Hydrogenation of Diol 7. Palladium on charcoal catalyst (10%, 2 mg) was added to a solution of the diol **7** (30 mg, 0.10 mmol) in ethyl acetate (5 mL) and the reaction mixture stirred under hydrogen for 12 h. The catalyst was removed by filtration, and the solvent was evaporated to obtain an oil which was dissolved in acetic anhydride (0.5 mL) and pyridine (1 mL). After the solution had been stirred for 12 h, the solvent was evaporated in vacuo to obtain the acetate **23** (29 mg, 84% theoretical), identical in all respects with the sample obtained from the peroxide mixture.

Hydrogenation of Diol 14. The diol **14** (5 mg, 0.017 mmol) was hydrogenated and the product acetylated, using the procedure above, to obtain the acetate **22** (5 mg, 87% theoretical) that was identical in all respects with the sample obtained from the peroxide mixture.

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Registry No.—**3,** 68914-58-9; **4,** 68914-59-0; **5,** 68914-60-3; **6,** 68914-61-4; **7,** 68914-62-5; **8,** 68914-63-6; **9,** 68914-64-7; **10,** 68914-65-8; **11,** 68914-66-9; **12,** 68914-67-0; **13,** 68914-68-1; **14,** 68964-12-5; **15,** 68914-69-2; **16,** 68964-13-6; **17,** 68914-70-5; **18,** 68964-55-6; **19,** 68914-71-6; **20,** 68914-72-7; **21,** 68964-14-7; **22,** 68914-73-8; **23,** 68964-15-8.

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Acyclic Diterpenes from the Marine Sponge *Didiscus* sp.

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The marine sponge *Didiscus* sp. contains six acyclic diterpenes: (3*E*,5*E*,10*E*)-7-hydroxy-13-keto-3,7,11,15-tetramethylhexadeca-1,3,5,10,14-pentaene (**4**), (3*Z*,5*E*,10*E*)-7-hydroxy-13-keto-3,7,11,15-tetramethylhexadeca-1,3,5,10,14-pentaene (**5**), (3*E*,5*E*,10*E*)-7-ethoxy-13-keto-3,7,11,15-tetramethylhexadeca-1,3,5,10,14-pentaene (**9**), (3*Z*,5*E*,10*E*)-7-ethoxy-13-keto-3,7,11,15-tetramethylhexadeca-1,3,5,10,14-pentaene (**10**), (3*E*,5*E*,10*E*)-7-ethoxy-3,7,11,15-tetramethylhexadeca-1,3,5,10,14-pentaene (**11**), and (3*Z*,5*E*,10*E*)-7-ethoxy-3,7,11,15-tetramethylhexadeca-1,3,5,10,14-pentaene (**12**).

Few diterpenes have been isolated from marine sponges.[1] The only linear diterpene that had previously been obtained from a sponge was the isonitrile **1** from a Hawaiian *Halichondria* species.[2] Other linear diterpenes such as phytol from *Gracilaria andersoniana*,[3] crinitol (**2**) from *Cystoseira crinita*,[4] and elaganolone (**3**) from *Cystoseira elegans*[5] had been found in marine algae. In this paper we wish to describe six closely related linear diterpenes from the marine sponge *Didiscus* sp.

During a routine thin-layer chromatographic screening of Caribbean sponges collected at Belize we observed that the crude ethanolic extract of *Didiscus* contained several compounds which exhibited strong ultraviolet absorption. The ethyl acetate soluble material from the ethanolic extract was chromatographed on Florisil to obtain three bands containing diterpenes. The major band was rechromatographed on silica gel to obtain a 3:1 mixture of two isomers, **4** and **5,** which could be separated by LC on μ-porasil.

The major diterpene **4** had the molecular formula $C_{20}H_{30}O_2$. The infrared spectrum indicated that the diterpene **4** contained a hydroxyl group (3470 cm^{-1}) and an unsaturated ketone (1690, 1620 cm^{-1}). The ^{13}C NMR spectrum contained signals for a carbonyl group at δ 207.1, the carbon of a tertiary alcohol at 73.0 (s), and ten olefinic carbons, indicating that **4** was acyclic. Every signal in the ^1H NMR spectrum could be assigned (Table I) and the assignment confirmed by decoupling. The terminal vinyl group gave signals at δ 6.42 (dd, 1 H, J = 17, 11 Hz), 5.22 (bd, 1 H, J = 17 Hz), and 5.07 (bd, 1 H, J = 11 Hz). The vinyl proton signal at δ 6.64 (dd, 1 H, J = 15, 11 Hz, C-5) was coupled to signals at 6.07 (d, 1 H, J = 11 Hz, C-4) and 5.82 (d, 1 H, J = 15 Hz, C-6). The vinyl proton signal at δ 6.13 (bs, 1 H) was coupled ($J < 1$ Hz) to two methyl singlets at 2.14 and 1.87, suggesting a β,β-dimethyl, α,β-unsaturated ketone group.[6] The remaining vinyl proton signal at δ 5.27 (bt, 1 H, J = 7 Hz) was coupled to a methyl singlet at 1.59 ($J < 1$ Hz) and to a methylene signal at 2.09 (m, 2 H), which was in turn coupled to a methylene signal at 1.66 (t, 2 H, J = 6.5 Hz). The remaining signals were a two-proton singlet at δ 3.05 and methyl singlets at 1.87 and 1.33. Since the UV spectrum [λ_{max} 282 nm (ϵ 41 200), 272 (ϵ 52 200), 261 (ϵ 41 200), 253 (ϵ 30 000)] suggested the presence of a triene, only two structures, **4** and **6,** can account for these data. The chemical shift data for the vinyl protons clearly favor structure **4.**

Treatment of ketone **4** with 4-phenyl-1,2,4-triazoline-3,5-dione in dichloromethane solution at room temperature gave an adduct **7.** The ^1H NMR spectrum of the adduct **7** contained an ABX system at δ 4.01 (m, 1 H, J = 16, 3, 3, Hz), 4.34 (dd, 1 H, J = 16, 4 Hz), and 5.64 (m, 1 H, J = 4, 3 Hz) with the signal at 4.01 long-range coupled to a signal at 4.73 (dd, 1 H, J = 8, 3 Hz) which was in turn coupled to a vinyl signal at 5.61 (dd, 1 H, J = 15, 8 Hz). These signals were assigned to the protons on the diazine ring and clearly eliminated structure **6.**

The minor isomer **5** appeared to be a geometrical isomer of **4.** It gave the same adduct **7** on treatment with 4-phenyl-1,2,4-triazoline-3,5-dione and both compounds could be hydrogenated over 10% palladium on carbon catalyst to obtain the same ketone **8** in high yield. The ketones **4** and **5** were therefore isomeric about the $^3\Delta$ double bond. The ^1H NMR

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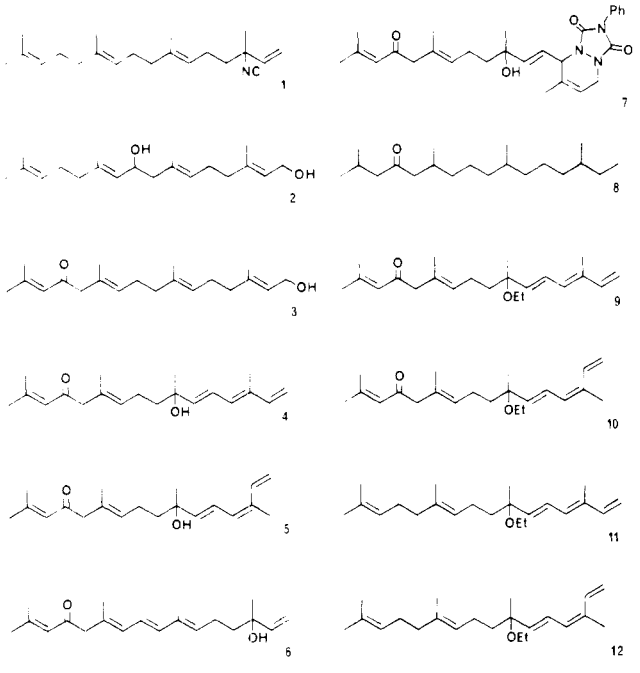
Table I. ^{1}H NMR Chemical Shift Data

H at C no.	4	5	9	10	11	12	multiplicity
1*E*	5.22	5.25	5.22	5.17	5.22	5.24	d, *J* = 17 Hz
1*Z*	5.07	5.15	5.05	5.05	5.04	5.04	d, *J* = 11 Hz
2	6.42	7.00	6.41	6.95	6.43	6.96	dd, *J* = 17, 11 Hz
4	6.07	6.01	6.04	6.02	6.07	6.00	d, *J* = 11 Hz
5	6.64	6.75	6.36	6.59	6.50	6.59	dd, *J* = 15, 11 Hz
6	5.82	5.74	5.72	5.66	5.72	5.63	d, *J* = 15 Hz
8	1.66	1.66	1.64	1.64	1.59	1.59	t, *J* = 6.5 Hz
9	2.09	2.09	2.07	2.07	2.02	2.02	m
10	5.27	5.27	5.25	5.25	5.11	5.11	t, *J* = 6.5 Hz
12	3.05	3.04	3.02	3.02	2.02	2.02	s (**4, 5, 9, 10**), m (**11, 12**)
13					2.02	2.02	m (**11, 12**)
14	6.13	6.09	6.11	6.11	5.11	5.11	s (**4, 5, 9, 10**), t (**11, 12**)
16	1.87	1.87	1.87	1.87	1.65	1.65	s
17	2.14	2.14	2.13	2.18	1.59	1.59	s
18	1.59	1.59	1.61	1.61	1.59	1.59	s
19	1.33	1.33	1.27	1.28	1.25	1.27	s
20	1.87	1.87	1.87	1.87	1.87	1.89	s
-OEt			1.17, 3.38	1.16, 3.38	1.16, 3.38	1.16, 3.38	t, *J* = 7 Hz q



spectrum of **5** contained signals for the C-2 proton at δ 7.00, the C-4 proton at 6.01, and the C-5 proton at 6.75. The C-2 and C-4 proton signals for ketone **5** are downfield from the corresponding signals in the spectrum of ketone **4**, while the C-4 proton signal was upfield, indicating that ketone **4** has the 3*E* geometry. This assignment was supported by the ^{13}C chemical shift data for C-20 which occurred at δ 12.1 in the 3*E* isomer **4** and at δ 19.9 in the 3*Z* isomer **5**. The 5*E* stereochemistry was assigned on the basis of a 15 Hz coupling constant between protons at C-5 and C-6 while the 10*E* geometry depends on the assignment of the signal at δ 16.6 in the ^{13}C NMR spectrum to the C-18 methyl group. Although the ketones **4** and **5** contain one asymetric center at C-7, they are racemic. In theory, the adduct **7** could have been formed as a mixture of diastereoisomers but only one isomer was detected, presumably due to the directing effect of the hydroxyl group. The ketones **4** and **5** are (3*E*,5*E*,10*E*)- and (3*Z*,5*E*,10*E*)-7-hydroxy-13-keto-3,7,11,15-tetramethylhexadeca-1,3,5,10,14-pentaene, respectively.

The minor constituents of the sponge were isolated as mixtures of 3*E* and 3*Z* isomers, and were identified by comparison of spectral data. The ethyl ethers **9** and **10** were obtained as a 4:1 mixture and each component could be separated with difficulty to ~90% isomeric purity. The absence of a hydroxyl signal in the infrared spectrum and the presence of ethoxyl signals at δ 1.17 (t, 3 H, *J* = 7 Hz) and 3.38 (q, 2 H, *J* = 7 Hz) in the ^{1}H NMR spectrum, together with the similarity of all other spectral data, suggested that the compounds **9** and **10** were the 7-ethoxy compounds corresponding to the hydroxy ketones **4** and **5**.

The two remaining compounds **11** and **12** were obtained as an inseparable 3:1 mixture of 3*E* and 3*Z* isomers. The infrared spectrum of the mixture did not contain either hydroxyl or carbonyl bands and the ultraviolet spectrum lacked the 253-nm band found in the spectra of the α,β-unsaturated ketones **4** and **5**. Comparison of the ^{1}H NMR spectrum of the mixture of **11** and **12** with the spectra of **9** and **10** allowed us to differentiate two sets of signals (Table I) corresponding to the 3*E* and 3*Z* isomers of 7-ethoxy-37,7,11,15-tetramethylhexadeca-1,3,5,10,14-pentaene.

In order to determine whether the ethyl ethers were artifacts of extraction, a small sample of the frozen sponge was extracted with methanol. The ^{1}H NMR spectra of the ether mixtures revealed the presence of ethyl ethers only.

Experimental Section

Infrared spectra were recorded on a Perkin-Elmer Model 137 spectrophotometer. Ultraviolet spectra were recorded on a Perkin-Elmer Model 124 double-beam spectrophotometer. Optical rotations were measured on a Perkin-Elmer Model 141 polarimeter, using a 10-cm microcell. ^{1}H NMR spectra were recorded on a Varian HR-220 NMR spectrometer, and ^{13}C spectra were recorded on a Varian CFT-20 NMR spectrometer; all chemical shifts are reported with respect to Me_4Si (δ 0). Low-resolution mass spectra were recorded on a Hewlett-Packard 5930A mass spectrometer. High-resolution mass spectra were supplied by the Chemistry Department at UCLA. All solvents used were either spectral grade or distilled from glass prior to use.

Collection and Extraction of *Didiscus* sp. The sponge *Didiscus* sp. was collected by SCUBA (−20 m) at Lighthouse Reef, Belize. The sponge was frozen and remained frozen until extraction. The sponge was steeped in ethanol for 48 h. The ethanolic extract was decanted and evaporated in vacuo to obtain a concentrate which was partitioned between ethyl acetate and water. (A smaller sample was lyophilized and extracted with methanol in a Soxhlet apparatus, the extract evaporated in vacuo, and the concentrate partitioned between ethyl acetate and water.) The ethyl acetate extracts were dried over sodium sulfate and the solvent evaporated to yield a gum (18 g, 5.6% dry weight).

Chromatography. The crude extract (8.5 g) was applied to a column (100 cm × 5 cm diameter) of Florisil and the material was eluted with solvents of increasing polarity from hexane to diethyl ether. The first UV absorbing fraction, eluted with 5% ether in hexane, consisted of a 3:1 mixture of compounds **11** and **12** (60 mg, 0.04% dry weight).

A second fraction, eluted with 15% ether in hexane, contained a 4:1 mixture of compounds **9** and **10** (400 mg, 0.26% dry weight). The major fraction, eluted with 20% ether in hexane, was a 3:1 mixture of compounds **4** and **5** (700 mg, 0.46% dry weight). The mixture of **4** and **5** was chromatographed on a column (50 cm × 2 cm diameter) of silica gel using 10% ether in hexane as eluant to remove fats. The isomers were separated on μ-porasil using 30% ether in hexane.

(3*E*,5*E*,10*E*)-7-Hydroxy-13-keto-3,7,11,15-tetramethylhexadeca-1,3,5,10,14-pentaene (4): oil; $[\alpha]^{20}_D$ 0; IR (CCl_4) 3470, 1690, 1620 cm^{-1}; UV (hexane) 253 nm (ε 30 000), 261 (ε 41 200), 272 (ε 52 200), 282 (ε 41 200); ^1H NMR ($CDCl_3$) see Table I; ^{13}C NMR (C_6D_6) δ 207.5 (s), 154.8 (s), 142.3 (d), 141.8 (d), 134.8 (s), 131.7 (d), 130.2 (s), 129.7 (d), 124.0 (d), 123.3 (d), 112.2 (t), 73.0 (s), 55.4 (t), 42.7 (t), 28.9 (q), 27.3 (q), 23.6 (t), 20.6 (q), 16.6 (q), 12.1 (q); HRMS, found 302.2246, $C_{20}H_{30}O_2$ requires 302.2246.

(3*Z*,5*E*,10*E*)-7-Hydroxy-13-keto-3,7,11,15-tetramethylhexadeca-1,3,5,10,14-pentaene (5): oil; IR (CCl_4) 3560, 1690, 1620 cm^{-1}; UV (hexane) 248 nm (ε 26 000), 254 (ε 33 850), 264 (ε 38 200), 274 (ε 28 600); ^1H NMR ($CDCl_3$) see Table I; ^{13}C NMR (C_6D_6) δ 207.5 (s), 154.6 (s), 141.1 (d), 133.9 (d), 133.3 (s), 130.2 (d), 129.6 (d), 123.4 (d), 122.9 (d), 114.0 (t), 72.9 (s), 55.4 (t), 42.7 (t), 28.8 (q), 27.2 (q), 23.6 (t), 20.5 (q), 19.9 (q), 16.6 (q) (one signal obscured by C_6D_6); HRMS, found 302.2246, $C_{20}H_{30}O_2$ requires 302.2246.

(3*E*,5*E*,10*E*)-7-Ethoxy-13-keto-3,7,11,15-tetramethylhexadeca-1,3,5,10,14-pentaene (9): oil; IR (CCl_4) 1690, 1620 cm^{-1}; UV (hexane) 254 nm (ε 28 000), 265 (ε 40 000), 275 (ε 51 000), 282 (ε 41 000); ^1H NMR see Table I; ^{13}C NMR (CCl_4) δ 207.1 (s), 153.3 (s), 141.0 (d), 140.0 (d), 134.2 (s), 130.9 (d), 129.4 (s), 129.0 (d), 125.3 (d), 122.7 (d), 112.0 (t), 76.3 (s), 57.0 (t), 55.1 (t), 40.2 (t), 27.3 (q), 22.8 (q), 22.4 (t), 20.2 (q), 16.0 (q), 15.9 (q), 11.8 (q); mass spectrum, *m/e* 330 (1), 284 (5), 201 (5), 186 (8), 86 (100).

(3*Z*,5*E*,10*E*)-7-Ethoxy-13-keto-3,7,11,15-tetramethylhexadeca-1,3,5,10,14-pentaene (10). This compound could not be separated completely from compound **9**. The ^1H NMR data (Table I) were deduced by subtraction.

Mixture of (3*E*,5*E*,10*E*)- and (3*Z*,5*E*,10*E*)-7-Ethoxy-3,7,11,15-tetramethylhexadeca-1,3,5,10,14-pentaene (11 and 12). A 3:1 mixture of geometrical isomers. The spectral data were recorded on the mixture and the ^1H NMR signals assigned according to peak heights (Table I): IR (CCl_4) 1610 cm^{-1}; UV (hexane) 265 nm (ε 38 000), 274 (ε 50 800), 281 (ε 40 000); mass spectrum, *m/e* 271 (1), 270 (1), 255 (11), 228 (11), 69 (100), 55 (75).

Hydrogenation of Ketone 4. A solution of ketone **4** (10 mg, 0.03 mmol) in anhydrous ether (10 mL) containing 10% palladium on carbon catalyst (2 mg) was stirred under an atmosphere of hydrogen for 18 h. The catalyst was removed by filtration and the solvent evaporated to yield the ketone **8** (9.5 mg, 95% theoretical): IR (CCl_4) 1720 cm^{-1}; ^1H NMR δ 0.83 (d, 9 H, *J* = 7 Hz), 0.85 (d, 3 H, *J* = 7 Hz), 0.88 (t, 3 H, *J* = 7 Hz), 0.90 (d, 3 H, *J* = 7 Hz), 1.2–1.3 (m, 16 H), 2.1–2.2 (m, 6 H); mass spectrum, *m/e* 296 (4), 263 (6), 239 (12), 196 (16), 100 (100).

This experiment was repeated with compounds **5**, **9**, and **10** to obtain the same ketone **8** in 85–95% yield.

Treatment of Compound 4 with 4-Phenyl-1,2,4-triazoline-3,5-dione. A solution of ketone **4** (10 mg, 0.033 mmol) and 4-phenyl-1,2,4-triazoline-3,5-dione (6 mg, 0.034 mmol) in dichloromethane (10 mL) was stirred at room temperature for 30 min. The solvent was evaporated in vacuo to obtain an adduct that was purified by preparative TLC on silica gel: yield 11 mg (70% theoretical); IR (CCl_4) 3470, 1770, 1710, 1690, 1610 cm^{-1}; UV (hexane) 234 nm (ε 15 400); ^1H NMR ($CDCl_3$) δ 1.29 (s, 3 H), 1.59 (s, 3 H), 1.64 (t, 2 H, *J* = 7 Hz), 1.82 (s, 3 H), 1.85 (s, 3 H), 2.11 (m, 2 H), 2.13 (s, 3 H), 3.02 (s, 2 H), 4.01 (m, 1 H, *J* = 16, 3, 3 Hz), 4.34 (dd, 1 H, *J* = 16, 4 Hz), 4.73 (bd, 1 H, *J* = 8 Hz), 5.22 (t, 1 H, *J* = 7 Hz), 5.61 (dd, 1 H, *J* = 15, 8 Hz), 5.64 (M, 1 H), 5.98 (d, 1 H, *J* = 15 Hz), 6.09 (bs, 1 H), 7.45 (m, 5 H); mass spectrum, *m/e* 477 (2), 459 (7), 242 (12), 119 (47), 83 (100). The same adduct was obtained from compound **5**.

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Registry No.—**4**, 68582-63-8; **5**, 68602-58-4; **7**, 68582-67-2; **8**, 68582-68-3; **9**, 68582-64-9; **10**, 68629-49-2; **11**, 68582-65-0; **12**, 68582-66-1; 4-phenyl-1,2,4-triazoline-3,5-dione, 4233-33-4.

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Pyrimidine Derivatives and Related Compounds. 32.[1] Acid-Catalyzed Hydrolysis of 1,3-Disubstituted 6-Carbamoyl(or Cyano)uracils. N(1)- and N(3)-Dealkylation of Uracils[2]

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Acid-catalyzed hydrolysis of 1-*sec*-alkyl-6-carbamoyl-3-methyluracil in refluxing 48% hydrobromic acid causes dealkylation at the 1 position to afford 3-methylorotic acid. 1-*sec*-Alkyl-6-carbamoyl(or cyano)-3-methyluracils undergo a similar N(1)-dealkylation when treated in 98% sulfuric acid, yielding 6-carbamoyl-3-methyluracil. In the case of 3-cyclohexyl-6-carboxyl(or carbamoyl)uracils, the N(3)-dealkylation is observed. It is clarified that the N(1)-dealkylation takes place, in general, more readily than the N(3)-dealkylation does.

We previously reported the synthesis of 6-cyano- and 6-carbamoyluracils by the reaction of 5-bromouracils with sodium cyanide.[3] Prior to that, in our laboratory[4] it was demonstrated that 5-cyanouracils undergo acid-catalyzed hydrolysis and decarboxylation, yielding 5-carbamoyluracils, 5-carboxyuracils, or uracils, depending upon the acidic conditions employed. In this connection we investigated the acid-catalyzed hydroysis of 6-cyano- and 6-carbamoyluracils. This paper describes that N-dealkylation of *N-sec*-alkyl-6-cyano(or carbamoyl)uracils readily proceeds together with

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