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(−)-*TRANS*-7(*S*)-METHOXYTETRADEC-4-ENOIC ACID AND RELATED AMIDES FROM THE MARINE CYANOPHYTE *LYNGBYA MAJUSCULA*

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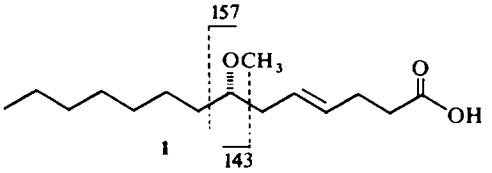
Key Word Index—*Lyngbya majuscula*; Oscillatoriaceae; blue-green alga; (−)-*trans*-7(*S*)-methoxytetradec-4-enoic acid; malyngamides A, B and C.

Abstract—(−)-*trans*-7(*S*)-Methoxytetradec-4-enoic acid and the related amides, malyngamides A, B and C, were found as constituents of shallow-water varieties of the marine blue-green alga *Lyngbya majuscula*.

INTRODUCTION

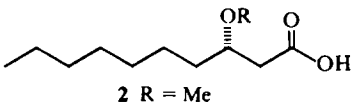
In our continuing studies of marine *Lyngbya* [1, 2] we find that (−)-*trans*-7(*S*)-methoxytetradec-4-enoic acid (**1**) is a major constituent in the lipid extracts of most shallow-water varieties of *L. majuscula*. Also present are various amides of **1**, 3 of which we have partially characterized and named malyngamides A, B, and C. Compound **1** and amides of **1** are not constituents of a deep-water variety of this blue-green alga.



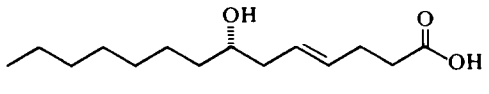
RESULTS AND DISCUSSION

Extraction of the wet or freeze-dried, shallow-water variety of *L. majuscula* with acetone followed by gel filtration and absorption chromatography of the extract produced an oily acid. ^{13}C NMR data showed that this compound had 15 carbons and 27 nonexchangeable hydrogens. One carbon was in a carboxylic acid group, two were olefinic methines in a 1,2-disubstituted double bond, one was a methine singly-bonded to oxygen, nine were methylenes and two were methyl carbons with one of them in a methoxyl group. The methoxyl group had to be attached to C-7 of a linear C_{14} carboxylic acid and the double bond had to be located between C-7 and the carboxylic acid group since the high resolution MS showed α-cleavage ions at *m/e* 143.14345 ($C_9H_{19}O^+$) and 157.08736 ($C_8H_{13}O_3^+$). Proton decoupling experiments on the methyl ester (see Experimental) suggested that the double bond was separated by one carbon from C-7 and by two carbons from the carboxylic acid group and the IR spectrum indicated that the geometry of the double bond was *trans* (970 cm^{-1}). The acid was therefore *trans*-7-methoxytetradec-4-enoic acid (**1**). The identification was confirmed by ozonolysis of **1** to give 3-methoxydecanoic acid (**2**).

The optical rotation of **2**, $[\alpha]_D$ +8.2° in $CHCl_3$, was comparable in magnitude but opposite in sign to the optical rotation of 3(*R*)-methoxybutanoic acid, $[\alpha]_D$ −11.6° (neat) [3] and 3(*R*)-methoxynonanoic acid, $[\alpha]_D$ −7.3° in $CHCl_3$, obtained by methylation of ricinoleic acid with methyl iodide and sodium hydride in DMF followed by ozonolysis. This showed that compound **2** had the *S* configuration at C-3 and **1** therefore the *S* configuration at C-7. To secure the assignments rigorously, **1** was demethylated with boron trifluoride and ethanethiol to *trans*-7(*S*)-hydroxytetradec-4-enoic acid (**3**) which had an $[\alpha]_D$ +2.5° in $CHCl_3$. By comparison a commercial sample of ricinelaidic acid (where C-12 is *R*) showed an $[\alpha]_D$ −2.1° in $CHCl_3$. Ozonolysis of **3** gave 3(*S*)-hydroxydecanoic acid (**4**) which had an $[\alpha]_D$ +17.5° in $CHCl_3$ that was intermediate in size but opposite in sign to those of 3(*R*)-hydroxynonanoic acid and 3(*R*)-hydroxydodecanoic acid in $CHCl_3$ (Table 1). 3(*S*)-Hydroxynonanoic acid (**5**) is reported to have $[\alpha]_D$ +19.8° in $CHCl_3$ [6]. In EtOH, **4** had $[\alpha]_D$ −16.6° compared with $[\alpha]_D$ −3.4° for **5** [6] and $[\alpha]_D$ +3.2° for 3(*R*)-hydroxynonanoic acid (Table 1). We expected **4** to have only a slightly higher levorotatory $[\alpha]_D$ than **5** in EtOH. No explanation can be made at this time for the



2 R = Me
4 R = H



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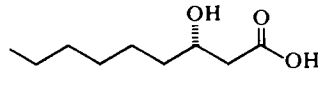

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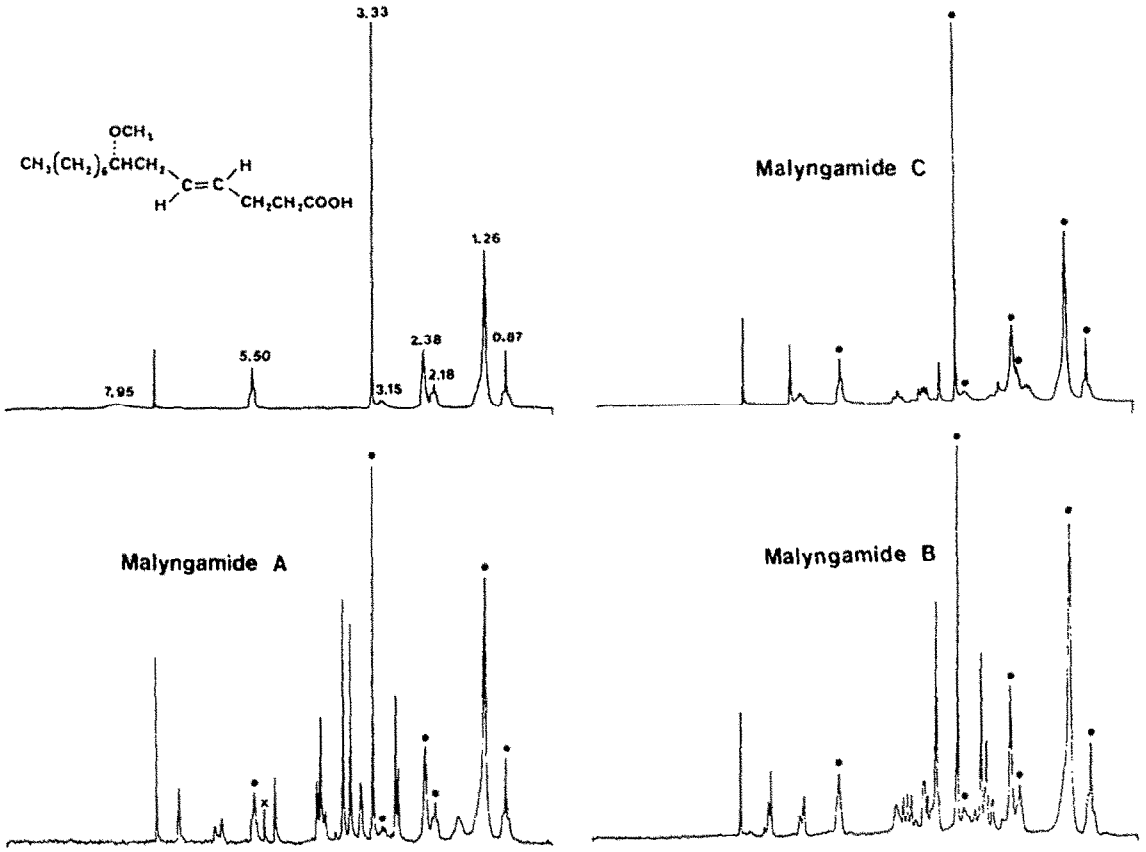


Fig. 1. 100 MHz PMR spectra of *trans*-7(*S*)-methoxytetradec-4-enoic acid (1) and malyngamides A, B and C in $CDCl_3$. The signals in the spectra of malyngamides A, B, and C corresponding to the *trans*-7(*S*)-methoxytetradec-4-enyl moiety are indicated by ●. The singlet at lowest field (δ 7.25) in the spectra of malyngamides A, B and C is residual $CHCl_3$.

discrepancy. These additional studies, however, clearly indicated that **1** has the 7*S* configuration.

Also present in the lipid extracts of shallow-water varieties of *Lyngbya majuscula* were *trans*-7(*S*)- methoxytetradec-4-enoic amides. In two varieties of this seaweed from Oahu, Hawaii (Kahala Beach and Kailua), we isolated a neutral, non-crystalline, optically active, chlorine-containing compound, malyngamide A, which exhibited absorptions in its PMR spectrum (Fig. 1) that were superimposable on those of **1**. Malyngamide A, which appeared to have the elemental formula $C_{29}H_{45}N_2O_6Cl$ on the basis of MS, could be readily hydrolysed to **1**. Since the IR spectrum of malyngamide A showed only amide-type carbonyl absorption, **1** most likely arose from cleavage of an amide functionality in malyngamide A. In the variety from Kailua, malyngamide A was accompanied by a closely-related compound, malyngamide B ($C_{28}H_{45}N_2O_6Cl$ suggested by high resolution MS of fragment ions at *m/e* 143 and 313), which also showed PMR signals that coincided with those of **1** (Fig. 1). In another shallow-water variety of *L. majuscula* from Fanning Island, we isolated a completely different compound, malyngamide C, of composition $C_{24}H_{38}NO_5Cl$. Malyngamide C also exhibited signals in its PMR spectrum that were the same as those of **1** (Fig. 1), except for the broad signal assigned to the C-2 and C-3 methylene protons which had shifted upfield in the PMR spectrum of malyngamide C. Acid hydrolysis of malyngamide C, however, led to **1**.

A deep-water variety of *L. majuscula* from Enewetak did not contain **1** or amides of **1**. The lipid extract contained two compounds, malyngamides D and E, which exhibited **1**-like absorptions in their PMR spectra, but the diagnostic fragment ion peak at *m/e* 143, which was intense in the EI mass spectra of **1** and all esters and amides of **1**, was absent. Moreover, acid hydrolysis of malyngamide E did not produce **1** but rather a different fatty acid. The PMR spectrum of the new acid, however, strongly suggested that it was a *trans*-7-methoxyalk-4-enoic acid since it showed signals for the C-2, C-3, C-4,

Table 1. Optical data for *R*-3-hydroxyalkanoic acids, CH_3-$(CH_2)_n$-CH(OH)-CH_2-CO_2H

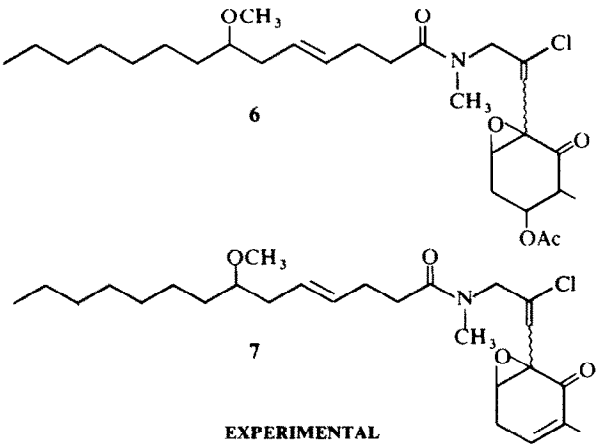
n	$[\alpha]_D$ EtOH	$[\alpha]_D$ $CHCl_3$	Reference
0	−17.3°		4[a]
1	−11	−35°	5[b]
2	−1°	−28°	5[c]
5	+3.2°	−19.6°	6[d]
8		−16.1°	7[e]

The temperature and concentration are (a) 25° and 12, (b) 25° and 2, (c) 24° and 2, (d) 20° and 5, and (e) 17° and 5.

C-5, C-6 and C-7 protons that were essentially identical with those of **1**.

No *trans*-7-methoxyalk-4-enoic acids or amides were detected in the lipid extract of a *L. semiplena* from Fanning Island. Compound **1** was found to be a major constituent in a cyanophyte tentatively identified as a *Crinalium* sp. (Oscillatoriaceae) from Fanning Island. *trans*-7-Methoxyalk-4-enoic acid and amides, however, were absent in several other specimens of Oscillatoriaceae, i.e. species of *Schizothrix*, *Oscillatoria*, *Symploca*, *Phormidium* and *Spirulina*.

Two *trans*-7-methoxytetradec-4-enoic amides, stylocheilamide and deactylstylocheilamide, have been isolated from the digestive gland of the sea hare *Stylocheilus longicauda* and proposed to have structures **6** and **7** [8]. The stereochemistry of the ring in **6** and **7** has been determined from X-ray crystallography of a degradation product, but the geometry of the chlorine-substituted double bond and the absolute configurations of the chiral centers remain unknown. Like the toxins associated with this gastropod mollusk [9], amides **6** and **7** appear to be dietary components and may be constituents of a *Lyngbya* sp.



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EXPERIMENTAL

PMR and ^{13}C NMR spectra were obtained at 100 MHz and 25 MHz on a spectrometer equipped with a Fourier transform system. Single frequency off-resonance decoupled ^{13}C NMR spectra were determined with the proton decoupler at δ 14. Proton chemical shifts are reported in δ ppm relative to TMS as internal standard. Carbon-13 chemical shifts are reported in δ relative to the solvent, i.e. $CDCl_3$ (δ = 76.9) or C_6D_6 (δ = 128), as internal standard. Electron impact MS were obtained at 70 eV. Elemental analyses were performed by Chemical Analytical Services, University of California, Berkeley.

Isolation: (*A*) trans-7(S)-*methoxytetradec-4-enoic acid*. *L. majuscula* was collected in shallow water at Kahala Beach, Oahu. The freeze-dried alga (680 g) was extracted twice with $CHCl_3$ (PMR inspection of the solvent showed the presence of more EtOH preservative than usual) and twice with MeOH. The combined extracts were evapd and the residual oily solid was soaked with $CHCl_3$–MeOH (3:1) and the mixture filtered. Evapn of the filtrate gave 37 g of a brown oil. The extract (34 g) was chromatographed on 550 g of Si gel with a hexane–$CHCl_3$ gradient. The fraction (1.69 g) eluted with 10–20% $CHCl_3$ in hexane was then chromatographed on 100 g of neutral Al_2O_3 with a hexane–$CHCl_3$ gradient. The first fraction (206 mg) was an oil, identified as ethyl linolenate on the basis of PMR and MS analyses. The second fraction was also an oil (247 mg). Further purification of 125 mg of fraction 2 on Sephadex LH-20 with MeOH–$CHCl_3$ (1:1) gave 76 mg of GLC-pure (10% SE-30 on Chromosorb P, 240°) Et *trans*-7(*S*)-methoxytetradec-4-enoate as a colorless oil, $[\alpha]_D^{26}$ −9° ($CHCl_3$, *c* 7.3); IR (neat) ν_{max} 2920, 2850, 2820, 1735, 970 cm^{-1}: PMR ($CDCl_3$) δ 5.49 (*m*, 2H), 4.14 (*q*, *J* = 7 Hz, 2H), 3.33 (*s*, 3H), 3.15 (*m*, 1H), 2.36 (*br s*, 4H), 2.19 (*bt*, 2H), 1.27 (*br s* with low field *sh*, 12H), 1.25 (*t*, *J* = 7 Hz, 3H), 0.88 (*bt*, *J* = 7 Hz, 3H). ^{13}C NMR ($CDCl_3$) δ 172.89 (C=O), 130.27 (=CH), 127.36 (=CH), 80.69, (OCH), 60.17 (OCH_2), 56.38 (OCH_3), 36.30 (CH_2), 34.19 (CH_2), 33.31 (CH_2), 31.81 (CH_2), 29.70 (CH_2), 29.26 (CH_2), 27.94 (CH_2), 25.21 (CH_2), 22.56 (CH_2), 14.20 (CH_3), 14.02 (CH_3); ^{13}C NMR (C_6D_6) δ 172.29 (C=O), 130.73 (=CH), ~128.0 (=CH, obscured by solvent peak), 80.97 (OCH), 60.10 (OCH_2), 56.40 (OCH_3), 36.94 (CH_2), 34.47 (CH_2), 33.94 (CH_2), 32.36 (CH_2), 30.33 (CH_2), 29.80 (CH_2), 28.48 (CH_2), 25.84 (CH_2), 23.20 (CH_2), 14.39 ($2CH_3$); MS *m/e* (rel. intensity) 285 (0.2), 284 (0.1, M^+), 253 (1.5), 239 (1), 207 (17), 185 (10), 143 (77), 111 (55), 97 (40), 83 (37), 69 (100).

A mixture of 20 mg of Et ester and 2 ml of 10% NaOH soln was refluxed for 5 hr, acidified with dil H_3PO_4 and extracted with CH_2Cl_2 to give 18 mg of *trans*-7(*S*)-methoxytetradec-4-enoic acid (**1**, 0.02% of dried alga) as a colorless oil, $[\alpha]_D^{26}$ −11.1° ($CHCl_3$, *c* 3.9). IR ($CHCl_3$) ν_{max} 3520, 3410, 2925, 2850, 1715, 970 cm^{-1}; PMR ($CDCl_3$) δ 7.95 (*br*, 1H, CO_2H), 5.50 (*br t*, 2H, C-4 and C-5 methines), 3.33 (*s*, 3H, OCH_3), 3.15 (*br p*, 1H, C-7 methine), 2.38 (*br*, 4H, C-2 and C-3 methylenes), 2.18 (*br t*, 2H, C-6 methylene), 1.26 (*br s* with low field *sh*, 12H, C-8 to C-13 methylenes), 0.87 (*br t*, 3H, C-14 methyl); ^{13}C NMR (C_6D_6) δ 179.08 (C=O), 130.29 (=CH), 127.49 (=CH), 80.98 (OCH), 56.32 (OCH_3), 36.94 (CH_2), 34.13 (CH_2), 33.95 (CH_2), 32.36 (CH_2), 30.25 (CH_2), 29.85 (CH_2), 28.14 (CH_2), 25.85 (CH_2), 23.21 (CH_2), 14.40 (CH_3); MS *m/e* (rel. intensity) 256 (0.1), 225 (0.1), 207 (0.5), 157 (1), 155 (2), 143 (100), 111 (22), 69 (80), 55 (25), 45 (22); high resolution MS *m/e* 157.08736 (calcd. for $C_8H_{13}O_3$, 157.08647), 155.07107 (calcd. for $C_8H_{11}O_3$, 155.07082), 143.14345 (calcd. for $C_9H_{19}O$, 143.14359). (Found: C, 70.1; H, 10.9. Calcd. for $C_{15}H_{28}O_3$: C, 70.3; H, 11.0%).

In another expt freshly collected *L. majuscula* from Kahala Beach was frozen and extracted twice with MeOH and then twice with $CHCl_3$. Work up of the combined extracts as described above led to the Me ester of **1** as a GLC-pure (10% SE-30 on Chromosorb P, 240°) colorless oil; IR ($CHCl_3$) ν_{max} 1735, 970 cm^{-1}; PMR ($CDCl_3$) δ 5.49 (*t*, C-4 and C-5 methines), 3.67 (*s*, CO_2CH_3), 3.33 (*s*, OCH_3 on C-7), 3.15 (*br p*, *J* = 6–7 Hz, C-7 methine), 2.37 (*br s*, C-2 and C-3 methylenes, →sharper *s* on irr. at 5.49), 2.18 (*br*, *t*, *J* = 6–7 Hz, C-6 methylene → sharp *d* on irr. at 5.49 and *br d* on irr. at 3.15), 1.26 (*br s* with low field *sh*, C-8, C-9 C-10, C-11, C-12, and C-13 methylenes), 0.88 (*bt*, *J* = 7 Hz, C-14 methyl); MS *m/e* (rel. intensity) 271 (2, M^+ + 1), 269 (2), 239 (13), 207 (36), 189 (13), 171 (27), 143 (100); high resolution MS *m/e* 171.102547 (calcd. for $C_9H_{15}O_3$, 171.102123), 143.143454 (calcd. for $C_9H_{19}O$, 143.143594).

trans-7(*S*)-Methoxytetradec-4-enoic acid could be obtained directly from the alga using the following procedure. Freeze-dried *L. majuscula* (1.24 kg), collected at Kahala Beach, Oahu in January 1977, was extracted successively with petrol, CH_2Cl_2, Me_2CO, and *iso*PrOH to give 1.5, 12, 9.5, and 2.2 g of extract, respectively. The Me_2CO extract was partitioned between EtOAc and aq. 0.2 M NaH_2PO_4. The EtOAc phase was washed with aq. Na_2HPO_4 and evapd to give 6.5 g of oil. Chromatography of 5 g of this oil on 150 g of Si gel gave 360 mg of a dark green oil that was eluted with 10–20% EtOAc in C_6H_6. Gel filtration on a 2.5 cm × 1.9 m column of Sephadex LH-20 with $CHCl_3$–MeOH (1:1) yielded a fraction (671–694 ml) which contained 290 mg of spectrally pure **1**.

Using similar procedures **1** was isolated in 0.02% yield or higher from shallow water varieties of *L. majuscula* collected at Enewetak and Kwajalein in the Marshall Islands and in the lagoon near Cartwright Point, Fanning Island. Compound **1** was also isolated from a *Crinalium* sp. collected in the lagoon near the Cable Station, Fanning Island and had $[\alpha]_D^{23.5}$ −14.1° ($CHCl_3$, *c* 0.34).

(*B*) *Malyngamide A*. Freeze-dried *L. majuscula* from Kahala Beach, Oahu was extracted successively with petrol, CH_2Cl_2, Me_2CO and *iso*PrOH. The CH_2Cl_2 extract (1.52 g) was applied

to a 180 × 2.5 cm column of Sephadex LH-20 and the chromatogram eluted successively with 645 ml of CH_2Cl_2, hexane (4:1), 630 ml of CH_2Cl_2–Me_2CO (3:2), and 425 ml of CH_2Cl_2–Me_2CO (1:4). After 325 ml of CH_2Cl_2–hexane (4:1) had passed through the column, 11 fractions were collected: A, 325–425 ml, 225 mg; B, 425–470 ml, 208 mg; C (mostly majusculamides [1] by PMR analysis), 470–555 ml, 168 mg; D (mostly majusculamides [1] by PMR analysis), 555–645 ml, 129 mg; E, 645–825 ml, 160 mg; F, 825–925 ml, 58 mg; G, 925–1025 ml, 207 mg; H, 1025–1275, 171 mg; I, 1275–1375 ml, 42 mg; J, 1375–1500 ml, 111 mg; K, 1500–1700 ml, 32 mg.

Chromatography of fraction B (165 mg) on neutral Al_2O_3 (20 g) with CH_2Cl_2–MeOH (49:1) followed by gel filtration on Sephadex LH-20 with $CHCl_3$–MeOH (1:1), chromatography on Bio-Beads SX-8 with C_6H_6 and HPLC on μ-Bondapak-CN with hexane and 1,2-dichloroethane (43:7) gave 13 mg of malyngamide A as a colorless oil, $[\alpha]_D^{25}$ −6.5° (CH_2Cl_2, *c* 0.77); MS *m/e* 554 and 552 (M^+, 1:3 rel. intensity), 517 (M^+ −Cl), 143; high resolution MS *m/e* 517.32630 (calcd. for $C_{29}H_{45}N_2O_6$, 517.32777).

(*C*) *Malyngamide B. L. majuscula* was collected at Kailua Beach Park, Oahu in February, 1976. The freeze-dried alga (37 g) was extracted successively twice with $CHCl_3$ and twice with MeOH. The combined extracts were reduced to 2.5 g of a dark green oil which was applied to a column of Si gel (60 g). The chromatogram was developed with hexane, hexane $CHCl_3$, $CHCl_3$ and $CHCl_3$–Me_2CO. Elution with 20–50% Me_2CO in $CHCl_3$ removed 105 mg of a black tar. Chromatography of this fraction on neutral Al_2O_3 gave, upon elution with $CHCl_3$–MeOH (97:3), 46.6 mg of a yellow oil. Gel filtration on Sephadex LH-20 with $CHCl_3$–MeOH (1:1) produced 32.2 mg of malyngamide B as a colorless oil; MS *m/e* 542 and 540 (M^+, 1:3 rel. intensity), 505 (M^+ −Cl); high resolution MS *m/e* 540.2949 (calc. for $C_{28}H_{45}N_2O_6{}^{35}Cl$, 540.2967).

(*D*) *Malyngamide C.* Wet *L. majuscula*, collected in shallow water near Cartwright Point, Fanning Island in April, 1977 was extracted with MeOH and CH_2Cl_2. The extracts were combined and evapd and the residue distributed between EtOAc and H_2O. Evapn of the EtOAc layer gave an oil (7.2 g) which was distributed between n-hexane and MeOH–H_2O (9:1). The MeOH–H_2O layer was then adjusted in concn to 3:1 and extracted with CCl_4, and finally to 65:35 and then extracted with $CHCl_3$. The $CHCl_3$ extract was evapd to give 358 mg of an oil which was then subjected to gel filtration on a 2.5 cm × 1.9 m column of Sephadex LH-20 with $CHCl_3$–MeOH (1:1). The fraction eluted from 555 to 607 ml contained 205 mg of spectrally pure malyngamide C, $[\alpha]_D^{23.5}$ −19.6° ($CHCl_3$, *c* 1.4); MS *m/e* 457 and 455 (M^+, 1:3 rel. intensity), 420 (M^+ −Cl), 315 and 313 (1:3 rel. intensity), 143; high resolution MS *m/e* 313.10962 (calcd. for $C_{15}H_{20}NO_4{}^{35}Cl$, 313.10809), 143.14359 (calcd. for $C_9H_{19}O$, 143.14359).

Ozonolysis of **1**. A soln of **1** (40 mg) in 15 ml MeOH was treated with excess O_3 for 30 min at −70°. The reaction mixture was added to 7 ml of HCO_2H and 3.5 ml H_2O_2. After a 30 min reflux, the soln was evapd and the residue distributed between dil HCl and $CHCl_3$. The acidic material in the $CHCl_3$ layer was transferred into $NaHCO_3$ and after acidification back into $CHCl_3$. Evapn of the dried $CHCl_3$ layer gave 8.5 mg of 3-methoxydecanoic acid (**2**) as a colorless oil, $[\alpha]_D$ +8.2° ($CHCl_3$, *c* 0.85); PMR ($CDCl_3$) δ 0.88 (*br t*, *J* = 7 Hz, 3H), 1.24 (*br s*, 10H), 1.51 (*br m*, 2H), 2.53 (*d*, *J* = 6 Hz, 2H), 3.39 (*s*, 3H), 3.64 (*br p*, *J* = 6 Hz, 1H), 6.6–8.2 (*br*, 1H); MS *m/e* (rel. intensity) 203 (4, M^+ +1), 201 (3), 143 (71), 103 (100); high resolution MS *m/e* 203.16475 (calcd. for $C_{11}H_{23}O_3$, 203.16473). (Found: C, 65.4; H, 11.0. Calcd for $C_{11}H_{22}O_3$: C, 64.9; H, 10.8%).

Alkaline hydrolysis of malyngamide A. The compound (25 mg) was suspended in 20 ml of 10% KOH in EtOH–H_2O (4:1) and the stirred mixture refluxed for 15 hr. The hydrolysate was concd *in vacuo* and distributed between H_2O and CH_2Cl_2. The aq. layer was separated, acidified and extracted with CH_2Cl_2 to give 9.5 mg of a brown oil. Gel filtration on Sephadex LH-20 with $CHCl_3$–MeOH (1:1) yielded 4.5 mg of **1** as a colorless oil, $[\alpha]_D^{26}$ −10.0° ($CHCl_3$, *c* 0.5).

Acid hydrolysis of malyngamide C. A mixture of the compound (56 mg) in 5 ml of 2 N HCl and 5 ml MeOH was refluxed for 2 hr under N_2. H_2O was added and extraction with $CHCl_3$ gave 38 mg of an oil from which 4 mg of **1**, $[\alpha]_D^{24}$ −10.0° ($CHCl_3$, *c* 0.4), and 15 mg of the corresponding Me ester were obtained after gel filtration on Sephadex LH-20.

Methylation of ricinoleic acid. The acid (218 mg) and NaH (750 mg of a 50% dispersion in mineral oil) were dissolved in 5 ml DMF. MeI (1 ml) was added to the stirred soln under N_2 and the soln was warmed to 40° for 24 hr. A second 1 ml aliquot of MeI was then added. After an additional 18 hr stirring at room temp., the mixture was diluted with 10 ml H_2O, acidified and extracted with $CHCl_3$. Evapn of the $CHCl_3$ soln left a brown oil which was chromatographed on Si gel (20 g). Elution with $CHCl_3$–MeOH (49:1) gave 50 mg of *O*-methylricinoleic acid as a colorless oil, $[\alpha]_D^{24.5}$ +10.2° ($CHCl_3$, *c* 3.1), PMR ($CDCl_3$) δ 9.94 (*bs*, CO_2H), 3.34 (*s*, OMe), 3.17 (*m*, C-12 CH).

3(R)-*Methoxynonanoic acid.* Ozonolysis of 35 mg of *O*-methylricinoleic acid and oxidative workup produced 13 mg of 3(*R*)-methoxynonanoic acid as a colorless oil, $[\alpha]_D^{25}$ −7.3° ($CHCl_3$, *c* 1.2); PMR ($CDCl_3$) δ 3.67 (*m*, C-3 CH), 3.41 (*s*, OMe).

Demethylation of **1**. To a stirred soln of 153 mg of **1** in 4 ml of ethanethiol was added 0.5 ml of BF_3–etherate [11]. After stirring at room temp. for 4 days, 10 ml of H_2O was added and the suspension was extracted with $CHCl_3$ (6 × 5 ml). The combined $CHCl_3$ extracts were dried (Na_2SO_4) and evapd to give 175 mg of brown oil. A portion (199 mg) of this oil was chromatographed on Si gel (18 g). Elution with $CHCl_3$–MeOH (97:3) separated 49 mg of unreacted **1** from 83 mg of crude *trans*-7(*S*)-hydroxytetradec-4-enoic acid (**3**). Purification of the yellow, oily **3** with activated charcoal gave 64 mg of a colorless solid which after two recrystallizations from pentane had mp 41–42.5°; $[\alpha]_D^{24.5}$ +2.5° ($CHCl_3$, *c* 2); PMR ($CDCl_3$) δ 6.43 (*bs*, 2OH), 3.59 (*m*, 1H). (Found: C, 69.3; H, 10.8. Calcd. for $C_{14}H_{26}O_3$: C, 69.4; H, 10.8%).

3(S)-*Hydroxydecanoic acid* (**4**). Ozonolysis of 43 mg of **3** as described above gave 9.6 mg of a colorless oily solid. Recrystallization from pentane gave **4** as a white granular solid, mp 43–44°, $[\alpha]_D^{25}$ +17.5° ($CHCl_3$, *c* 0.4); $[\alpha]_D^{25}$ −16.6° (EtOH, *c* 0.4). PMR ($CDCl_3$) δ 5.10 (*bs*, OH and CO_2H), 4.01 (*bm*, C-3 CH).

Identification of cyanophytes. The filamentous blue-green alga from Reefer 8 pinnacle at Enewetak Atoll in the Marshall Islands has been previously identified as *Lyngbya gracilis* Gomont [10]. A re-examination of this cyanophyte shows that its morphology does not agree with the published description of *L. gracilis* from Enewetak [12]; however, it is entirely consistent with descriptions of *L. majuscula* Gomont [13, 14]. All other cyanophytes used in this study were identified by comparing morphological features with published descriptions [14]. Voucher specimens of all algal collections have been retained.

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