137.9s	77.0d	76.6d	73.9d	73.4d	28.5d	28.5d	138.1s
7	125 4d	126 8d	61.8d	123.3d	125 0d	130 4d	122.3d	37.0d	37.4d	51.0d	50.1d	10.2d	10 2d	124.2d
8	29 6t	29 6t	27.0t	28.9t	29.6t	70.1d	[c]28.7t	39.1t	38.8t	22.8t	22.2t	8.3t	8.2t	[d]29.6t
9	157.1d	156.8d	152 5d	156.8d	158.0d	43 6t	157.4d	20.2t	20.4t	40.5t	40 4t	25.7d	26.1d	157.8d
10	32 8d	32 3d	32 4d	33 5d	38.1d	137.2s	32.7d	74.9s	74.2s	152.1s	152.2s	37 6d	32.9d	33.3d
11	28 1t	28 0t	28.3t	27.9t	33.7t	127.6d	37.6t	38 0d	38.4d	86.5s	86 9s	30.1t	35.8t	39.6t
12	25 5t	25 4t	25.5t	25 2t	25.5t	121.3d	25.7d	34.3t	34.5t	35.7t	35.1t	25.7t	25.7t	25.7t
13	123 4d	123 1d	123 2d	123 3d	123.7d	145.2d	124.4d	26.1t	26.3t	26 3t	26.0t	123.1d	123 8d	124.6d
14	132 4s	132.7s	132 7s	132 1s	131 8s	70 9s	130.9s	124 6d	124.9d	83.4d	83.5d	133.0s	132.3s	131.2s
15	17 8q	17.8q	17.8q	17.6q	17.6q	29.8q	17 4q	131.5s	140.2s	71.3s	82.2s	17.7q	17.7q	17.6q
16	25.7q	25 7q	25.7q	25.5q	25.6q	29 8q	25 4q	25 7q	25.6q	24 9q	24.5q	25.9q	25.6q	25.7q
17	71.9t	71 5t	71.8t	71.2t	66.2t	71.6t	17.0q	16 3q	16 5q	16.0q	15.8q	64.2t	17.4q	20.2q
18	173 2s	171.7s	171 4s	172.0s	203 1d	173.2s	203.5d	21.3q	22.3q	107.3t	107.3t	72.3t	72.3t	203.6d
19	194 4d	194 0d	193.7d	193.7d	194.3d	119.7t	194.2d	16.4q	16.0q	24.6q	22.6q	174.6s	174.7s	194.2d
20	20.5q	19 9q	20 6q	17 2q	20 2q	19.2q	17.1q	17.7q	17.7q	27.4q	22.6q	23.5q	23.7q	17.6q
21		169.9s			171 2s						170.5s	170.9s		
22		21 3q			21 0q						22 6q	20.9q		

[a] Data taken from literature [4, 6, 13, 12, 10, 7]. [b] These assignments may be reversed. [c] These assignments are amended from the original published data [6]. [d] These assignments are amended from the original published data[7].

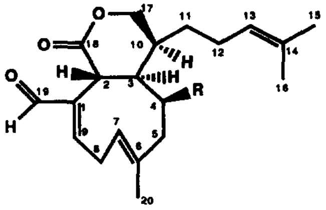
3. This deduction is also supported by the rather shielded nature of the C6 and C7 ^{13}C NMR resonances of **3**. The stereochemistry of the oxirane was proposed from the results of a 2D-NOESY experiment performed on **3** (supplementary data). The significant nOe's that were observed are between the proton with a resonance at δ3.82 (H2) and the protons with resonances at δ2.92 (H7) and δ2.62 (H8ax). These results clearly indicate that these three protons must be on the same side of the molecule. Further from the Dreiding model of **3**, it is evident that if H7 is β the methyl group at C6 must be α. The model of **3** constructed with the aforementioned nOe's in mind also produces a 90° dihedral angle between H7 and H8eq, which is expected as these two protons were found to have a 0 Hz coupling. All of the findings concerning the stereochemistry of the epoxide function of **3** are consistent with the findings of Kashmann and Groweiss for their semi-synthetic epoxides [5]. Compound **3** is thus (2*R*, 3*R*, 4*S*, 6*R*, 7*R*, 9*E*, 10*R*)-17, 6:7-epoxyxenic-4-hydroxy-9, 13-dien-1-al-18-oic acid lactone.

Compound **4** has the molecular formula $C_{22}H_{32}O_5$ by mass spectrometry. Apparent in the ^{13}C NMR data of **4** are resonances for two aldehydic carbonyl carbons and an acetate carbonyl carbon [203.1 (d), 194.3 (d), 171.2 (s)] as well as for three carbon carbon double bonds [148.1 (s), 158.0 (d), 137.7 (s), 125.0 (d), 123.7 (d), 131.8 (s)], indicating **4** to be monocyclic. On comparison of the ^{13}C NMR data for **4** with those for dictyodial (**10**) [6] and 4β-hydroxydictyodial (**11**) [7] it is evident that **4** is the 17-acetoxy derivative of 4β-hydroxydictyodial and is thus (2*R*, 3*R*, 4*S*, 6*E*, 9*E*, 10*R*)-17-acetoxyxenic-4-hydroxy-6, 9, 13-trien-1, 2-dial.

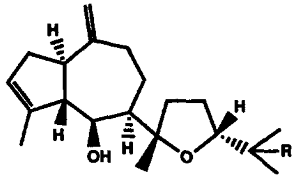
Compound **5** was the final xenicane derivative to be isolated from this investigation of *D. divaricata*. The molecular formula of **5**, $C_{22}H_{32}O_5$, together with its ^{13}C NMR data, indicates the molecule to be tricyclic. Also evident from the ^{13}C NMR data were signals for an cyclopropyl moiety [10.2 (d), 8.3 (t), 25.7 (d)], an acetate carbonyl carbon [170.9 (s)], an α, β-unsaturated γ-lactone [128.6 (s), 166.6 (s), 174.6 (s), 72.3 (t)], and a secondary alcohol function [70.1 (d)], with the latter two functions also being supported by IR and UV data [3450, 1755, 1735 cm^{-1}, 229 nm, (ε 12200)]. It became obvious when all of the above deductions are considered as a whole that **5** must be a crenulide derivative of the type previously reported [9, 10]. When the ^{13}C NMR data for **5** were compared to those for **13** (see Table I) it is clear that **5** is the 17-acetoxy derivative of **13**. Compound **5** is thus 17-acetoxy-4α-hydroxycrenulide.

The three remaining isolates were all hydroazulenoid diterpenes of the pachydityol A (**14**) type [11]. Of the three such compounds isolated in this investigation, the known compound, dictyol C (**8**) was the first to be fully characterised, and was identified by comparison with published spectroscopic data [3].

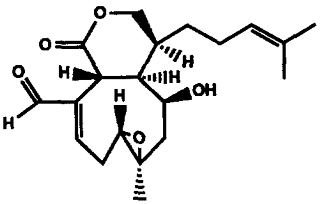
Compound **6** was obtained as an oil and had many spectroscopic similarities to the known compound, dictyol H (**15**) [12]. The molecular formula of $C_{20}H_{32}O_3$ was deduced from the ^{13}C NMR and mass spectrometric data of **6**, which suggested it to be the deacetoxy form of **15**. Closer



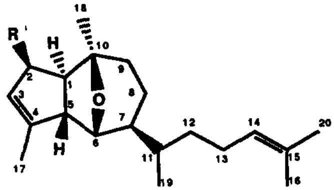
1 R=OH
2 R=H
9 R=OAc



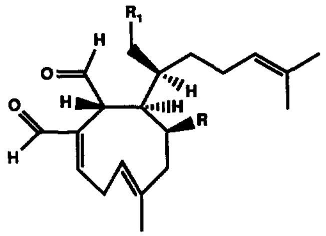
6 R=OH
15 R=OAc



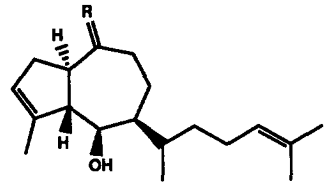
3



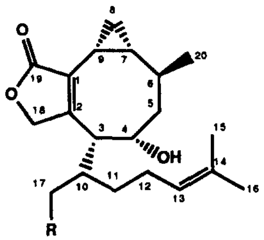
7 R=OH
16 R=H



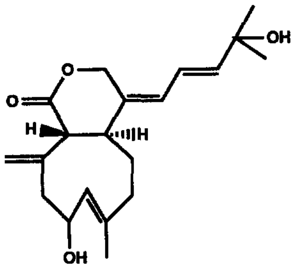
4 R=OH, R_1=OAc
10 R=R_1=H
11 R=OH, R_1=H



8 R= α CH_3, β OH
14 R=H_2



5 R=OAc
13 R=H



12

comparison of the ^{13}C and ^{1}H NMR data for **6** and **15** further supported this proposal (see Table I). A surprising feature was apparent, however, when the two sets of ^{13}C NMR data were compared; a difference in chemical shift of about 10 ppm was observed for C15 in the acetate, **15**, than in the alcohol, **6**. This larger than expected difference may be due in part to the proximity of the furan moiety. Alvarado *et al.*, however, did not resolve the relative stereochemistry of the tetrahydrofuran moiety present in dictol H (**15**) [12], and so, in an attempt to propose the relative stereochemistry at C11 and C14 in **15** and **6** a 2D-NOESY spectrum was recorded for **6** (Fig. 1). These data clearly illustrate that H14 and the C11 methyl group are on the same face of the furan moiety. The proposed relative stereochemistry at all centres for **6** is thus 1*R**, 5*S**, 6*R**, 7*R**,11*S**, 14*R**. As the optical rotations for **15** and **6** have the same sign and are of a similar magnitude (+45.7°, +7.1°) it is proposed that both have the same relative stereochemistry at all chiral centres.

Compound **7** was isolated as an oil, of the molecular formula $C_{20}H_{32}O_2$, and by ^{13}C NMR spectroscopy was shown to contain two carbon-carbon double bonds [134.0 (d), 146.9 (s), 124.6 (d),131.5 (s)]; the molecule was thus tricyclic. Further, from the ^{13}C NMR and IR spectroscopic data the presence of a secondary alcohol [70.5 (d), 3410 cm^{-1}] and an ether linkage [77.0 (d), 74.9 (s)] were implied. The unusually deshielded nature of two further carbons, C1 and C5, [62.8 (d), 57.0 (d)] suggested the presence of a highly strained bridging group. When all of the aforementioned observations and the relevant spectroscopic data were compared with the corresponding data for dictyoxide (**16**) [13] it seemed likely that **7** was a mono-hydroxy derivative of **16**. Assignment of the hydroxy function in **7** to C2 was made on the basis of results from 2D ^{13}C-^{1}H (see Tables 1 and 2) and ^{1}H-^{1}H NMR correlated spectroscopy (Fig. 2). From models and the magnitude of the interproton coupling between H2 and H3 (J 2-3 Hz) and H2 and H1 (J 4 Hz), it is clear that the hydroxy function and H1 are *trans*. If H1 and H2 were *trans* $J_{H1\text{-}H2}$ would be expected to be much greater than 4Hz. The relative stereochemistry for **7** is thus as shown in **7**.

The results presented in this current report on xenicane and hydroazulenoid ('extended sesquiterpenes') classes of compounds, coupled with the literature data on dolabellane class compounds from *D. divaricata* [1, 2], show that this taxon is capable of producing diterpenes of all of the structural types common to the family Dictyotaceae, namely, xenicanes, 'extended sesquiterpenes' and dolabellanes [14]. The bicyclic hydroazulenoid compounds (**6-8**) may be derived from 'extended germacrene' derivatives, still to be found in *D. divaricata*. The xenicane-type compounds obtained include the dictyodial derivative **4**, which is a possible intermediate for the more elaborate crenulide derivative **5**, and the three xeniolide derivatives (**1-3**) [15]. The structural variations of the latter three compounds (**1-3**) are unprecedented in the algal literature. Biosynthetically xeniolide derivatives with the carboxylic function at C-18 are not unexpected in the genus *Dictyota*, although extensive research into the secondary metabolite chemistry of this and related taxa has to date only yielded four xeniolide-derivatives possessing a carboxylic function at C-17 [16] of the xenicane ring system.

Figure 1. Contour plot of a 300MHz 2D NOESY spectrum of a solution of **6** in $CDCl_3$, T=303K. A 1Kx512W data matrix has been transformed with sine-bell filters in both domains. 16 scans were made for each of 256 individual transients.

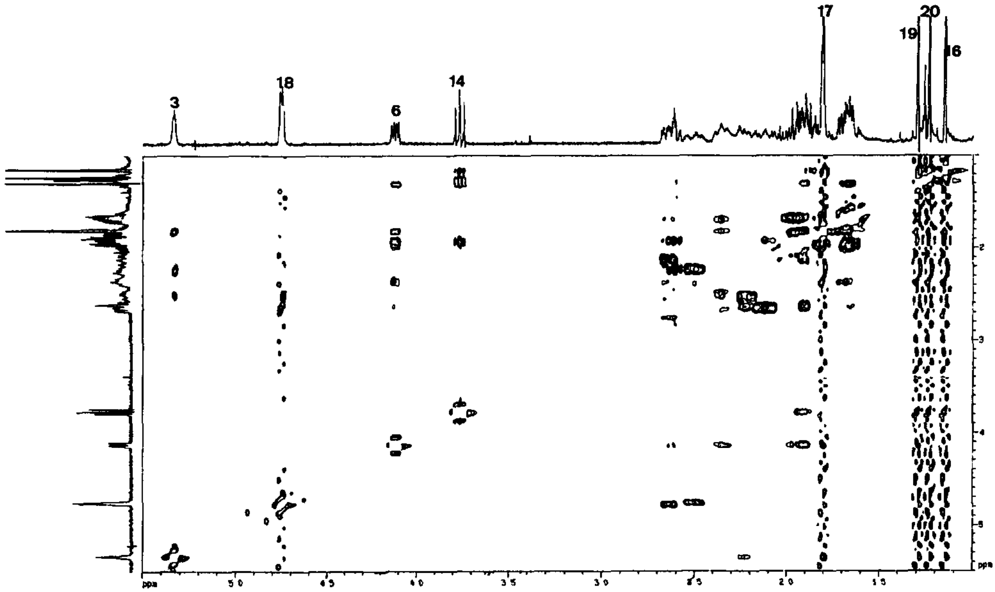


Figure 2. Contour plot of a 300MHz ^1H-^1H Total Correlation (TOCSY) spectrum of a solution of **7** in $CDCl_3$, T=298K. A 1Kx1K data matrix has been transformed with sine-bell filters in both domains. 32 scans were made for each of 256 individual transients.

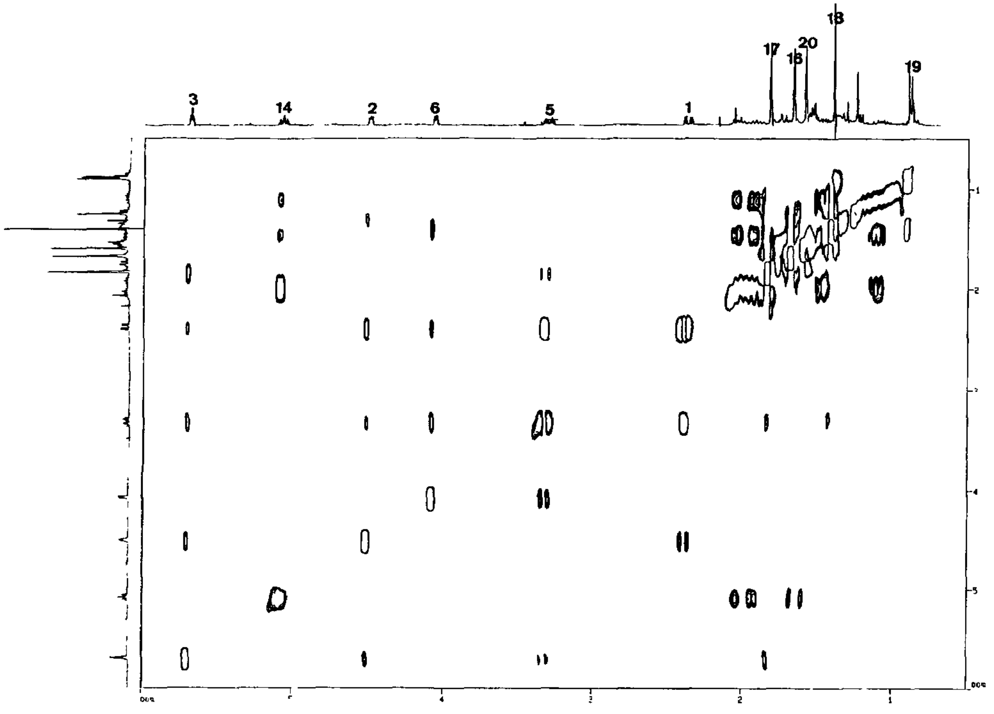


Table II ^{1}H NMR data for compounds **1**-**7** and **9**. All assignments are unambiguous and based primarily on ^{13}C and ^{1}H 2D correlated spectroscopy employing either ^{13}C or^{1}H detection.

Carbon	1	9	3	2
2	3.82 s	3.83s	3.82s	3.27 s
3	2.02 d, *J* 4 7	2.18, brd, *J* 3.2	1.86 brd, *J* 3.3	1.78 m
4	4.40 m	5 47 dd, *J* 3.0, 3.2	4.40 brd, *J* 3.3	1.68 m
5	2 20 dd, *J* 3.1, 13.2	2.22 dd, *J* 3 5, 13.1	1.26 brd, *J* 14.1	2.31 brd, *J* 12.0
	2.36 dd, *J* 2 1, 13.2	2 56 dd, *J* 3.0, 13.1	2.42 dd, *J* 3.1, 14.1	2.08 ddd, *J* 4.7, 12.0, 12.3
7	5.30 brd, *J* 11.2	5 38 brd, *J* 12 0	2.92 d, *J* 10.8	5.39 brd, *J* 10.6
8	3.08 ddd, *J* 2.8, 8.6, 16.7	3.14 ddd, *J* 3.3, 8.6, 16.7	2.62 ddd,*J* 3.0, 10 8, 16.7	3.04 ddd, *J* 3.1, 8.5, 16.1
	3 52 ddd, *J* 2.7, 11.2, 16 7	3 51 ddd, *J* 2 6, 12 0, 16.7	3.03 dd, *J* 9.1, 16.7	3.39 ddd, *J* 3.1, 10.6, 16.1
9	6 94 dd, *J* 2 7, 8.6	6.99 dd,*J* 2.6, 8.6	6.98 dd, *J* 3.0, 9 1	6.94 dd, *J* 3.1, 8 5
10	2.49 m	2.50 m	2 57 m	2.53 m
11	1.24 m, 1.36 m	1 31 m, 1.36 m	1.30 m	1.23 m, 1.28 m
12	1.94 brddd, *J* 7 0, 7 2, 8.0	1.94 brt, *J* 7.5	1 92 m	1.93 m, 1.97 m
	1.94 brddd, *J* 7.0, 7.2, 8.0	1.97brt, *J* 7.5		
13	5.02 dd, *J* 7.2,7.2	5.02 ddqq, *J* 1 4, 1.4, 7 2, 7.2	4.99 dd, *J* 7.2, 7.2	5 03 brdd, *J* 7.1, 7.3
15	1.58 s	1.59 s	1.56 s	1.59 s
16	1.66 s	1.67 s	1.65 s	1.66 s
17	4.39 m	3 84 dd, *J* 11.2, 12.5	4.46 m	4.09 dd, *J* 9.0, 11 1
		4.41 ddd, *J* 1 6, 5.5, 11.2		4.34 dd, *J* 4 6, 11.1
19	9.29 s	9 32 s	9.40 s	9.26 s
20	2 00 s	1.92 s	1.65 s	1.80 s
21		2 08 s		

Table II continued

Carbon	4	7	6	5
1		2.37 dd, *J* 4 0, 11.9	2.65 m	
2	3 61 s	4.51 brs	2.26 m, 2.48 m	
3	2 08 m	5.69 brs	5.34 brs	3.37 brd, *J* 8.0
4	4.39 brm			4.33 brs
5	2 12 m, 2 47 dd, *J* 2 1, 13.0	3.32 brd, *J* 11.9	2 36 m	1.89 m, 1.77 brd, *J* 5.8
6		4 08 dd, *J* 2 3, 4.2	4.14 dd, *J* 3.7, 8.2	1 24 m
7	5.33 brd, *J* 10 3	1.37 m	1.90 m	1.48 m
8	3 12 ddd, *J* 3.1, 8 4, 16.7 3 44 ddd, *J* 2 9, 11 8, 16 7	1.93 m	1.69 m	0.36 ddd, *J* 5 3, 5.4, 5.4, 1.02 m
9	7.07 dd, *J* 2 9, 8 4	1 54 m	2.12 m, 2 66 m	2 09 m
10	2 39 m			1.94 m
11	1 05 m, 1 43 m	1.46 m		1.37 m
12	1.82 m	1.08 m	1.68 m,1.98 m	0 97 m, 2.01 m[b]
13	5.01 brt, *J* 7.0	2 00 m	1 90 m	5 06 brdd, *J* 7.1, 7.5
14		5 08 brdd, *J* 7.0, 7.2	3.77 dd, *J* 6 8, 7.7	
15	1.56 s			1 59 s
16	1 66 s	1.68 s	1.15 s	1.69 s
17	4.18 dd, *J* 7 3, 11 4 4.45 dd, *J* 4.4,11 4	1.83 m	1 80 brs	4.19 m
18	9.72 s	1.41 s	4.75 m	4.73 dd, *J* 3.0, 17.3 4.97 dd, *J* 2.5,17.3
19	9.37 s	0.90 d, *J* 6.2	1.30 s	
20	1.97 s	1.60 s	1.24 s	1 02 d, *J* 6.9
21	2 08 s			2 09 s

[a] Unless otherwise stated the NMR solvent was $CDCl_3$ containing TMS (δ 0). [b] These assignments may be reversed.

EXPERIMENTAL

GENERAL PROCEDURES. All solvents were HPLC grade. Silica gel (type 60, Merck) was used for column chromatography and aluminum-backed plates coated with silica gel 60 F_{254} 0.2 mm thick (Merck) were used for TLC. HPLC was carried out with a Waters 6000A solvent delivery system connected to a Rheodyne HPLC injector, using Knauer columns (25 cm x 8 mm, LiChrosorb Si60 5μm, normal phase and 25 cm x 4 mm, filled with Spherisorb ODS 2 5 μm, reversed phase). Melting points were determined using a Wild Ltd. (Heerbrugg, Switzerland) microscope fitted with a Mettler FP52 hot-stage apparatus and are uncorrected. Optical rotations were measured with a Perkin-Elmer 141 polarimeter using a 10 cm cell with $CHCl_3$ as solvent. Infrared spectra were recorded on a Perkin-Elmer 781 infrared spectrometer as either liquid films or Nujol mulls. Ultraviolet spectra were obtained in ethanol, on a Perkin-Elmer Lambda 3 UV/VIS spectrometer. ^1H and ^{13}C NMR spectra were recorded on a Bruker AMX-300 spectrometer operating at a basic frequency of 300 MHz. Mass spectra were recorded on either a Hitachi-Perkin-Elmer RMM-6M (EI and CI) or a ZAB2-SEQ (FAB) mass spectrometer.

MATERIAL INVESTIGATED. All plant materials were collected at depths of 0-10 m. After collection algae are frozen and then freeze dried prior to extraction. Voucher specimens are deposited at the James Cook University's Botany Department Herbarium (JCT A7753).

EXTRACTION AND CHROMATOGRAPHY. Freeze-dried *D. divaricata* tissue (253 g) was steeped in methylene chloride (2 litres) and then in methanol (2 litres). The resultant methylene chloride solubles, 20 g (7.9%), were then chromatographed over silica. Material was eluted from the column with gradient mixtures of hexane through to ethyl acetate and eventually to methanol. In all, 21 separate fractions were obtained from this initial chromatography.

(2*R*, 3*R*, 4*S*, 6*E*, 9*E*, 10*R*)-17, 4-hydroxyxenic-6, 9, 13-trien-1-al-18-oic acid lactone, **1**: Fraction 10 from the initial chromatography was further chromatographed by HPLC using reversed-phase material with acetonitrile and water (7:3) as the eluant, to afford **1** as an oil (60 mg, 0.02%); $[\alpha]^{25}_{D}$ -151.3° (c=0.3, $CHCl_3$); IR (film) ν_{max} 3450, 2900, 1730, 1690 cm^{-1}; UV λ_{max} (EtOH) 228 nm (ε 7750); ^1H NMR (see Table II); ^{13}C NMR (see Table I); EIMS, *m/z* (% rel. int.), 332 ($M^{+\cdot}$, 3), 287 (3), 217 (4), 175 (6), 151 (11), 133 (13), 69 (63), 41 (100).

(2*R*, 3*R*, 6*E*, 9*E*, 10*R*)-17-xenic-6, 9, 13-trien-1-al-18-oic acid lactone; **2**: Fraction 7 from the initial separation was rechromatographed over silica to give 11 further fractions. Fraction 2 from this second chromatography was further separated by HPLC using reversed phase material and methanol water (4:1) as eluant to yield **2** as an oil (150 mg, 0.06%); $[\alpha]^{25}_{D}$ -189.5° (c=0.2, $CHCl_3$); IR (film) ν_{max} 2910, 1720, 1685 cm^{-1}; UV λ_{max} (EtOH) 227 nm (ε 4750); ^1H NMR (see Table II); ^{13}C NMR (see Table I); HREIMS, obsd. *m/z* 317.181, $C_{20}H_{29}O_3$ requires *m/z* 317.211; EIMS *m/z* (% rel. int.), 317 ($M{+}H^{+\cdot}$, 21), 316 (8), 299 (15), 298(16), 271 (10),255 (9), 201 (9), 189 (14), 161 (16), 147 (20), 135 (37), 109 (47), 69 (71), 41 (100).

(2*R* 3*R*, 4*S*,, 6*R*, 7*R*, 9*E*, 10*R*)-17, 6, 7-epoxyxenic-4-hydroxy-9, 13-dien-1-al-18-oic acid lactone; **3**: After the HPLC had been performed on fraction 10 to afford **1** the remaining material was rechromatographed by HPLC over normal phase silica employing hexane and ethyl acetate (3:7) as the eluant to afford **3** as an oil (17 mg, 0.007%); $[\alpha]^{25}_{D}$ -178.3° (c=0.06, $CHCl_3$); IR (film) ν_{max} 3450, 2910, 1720, 1690 cm^{-1}; UV λ_{max} (EtOH) 228 nm (ε 7430); ^1H NMR (see Table II); ^{13}C NMR (see Table I); CIMS, *m/z* (% rel. int.), 349 ($M{+}H^{+\cdot}$, 49), 331 (13), 313 (4), 155 (4), 109 (7) , 58 (56), 57 (100).

(2*R*, 3*R*, 4*S*,, 6*E*, 9*E*, 10*R*)-17-acetoxyxenic-4-hydroxy-6, 9, 13-trien-1, 2-dial; **4**: Also derived from initial fraction 7 was **4**, this time from the separation of fraction 6 from the chromatography of initial fraction 7, over normal phase using a hexane ethyl acetate mixture (7:3), **4** an oil (43 mg,0.02%); $[\alpha]_D^{25}$ -128.8° (c=0.08, $CHCl_3$); IR (film) ν_{max} 3460, 2910, 1740, 1710, 1680 cm^{-1}; UV λ_{max} (EtOH) 224 nm (ε 3930); ^1H NMR (see Table II); ^{13}C NMR (see Table I); CIMS, obsd. *m/z* 375.23, $C_{22}H_{31}O_5$ requires *m/z* 375.22; CIMS, *m/z* (% rel. int.), 375 ($M\text{-}H^{+\cdot}$, 8), 349 (4), 333 (8), 315 (9), 155 (10), 57 (100).

17-acetoxy-4α-hydroxycrenulide; **5**: From the same fraction that **4** was derived also came the slightly more polar metabolite **5** as an oil (12 mg, 0.005%), $[\alpha]_D^{25}$ +45.0° (c=0.06, $CHCl_3$); IR (film) ν_{max} 3450, 2920, 1755, 1735 cm^{-1}; UV λ_{max} (EtOH) 229 nm (ε 12200); ^1H NMR (see Table II); ^{13}C NMR (see Table I); HREIMS, obsd. *m/z* 376.229, $C_{22}H_{32}O_5$ requires *m/z* 376.225; EIMS *m/z* (% rel. int.), 376 ($M^{+\cdot}$, 7), 333 (16), 217 (6), 189 (7), 145 (12), 117 (10), 109 (18), 107 (13), 105 (18), 97 (13), 82 (33), 43 (100).

Deacetoxydictyol H; **6**: HPLC separation of fraction 3, from the second fractionation of preliminary fraction 7, with reverse phase material and methanol-water (4:1) as the eluant afforded **6** as a yellow oil (70 mg, 0.03%); $[\alpha]_D^{25}$ +45.7° (c=0.002, $CHCl_3$); IR (film) ν_{max} 3425, 2930, 1635 cm^{-1}; ^1H NMR (see Table II); ^{13}C NMR (see Table I); HREIMS, obsd. *m/z* 302.223, $C_{20}H_{30}O_2$ requires *m/z* 302.225; EIMS *m/z* (% rel. int.), 302 ($M\text{-}H_2O^{+\cdot}$, 13), 287 (7), 284 (7), 243 (15), 199 (12), 198 (12), 185 (15), 175 (12), 173 (11), 159 (24), 157 (18), 143 (100), 125 (38).

2-Hydroxydictyoxide; **7**: Fraction 9 from the preliminary fractionation of the dichloromethane solubles afforded, after HPLC separation over reversed phase material with methanol water (3:2) as eluant, **7** a viscous oil (15 mg, 0.006%); $[\alpha]_D^{25}$ -37.8° (c=0.09, $CHCl_3$); IR (film) ν_{max} 3410, 2910, 1740 cm^{-1}; ^1H NMR (see Table II); ^{13}C NMR (see Table I); HREIMS, obsd. *m/z* 304.237, $C_{20}H_{32}O_2$ requires *m/z* 304.240; EIMS, *m/z* (% rel. int.), 304 ($M^{+\cdot}$, 12), 286 (14), 271 (6), 243 (10), 225 (8), 215 (14), 207 (36), 191 (37), 189 (25), 175 (30), 161 (24), 159 (26), 135 (48), 121 (43), 109 (100), 95 (72).

Dictyol C; **8**: The known compound dictyol C was found to be the major component of fraction 8 from the preliminary chromatography of the dichloromethane solubles. It was eventually purified from this fraction by HPLC to yield 120 mg (0.05%) of material with identical physical and spectroscopic properties to those previously reported [3].

Acetylation of **1** (35 mg) afforded **9** (15 mg) an oil, $[\alpha]_D^{25}$ -204.0° (c=0.13, $CHCl_3$); IR (film) ν_{max} 2920, 1740, 1725, 1690 cm^{-1}; UV λ_{max} (EtOH) 226 nm (ε 5480); ^1H NMR (see Table II); ^{13}C NMR (see Table I); HREIMS 374.198 obsd. *m/z*, $C_{22}H_{30}O_5$ requires *m/z* 374.209; EIMS, *m/z* (% rel. int.), 374 (M^+ ,5), 332 (3), 314 (4), 285 (5), 269 (6), 215 (6), 187 (9), 175 (10), 161 (10), 147 (12), 69 (36), 43 (100).

ACKNOWLEDGEMENT-We thank Mr. Rocky de Nys, Department of Chemistry and Biochemistry, James Cook University of North Queensland, Australia, for collection of the algal material, and Dr. Ian Price, Department of Botany, James Cook University of North Queensland for species assignment. We also thank Dr. L. Botz for his suggestions and assistance in some of our preliminary separation work. Mass spectral data were provided by the Mass Spectral Service of the ETH Chemistry Department.

REFERENCES

1. Crews, P.; Klein, T. E.; Hogue, E. R.; Myers, B. L. **1982**, *J. Org. Chem.,47*, 811-815.
2. Sun, H. H.; McConnell, O. J.; Fenical, W.; Hirotsu, K.; Clardy, J. **1981**, *Tetrahedron, 37*, 1237-1242.
3. Danise, B.; Minale, L.; Riccio, R.; Amico, V.; Oriente, G.; Piattelli, M.; Tringali, C.; Fattorusso,E.; Magno, S.; Mayol, L. **1977**, *Experientia, 33*, 413-415.
4. Kashmann, Y.; Groweiss, A. **1980**, *J. Org. Chem., 45*, 3814-3824.
5. Groweiss, A.; Kashmann, Y. **1983**, *Tetrahedron, 39*, 3385-3396.
6. Finer, J.; Clardy, J.; Fenical, W.; Minale, L.; Riccio, R.; Battaile, J.; Kirkup, M.; Moore, R. E. **1979**, *J. Org. Chem., 44*, 2044-2047.
7. Kirkup, M.; Moore, R. E. **1983**, *Phytochemistry, 22*, 2539-2541.
8. Horeau, A. *Determination of the Configuration of Secondary Alcohols* in 'Stereochemistry Fundamentals and Methods', Hogan, H. B. ed., Georg Thieme (Stuttgart) **1977**, *3*, 51.
9. Sun, H. H.; McEnroe, F. J.; Fenical, W. **1983**, *J. Org. Chem., 48*, 1903-1906.
10. Midland, S. L.; Wing, R. M.; Sims, J. J. **1983**, *J. Org. Chem., 48*, 1906-1909.
11. Hirschfeld, D. R.; Fenical, W.; Lin, G. H. Y.; Wing, R. M.; Radlick, P.;Sims, J. J. **1973**, *J. Amer.Chem.Soc., 95*, 4049-4050.
12. Alvarado, A. B.; Gerwick, W. H. **1985**, *J. Nat. Prod., 48*, 132-134.
13. Amico, V.; Oriente, G.; Piattelli, M.; Tringali, C. **1979**, *Phytochemistry, 18*, 1895-1897.
14. Faulkner, D. J. **1984**, *Nat. Prod. Rep., 1*, 251-280.
15. Fenical, W. in *Marine Natural Products*, Scheuer, P. ed., Academic Press, New York, **1978**, *2*, 207.
16. Ravi, B. N.; Wells, R. J. **1982**, *Aust. J. Chem., 35*, 121-128.