olefinic protons and revealed one quaternary (1.11) and three vinyl methyl groups [1.71 (3 H) and 1.64 (6 H)].

The skeletal structure of 1 was determined by its isomerization to (+)-δ-selinene (2) on treatment with *p*-toluenesulfonic acid. The optical[5] and spectral properties of 2 were identical to those reported in the literature.[5,6]

Since 1 possesses a selinane carbon skeleton its two double bonds must be placed at the 4,5 and the 7,11 positions as both olefinic links are quaternary. The configuration at C-10 is fixed by the formation of dextrarotatory δ-selinene on isomerization. Double resonance experiments at 270 MHz permitted the assignment of the chemical shifts and *J* values for several protons in 1. H-6β absorbs at δ 2.32 and appears as a broad doublet coupled by 15 Hz to H-6α. The latter occurs as a doublet of doublets at δ 3.16, coupled to H-6β by 15 Hz and to H-8α by 2 Hz. A near coplanar W arrangement is present between H-6α and H-8α in conformer 3, accounting for the long-range coupling. The location of H-6α in the deshielding region of both double bonds[7] explains its rather large downfield shift. H-8α appears at δ 2.44 as a broad doublet ($J_{8\alpha,6\alpha}$ = 2 Hz, $J_{8\alpha,8\beta}$ = 13 Hz, $J_{8\alpha,9}$ = 5 Hz) and H-8β at 2.05 as a broad triplet ($J_{8\beta,8\alpha} = J_{8\beta,9\alpha}$ = 13 Hz).

Experimental Section

IR spectra were taken on a Perkin-Elmer 700 spectrophotometer as neat liquids. ^{1}H NMR were recorded on a Perkin-Elmer R-24B spectrometer at 60 MHz and a Bruker 270 HX spectrometer at 270 MHz in C_6D_6. ^{13}C NMR spectra were obtained with a JOEL PFT-100 spectrometer in $CDCl_3$. Low-resolution mass spectra were recorded on a Finnigan 1015 D GC–mass spectrometer and high-resolution mass spectra on a CEC-21-110B spectrometer. Ultraviolet spectra were determined with a Perkin-Elmer 202 spectrophotometer in 95% EtOH. Optical rotations were measured in $CHCl_3$ on a Zeiss type VDr Na polarimeter. Brinkman silica gel HF-254 + 366, Type 60 (500 μm, activated 0.5 h at 100 °C), was used for TLC. All solvents were reagent grade.

Isolation of (+)-Selin-4,7(11)-diene. (1). Approximately 160 mg of the 3:1 hexane–benzene eluant of the crude algal extract[8] was dissolved in ether and spotted on TLC plates. The plates were developed three times in hexane, drying between developments, and the spots were extracted with ether to give 89 mg of 1 as a colorless oil (0.08%, dry weight of alga): R_f 0.84; $[\alpha]^{24}_D$ +34° (*c* 0.90); UV λ_{max} 218 nm (ε 4800); IR ν_{max} 2960, 2920, 2860, 1450, 1370, 1230, 1120, 875 cm^{-1}; ^{1}H NMR (270 MHz) δ 1.1–1.6 (m), 1.11 (3 H, s), 1.64 (6 H, s), 1.71 (3 H, s), 1.87 (br m), 2.05 (1 H, br t, *J* = 13 Hz), 2.32 (1 H, br d, *J* = 15 Hz), 2.44 (1 H br d, *J* = 2, 5, 13 Hz), 3.46 (1 H, dd, *J* = 2, 15 Hz); ^{13}C NMR δ 19.1, 19.4, 20.1 (2), 24.5, 26.1, 29.9, 32.9, 34.8,[9] 39.7, 42.2, 119.8,[9] 123.7,[9] 131.7,[9] 135.2;[9] mass spectrum *m/e* 204 (68), 189 (76), 161 (60), 147 (28), 133 (72), 119 (60), 105 (88), 91 (84), 81 (40), 79 (40), 77 (40), 67 (36), 55 (56), 41 (100). High-resolution mass spectrum Calcd for $C_{15}H_{24}$: 204.1878. Found: 204.1891.

Isomerization of (+)-Selin-4,7(11)-diene (1). (+)-δ-Selinene (2). A solution of 50 mg of 1 and a crystal of *p*-toluenesulfonic acid monohydrate in 5 mL of benzene was heated at reflux for 1 h. The benzene was removed and the residue was purified by TLC (hexane) to give 39 mg (78%) of (+)-δ-selinene as a colorless oil: R_f 0.65; $[\alpha]^{24}_D$ +196° (*c* 4.6); UV λ_{max} 248 (ε 14 300); IR ν_{max} 2960, 2920, 2870, 1620, 1480, 1370, 1210, 870 cm^{-1}; ^{1}H NMR (270 MHz) δ 0.94 (3 H, s), 1.05 (3 H, d, *J* = 7 Hz), 1.06 (3 H, d, *J* = 7), 1.24–1.57 (m), 1.69 (3 H, s), 1.95–2.31 (m), 6.12 (1 H, s); ^{13}C NMR[10] δ 18.7 (2), 21.4, 21.9, 23.3 (2), 32.8, 35.6, 37.7, 38.1, 117.0; mass spectrum *m/e* 204 (57), 189 (70), 161 (100), 147 (18), 133 (43), 119 (41), 105 (63), 91 (59), 81 (39), 67 (23), 55 (33), 43 (53), 41 (53). High-resolution mass spectrum Calcd for $C_{15}H_{24}$: 204.1878. Found: 204.1885.

Acknowledgments. This work was supported by a grant from the National Institutes of Health (1 R01 CA 16267). We are grateful to Professors P. J. Scheuer and R. E. Moore, University of Hawaii, for the use of their laboratory during collecting trips, to Dr. M. R. Brennan, S.L., Dr. B. J. Burreson, M. Serraon, and D. Dalietos for assistance in collecting the alga and to Mr. J. B. Keenaghan, Astra Pharmaceutical Products, Inc., for the low-resolution mass spectra. The high-resolution mass spectra were provided by the faculty at MIT, Grant FR00317 (Principal Investigator K. Biemann). The ^{13}C-NMR spectra were recorded at the facility at the University of Connecticut Health Center, Grant RR0639 (Principal Investigator J. Glasel). The 270-MHz ^{1}H-NMR spectra were obtained at the Yale facility, Grant 1-P07-PR00798 (Principal Investigator M. Saunders).

Registry No.—1, 41071-31-2; 2, 28624-28-4.

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Marine Natural Products: Cembrene-A and Cembrene-C from a Soft Coral, *Nephthea sp.*

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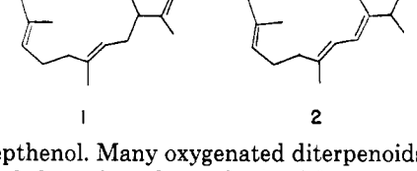
Previously we reported the isolation of two new cembrene derivatives, nephthenol and epoxynephthenol acetate, from a soft coral, *Nephthea* species.[2] Since then, nephthenol has been identified as a component in another soft coral[3] and also synthesized.[4] In this paper we report the isolation of two cembrene hydrocarbons, 1 and 2, from the *Nephthea sp.* that



1 2

yielded nepthenol. Many oxygenated diterpenoids having a cembrane skeleton have been obtained from marine organisms, but the only report to date of a cembrene hydrocarbon from marine sources is the recent paper by Herin and Tursch,[5] wherein the isolation of cembrene-A from another soft coral is described. Cembrene-A (1) has been isolated previously from several terrestrial sources.[6] The hydrocarbon 2 was initially reported as a component of the oleoresin of *Pinus koraiensis*,[7a] but later work[7b] revealed that it was an artifact; 2 has also been obtained in trace amounts from strong base-catalyzed isomerization of cembrene-A.[6b]

The hydrocarbon 1 has earlier been assigned various names: neocembrene,[6a] cembrene-A,[6c] and neocembrene-A.[6b] Although neocembrene has chronological precedence in the literature, we have chosen to use the name cembrene-A. This name allows for convenient construction of trivial names for still other double-bond isomers of cembrene in a manner

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analogous to the suggestions[8] for nomenclature of germacrenes, the corresponding biogenetically equivalent sesquiterpene hydrocarbons. Similarly, we suggest that compound **2** be designated cembrene-C[9] rather than α-pinacene, the name assigned to this hydrocarbon when it was first reported.[7a]

The hydrocarbons cembrene-A (**1**) and cembrene-C (**2**) were obtained from soft coral collected at Enewetak, Marshall Islands. Freshly collected specimens were preserved immediately in isopropyl alcohol and later recovered by filtration, air-dried, and soaked in hexane at room temperature. The concentrate of the isopropyl alcohol extract was extracted with benzene. These benzene and hexane extracts were combined and chromatographed over Florisil. One of the chromatographic fractions was a clear oil that was shown by gas chromatography to consist predominantly of only two components (**1** and **2**) present in approximately equal amounts. Chromatography of part of this fraction over silica gel yielded a pure sample of cembrene-A but led to complete loss of the second component. Cembrene-A was identified by comparison of its spectral and gas chromatographic properties with those of an authentic sample.[10]

Cembrene-C (**2**), isolated by preparative GC, was optically inactive and had the same elemental composition as cembrene-A, $C_{20}H_{32}$ (M^+, 272). On catalytic hydrogenation both compounds yielded the same saturated hydrocarbon, thus establishing that cembrenes-A and -C have the same carbon skeleton. The NMR spectrum of cembrene-C appeared identical with that reported for α-pinacene[7] and revealed that the molecule possessed an isopropyl group and four double bonds: two isolated trisubstituted double bonds and two conjugated double bonds, UV max 252 nm (ε 18 403) and shoulders at 246 (16 230) and 260 (13 350). The conjugated double bonds had associated with them a two-proton NMR signal at δ 5.98 (AB quartet with intense overlapping central lines and very weak outer members, J = 10–12 Hz) that was coupled to one vinyl methyl signal (δ 1.73). In order to account for the three vinyl methyl groups and the allylic nature of the isopropyl methine proton (δ 2.26), the conjugated double-bond unit must be positioned as in **2**. Confirmation of this structure was obtained by oxidative degradation. Both Lemieux–von Rudloff oxidation[11] and ozonolysis of cembrene-C yielded levulinic acid as the only isolable acidic product and 6-methyl-2,5-heptanedione as the sole neutral product. A micro-ozonolysis experiment[12] led to the identification of glyoxal as the remaining oxidation fragment. Cembrene-C thus has the same overall structure as proposed for the stereoisomeric α-, β-, and γ-pinacene and corresponds by NMR to α-pinacene. The isomeric pinacenes are reported[7a] to differ only in configuration at the conjugated diene site, but no specific geometry has been assigned to any of the isomers. Our data do not permit assignment of this stereochemistry either.

Cembrenes-A and -C appear to be present in the crude extract and are not just artifacts derived from nephthenol during the isolation process. Thus, the low-boiling distillate from a falling film distillation [110 °C (2–3 mm)] of the original hexane extract exhibits the diagnostic low-field NMR signals for the conjugated diene (δ 5.98) of cembrene-C and for the *exo*-methylene of cembrene-A (δ 5.8). Furthermore, nephthenol survives chromatographies over Florisil and silica gel, as does synthetic nephthenol. Although chromatography over silica gel led to a complete loss of **2**, both **1** and **2** survived chromatography over Florisil (very little separation), and no isomerization of **1** to **2** appeared to occur on the latter adsorbent, as judged by GC analysis of eluted material.

All attempts to prepare a Diels–Alder addition product of **2** failed (maleic anhydride, sulfur dioxide, 4-phenyl-1,2,4-triazoline-3,5-dione[13]). This indicates that the conjugated diene system in **2** is s-trans.

Experimental Section

Infrared spectra were taken on a Beckman IR-8 spectrophotometer and Ultraviolet spectra on a Carey Model 118 spectrophotometer using 1-cm matched quartz cells. NMR spectra were acquired on Varian T-60 and XL-100 spectrometers in the solvents specified; signals are reported in parts per million (δ) downfield from internal tetramethylsilane. Mass spectra were obtained on Hitachi RMU-7 and Finnigan Model 1015 spectrometers and optical rotations on Perkin-Elmer 141 digital readout or Gaertner polarimeters. Microanalyses were obtained from Mr. E. Meier, Department of Chemistry, Stanford University, Palo Alto, Calif. Chromatographic adsorbents used were Florisil (Fischer, 100–200 mesh) and silicic acid (Mallinckrodt, SilicAR CC-7 and Brinkman TLC mesh). Gas chromatographic analyses were conducted on Varian Aerograph Models 1200 and 1700 using the following columns: A, 6 ft × 0.5 in, 10% FFAP on 60–80 mesh Chromosorb W (Applied Science Laboratories, State College, Pa.); B, 10 ft × 0.25 in, 20% FFAP on 60–80 Chromosorb W; C, 6 ft × 0.125 in, 3% OV-225 on 100–120 mesh Gas-Chrom Q (Applied Science Laboratories, State College, Pa.); D, 6 ft × 0.125 in, OV-1 on 100–120 mesh Gas-Chrom Q.

Isolation of Cembrene-A and Cembrene-C. *Nephthea sp.*, 3 kg, was obtained preserved in isopropyl alcohol from Enewetak, Marshall Islands. The specimens were recovered by filtration, air-dried, and then soaked in hexane at room temperature for 1 week. The isopropyl alcohol solution was concentrated on a rotary evaporator, and the aqueous concentrate was extracted with benzene. Evaporation of the combined hexane and benzene solutions gave 172 g of dark, viscous residue. This entire extract was chromatographed on Florisil (900 g). Elution was initiated with hexane, and from the first 2 L of eluate, 55 g of oil was recovered. Rechromatography of this material over Florisil (900 g), employing hexane as solvent (250-mL fractions), afforded 2.7 g (fraction 9) of a colorless oil, which was shown by gas chromatographic analysis to consist of only two components present in approximately equal amounts.

Chromatography of 75 mg of this two-component fraction on 10 g of TLC-mesh silica gel yielded 35 mg of pure cembrene-A; the second hydrocarbon was not recovered from this adsorbent. The purified sample of cembrene-A exhibited IR and NMR spectra identical with those reported[6a,c] and also obtained from an authentic sample, but it showed a negligible rotation,[14] $[\alpha]_D$ −0.37°. Cembrene-A from *Nephthea* was indistinguishable from an authentic sample by gas chromatography, and the two samples gave virtually the same mass spectra under similar conditions on the same instrument.

Purification and Identification of Cembrene-C. Cembrene-C was isolated by preparative gas chromatography, column B, 155 °C; UV max (isooctane) 252 nm (ε 18 403), with shoulders at 246 (16 230) and 260 (13 500); IR (neat) 3060, 1660, 1605, 1440, 1375, 1355, 860, 840 cm^{-1}; NMR ($CDCl_3$) δ 1.04 (d, 6, J = 7 Hz, isopropyl methyls), 1.52, 1.58 (s, 3 each, vinyl methyls of isolated double bonds), 1.73 (s, 3, vinyl methyl, conjugated double bond), 2.12 (allylic methylene H's), 2.26 (heptet, isopropyl methine), 5.02 (br m, 2, nonconjugated vinyl protons), 5.98 (AB q, with intense overlapping inner members, 2, J = 10–12, vinyl protons, conjugated double bond); mass spectrum (70 eV), m/e (relative intensity) 272 (39, M^+), 257 (2), 229 (7), 189 (5), 161 (16), 137 (23), 136 (100), 135 (13), 121 (86), 119 (13), 107 (22), 105 (20), 93 (73), 91 (23), 81 (23), 79 (21), 77 (23), 67 (21), 55 (18), 53 (18).

Anal. Calcd for $C_{20}H_{32}$: C, 88.16; H, 11.84. Found: C, 87.98; H, 11.62.

Hydrogenation of Cembrene-C. A small sample of cembrene-C (5 mg, 83% cembrene-C and 17% cembrene-A by GC analysis) in 95% ethanol was added to a suspension of prereduced PtO_2 in a few milliliters of ethanol and stirred under hydrogen (1 atm) for 48 h. Gas chromatographic analysis on columns A and D showed only one peak, and this was found to have the same retention time (peak enhancement) on both columns as the product obtained from hydrogenation of cembrene-A under the above conditions.

Permanganate–Periodate Oxidation of Cembrene-C. A solution of cembrene-C (32 mg) in 1 mL of *tert*-butyl alcohol was added to a solution prepared by adding 19 mL of *tert*-butyl alcohol and 75 mg of K_2CO_3 to 38.3 mL of Lemieux–von Rudloff reagent.[11] The mixture was then stoppered and shaken (Parr apparatus) for 24 h with occasional checks to ensure that the pH was maintained at 8–9. The reaction was quenched by the addition of 1.6 g of $K_2S_2O_5$, whereupon a clear yellow solution was obtained. The pH was adjusted to 8 with K_2CO_3 (0.3 g more of $K_2S_2O_5$ was added to discharge the brown color),

and the *tert*-butyl alcohol was removed on a rotary evaporator at 40 °C. The concentrated aqueous solution was extracted with peroxide-free ether to obtain neutral fragments and then acidified and extracted continuously with ether for 14 h to isolate the acidic products.

The neutral fraction was shown by GC analysis to contain only one component. A few milligrams of this was purified by preparative GC and identified as 6-methyl-2,5-heptanedione from the following spectral data: NMR (100 MHz, CCl_4, Fourier transform) 1.08 (d, 6), 2.11 (s, 3), 2.58 (5) [lit.[15] 1.05 (d, 6), 2.06 (s, 3), 2.54 (5)]; mass spectrum (11 eV) *m/e* 142 (0.5, M^+), 99 (100), 71 (7), 43 (5); chemical ionization MS, 183 $(M + 43)^+$, 171 $(M + 29)^+$, 143 $(M + 1)^+$ (base peak), 125 $[(M + 1) - 18]^+$, 99 $(M - 43)^+$, 71 $(M - 71)^+$.

The sole significant acidic product was identified as levulinic acid by the GC retention times of the acid and its methyl ester (from diazomethane treatment) on columns A and B, respectively, in comparison to authentic reference samples.

Ozonolysis of Cembrene-C. Ozone was bubbled through a solution of 1 mg of cembrene-C in 2 mL of ethyl acetate at −70 °C for 6 min, at which time the solution remained blue. Part of the ozonolysis mixture was treated with *o*-phenylenediamine according to the procedure of Moore and Brown[12] to convert any glyoxal to quinoxaline. The latter was identified in the final reaction mixture by GC analysis on columns A and C (peak enhancement using an authentic sample).

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Registry No.—**1**, 31570-39-5; **2**, 64363-64-0; 6-methyl-2,5-heptanedione, 13901-85-4.

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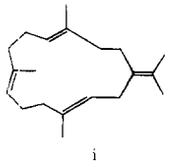

i

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Controlled-Potential Reduction of Cyclopropyl Ketones

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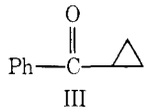
There are many instances of cyclopropyl systems reacting in a manner similar to double bonds. For example, addition reactions to cyclopropanes resulting in ring opening to 1,3-disubstitution products have been found with iodine,[1] bromine,[2] hydrogen bromide,[2,3a,b] hydrogen,[3b] and malonic ester anion.[4] Cyclopropyl rings have been used as double bond equivalents in Friedel–Crafts alkylations[5] and in Diels–Alder reactions.[6] Spectral studies have shown that cyclopropyl rings can affect absorption maxima in the ultraviolet region in much the way as does a double bond.[7]

We wished to see if this analogy could be realized in the electrochemical reduction of cyclopropyl ketones as compared to α,β-unsaturated ketones. Although there have been polarographic studies[8] of such systems there are no reported controlled potential reductions *with product isolation*. The polarography carried out revealed that the half-wave reduction potentials for cyclopropyl ketones is in between that of saturated ketones and α,β-unsaturated ketones, thus indicating a possible interaction of the cyclopropyl ring with the carbonyl group.

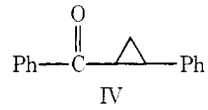
The reduction of α,β-unsaturated ketones follows the scheme shown in Scheme I. Which of the pathways obtains depends on the structure of the ketone and the potential at which the reduction is carried out. In some cases it is only possible to effect 2-e additions.

A similar scheme for cyclopropyl ketones would be Scheme II. Products B′, C′, and E′ could reflect interactions between the initially formed 1-e addition product and the cyclopropyl ring, I ↔ II, and would indicate an analogy to the olefinic system. The behavior of radicals of type I produced by chemical means has been studied by Neckers et al.[9]

Two ketones were subjected to polarography and controlled potential reduction, phenyl cyclopropyl ketone, III, and *trans*-1-benzoyl-2-phenylcyclopropane, IV.

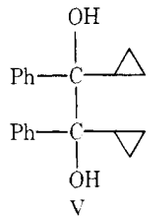


III

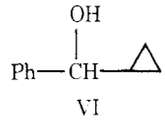


IV

From the controlled-potential reduction of ketone III, an 80% material balance was obtained which consisted of 40% starting ketone, III, 43% dimeric glycol, V, and 17% of the 2-e reduction product, cyclopropylphenylcarbinol, VI. These products provide no evidence for the interaction I ↔ II nor the analogy of this system with the double bond counterpart.



V



VI

The ketone IV on controlled-potential reduction provided (90% recovery) a mixture of the starting material, 25%, and γ-phenylbutyrophenone, VII. This result can be explained in terms of the increased importance of the type of interaction shown above, I ↔ II, when a phenyl is present to stabilize radical character as in IIa.

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