on Chromosorb with temperature programming from 80 to 250 °C). The yields of **1**, **2a**, and **3a**, determined by GLC with respect to the internal standard, were 8, 16, and 5%, respectively. In a separate experiment, the product mixture was separated briefly by column chromatography (silica gel with low boiling petroleum ether as eluant). Each component was purified by GLC. Olefin **1** was characterized by comparison against authentic specimen.[6] Olefin **3a** melted at 119.5–121 °C (lit. 116–117 °C,[2] 125–125.5 °C[3]) and gave the same NMR as that reported.[2] GLC purified **2a** gave the following spectral and analytical data: IR (liquid film) 3090, 3020, 1630 (broad and weak), 1035 cm^{-1}; NMR ($CDCl_3$) δ 0.4–0.7 (m, 8), 1.07 (d, 12, J = 7 Hz), 1.1–1.5 (m, 2), 3.05 (heptet, 2, J = 7 Hz). Anal. Calcd for $C_{14}H_{24}$: C, 87.4; H, 12.6. Found: C, 87.5; H, 12.3.

Similar treatment of dicyclopropyl ketone (2.09 g, 19 mmol) and 3-pentanone (1.64 g, 19 mmol) with the titanium(0) reagent gave 1.30 g of an olefinic fraction, bp 40–82 °C at 4 mmHg. GLC analysis of the fraction showed the existence of three major components (74% of the total peak area) and many minor components. The three components were characterized as **1** (3%), **2b** (21%), and **3b** (7%). GLC purified **2b** gave the following data: IR (liquid film) 3080, 3020, 1635, 1010 cm^{-1}; NMR (CCl_4) δ 0.3–0.8 (m, 8), 0.95 (t, 6, J = 7.5 Hz), 1.0–1.4 (m, 2), 2.23 (quartet, 4, J = 7.5 Hz). Anal. Calcd for $C_{12}H_{20}$: C, 87.7; H, 12.3. Found: C, 87.7; H, 12.2.

In both coupling reactions, the ratio of **1**:**2**:**3** given in the text is an average of two to four runs.

1,2-Dicyclopropylstilbene. To 26.6 g (140 mmol) of titanium tetrachloride in 300 mL of dry dioxane 10.2 g (70 mmol) of cyclopropyl phenyl ketone was added. Under a nitrogen atmosphere, 18.3 g (280 mg atom) of zinc powder was then added in one portion and the resulting mixture was refluxed for 8 h.[11] After cooling down the mixture, 400 mL of water was added and organic material was extracted with three portions of benzene. The combined benzene solution was washed with saturated sodium chloride solution and dried over anhydrous magnesium sulfate. Evaporation of the solvent gave a solid residue which was recrystallized from ether to give 2.09 g (23%) of crystalline product **4a**, mp 147.5–148.5 °C. The mother liquid of the recrystallization was concentrated and the residue was placed on top of a silica gel column (50 g), and elutions were carried out with hexane. From relatively later fractions, the second product **4b**, mp 78–79 °C (from ethanol), 1.85 g (20%), was obtained. Olefins **4a** and **4b** were characterized as isomeric 1,2-dicyclopropylstilbene from the following data. Olefin **4a:** NMR ($CDCl_3$) δ 0.0–0.6 (m, 8), 1.2–1.6 (m, 2), 7.0–7.5 (m, 10); mass m/e 260 (M^+); UV_{max} (hexane) 242 nm (ε 6400). Anal. Calcd for $C_{20}H_{20}$: C, 92.3; H, 7.7. Found: C, 92.2; H, 7.8. Olefin **4b:** NMR (CCl_4) δ 0.1–0.4 (m, 4), 0.5–0.8 (m, 4), 2.0–2.3 (m, 2), 6.6–7.0 (m, 10); mass m/e 260 (M^+); UV_{max} (hexane) 254 nm (ε 8400). Anal. Calcd for $C_{20}H_{20}$: C, 92.3; H, 7.7. Found: C, 92.5; H, 7.9. Olefin **4a**, which may be the same substance as that described by Bennett and Bunce (mp 139.8–140.2 °C),[16] is assigned as a trans isomer. Heating of either **4a** or **4b** in 1,2-dichloroethane[17] at 100 °C for 44 h resulted in the formation of a mixture with the same composition (**4a**/**4b** = 75:25). Regarding the UV data, it is reported that the trans isomer of 1,2-dialkylstilbenes exhibits the maximum at wavelengths shorter than that for the cis isomer.[18]

NMR Examination of 2a and 1. Forty-six milligrams of **2a** was placed in an NMR tube and ca. 0.8 mL of Freon 12 was condensed in the tube. The tube was sealed and NMR measurements were performed at several temperatures (down to −160 °C). The methyl signal coalesced at −105 °C as described in the text. The signals due to the methine protons coalesced at −95 °C and they appeared at δ 2.44 and 3.57 at −140 °C or below. Thus, $\Delta G_c^{\ddagger}$ at 178 K is calculated to be 8.5 kcal/mol.[13] The signals due to the cyclopropyl groups also changed their shapes and split at least into four signals at ca. δ 0.3, 0.6, 0.9, and 1.7 at −140 °C or below.

On the other hand, NMR signals of **1** remained practically unchanged down to −160 °C. Slight line broadenings observed may be due to the viscosity increase.

Acknowledgment. The present research was supported by the funds (a Grant-in-Aid for Scientific Research, No. 047002 and 154145) provided by the Ministry of Education of Japan, to which we are grateful.

Registry No.—**1**, 23534-93-2; **2a**, 65045-41-2; **2b**, 65045-42-3; **3a**, 7090-88-2; **3b**, 868-46-2; **4a**, 65045-43-4; **4b**, 65045-44-5; titanium trichloride, 7705-07-09; potassium, 7440-09-7; dicyclopropyl ketone, 1121-37-5; 2,4-dimethyl-3-pentanone, 565-80-0; 3-pentanone, 96-22-0; titanium tetrachloride, 7550-45-0; cyclopropylphenyl ketone, 3481-02-5.

References and Notes

(1) J. E. McMurry and M. P. Fleming, *J. Org. Chem.*, **41**, 896 (1976), and references cited therein.
(2) R. F. Langler and T. T. Tidwell, *Tetrahedron Lett.*, 777 (1975).
(3) D. S. Bonse and T. H. Morton, *Tetrahderon Lett.*, 781 (1975).
(4) G. A. Olah and G. K. S. Prakash, *J. Org. Chem.*, **42**, 580 (1977), and references cited therein.
(5) J. E. McMurry and L. R. Krepski, *J. Org. Chem.*, **41**, 3929 (1976).
(6) S. Nishida, I. Moritani, E. Tsuda, and T. Teraji, *Chem. Commun.*, 781 (1969); A. Nierth, H. M. Ensslin, and M. Hanack, *Justus Liebigs Ann. Chem.*, **733**, 187 (1970); T. Teraji, I. Moritani, E. Tsuda, and S. Nishida, *J. Chem. Soc. C*, 3252 (1971).
(7) Control experiments proved that olefin **1** is stable under the $TiCl_3$–K coupling reaction conditions.
(8) McMurry and Krepski[5] also report that crossed olefin is produced in an amount greater than the statistical value in the reaction of diaryl ketones and dialkyl ketones.
(9) Average of two runs.
(10) Average of four runs.
(11) T. Mukaiyama, T. Sato, and J. Hanna, *Chem. Lett.*, 1041 (1973).
(12) The signal due to methine protons also coalesced, see Experimental Section.
(13) H. Kessler, *Angew. Chem., Int. Ed. Engl.*, **9**, 219 (1970).
(14) Overlappings of the signals with those of 2-propyl group did not allow for clear observations of their coalescence; see Experimental Section.
(15) H. Kwart and S. Alekman, *J. Am. Chem. Soc.*, **90**, 4482 (1968); C. Roussel, M. Chanon, and J. Metzger, *Tetrahedron Lett.*, 1961 (1971).
(16) J. G. Bennett, Jr., and S. C. Bunce, *J. Org. Chem.*, **25**, 73 (1960).
(17) We frequently observed that styrene and stilbene derivatives isomerized easily in halogenoalkanes, or in the presence of a trace amount of polyhalogenomethanes such as bromotrichloromethane, at 100–150 °C (S. Nishida, K. Ishikura, N. Shimizu, T. Imai, and F. Kataoka, unpublished results).
(18) H. Suzuki, *Bull. Chem. Soc. Jpn.*, **25**, 145 (1952).

Sesquiterpenoids from the Hawaiian Marine Alga *Laurencia nidifica*. 7. (+)-Selin-4,7(11)-diene

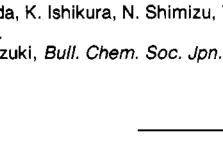
Hao H. Sun and Karen L. Erickson*

Jeppson Laboratory, Clark University, Worcester, Massachusetts 01610

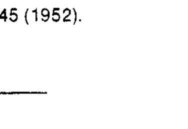
Received October 11, 1977

The selinane skeleton is one of the most common in sesquiterpenoids of terrestrial origin. Its presence in marine organisms has also been noted in a gorgonian,[1] a sponge,[2] and a brown alga.[3] Very recently the prolific *Laurencia* genus has been found to produce (−)-selin-7-ene derivatives.[4] We report here the isolation of (+)-selin-4,7(11)-diene (**1**) from the green variety of the Hawaiian marine alga *Laurencia nidifica*. To our knowledge this material has not been previously recorded as naturally occurring.

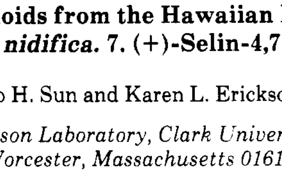
(+)-Selin-4,7(11)-diene (**1**) was isolated as an unstable



1



2



3

colorless oil in 0.08% yield from the dry alga. High resolution mass spectroscopy established its molecular formula as $C_{15}H_{24}$. Its infrared spectrum showed only carbon–hydrogen absorptions. ^{13}C NMR indicated the presence of four quaternary olefinic carbons (119.8, 123.7, 131.7, 135.2) and a fifth quaternary center at 34.8. ^1H NMR confirmed the absence of 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.

References and Notes

(1) A. J. Weinheimer, W. W. Youngblood, P. H. Washecheck, T. K. B. Karns, and L. S. Ciereszko, *Tetrahedron Lett.*, 497 (1970).
(2) L. Minale, R. Riccio, and G. Sodano, *Tetrahedron*, **30**, 1341 (1974).
(3) E. Kurosawa, M. Izawa, K. Yamamoto, T. Masamune, and T. Irie, *Bull. Chem. Soc. Jpn.*, **39**, 2509 (1966).
(4) B. M. Howard and W. Fenical, *J. Org. Chem.*, **42**, 2518 (1977), and ref 11 therein; A. F. Rose and J. J. Sims, *Tetrahedron Lett.*, 2935 (1977).
(5) L. Ruzicka and M. Stoll, *Helv. Chim. Acta*, **6**, 846 (1923); G. Büchi, M. S. v. Wittenau, and D. M. White, *J. Am. Chem. Soc.*, **81**, 1968 (1959); M. L. Maheshwari, T. C. Jain, R. B. Bates, and B. C. Bhattacharyya, *Tetrahedron*, **19**, 1079 (1963). The latter reference reports $[\alpha]^{30}{}_D$ +265.5° for **2** and $[\alpha]^{30}{}_D$ −191° for its enantiomer.
(6) G. Mehta and B. P. Singh, *Tetrahedron Lett.*, 3961 (1975); A. F. Thomas, M. Ozainne, R. Decorzant, and F. Näf, *Tetrahedron*, **32**, 2261 (1976).
(7) L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," 2nd ed, Pergamon Press, New York, N.Y., 1969, p 83.
(8) S. M. Waraszkiewicz, H. H. Sun, and K. L. Erickson, *J. Org. Chem.*, in press.
(9) Quaternary carbons.
(10) Quaternary carbons were not recorded.

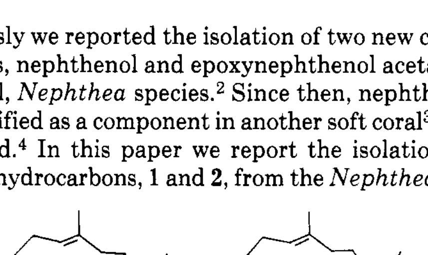
Marine Natural Products: Cembrene-A and Cembrene-C from a Soft Coral, *Nephthea sp.*

David J. Vanderah,[1] Neal Rutledge, Francis J. Schmitz,* and Leon S. Ciereszko

Department of Chemistry, University of Oklahoma, Norman, Oklahoma 73019

Received October 13, 1976

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

