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TROPICAL MARINE ALGAE, VII.[1] THE CHEMICAL COMPOSITION OF MARINE ALGAE FROM NORTH QUEENSLAND WATERS

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ABSTRACT.—Details of the secondary metabolite content of seven species of red algae (Rhodophyta), four species of brown algae (Phaeophyta), two species of blue-green algae (Cyanophyta), and six species of green algae (Chlorophyta) from coastal waters of North Queensland, Australia, between 15° S and 20° S of the equator, are reported. Although many of these metabolites are not new natural products, several as yet unreported compounds were identified. A specimen of the red alga *Laurencia majuscula* yielded the novel metabolites (1*Z*,8*R**,9*R**)-8-bromochamigra-1,11(12)-dien-9-ol [**31**], and (1*R**,2*S**,3*R**,5*S**,8*S**,9*R**)-2,3,5,9-tetramethyltricyclo[6.3.0.0^{1,5}]undecan-3-ol [**32**]. A sample of *Dictyopteris delicatula* afforded the novel metabolite (1*R**,3*R**,4*S**,11*R**)-3,4;7,8-bisepoxydolabellan-12(18)-ene [**54**]. A specimen of a shallow-water *Lyngbya* sp. yielded the novel metabolite 8′-deacetoxymalyngamide C [**60**], and from a collection of *Chlorodesmis fastigiata* the novel metabolite (2*E*,6*E*,10*E*)-1-acetoxy-3-acetoxymethyl-7,11,15-trimethylhexadeca-2,6,10,14-tetraene [**66**] was isolated.

Australian waters contain representatives of all major families of marine macroalgae, with the southern coastline supporting a much higher species richness than other coasts. Moving northward from the southern coast, there is also a general decrease in the seaweed biomass on the rocky shores (1). There is also a gradient in macroalgal biomass in northeastern Australia, from comparatively high biomass on mainland rocky shores and nearshore fringing coral reefs to low biomass on shelf reefs of the Great Barrier Reef (2). On reefs remote from the coast, comparatively few larger, prominent algae occur, including *Chlorodesmis*, a genus whose representatives are known to possess chemical constituents with significant antifeedant properties (3), and *Halimeda*, which have also been shown to be chemically defended (4). No systematic chemical investigation of tropical marine algae in Australia has been undertaken, although extensive taxonomic work has been carried out by Price and his students (5). We have investigated the chemical content of at least 20 distinct species of algae from the coastal islands and reefs around Townsville, North Queensland, Australia and here report the results of those investigations. Although the structures of many of the compounds are known, five new metabolites are here reported for the first time.

RESULTS AND DISCUSSION

Table 1 lists all the algal species and specimens whose chemistry was investigated in the period of this study. Sixty-seven secondary metabolites **1–67** from 19 different algal species were isolated and characterized. The algae investigated fall into the following four categories: species not previously investigated that yielded new natural products [*Plocamium hamatum* J. Agardh (A6919, A7578, A7580), *Laurencia tenera* Tseng (A7531), *Portieria hornemannii* (Lyngbye) P.C. Silva (A7579, A7376, A7581, A7582, A7583)] or that afforded no secondary metabolites [*Galaxaura oblongata* (Ellis & Solan-

[1]For Part VI, see Coll and Wright (27).

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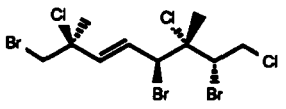
TABLE 1. A Listing of All Algal Species Investigated During the Five-year Period July 1984 to August 1988.

Division	Species	Location	Date	Depth	Voucher specimen number[a]	Isolates	Original reference for isolates
Rhodophyta, Gigartinales							
Plocamiaceae	*Plocamium hamatum* J. Agardh	Potter Reef	6/7/84	1–6 m	A6919	**1–4**	(24)
	Pl. hamatum	Pelorus & Orpheus Islands channel	6/12/84	1–6 m	A7578	**5**	(24)
	Pl. hamatum	Rib Reef	11/7/85	3–10 m	A7580	**2, 3, 5–7**	(24,28,29)
Rhizophyllidaceae	*Portieria hornemannii* (Lyngbye) P.C. Silva	Florence Bay	13/7/84	1–3 m	A7579	**8**	(27)
	Po. hornemannii	Rib Reef	10/7/85	1–6 m	A7376	**9–14**	(23)
	Po. hornemannii	Florence Bay	28/6/87	0–6 m	A7581	**8, 11, 15**	(23,27)
	Po. hornemannii	Korea Reef	28/7/87	0–6 m	A7582	**8, 11, 12, 16–21**	(23,27)
	Po. hornemannii	Feather Reef	28/7/87	0–8 m	A7583	**8, 15, 22, 23**	(27)
Rhodophyta, Ceramiales							
Rhodomelaceae	*Laurencia majuscula* (Harvey) Lucas	Zoe Bay	7/7/85	1–4 m	A7575	**24–28**	(7)
	L. majuscula	Zoe Bay	8/7/86	2–3 m	A7576	**24–30**	(7)
	L. majuscula	Florence Bay	13/10/87	2–6 m	A7577	**24–27, 31, 32**	(6,7)
	Laurencia implicata J. Agardh	Britomart Reef	9/7/85	1–6 m	A7573	**33, 35, 36, 44, 45**	(30,32,33)
	L. implicata	Florence Bay	13/10/87	2–6 m	A7574	**37–42**	(25,34)
	L. implicata	Davies Reef	5/6/84	3–6 m	A7572	**34, 35, 43–46**	(30–33)
	Laurencia tenera Tseng	Florence Bay	28/6/87	0–6 m	A7531	**47, 48**	(26)
Rhodophyta, Nemaliales							
Galaxauraceae	*Galaxaura oblongata* (Ellis & Solander) Lamouroux	Geoffrey Bay	13/7/84	0–3 m	A7584		(6)
	G. oblongata	John Brewer Reef	29/10/85	4–10 m	A7585		(6)
	Galaxaura marginata (Ellis & Solander) Lamouroux	John Brewer Reef	29/10/85	4–10 m	A7586		(6)
Phaeophyta, Dictyotales							
Dictyotaceae	*Dictyota volubilis* Kützing	Geoffrey Bay	13/7/84	1–3 m	A7567	**49–54**	(6,35–37,39)
	Dictyota volubilis	Geoffrey Bay	29/7/85	1–3 m	A7568	**49, 50, 53, 55–57**	(35–39)

TABLE 1. Continued.

Division	Species	Location	Date	Depth	Voucher specimen number[a]	Isolates	Original reference for isolates
	Dictyopteris delicatula Lamouroux	Geoffrey Bay	13/7/84	1–3 m	A7569	**54**	(6)
	Padina sp. a	Broadhurst Reef	21/11/85	14 m	A7570		(6)
	Padina sp. b	John Brewer Reef	29/10/85	6–18 m	A7571		(6)
Cyanophyta, Nostocales							
Oscillatoriaceae	*Lyngbya* sp. a	Myrmidon Reef	13/6/85	5–20 m	A7565		(6)
	Lyngbya sp. b	Broadhurst Reef	16/11/86	2–6 m	A7566	**58–60**	(6,19,20)
Chlorophyta, Siphonocladales							
Siphonocladaceae	*Boodlea composita* (Harvey) Brand	Florence Bay	11/8/84	0–4 m	A7559	**61**	(6)
Chlorophyta, Bryopsidales							
Halimedaceae	*Halimeda* sp.	Lt. Broadhurst Reef	23/11/85	2–4 m	A7560		(6)
Udoteaceae	*Tydemania expeditionis* Weber-van Bosse	Lt. Broadhurst Reef	23/11/85	10–15 m	A7201	**62–64**	(40)
Caulerpaceae	*Caulerpa ? peltata* Lamouroux	Slashers Reef	11/7/85	10–15 m	A7561		(6)
	Caulerpa racemosa (Forsskål) J. Agardh	Fairy Reef	9/8/84	10–15 m	A7462		(6)
	Chlorodesmis fastigiata (C. Agardh) Ducker	John Brewer Reef	26/2/87	4–10 m	A7563	**65, 66**	(6,21)
	Ch. fastigiata	Potter Reef	6/7/84	3–6 m	A7564	**66**	(6)

[a]Voucher specimens are lodged in the James Cook University's Botany Department Herbarium (JCT).



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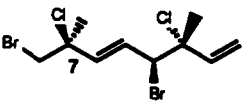

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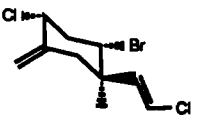

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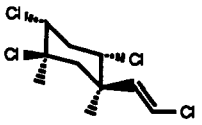

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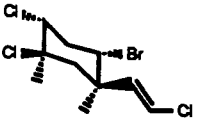

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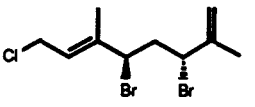

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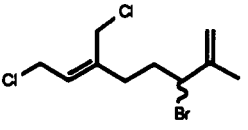

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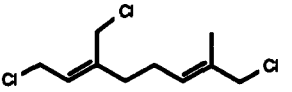

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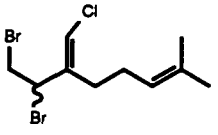

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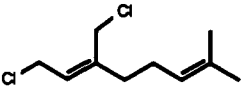

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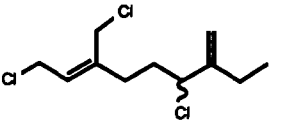

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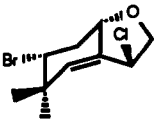

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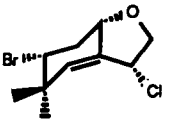

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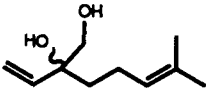

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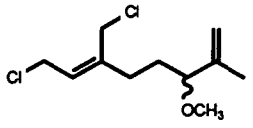

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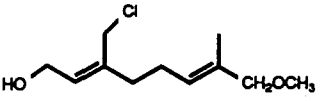

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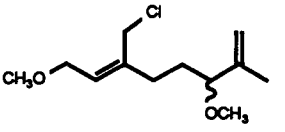

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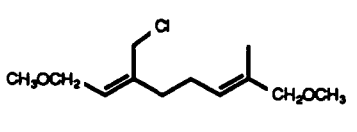
der) Lamouroux (A7584, A7585), *Galaxaura marginata* (A7586), *Padina* sp. (A7570, A7571)] and species previously investigated that afforded novel metabolites [*Laurencia implicata* J. Agardh (A7574), *Laurencia majuscula* (Harvey) Lucas (A7575, A7576, A7577), *Dictyota volubilis* Kützing (A7567), *Dictyopteris delicatula* Lamouroux (A7569), *Lyngbya* sp. (A7566), *Chlorodesmis fastigiata* (C. Agardh) Ducker (A7563)] or that contained only known secondary metabolites [*Caulerpa racemosa* (Forsskål) J. Agardh (A7462), *Caulerpa ? peltata* Lamouroux (A7561), *Tydemania expeditionis* Weber-van Bosse (A7201), *Halimeda* sp. (A7560), *Boodlea composita* (Harvey) Brand (A7559), *Chlorodesmis fastigiata* (A7564), *Lyngbya* sp. (A7565), *Dictyota volubilis* (A7568), *Laurencia implicata* (A7572, A7573)]. For all known compounds, agreement with the



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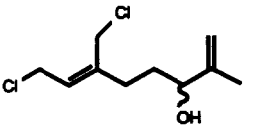

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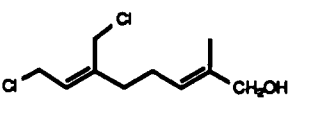

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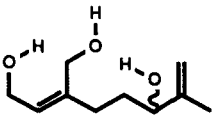

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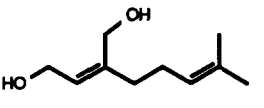

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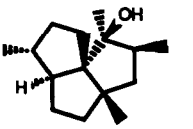

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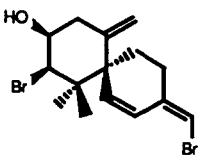

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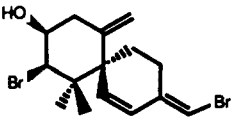

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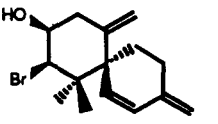

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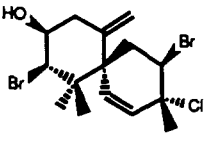

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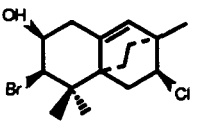

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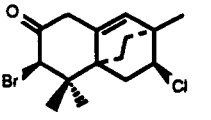

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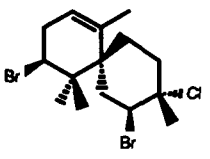

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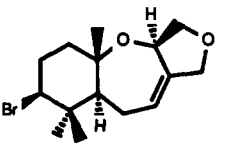

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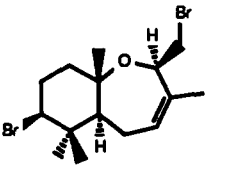

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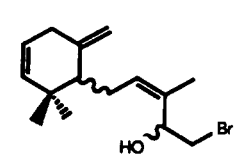
reported physical data, including $[\alpha]_D$ and ^1H- and ^{13}C-nmr data, was obtained before identification was regarded as complete. Absence of an entry in the 'Isolates' column of Table 1 indicates that the extract of that alga was predominantly fats and sterols. These metabolites were not further investigated in this study. The details of these investigations as well as those of the algae with voucher specimen numbers A7580, A7573, A7572, A7567, A7568, A7559, and A7201 are reported elsewhere (6).

TWO NEW RHODOPHYTA METABOLITES **31** AND **32**.—A collection of *Laurentia majuscula* (A7577) afforded the known chamigrene derivatives **25**, **26** and **27** (7) and a new chamigrene derivative **31**. Two triquinane derivatives, the known triquinane derivative **24** (7) and a new triquinane derivative **32** were also identified.

The chamigrene derivative **31** had the molecular formula $C_{15}H_{23}OBr$ and, by ^{13}C-nmr spectroscopy, contained two carbon-carbon double bonds; thus, it was bicyclic. Double resonance experiments permitted several structural fragments to be developed. Irradiation at δ 4.46 removed a 10.3 Hz coupling from the signal at δ 3.76, while irradiation at δ 3.76 collapsed the δ 4.46 doublet to a singlet, the double doublet at δ



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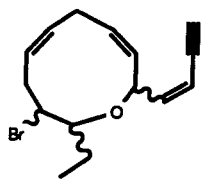

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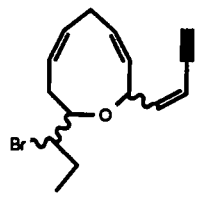

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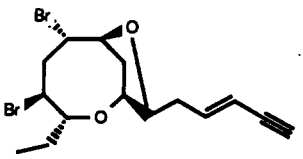

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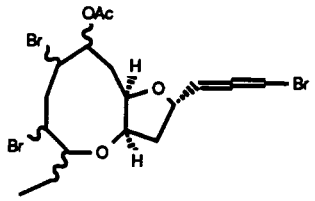

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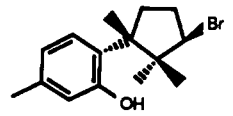

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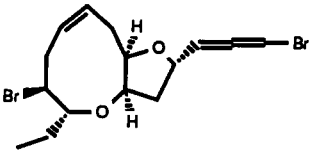

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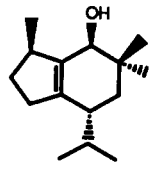

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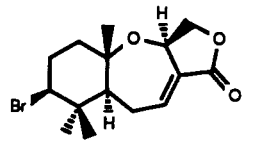

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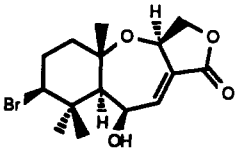

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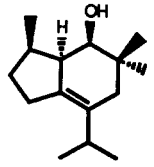

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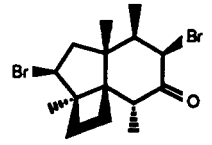

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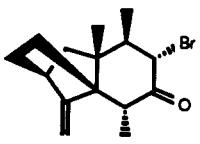

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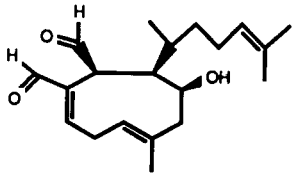

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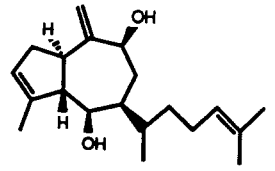

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2.61 to a doublet, and the multiplet at δ 2.35 to a broad doublet. Irradiation at either δ 2.61 or 2.35 collapsed the multiplet at δ 3.76 to a double doublet and the other proton signal (δ 2.61 or 2.35) to a doublet (-CH_2-CHX-CHX-). Irradiation at δ 5.29 sharpened the signals at δ 2.23 and 2.02, while irradiation at either of the latter sharpened the δ 5.29 signal and collapsed the other to a singlet (=CH-CH_2-). Short and long range ^{13}C-^{1}H correlation experiments (Table 2) associated all protons with their directly bonded carbon atoms and enabled carbon connectivities to be confirmed. Based on the co-occurrence of chamigrene derivatives in the algae, structure **31** was proposed. The magnitude of the coupling constants ($J_{8,9}$ = 10.9 Hz, $J_{9,10}$ = 11.5 Hz) dictated that all three protons were axial. The Br (^{13}C-nmr 77.0 ppm) and OH (ir 3390 cm^{-1}, 72.0 ppm) substituents on the cyclohexane ring containing the *exo*-vinylmethylene

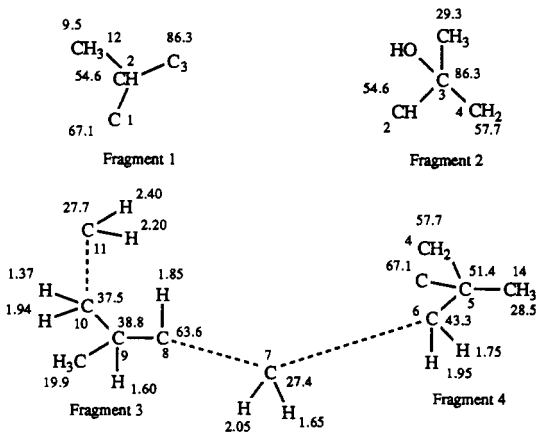
TABLE 2. ^{13}C- and ^{1}H-nmr Data for **31**.[a]

Carbon	^{13}C (ppm)	^{1}H (δ)	^{1}H-^{13}C Long Range Correlations
C-1	132.9 (s)		
C-2	119.4 (d)	5.29 (brs)	
C-3	30.5 (t)	2.02 (brd, J = 15.2 Hz) 2.23 (brd, J = 15.2 Hz)	
C-4	46.3 (s)		
C-5	25.8 (t)	1.60 (m), 1.85 (m)	
C-6	27.5 (t)	1.70 (m), 1.85 (m)	
C-7	42.8 (s)		
C-8	77.0 (d)	4.46 (d, J = 10.3 Hz)	
C-9	72.0 (d)	3.76 (ddd, J = 5.7, 10.3, 11.5 Hz)	
C-10	39.0 (t)	2.35 (ddt, J = 11.5, 13.3, 1.5 Hz) 2.61 (dd, J = 5.7, 13.3 Hz)	
C-11	143.1 (s)		
C-12	114.8 (t)	4.73 (s), 5.07 (t, J = 1.7 Hz)	46.3, 114.8
C-13	23.9 (q)	1.12 (s)	18.7, 23.9, 25.8, 42.8, 46.3, 77.0
C-14	18.7 (q)	0.94 (s)	18.7, 23.9, 42.8, 77.0
C-15	23.0 (q)	1.58 (s)	23.0, 25.8, 27.5, 46.3, 114.8

[a]Assignments are based on short (J = 125 Hz) and long (J = 10 Hz) range ^{13}C-^{1}H correlations.

group [114.8(t), 143.1(s) ppm] must both be equatorial. This chamigrene derivative **31** is unique in the literature in having both the hydroxyl and bromine substituents equatorial. In all other reports (8–16), chamigrenes with 8-bromo and 9-hydroxyl functionalities possess an equatorial 8-bromo function with an adjacent axial hydroxyl group. Jones oxidation of **31** afforded the ketone **69** identified only on the basis of its ^{1}H-nmr spectral data. It rearranged to the related α,β-unsaturated ketone **70** on standing overnight at −40°. The structure of the rearranged ketone **70** was consistent with its ^{1}H- and ^{13}C-nmr spectral data. The new chamigrene derivative **31** is thus (1*Z*,8*R**, 9*R**)-8-bromochamigra-1,11(12)-dien-9-ol.

A non-halogenated sesquiterpene alcohol **32** of the molecular formula $C_{15}H_{16}O$



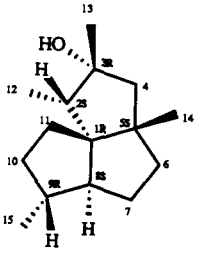
SCHEME 1. Dotted lines indicate connectivities established from ^{1}H homonuclear decoupling experiments.

TABLE 3. ^{13}C-nmr Data for **24** and ^{13}C- and ^{1}H-nmr Data for **32**.[a]

Carbon	^{13}C (ppm)			^{1}H (δ) Shifted **32**	^{1}H-^{13}C Long Range Correlations **32**
	24	Unshifted **32**	Shifted **32**		
C-1	70.0 (s)	65.9 (s)	67.1 (s)		
C-2	85.2 (s)	53.9 (d)	54.6 (d)	2.26 (q, J = 7.2 Hz)	
C-3	41.1 (d)	81.1 (s)	86.3 (s)		
C-4	47.5 (t)	55.7 (t)	57.7 (t)	2.42 (d, J = 13.7 Hz) 2.96 (d, J = 13.7 Hz)	18.5, 54.6, 57.7, 67.1 86.3
C-5	49.8 (s)	50.2 (s)	51.4 (s)		
C-6	41.9 (t)	42.7 (t)	43.3 (t)	1.75 (m), 1.95 (m)	
C-7	29.1 (t)	26.9 (t)	27.7 (t)	2.20 (m), 2.40 (m)	
C-8	57.8 (d)	63.9 (d)	63.6 (d)	1.85 (m)	
C-9	42.5 (d)	38.4 (d)	38.8 (d)	1.60 (m)	
C-10	36.4 (t)	37.1 (t)	37.5 (t)	1.37 (m), 1.94 (m)	
C-11	27.8 (t)	26.9 (t)	27.4 (t)	1.65 (m), 2.05 (m)	
C-12	22.3 (q)	8.3 (q)	9.5 (q)	1.75 (d, J = 7.2 Hz)	9.5, 54.6, 67.1, 86.3
C-13	12.4 (q)	27.8 (q)	29.3 (q)	2.49 (s)	29.3, 54.6, 57.7, 86.3
C-14	26.7 (q)	26.3 (q)	28.5 (q)	1.57 (s)	28.5, 43.3, 51.4, 57.7, 67.1
C-15	19.5 (q)	19.7 (q)	19.9 (q)	1.09 (d, J = 6.5 Hz)	19.9, 37.5, 38.8, 63.6

[a]Assignments for **32** are based on short (J = 125 Hz) and long (J = 10 Hz) range ^{13}C-^{1}H correlations.

was also isolated. On the basis of its spectral similarity with **24** it was presumed to be a triquinane derivative (Table 3). Because **32** contained no sp^2 carbons in the ^{13}C-nmr spectrum, the molecule was tricyclic. The presence of a tertiary alcohol function was indicated in the ^{13}C-nmr and infrared spectra (singlet at 81.1 ppm; ν max 3450 cm^{-1}). As in the case of triquinane **24**, the ^{1}H-nmr spectrum of **32** contained all its proton resonances between δ 0.8 and 1.8. Four methyl resonances were discernible: doublets at δ 0.80 (J = 6.5 Hz) and 0.90 (J = 7.2 Hz) and singlets at δ 1.10 and 1.16; all other proton resonances were masked by superimposition of signals. ^{1}H double resonance experiments were performed after addition of the shift reagent Eu(fod)$_3$, and the shift-reagent treated sample was then subjected to two-dimensional long and short range ^{13}C-^{1}H shift-correlated nmr spectral studies, the results of which appear in Table 3. The short range experiments permitted unambiguous association of carbons to their attached protons, and the long range experiments enabled four molecular fragments to be deduced (Scheme 1). Thes four fragments could then be linked on the basis of the following proton double resonance experiments. Thus irradiation at δ 1.65 sharpened signals at δ 1.75, 1.85, 1.95, and 2.05 in the "shifted" ^{1}H-nmr spectrum of **32**, while irradiation at δ 1.37 affected signals at δ 1.60, 1.94, 2.20, and 2.40. The remaining connectivities were established from the long range correlation experiment. Thus the



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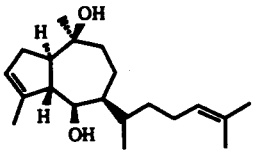

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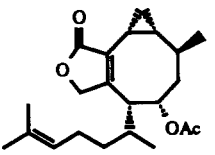

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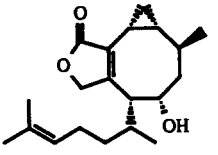

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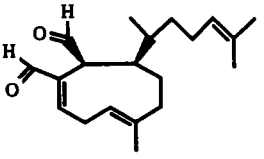

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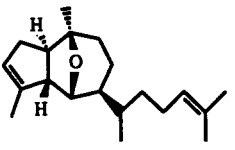

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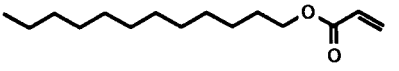

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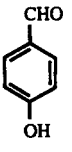

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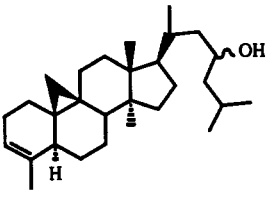

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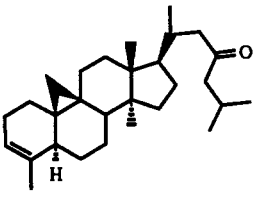

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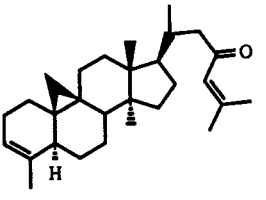

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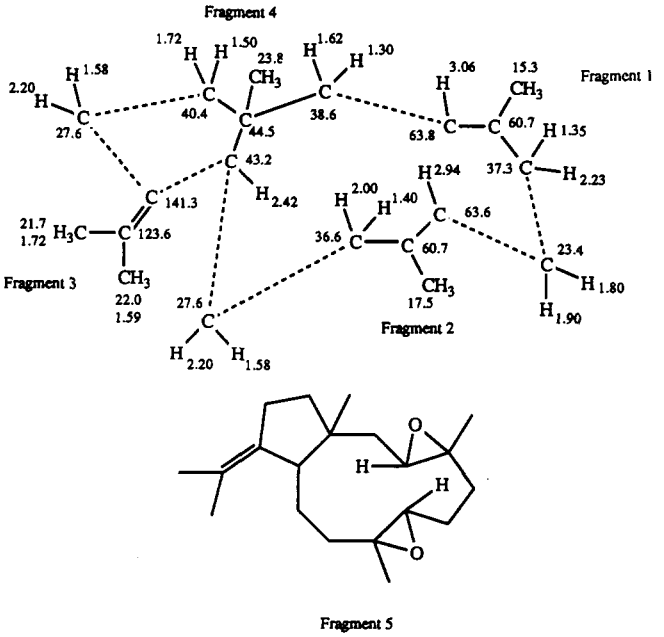
carbon with resonance at 63.6 ppm must bond to the carbon whose resonance occurs at 67.1 ppm, as must the carbon resonating at 27.7 ppm leading to the triquinane structure. Stereochemical assignments for **32** were based on direct comparison of ^{13}C-nmr data for **32** with that for **24** (Table 3) and the $\Delta\delta$ values for the methyl groups on addition of shift reagent (see Experimental). The new triquinane **32** is thus (1*R**,2*S**, 3*R**,5*S**,8*S**,9*R**)-2,3,5,9-tetramethyltricyclo[6.3.0.$0^{1,5}$]undecan-3-ol.

A NEW PHAEOPHYTA METABOLITE **54**.—A specimen of *Dictyopteris delicatula* (A7569) afforded a single diterpene **54** with molecular formula $C_{20}H_{32}O_2$, which contained a single carbon-carbon double bond as indicated by ^{13}C-nmr spectroscopy. The compound was tetracyclic and by ir spectroscopy lacked carbonyl and hydroxyl functions. The presence of four oxygenated carbons was indicated in the ^{13}C-nmr spectrum of **54** and because of their unusually shielded nature (60–64 ppm), the presence of two epoxides was proposed. This accounted for two of the rings required by the molecular formula; the diterpene skeleton was thus bicyclic. The nature of the ring system was deduced on the basis of short and long range two-dimensional ^{13}C-^{1}H shift correlated nmr experiments (Table 4). These data led to the establishment of four molecular fragments (Scheme 2). Connectivities between the fragments were established on the basis of homonuclear ^{1}H-nmr double resonance experiments (see Experimental). In this way the basic dolabellane skeleton was deduced for **54** with two epoxide groups (fragment

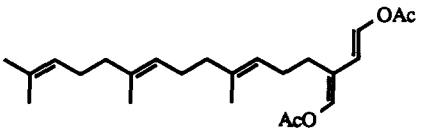
TABLE 4. ^{13}C-nmr Data for **68** and ^{13}C- and ^{1}H-nmr Data for **54**.[a]

Carbon	^{13}C (ppm)		^{1}H (δ) **54**	^{13}C-^{1}H Long Range Correlations **54**
	68	**54**		
C-1	42.9 (s)	44.5 (s)		
C-2	37.9 (t)	38.6 (t)	1.62 (m), 1.30 (m)	
C-3	63.0 (d)	63.8 (d)	3.06 (dd, J = 3.0, 11.3 Hz)	38.6, 63.8
C-4	61.8 (s)	60.7 (s)		
C-5	36.3 (t)	37.3 (t)	2.23 (ddd, J = 3.6, 3.6, 13.3 Hz) 1.35 (m)	
C-6	24.5 (t)	23.4 (t)	1.80 (m), 1.90 (m)	
C-7	142.3 (d)	63.6 (d)	2.94 (d, J = 7.5 Hz)	23.4, 63.6
C-8	135.5 (s)	60.7 (s)		
C-9	209.1 (s)	36.6 (t)	2.00 (dddd, J = 2.5, 4.5, 13.9, 15.6 Hz) 1.40 (m)	
C-10	29.6 (t)	27.6 (t)	2.20 (m), 1.58 (m)	
C-11	48.6 (d)	43.2 (d)	2.42 (brs, J = 12.0 Hz)	
C-12	87.1 (s)	141.3 (s)		
C-13	43.5 (t)	27.6 (t)	2.20 (m), 1.58 (m)	
C-14	41.0 (t)	40.4 (t)	1.72 (m), 1.50 (m)	
C-15	23.8 (q)	23.8 (q)	1.23 (s)	23.8, 38.6, 40.4, 43.2, 44.5
C-16	15.4 (q)	15.3 (q)	1.20 (s)	15.5, 37.3, 60.7, 63.8
C-17	11.9 (q)	17.5 (q)	1.43 (q)	17.5, 36.6, 60.7, 63.6
C-18	34.2 (d)	123.6 (s)		
C-19	17.7 (q)	21.7 (q)	1.59 (brs)	21.7, 22.0, 27.6, 123.6, 141.3
C-20	18.1 (q)	22.0 (q)	1.72 (brs)	22.0, 21.7, 123.6, 141.3

[a]Assignments for **54** are based on short (J = 125 Hz) and long (J = 10 Hz) range ^{13}C-^{1}H correlations.



SCHEME 2. Dotted lines indicate connectivities established from ^{1}H homonuclear decoupling experiments.



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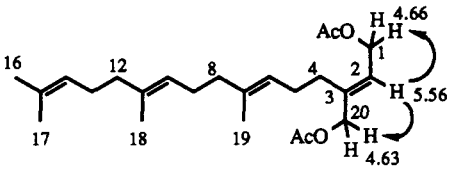

Arrows indicate nOe

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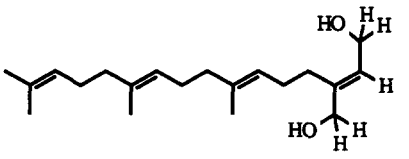

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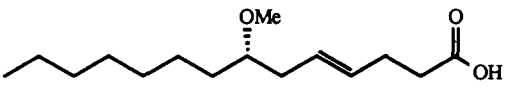
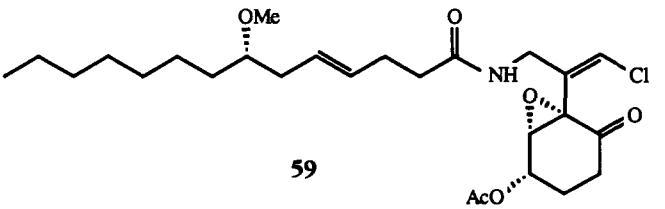


58



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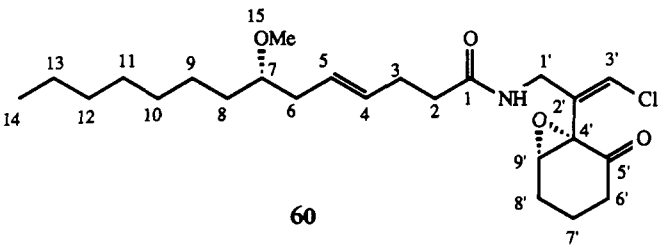
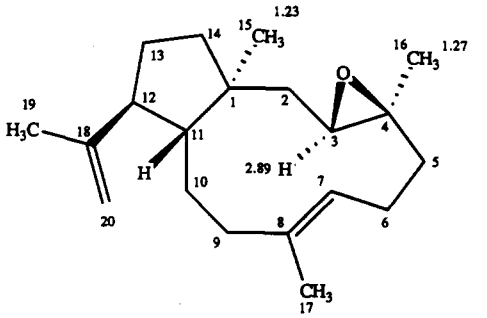


60

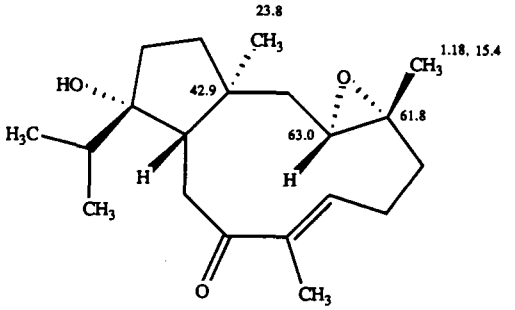
5, Scheme 2). The proposed structure contains six chiral centres. On the basis of literature precedents as well as ^{13}C and ^{1}H nmr comparisons of data for **54** with those for the known dolabellane derivatives **67** (17) and **68** (18), (Table 4), the ring junction stereochemistry (C-1–C-11) in **67** and **68** was trans, and the same is proposed for **54**. The 3,4-epoxide group in **54** is believed to have the same relative stereochemistry as **68** and the opposite to **67**, based on the extreme similarity between ^{13}C- and ^{1}H-nmr data between **68** and **54** in this region. NOe experiments performed in an attempt to resolve the stereochemistry at C-7 and C-8 were inconclusive. The new dolabellane derivative **54** is thus (1*R**,3*R**,4*S**,11*R**)-3,4;7,8-bisepoxydolabellan-12(18)-ene.

A NEW CYANOPHYTA METABOLITE **60**.—A blue-green alga, *Lyngbya* sp. (A7566), yielded three compounds of interest, **58**, **59**, and **60**.

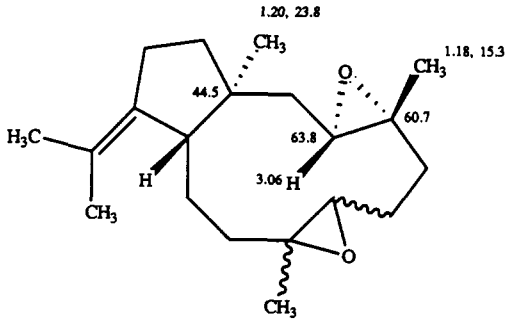
Compound **58** was the known *Lyngbya* metabolite (7*S*)-7-methoxytetradec-4-enoic acid (19) with which it was shown to be identical in all respects including specific rota-



67



68

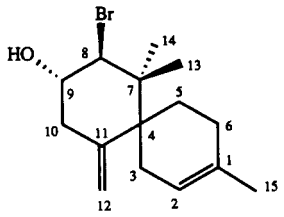


54

tion. The *E* configuration of the double bond was confirmed by obtaining the ^{1}H-nmr spectrum for **58** using C_6D_6 as the solvent. Under these conditions, the two vinyl protons showed $J_{4,5}$= 15.2 Hz, consistent with the earlier assignment of the *E* configuration for the Δ^4 double bond, based on ir spectroscopy. Isolate **59**, molecular formula $C_{26}H_{40}NO_6Cl$, was identified as malyngamide C (19), whose complete structure was recently published by Ainslie *et al.* (20).

Compound **60**, molecular formula $C_{24}H_{38}NO_4Cl$, was closely related to malyngamide C **59**. The ^{1}H-nmr spectra of **59** and **60** were virtually identical except for a one-proton multiplet at δ 5.4, broadening of the epoxy methine signal at δ 4.54 (brs), and the absence of an acetoxy methyl resonance at δ 2.1 in the spectrum of **60**. It appeared that **60** was a deacetoxymalyngamide C. This was confirmed by detailed comparison of the ^{13}C- and ^{1}H-nmr spectra of **59** and **60** (see Experimental). The new metabolite **60** is 8′-deacetoxymalyngamide C.

A NEW CHLOROPHYTA METABOLITE **66**.—From a sample of *Chlorodesmis fas-*



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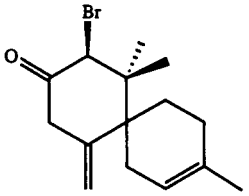

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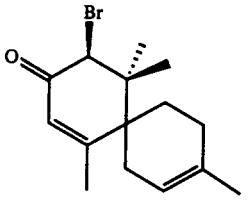

70

tigiata (A7563) two diterpenes, **65** and **66**, were isolated. Compound **65** was readily identified as the known isolate didehydrotrifarin, a tetraprenyl bisdienylacetate believed to have significant feeding deterrent properties (21).

The more polar metabolite **66** had the molecular formula $C_{24}H_{38}O_4$ and showed signals in the ^{13}C-nmr spectrum for four carbon-carbon double bonds and two acetoxyl carbonyl groups. The molecule was thus acyclic. The ^{1}H-nmr spectrum evidenced the presence of four vinyl methyl groups, two acetoxy methyl groups, and four vinyl protons. Comparison of the ^{13}C- and ^{1}H-nmr spectra of **65** and **66** showed that each compound contained the same unsubsituted tris-isoprene moiety. The terminal 1,4-diacetoxybutadiene function of **65** was, however, not present and instead a 1,4-diacetoxybut-2-enyl moiety was present in **66**. This was revealed by the following homonuclear proton double resonance experiment in which irradiation at δ 5.56 (H-2) collapsed the doublet at δ 4.66 (H-1, H-1′) to a singlet and sharpened the broad two-proton singlet at δ 4.63 (H-20, H-20′). The C-1 and C-20 methylene carbons (58.6, 61.0 ppm) bore the acetoxyl groups. The configuration of the 2,3 double bond was determined to be *E* based on nOe experiments, in which low power irradiation at δ 5.56 caused enhancement of the signals at δ 4.66 (1%) and 4.63 (1%). Compound **66** is thus (2*E*,6*E*,10*E*)-1-acetoxy-3-acetoxymethyl-7,11,15-trimethylhexadeca-2,6,10,14-tetraene.

EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—Melting points were measured on a Reichert microscope hot-stage apparatus and are uncorrected. Mass spectra were recorded on a JEOL D-100 mass spectrometer with peak matching unit. All ^{1}H-nmr and ^{13}C-nmr spectra were recorded using a Bruker AM300 nmr spectrometer. Unless otherwise stated the nmr solvent is $CDCl_3$ containing a trace of $CHCl_3$, which is used as the internal reference for ^{1}H-nmr measurements (δ 7.26). Ir spectra were recorded on a Perkin-Elmer 297 infrared spectrometer as either liquid films or Nujol mulls, and uv spectra were recorded in EtOH on a Varian 634 uv spectrophotometer. Optical rotations were recorded with a Perkin-Elmer 141 polarimeter using $CHCl_3$ as solvent at 20°.

Si gel (type 60, Merck) was used for vacuum liquid chromatography (vlc) (22), and plastic-backed plates coated with Si gel F_{254} (Merck) were used for tlc. Hplc was carried out with either a Waters 6000A or 4500A solvent delivery system connected to a Waters U6K injector and a Waters R401 differential refractometer. Hplc columns were from Techsil (250 × 8 mm, filled with Techsil 5 μm silica) and Hewlett-Packard (250 × 8 mm, filled with Si-100 7 μm). These hplc columns were used either in series or alone. All solvents were distilled prior to use.

PLANT MATERIAL.—All plant material was collected by divers using self-contained underwater breathing apparatus (scuba). After collection, plant materials were deep frozen until they were either freeze-dried or wet-extracted with MeOH or MeOH/CH_2Cl_2 mixtures. Voucher specimens were deposited with the James Cook University's Botany Department Herbarium (JCT) (Table 1).

ISOLATION FROM *L. MAJUSCULA*.—A sample of the alga (130 g) was collected from Florence Bay, Magnetic Island, and wet-extracted with 500 ml of a MeOH-CH_2Cl_2 (1:1). The CH_2Cl_2-soluble portion of the resultant extract (2.0 g, 1.5%) was separated by vlc (22) on Si gel using a step gradient solvent elution from light petroleum ether to EtOAc to afford 11 fractions of 100 ml each. Hplc separation of combined fractions 1–3 using two 250 × 8 mm normal phase silica columns in series, one with Techsil 5 silica

packing and the other with Hewlett Packard Si-100 7 μm packing, and light petroleum ether-EtOAc (97:3) as the eluent, afforded the chamigrene **31** and two triquinane derivatives **24** (7) and **32**. From fractions 4–11 the metabolites **25**, **26**, and **28** were obtained and identified on the basis of their ^{1}H- and ^{13}C-nmr spectroscopic data, which were all identical with those reported in the literature (7).

CHARACTERIZATION OF (1*Z*,8*R**,9*R**)-8-BROMOCHAMIGRA-1,11(12)-DIENE-9-OL [**31**].—A clear oil (14 mg, 0.001%): [α]D −58.9° (*c* = 0.4); hrms found 298.093, calcd 298.093 for $C_{15}H_{23}O^{79}Br$; eims *m/z* (% rel. int.) $[M]^+$ 298 (4), 283 (11), 219 (30), 217 (8), 203 (18), 202 (25), 201 (88), 185 (10), 175 (12), 173 (25), 163 (11), 161 (12), 159 (29), 157 (13), 147 (26), 145 (48), 135 (45), 133 (35), 121 (37), 119 (100), 117 (18); ir ν max (film) cm^{-1} 3360, 2900, 1440, 1100, 890, 790; ^{1}H nmr ($CDCl_3$, 300 MHz) and ^{13}C nmr ($CDCl_3$, 75 MHz) see Table 2. NOe experiments: irradiation at δ 0.94 caused enhancement of the signals around δ 1.60 (1%) and specific enhancement of the δ 3.76 resonance (3%). Irradiation at δ 1.21 caused enhancement of the resonances at δ 2.23 (3%) and δ 4.46 (4%). Irradiation at δ 4.73 caused enhancement of the signal at δ 2.02 (1%).

JONES OXIDATION OF **31**.—To a stirred solution of **31** (12 mg, 0.04 mmol) in Me_2CO (2 ml) Jones reagent was added until the solution had a permanent orange coloration. Addition of MeOH (2 ml) followed by removal of Me_2CO in vacuo yielded 1.5 ml of a green solution that was diluted to 4.5 ml with H_2O. Extraction of this solution with Et_2O (3 × 5 ml) followed by drying over $MgSO_4$ and solvent removal in vacuo afforded **69** (3 mg): ^{1}H nmr ($CDCl_3$, 300 MHz) δ 0.94 (s, 3H, Me-13), 1.12 (s, 3H, Me-14), 1.62 (s, 3H, Me-15), 1.30–2.40 (m, 6H), 3.23 (d, 1H, *J* = 14.3 Hz, H-10), 3.43 (d, 1H, *J* = 14.3 Hz, H-10), 4.80 (s, 1H, H-12), 5.06 (s, 1H, H-12), 5.13 (s, 1H, H-8), 5.34 (brs, 1H, H-2).

ALLYLIC REARRANGEMENT OF **69**.—Allowing **69** to stand in the freezer in a $CDCl_3$ solution overnight at −4° facilitated allylic rearrangement to afford **70** in a quantitative yield (3 mg): [α]D −58.5° (*c* = 0.2); ir ν max (film) cm^{-1} 2920, 1670, 1440, 1375, 870; ^{1}H nmr ($CDCl_3$, 300 MHz) δ 0.99 (s, 3H, Me-13), 1.24 (s, 3H, Me-14), 1.69 (s, 3H, Me-15), 1.58–2.13 (m, 5H), 2.00 (s, 3H, Me-12), 2.35 (d, 1H, *J* = 18.1 Hz, H-3), 5.10 (s, 1H, H-8), 5.49 (brs, 1H, H-2), 6.00 (s, 1H, H-10); ^{13}C nmr ($CDCl_3$, 75 MHz) 18.6 (q), 23.2 (q), 24.0 (q), 24.6 (q), 28.1 (t), 26.9 (t), 29.9 (t), 46.1 (s), 47.4 (s), 67.5 (d), 121.3 (d), 125.6 (d), 135.4 (s), 169.6 (s), 190.1 (s) ppm.

CHARACTERIZATION OF (1*R**,2*S**,3*R**,5*S**,8*S**,9*R**)-2,3,5,9-TETRAMETHYLTRICYCLO-[6.3.0.0^{1,5}]UNDECAN-3-OL [**32**].—A clear oil (14 mg, 0.001%): [α]D −19.4° (*c* = 0.3); hrms found 222.198, calcd 222.198 for $C_{15}H_{26}O$; eims *m/z* (% rel. int.) $[M]^+$ 222 (2), 203 (4), 201 (15), 175 (12), 164 (10), 149 (13), 145 (9), 135 (75), 133 (12), 111 (15), 109 (33), 107 (30), 105 (20), 98 (100), 95 (52), 91 (23); ir ν max (film) cm^{-1} 3450, 2900, 2850, 1440, 1360, 910; ^{1}H nmr ($CDCl_3$, 300 MHz) δ 0.8 (d, 3H, *J* = 6.5 Hz), 0.9 (d, 3H, *J* = 7.2 Hz), 1.1 (s, 3H), 1.1 (s, 3H), 1.0–1.8 (complex multiplet, 14H), ^{13}C nmr ($CDCl_3$, 75 MHz) see Table 3; ^{1}H nmr ($CDCl_3$, 300 MHz) and ^{13}C nmr ($CDCl_3$, 75 MHz), after an equimolar amount of Eu(fod)$_3$ shift reagent had been added, see Table 3.

ISOLATION FROM *D. DELICATULA*.—A sample of the alga collected from Geoffrey Bay, Magnetic Island, was frozen and subsequently freeze-dried. The dried tissue (174.3 g) was extracted with 3 liters of CH_2Cl_2 to afford 17.2 g (9.9%) of CH_2Cl_2 solubles. Of these solubles, 6.4 g was separated by vlc on Si gel using a step gradient solvent elution from light petroleum ether to EtOAc to afford 15 fractions of 100 ml each. Hplc separation of combined fractions 6–8 using two 250 × 8 mm normal phase silica columns in series, one with Techsil 5 silica packing and the other with Hewlett Packard Si-100 7μm packing, and hexane-EtOAc (94:6) as the eluent afforded a single diterpene **54**.

CHARACTERIZATION OF (1*R**,3*R**,4*S**,11*R**)-3,4;7,8-BISEPOXYDOLABELLAN-12(18)-ENE [**54**].—A clear oil (76 mg, 0.12%): [α]D +86.0° (*c* = 0.4); hrms found 304.240, calcd 304.240 for $C_{20}H_{32}O_2$; eims *m/z* (% rel. int.) $[M]^+$ 304 (2), 288 (1), 261 (1), 245 (2), 217 (2), 201 (1), 193 (4), 189 (2), 181 (4), 175 (5), 161 (4), 149 (7), 136 (11), 135 (29), 134 (19), 133 (17), 121 (29), 107 (28), 95 (24), 81 (20), 42 (100); ir ν max (film) cm^{-1} 2930, 1455, 1385, 1260, 1090, 895, 690; ^{1}H nmr ($CDCl_3$, 300 MHz) and ^{13}C nmr ($CDCl_3$, 75 MHz) see Table 4. Double resonance experiments: irradiation at δ 3.06 simplified resonances at δ 1.30 and δ 1.62. Irradiation at δ 1.62 collapsed the doublet of doublets at δ 3.06 to a doublet and simplified the resonance at δ 1.30. Irradiation at δ 2.94 simplified the complex resonance at δ 1.85. Irradiation at δ 1.80 reduced the doublet at δ 2.94 to a sharp singlet while the δ 1.90, 1.35, and 2.23 resonances were all simplified. Irradiation at δ 2.42 sharpened the signals at δ 1.72 and 1.59 while also affecting the δ 2.20 and 1.58 resonances. Irradiation at δ 1.58 affects signals at δ 1.40, 1.50, 2.00, 2.20, and 1.72. Irradiation at δ 2.20 affected resonances at 1.40, 1.50, 1.58, 2.00, and 1.72.

ISOLATION FROM *LYNGBYA* SP.—A sample (1470 g) of a shallow water *Lyngbya* sp. was collected from Broadhurst Reef and deep frozen. The frozen material was freeze-dried, and the dry tissue (565.7 g) was extracted with 4 liters of CH_2Cl_2. The CH_2Cl_2-soluble material (12.7 g, 2.3%) was separated by vlc

on Si gel using a step gradient solvent elution from hexane to Et_2O to afford 17 fractions of 100 ml each. Fractions 7–12 were predominantly a single compound **58**. Hplc separation of fraction 14, using the column system previously described and light petroleum ether-EtOAc (3:2) as the eluent, afforded two compounds **59** and **60**.

CHARACTERIZATION OF **58**.—A clear oil (200 mg, 0.035%): $[\alpha]_D -12.8°$ ($c = 0.22$) [lit. (23) $-11.1°$]; hrms found 225.181, calcd 225.185 for $C_{14}H_{25}O_2$; eims *m/z* (% rel. int.) $[M-OMe]^+$ 225 (1), 157 (2), 143 (88), 111 (20), 97 (5); ir ν max (film) cm^{-1} 3150, 2930, 1710, 1445, 1095, 975; ^1H nmr ($CDCl_3$, 300 MHz) and ^{13}C nmr ($CDCl_3$, 75 MHz) were identical with those previously published (27); ^1H nmr (C_6D_6, 300 MHz) δ 0.90 (m, 3H, Me-14), 1.28 (m, 10H, H_2-9, -10, -11, -12, -13), 1.45 (m, $2H_2$-8), 2.16 (m, 6H, H_2-2, -3, -6), 3.05 (m, 1H, H-7), 3.17 (s, 3H, 15-OMe), 5.35 (dt, 1H, $J = 15.2$, 6.1 Hz, H-4) 5.49 (dt, 1H, $J = 15.1$, 6.1 Hz, H-5).

CHARACTERIZATION OF **59**.—A clear oil (42 mg, 0.007%): $[\alpha]_D -23.1°$ ($c = 0.6$) [lit. (24) $-32.4°$]; hrms found 498.255, calcd 498.254 for $C_{26}H_{39}O_6N^{37}Cl$; eims *m/z* (% rel. int.) $[M-H]^+$ 498 (1), 355 (2), 320 (1), 301 (2), 266 (2), 155 (13), 143 (32), 85 (18), 69 (100); ir ν max (film) cm^{-1} 3380, 3300, 2930, 2860, 1745, 1715, 1655, 1525, 1455, 1435, 1370, 1235, 1095, 1040, 975, 895, 855; ^1H nmr ($CDCl_3$, 300 MHz) δ 0.86 (m, 3H, Me-14), 1.25 (brs, 10H, H_2-9, -10, -11, -12, -13), 1.42 (m, 2H, H_2-8), 2.01 (m, 2H, H_2-7), 2.14 (s, 3H, 11′-OAc), 2.17 (t, 1H, $J = 5.2$ Hz, H-2′), 2.25 (m, 2H, H_2-6), 2.35 (m, 1H, H-6′), 2.29 (m, 2H, H_2-3), 2.29 (m, 1H, H-2), 2.60 (dt, 1H, $J = 4.0$, 17.8 Hz, H-6″), 3.12 (m, 1H, H-7), 3.30 (s, 3H, 15-OMe), 3.64 (s, 1H, H-9′), 3.85 (dd, 1H, $J = 4.8$, 14.7 Hz, H-1″), 3.97 (dd, 1H, $J = 4.8$, 14.7 Hz, H-1′), 5.44 (m, 1H, H-8′), 5.46 (m, 1H, H-4), 5.46 (m, 1H, H-5), 6.10 (bt, 1H, $J = 4.8$ Hz, NH), 6.39 (s, 1H, H-3′); ^{13}C nmr ($CDCl_3$, 75 MHz) 14.1 (q), 20.9 (q), 21.5 (t), 22.6 (t), 25.3 (t), 28.4 (t), 29.3 (t), 29.7 (t), 31.8 (t), 33.3 (t), 35.0 (t), 36.3 (t), 36.3 (t), 40.3 (t), 56.4 (q), 61.5 (s), 62.6 (d), 68.4 (d), 80.7 (d), 122.8 (d), 127.6 (d), 130.7 (d), 133.1 (s), 170.4 (s), 172.4 (s), 200.9 (s) ppm.

CHARACTERIZATION OF 8′-DEACETOXYMALYNGAMIDE C [**60**].—A yellow oil (54 mg, 0.0096%): $[\alpha]_D +5.8°$ ($c = 0.8$); hrms found 422.234, calcd 422.242 for $C_{24}H_{35}O_3N^{37}Cl$; eims *m/z* (% rel. int.) $[M-H]$ 440 (<1), $[M-H-H_2O]$ 422 (1), 404 (1), 315 (1), 243 (3), 208 (4), 148 (3), 143 (35), 111 (12), 83 (10), 69 (100); ir ν max (film) cm^{-1} 3380, 3300, 2930, 2860, 1760, 1710, 1655, 1530, 1455, 1365, 1095, 970, 790, 765; ^1H nmr ($CDCl_3$, 300 MHz) δ 0.88 (m, 3H, Me-14), 1.27 (brs, 10H, H_2-9, -10, -11, -12, -13), 1.42 (m, 2H, H_2-8), 2.15 (m, 2H, H_2-6), 2.17 (m, 2H, H_2-11), 2.20 (m, 2H, H_2-8), 2.30 (m, 2H, H_2-7′), 2.24 (m, 1H, H-6′), 2.31 (m, 2H, H_2-3), 2.33 (m, 2H, H_2-2), 2.57 (dt, 1H, $J = 17.2$, 4.2 Hz, H-6″), 3.14 (m, 1H, H-7), 3.32 (s, 3H, 15-OMe), 3.54 (brs, 1H, H-9′). 3.86 (dd, 1H, $J = 4.8$, 14.6 Hz, H-1″), 3.99 (ddd, 1H, $J = 1.3$, 5.6, 14.6 Hz, H-1′) 5.47 (m, H-4), 5.47 (m, 1H, H-5), 6.18 (brt, 1H, $J = 5.6$ Hz, NH), 6.36 (s, 1H, H-3′); ^{13}C nmr ($CDCl_3$, 75 MHz) 14.1 (q), 16.7 (t), 22.6 (t), 23.3 (t), 25.3 (t), 28.5 (t), 29.3 (t), 29.7 (t), 31.8 (t), 33.3 (t), 36.3 (t), 36.4 (t), 37.2 (t), 40.6 (t), 56.4 (q), 60.5 (s), 62.9 (d), 80.7 (d), 122.0 (d), 127.5 (d), 130.7 (d), 134.1 (s), 172.3 (s), 208.3 (s) ppm.

ISOLATION FROM *C. FASTIGIATA*.—A sample (43 g) collected from John Brewer Reef was wet-extracted with 3.5 liters of MeOH to provide 1.27 g (0.3%) of CH_2Cl_2-soluble material. Vlc of this extract on Si gel using a step gradient solvent elution from light petroleum ether to Et_2O afforded 10 fractions of 75 ml each. Hplc separation of fraction 2, using the two columns in series as described previously and light petroleum ether-EtOAc (9:1) as eluent, afforded a single diterpene **65**. Hplc separation of fraction 3, as for fraction 2, except the eluent was light petroleum ether-EtOAc (88:12), afforded another diterpene **66**.

CHARACTERIZATION OF **65**.—A clear oil (52 mg, 4.09%) with ^1H-nmr, ^{13}C nmr, uv, and ir spectral data identical to those previously reported (29).

CHARACTERIZATION OF (2*E*,6*E*,10*E*)-1-ACETOXY-3-ACETOXYMETHYL-7,11,15-TRIMETHYLHEXADECA-2,6,10,14-TETRAENE [**66**].—An optically inactive clear oil (32 mg, 2.52%): hrms found 390.276, calcd 390.276 for $C_{24}H_{38}O_4$; eims *m/z* (% rel. int.) $[M]^+$ 390 (<1), 330 (<1), 321 (<1), 269 (<1), 229 (<1), 227 (<1), 204 (1), 201 (4), 159 (9), 81 (63), 69 (94), 43 (100); ir ν max (film) cm^{-1} 2925, 1738, 1445, 1370, 1225, 1025; ^1H nmr ($CDCl_3$, 300 MHz) δ 1.59 (s, 9H, Me-17, -18, -19), 1.68 (s, 3H, Me-16), 1.90–2.20 (m, 12H, H_2-4, -5, -8, -9, -12, -13), 2.05 (s, 3H, Me-22), 2.06 (s, 3H, Me-24), 4.63 (s, 2H, H_2-20), 4.66 (d, 2H, $J = 7.0$ Hz, H_2-1), 5.10 (m, 3H, H-6, -10, -13), 5.56 (t, 1H, $J = 7.0$ Hz, H-2); ^{13}C nmr ($CDCl_3$, 75 MHz) 16.0 (q), 16.0 (q), 17.6 (q), 20.9 (q), 20.9 (q), 25.7 (q), 26.3 (t), 26.6 (t), 26.7 (t), 35.1 (t), 39.7 (t), 39.7 (t), 60.4 (t), 61.7 (t), 123.1 (d), 123.9 (d), 124.1 (d), 124.3 (d), 131.3 (s), 135.0 (s), 136.0 (s), 139.5 (s), 170.8 (s), 170.8 (s) ppm. Double resonance experiments: irradiation at δ 5.56 (H-2) caused collapse of the doublet at δ 4.66 (1-CH_2) to a singlet and enhancement of the signals at δ 5.10 and 4.63.

HYDROLYSIS OF **66**.—To 8.27 mg (0.021 mmol) of **66** in MeOH (2 ml), 0.06 mmol of NaOH [0.29 ml of a solution prepared by dissolving 91.6 mg of NaOH in MeOH-H_2O (4:1)] was added. The resulting solution was stirred at room temperature for 30 min, and all solvents were removed in vacuo. The aqueous solution and solids remaining were extracted with 4 × 25-ml portions of Et_2O. Removal of Et_2O followed by purification of the crude product afforded 2 mg (31% yield) of the diol (2*E*,6*E*,10*E*)-3-hydroxymethyl-7,11,15-trimethylhexadeca-2,6,10,14-tetraen-1-ol [**71**]. An optically inactive clear oil; ir ν max (film) cm^{-1} 3380, 2920, 1620, 1505, 1465, 1345, 1230, 968, 960; ^1H nmr ($CDCl_3$, 300 MHz) δ 1.60 (s, 3H, Me-16), 1.60 (s, 3H, Me-18), 1.60 (s, 3H, Me-19), 1.68 (s, 3H, Me-17), 1.90–2.20 (m, 12H, H_2-4, -5, -8, -9, -12, -13), 4.18 (s, 2H, H_2-20), 4.21 (d, 2H, J = 7.0 Hz, H_2-1), 5.10 (m, 1H, H-6), 5.10 (m, 1H, H-10), 5.10 (m, 1H, H-14), 5.64 (t, 1H, J = 7.0 Hz, H-2); ^{13}C nmr ($CDCl_3$, 75 MHz) 16.1 (q), 16.1 (q), 17.7 (q), 25.7 (q), 26.6 (t), 26.6 (t), 26.7 (t), 35.8 (t), 39.7 (t), 39.7 (t), 58.6 (t), 6.10 (t), 123.5 (d), 124.1 (d), 124.4 (d), 126.7 (d), 131.3 (s), 135.1 (s), 135.9 (s), 143.7 (s) ppm.

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