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FURTHER BIOACTIVE ACETYLENIC COMPOUNDS FROM THE CARIBBEAN SPONGE *CRIBROCHALINA VASCULUM*

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ABSTRACT.—In addition to the known 3-hydroxydocosa-(4*E*,15*E*)-dien-1-yne [**1**], 3-hydroxy-16-methyleicos-(4*E*)-en-1-yne [**2**], and 3-hydroxy-19-methyleicos-(4*E*)-en-1-yne [**3**], the lipophilic extract of the Caribbean sponge *Cribrochalina vasculum* was shown to contain four new bioactive acetylene metabolites, (3*R*)-hydroxy-14-methyldocos-(4*E*)-en-1-yne [**4**], (3*R*)-hydroxy-16-methyleicos-1-yne [**7**], (3*R*)-hydroxy-19-methyleicos-1-yne [**8**], and docosa-(3*E*,15*Z*)-dien-1-yne [**9**], whose structures were elucidated on the basis of chemical and spectral studies. The previously unassigned chirality at C-3 of the known compounds **1–3** has been also established as *R*.

Cribrochalina vasculum Lamarck (family Niphatidae van Soest, order Haplosclerida Topsent) is a very conspicuous sponge, generally funnel- or bowl-shaped but often irregular. The external color is purple to purple-brown with greenish yellow areas, while the inside of the sponge is yellowish drab. Recently its lipid metabolites have been investigated; Carballeira and Reyes (1) studied the phospholipid fatty acid fraction of a sample collected near Puerto Rico, which revealed the new 23-methylpentacosa-5,9-dienoic acid. In 1990 Gunasekera and Faircloth (2) reported the isolation of five new acetylenic alcohols **1–3**, **5**, and **6** from the sponge *C. vasculum* collected in Belize. These compounds showed in vitro immunosuppressive activity on mixed lymphocyte reaction (MLR) assays and in vitro antitumor activity against the mouse leukemia P-388 cell line.

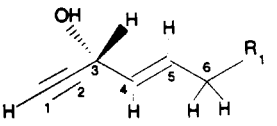
During a recent expedition in search of biologically active compounds of Porifera along the coasts of the Bahamas Islands, we collected several samples of this organism at a depth of 7 m by scuba diving. An accurate analysis of the extracts of this sponge revealed that the Bahamas collection also contains acetylenic metabolites. However, moderate variations were observed between this collection and the Belize collection. The major compounds **1–3** co-occur in both specimens, but the Bahamas sample contains large amounts of a new alkynol **4** with a methyl branched alkyl chain and the characteristic 1-yn-4-en-3-ol functionality in place of the metabolites **5** and **6** of the Belize collection. Minor quantities of **7** and **8**, the 4,5-dihydroderivatives of **2** and **3**, respectively, were also obtained. A small amount of the hydrocarbon **9** was also isolated from the less polar fraction.

These acetylenic compounds isolated from the sponge exhibited a strong toxicity in the brine shrimp (*Artemia salina*) assay (3).

RESULTS AND DISCUSSION

The MeOH/toluene extract of the sponge was partitioned between EtOAc and H_2O. The EtOAc-soluble fraction on chromatography following the reported experimental procedures (2) gave alcohols **1–4** and small quantities of **7–9**.

The stereochemistry at C-3 of the compounds **1–3** has not been previously described. We have determined the configuration at C-3 as *R* on the basis of the results obtained on their *p*-bromobenzoates **10–12** by applying the circular dichroic excitation method described by Nakanishi and co-workers (4–6). This nonempirical method

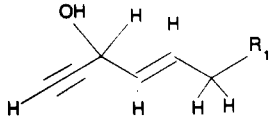


1 $R_1=(CH_2)_8\overset{15}{C}H=CH-(CH_2)_5\overset{22}{C}H_3$

2 $R_1=(CH_2)_9\overset{16}{C}H(\overset{21}{C}H_3)-(CH_2)_3\overset{20}{C}H_3$

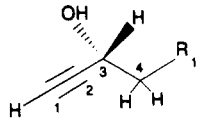
3 $R_1=(CH_2)_{12}\overset{19}{C}H(CH_3)_2$

4 $R_1=(CH_2)_7\overset{14}{C}H(\overset{23}{C}H_3)-(CH_2)_7\overset{22}{C}H_3$



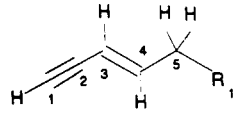
5 $R_1=(CH_2)_{13}-CH_3$

6 $R_1=(CH_2)_8\overset{15}{C}H=CH-(CH_2)_4\overset{21}{C}H(CH_3)_2$

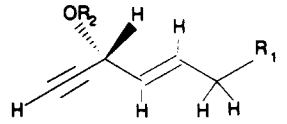


7 $R_1=(CH_2)_{11}\overset{16}{C}H(\overset{21}{C}H_3)-(CH_2)_3\overset{20}{C}H_3$

8 $R_1=(CH_2)_{14}\overset{19}{C}H(CH_3)_2$



9 $R_1=(CH_2)_9\overset{15}{C}H=CH-(CH_2)_5\overset{22}{C}H_3$

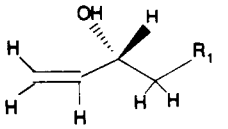


10 $R_1=(CH_2)_8-CH=CH-(CH_2)_5-CH_3$

11 $R_1=(CH_2)_9-CH(CH_3)-(CH_2)_3-CH_3$

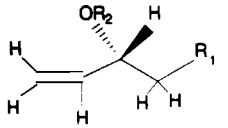
12 $R_1=(CH_2)_{12}-CH(CH_3)_2$

13 $R_1=(CH_2)_7-CH(CH_3)-(CH_2)_7-CH_3$



14 $R_1=(CH_2)_{11}-CH(CH_3)-(CH_2)_3-CH_3$

15 $R_1=(CH_2)_{14}-CH(CH_3)_2$



16 $R_1=(CH_2)_{11}-CH(CH_3)-(CH_2)_3-CH_3$

17 $R_1=(CH_2)_{14}-CH(CH_3)_2$

$R_2=p\text{-}BrC_6H_4COO^-$

based on the coupled oscillator theory was previously applied to compounds strictly related to **1–4**, **7**, and **8** (7,8). The *p*-bromobenzoates **10–12**, prepared by the usual procedure, showed a positive first Cotton effect (Figure 1) at λ 238 nm ($\Delta\epsilon$ 1.3), which indicated the *R* configuration for these compounds.

Compound **4** was isolated as an optically active colorless oil. Combination of hrms and ^{13}C-nmr spectroscopy gave its molecular formula $C_{23}H_{42}O$. Comparison of the downfield nmr data of **4** showed similarities to metabolites **1–3**, **5**, and **6**. The ir spectra of **2**, **3**, and **4** (2) were comparable. These data established the presence of the same 1-yn-4-en-3-ol functionality in these compounds.

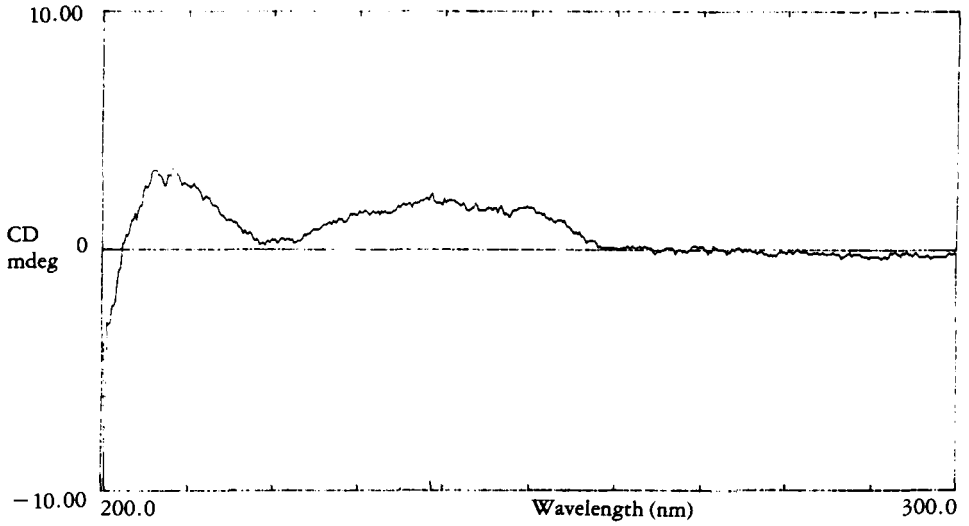


FIGURE 1. Cd spectrum of compound **13**; compounds **10–12** showed almost identical cd spectra.

The remaining portion of compound **4** should contain an alkyl chain with a methyl branching, to satisfy the molecular formula and its ^{13}C- and ^{1}H-nmr data. The ^{1}H-nmr spectrum contained a distorted methyl triplet at δ 0.86 ($J = 6.5$ Hz), a large signal at δ 1.24 corresponding to a normal aliphatic chain, and a 3H doublet at δ 0.81 ($J = 6.5$ Hz), which confirmed methyl branching. The position of branching at C-14 was deduced by the mass spectral fragmentation pattern (9). The spectrum showed two relatively intense peaks, at *m/z* 221.1901 (calcd for $C_{15}H_{25}O$ 221.1906, 38%) and 193.1587 (calcd for $C_{13}H_{21}O$, 193.1593 36%), separated by 28 amu, corresponding to the ions $[HC{\equiv}C\text{-}CH(OH)CH{=}CH(CH_2)_8\text{-}CH(CH_3)]^+$ and $[HC{\equiv}C\text{-}CH(OH)\text{-}CH{=}CH\text{-}(CH_2)_8]^+$ and the absence of a peak at *m/z* 207.

The stereochemistry at C-3 was assigned to be *R* as shown, due to the positive first Cotton effect observed for its *p*-bromobenzoate **13** (λ_{ext} 238 nm, $\Delta\epsilon$ 1.3).

Compound **7** was shown to be the dihydroderivative of **2**. Its molecular formula was deduced from ms and ^{13}C-nmr spectrometry to be $C_{21}H_{40}O$. Comparison of its nmr data with those of **2** (see Experimental) clearly indicated that the 4-en-1-yn-3-ol functionality is modified to a 1-yn-3-ol group. This was confirmed by the lack of sp^2 carbon signals in the ^{13}C-nmr spectrum of **7**, and by its ^{1}H-nmr spectrum which exhibited a doublet at δ 2.47 ($J = 2$ Hz), attributable to the acetylenic hydrogen coupled with the C*H*-OH proton resonating as a complex multiplet at δ 4.39. This was in turn coupled with the OH signal at δ 1.76 (1H, d, $J = 5.5$ Hz) and with the complex multiplet (δ 1.70, 2H) due to magnetically non-equivalent H_2-4 protons. The above assignments were deduced by interpretation of the ^{1}H-^{1}H COSY spectrum and confirmed by the ^{13}C-nmr spectrum which contained the pertinent carbon atoms at δ 72.7 (C-1), 85.0 (C-2), 62.4 (C-3), 37.7 (C-4).

The remaining part of **7** accounted for a molecular composition of $C_{17}H_{35}O$. Its structure was clear from the upfield region of the ^{1}H-nmr spectrum which showed the characteristic signals of a methyl branched alkyl long chain (see Experimental).

The methyl branching on the long chain must occur at C-16 as indicated by relatively intense peaks in the mass spectrum at *m/z* 251.2369 (calcd for $C_{17}H_{31}O$, 251.2376, 30%) $[HC{\equiv}C\text{-}CH(OH)\text{-}(CH_2)_{12}CH(CH_3)]^+$ and 223.2057 (calcd for $C_{15}H_{27}O$, 223.2063, 28%) $[HC{\equiv}C\text{-}CH(OH)\text{-}(CH_2)_{12}]^+$, and by the absence of a peak at *m/z* 237.

The *R* configuration at C-3 was assigned by selective hydrogenation of the acetylene group using the Lindlar catalyst to the corresponding enol **14**, whose chirality at C-3 was identified by applying the Nakanishi method (6) to its *p*-bromobenzoate **16**. Compound **16** showed a negative first Cotton effect (λ_{ext} 240 nm, $\Delta\epsilon$ −1.52; Figure 2), indicating an *R* configuration at C-3.

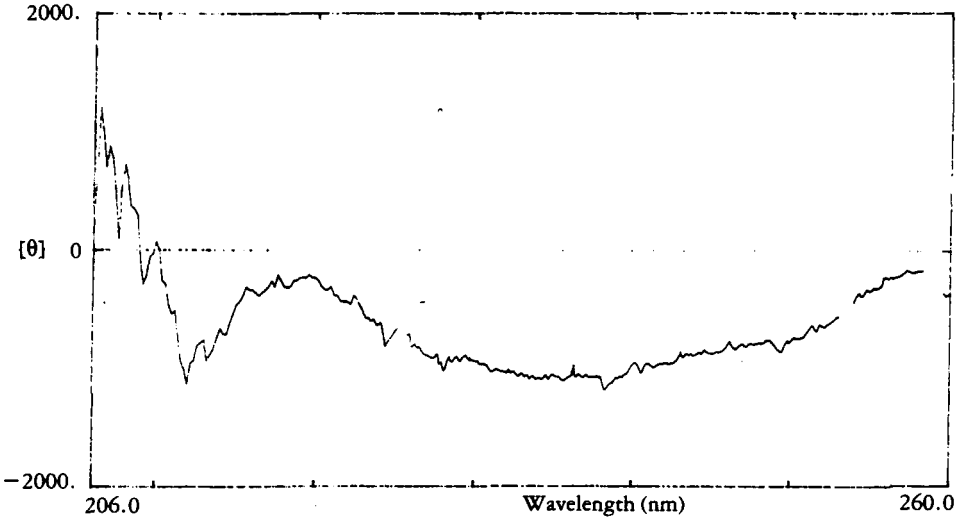


FIGURE 2. Cd spectrum of compound **16**; compound **17** showed almost identical cd spectrum.

Compound **8** was isomeric ($C_{21}H_{40}O$) with **7**. Its ir, ^{1}H- and ^{13}C-nmr spectra indicated that the two compounds had the same enol function linked to a long alkyl chain with methyl branching. The ^{1}H-nmr spectrum of **8** indicated a terminal isopropyl group which resonated as a 6H doublet at δ 0.85 (J = 6.5 Hz). The ^{13}C-nmr spectrum which contained signals at δ 22.68 (q, C-20 and C-21) and at δ 27.95 (d, C-19), confirmed the presence of the isopropyl group. The *R* stereochemistry at C-3 was determined following the same experimental procedure described for **7**.

As it has been reported for several other naturally occurring acetylene metabolites, these compounds **1–4**, **7**, and **8** are also toxic toward brine shrimp [*A. salina* (LC_{50} μg/ml), **1** (0.4), **2** (0.8), **3** (0.8), **4** (0.03), **7** (1.2), **8** (1.0)]. By testing the bioactivity of the fractions obtained by the chromatographic separation of the sponge extract, we noticed that toxicity against brine shrimp was not confined to fractions containing the acetylene alcohols. The toxicity was also exhibited by the fraction containing the most lipophilic metabolites. This fraction on hplc gave another bioactive compound **9** (LC_{50} μg/ml 1.1). This compound analyzed for $C_{22}H_{38}$ by ms, and was shown to contain a 3-en-1-yne functionality by its ir (ν max 3300, 2125 cm^{-1}) and uv absorption (λ max 225 nm, ε 14000), and ^{13}C-nmr [δ 79.0 (C-1), 81.5 (C-2), 108.2 (C-3), 145.9 (C-4), 31.8 (C-5)], and ^{1}H-nmr spectra [1H doublet at δ 3.09 (J = 2 Hz, H-1), a broad double doublet at δ 5.42 (J = 2, 18 Hz, H-3) a double triplet at δ 6.02 (J = 6.5, 18 Hz, H-4), and a broad quartet at δ 2.32 (J = 6.5 Hz, 5-H)]. The ^{1}H-^{1}H connectivities were deduced by homonuclear decoupling experiments and a 2D COSY plot.

The ^{1}H-nmr spectrum further indicates a broad signal (δ 1.24) integrating for 24 protons, a methyl triplet at δ 0.86, a further allylic signal integrating for four hydrogens at δ 2.03, and an additional olefinic signal (2H) at δ 5.36. The above arguments and consideration on the molecular formula established that in **9** the 3-en-1-yne function is linked to a normal long-chain alkenyl group.

The location of the isolated double bond at C-15 was determined by periodate-permanganate oxidation (10) of **9**. This gave a mixture of products, which was analyzed by gc-ms to reveal heptanoic acid as the major product. The sterochemistry of the conjugated double bond was assigned as *E* on the basis of the large vicinal coupling (H-3/H-4) of 15 Hz. The geometry of the isolated double bond could not be determined by ^{1}H nmr as the two olefinic signals appeared at the same chemical shift value. The assignments of the *Z* configuration was based on the interpretation of the ^{13}C-nmr spectrum, where the methylene carbons, allylic to the isolated double bond, resonate at δ 27.33, a value in good agreement with a *Z* configuration at C-15. A significantly lower value was reported for methylene carbons linked to an *E*-oriented double bond (11). On the basis of the above spectral and chemical data structure **9** was established as docosa-(3*E*,15*Z*)-dien-1-yne.

The reported results show moderate differences in the chemistry of two samples of *C. vasculum* coming from the Bahamas and Belize. In any case both *Cribrochalina* specimens are able to synthesize characteristic acetylene metabolites whose bioactivity points to a precise ecological role.

EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—Hreims of compounds **1–4** and **7–9** were obtained at 70 eV on a Kratos MS 50 spectrometer. Ft-ir were recorded on a Bruker IFS-48. Optical rotations were taken on a Perkin-Elmer 141 polarimeter in MeOH. Cd spectra of compounds **10–14**, **16**, and **17** (**10–14**, *n*-hexane; **16**, **17**, iPrOH) were recorded on a Jasco J500A spectrometer. Combined glc-ms analysis was performed on a Hewlett-Packard 5890 gas chromatograph with a mass selective detector MSD HP 5970 MS and a split/splitness injector for capillary columns, using a fused-silica column, 25 m × 0.20 μm HP-5 (cross-linked 25% Ph Me silicone, 0.33 μm film thickness). ^{1}H- and ^{13}C-nmr spectra were recorded in $CDCl_3$ on a Bruker AMX-500 spectrometer, and the solvent was used as an internal standard (^{1}H δ 7.26, ^{13}C δ 77.0). Assignments in the ^{1}H-nmr spectra were confirmed by spin-spin decoupling and ^{1}H-^{1}H COSY experiments ($CDCl_3$). The nature of each carbon resonance was deduced from a set of DEPT experiments.

Mplc was performed on a Buchi apparatus. Hplc was performed on a Varian Model 5000 with a Hibar RP-18 Lichrospher super 100 column using a dual cell refractometer detector.

EXTRACTION AND ISOLATION OF COMPOUNDS **1–4** AND **7–9**.—The marine sponge *C. vasculum* was collected by scuba along San Salvador Island, Bahamas, at a depth of 7 m. A voucher specimen is deposited in the Dipartimento di Chimica delle Sostanze Naturali, University of Naples.

The freshly thawed sponge (750 g, wet wt) was extracted with MeOH-toluene (3:1) (300 ml × 4), and the concentrated extract was partitioned between EtOAc and H_2O. The EtOAc-soluble fraction (4 g) was chromatographed over Si gel. The fraction eluted with petroleum ether (100 mg) was further purified by hplc [Hibar Lichrospher RP-18, 5 μm, MeOH-H_2O (9:1)] and afforded 7 mg of **9**, while the more polar fraction, eluted in petroleum ether-Et_2O (9:1) (900 mg), was purified by hplc (RP-18, 5 μm, 250 × 10 mm, 7% H_2O/MeOH) to yield six related compounds **1** (30 mg), **2** (40 mg), **3** (50 mg), **4** (21 mg), **7** (10 mg), and **8** (8 mg).

(3R)-Hydroxy-14-methyldocos-(4E)-en-1-yne [**4**].—[α]D 1.8 (*c* = 2.5, MeOH); ir ($CHCl_3$) ν max 3605, 3305 cm^{-1}; ^{1}H nmr ($CDCl_3$) δ 0.81 (3H, d, *J* = 6.5 Hz, H-23), 0.86 (3H, t, *J* = 6.5 Hz, H-22), 1.24 (29H, broad, CH and CH_2 groups), 1.84 (1H, d, *J* = 5 Hz, 3-OH), 2.04 (2H, ddt, *J* = 7, 1, 7 Hz, H-6), 2.56 (1H, d, *J* = 2.0 Hz, H-1), 4.81 (1H, dddd, *J* = 6, 5, 2.0, 1.5 Hz, H-3), 5.58 (1H, ddt, *J* = 15.3, 6, 1.5 Hz, H-4), 5.89 (1H, ddt, *J* = 15.3, 1.5, 7 Hz, H-5); ^{13}C nmr ($CDCl_3$) δ 14.09 (C, q), 19.68 (C, q), 22.65 (C, t), 27.08 (2C, t), 27.04 (C, t), 28.82 (C, t), 29.17 (C, t), 29.45 (C, t), 29.59 (C, t), 29.72 (C, t), 29.97 (2C, t), 31.94 (C, t), 31.93 (C, t), 32.73 (C, d), 37.06 (C, t), 37.07 (C, t), 62.75 (C, d), 73.90 (C, d), 83.34 (C, s), 128.35 (C, d), 134.54 (C, d); hrms *m/z* 334.3235 (calcd for $C_{23}H_{42}O$, 334.3237); ms *m/z* 334 (40), 316 (38), 305 (20), 291 (37), 277 (34), 263 (34), 249 (30), 235 (33), 221 (38), 193 (36), 179 (35), 165 (40), 151 (45), 137 (55), 123 (65), 109 (100).

(3R)-Hydroxy-16-methyleicos-1-yne [**7**].—[α]D 2.1 (*c* = 1.7, MeOH); ir (KBr) ν max 3500, 3360, 2360, 1616 cm^{-1}; ^{1}H nmr ($CDCl_3$) δ 0.81 (3H, t, *J* = 6.5 Hz, H-21), 0.86 (3H, t, *J* = 6.5 Hz, H-20), 1.24 (29H, broad, CH and CH_2 groups), 1.70 (2H, m, H-4), 1.76 (1H, d, *J* = 5.5 Hz, 3-OH), 2.47 (1H, d, *J* = 2 Hz, H-1), 4.39 (1H, m, H-3); ^{13}C nmr ($CDCl_3$) δ 14.11 (C, q), 19.70 (C, q), 22.68 (C, t), 25.00 (C, t), 27.07 (C, t), 27.09 (C, t), 27.95 (C, t), 28.81 (C, t), 29.17 (C, t), 29.45 (C, t), 29.59 (C, t), 29.67

(C, t), 30.01 (2C, t), 31.91 (C, t), 32.70 (C, d), 37.70 (C, t), 62.34 (C, d), 72.70 (C, d), 85.01 (C, s); hrms *m/z* 308.3117 (calcd for $C_{21}H_{40}O$, 308.3121); ms *m/z* 308 (41), 290 (39), 279 (32), 265 (30), 251 (30), 223 (28), 209 (30), 181 (28), 167 (30), 125 (40), 111 (60), 97 (70), 83 (75), 69 (80), 55 (100).

(3R)-Hydroxy-19-methyleicos-1-yne [**8**].—[α]D 1.9 (*c* = 2.0, MeOH); ir (KBr) ν max 3500, 3360, 2360, 1616 cm^{-1}; ^1H nmr ($CDCl_3$) δ 0.85 (6H, d, *J* = 6.5 Hz, H-20, H-21), 1.26 (29H, broad), 1.69 (2H, m, H-4), 1.74 (1H, d, *J* = 6.1 Hz, 3-OH), 2.47 (1H, d, *J* = 2 Hz, H-1), 4.38 (1H, m, H-3); ^{13}C nmr ($CDCl_3$) δ 22.68 (2C, q), 27.02 (C, t), 27.39 (C, t), 27.95 (C, d), 28.81 (C, t), 29.17 (C, t), 29.45 (C, t), 29.59 (C, t), 29.67 (C, t), 29.95 (C, t), 31.90 (C, t), 37.67 (C, t), 62.36 (C, d), 72.70 (C, d), 85.01 (C, s); hrms *m/z* 308.3115 (calcd for $C_{21}H_{40}O$, 308.3121); ms *m/z* 308 (40), 293 (37), 290 (22), 279 (25), 265 (50), 111 (65), 97 (70), 55 (100).

Docosa-(3E,15Z)-dien-1-yne [**9**].—Ir ($CHCl_3$) ν max 3300, 2100 cm^{-1}; uv (hexane) λ max 225 nm (ε 1400); ^1H nmr ($CDCl_3$) δ 0.86 (3H, t, *J* = 6.5 Hz, H-22), 1.24 (24H, broad, CH_2 groups), 2.03 (4H, m, H-14, -17), 2.32 (2H, bq, *J* = 6.5 Hz, H-5), 3.09 (1H, d, *J* = 2 Hz, H-1), 5.36 (2H, t, *J* = 5.5 Hz, H-15, -16), 5.42 (1H, bd, *J* = 18, 2 Hz, H-3), 6.02 (1H, dd, *J* = 6.5, 18 Hz, H-4); ^{13}C nmr ($CDCl_3$) δ 13.89 (C, q), 22.63 (C, t), 27.33 (2C, t), 28.81 (C, t), 28.96 (2C, t), 29.16 (C, t), 29.27 (C, t), 29.42 (C, t), 29.51 (C, t), 29.73 (2C, t), 31.83 (C, t), 79.00 (C, d), 81.50 (C, s), 108.2 (C, d), 129.8 (2C, d), 145.9 (C, d); hrms *m/z* 302.2971 (calcd for $C_{22}H_{38}$, 302.2975); ms *m/z* 302 (30), 273 (38), 259 (30), 245 (32), 231 (35), 217 (34), 161 (30), 147 (30), 119 (40), 105 (42), 65 (100).

CATALYTIC HYDROGENATION OF COMPOUNDS **7** AND **8**.—The acetylenic compound (3 mg) in hexane (5 ml) was stirred, in an atmosphere of H_2, at a constant speed over a magnetic stirrer for 45 min, with a catalytic amount of Lindlar catalyst. The residue was purified by plc (Kieselgel 60 F254, Merck, 0.5 mm) Si/$AgNO_3$ using C_6H_6-Et_2O (8:2) to give 1 mg of each olefin **14** and **15**.

p-BROMOBENZOYLATION OF COMPOUNDS **1–4**, **14**, AND **15** AND SEPARATION OF BENZOATES BY PLC.—Solutions of each of the acetylenic compounds (1 mg) in dry pyridine (1 ml) were treated with *p*-bromobenzoylchloride (25 mg) and 4-dimethylaminopyridine (4 mg), and the mixtures were stirred overnight under N_2. Usual procedure gave 1 mg of each benzoate **10–13**, **16**, and **17**.

OXIDATION OF **9**.—To **9** (2.17 mg) in tert-butyl alcohol (6.02 ml), 0.04 M K_2CO_3 aqueous solution (0.9 ml) and an aqueous solution (5.42 ml) containing 0.023 M $KMnO_4$ and 0.09 H $NaIO_4$ were added. The reaction was allowed to proceed at 37° for 18 h. After acidification with 5 N H_2SO_4, the solution was decolorized with aqueous 1 M $NaHSO_3$ and extracted with Et_2O (2 × 10 ml). After drying over $CaSO_4$, the combined ethereal extracts were concentrated to 0.5 ml. The resulting solution, analyzed by glc-ms, was found to contain *n*-eptanoic acid.

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