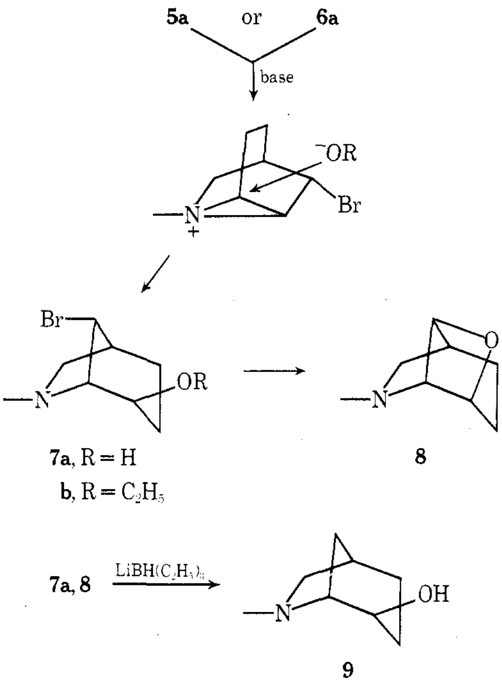

The astounding rate enhancement observed for **1a**, **5a**, and **6a** is reminiscent of the acceleration found for bicyclic α-amino halides compared with carbocyclic analogs $(\sim 10^3-10^8)^{2g-i}$ and the observation that most α-amino halides exist in the iminium salt form.[9] Apparently, favorably disposing nitrogen for displacement of halogens results in extremely rapid reactions. In the present case, locking the geometry such that the departing halogen and the attacking nitrogen are rigidly held antiplaner provides an especially favorable orientation for facile participation.[10]

Acknowledgment. The authors wish to express their gratitude to Dr. Grant Krow for a spectrum of **9** and helpful discussions. L.R. expresses his thanks to NDEA for a fellowship.

Supplementary Material Available. The synthesis and characterization of the compounds employed in this investigation along with other experimental details will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Business Office, Books and Journals Division, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.50 for photocopy or $2.50 for microfiche, referring to code number JOC-75-2567.

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(1) For reviews and discussions of the voluminous studies concerning participation and rearrangements in bicyclo systems and the attendant controversy concerning the nature of the intermediates see (a) J. A. Berson in "Molecular Rearrangements," P. de Mayo, Ed., Interscience Publishers, New York, N.Y., 1963, Part I, p 213; (b) G. A. Olah and P. v. R. Schleyer, Ed., "Carbonium Ions," Wiley, New York, N.Y., 1972, Vol. III; (c) G. D. Sargent, Quart. Rev. (*London*), **20**, 301 (1966); (d) P. D. Bartlett, Ed., "Nonclassical Ions," W. A. Benjamin, New York, N.Y., 1965; (e) H. C. Brown, "Boranes in Organic Chemistry," Cornell University Press, Ithaca, N.Y., 1972.

(2) For examples of investigations suggesting assistance by nitrogen in bicyclic systems see (a) J. W. Huffman, T. Kamiya, and C. B. S. Rao, *J. Org. Chem.*, **32**, 700 (1967); (b) S. Archer, M. R. Bell, T. R. Lewis, J. W. Schulenberg, and M. J. Unser, *J. Am. Chem. Soc.*, **79**, 6337 (1957), and **80**, 4677 (1958); (c) S. Archer, T. R. Lewis, M. R. Bell, and J. W. Schulenberg, *ibid.*, **83**, 2386 (1961); (d) J. D. Hobson and W. D. Riddell, *Chem. Commun.*, 1180 (1968); (e) G. Büchi, D. L. Coffen, K. Kocis, P. E. Sounet, and F. E. Ziegler, *J. Am. Chem. Soc.*, **88**, 3099 (1966); (f) L. A. Paquette and J. F. Kelly, *J. Org. Chem.*, **36**, 442 (1971); (g) H. O. Krabbenhoft, J. R. Wiseman, and C. B. Quinn, *J. Am. Chem. Soc.*, **96**, 258 (1974); (h) R. D. Fisher, T. D. Bogard, and P. Kovacic, *ibid.*, **94**, 7599 (1972), and **95**, 3646 (1973); (i) P. G. Gassman, R. L. Cryberg, and K. Shudo, *ibid.*, **94**, 7600 (1972).

(3) Pertinent studies of rearrangement and participation of oxygen containing bicyclics include (a) J. C. Martin and P. D. Bartlett, *J. Am. Chem. Soc.*, **79**, 2533 (1957); (b) L. A. Paquette and P. C. Storm, *ibid.*, **92**, 4295 (1970); (c) L. A. Spurlock and R. G. Fayter, Jr., *ibid.*, **94**, 2707 (1972); (d) J. Wolinsky, R. O. Hutchins, and J. H. Thorstenson, *Tetrahedron*, **27**, 753 (1971).

(4) R. E. Ireland and H. A. Smith, *Chem. Ind.* (*London*), 1252 (1959), invoked sulfur involvement in the solvolysis of 8-thiabicyclo[3.2.1]octyl derivatives.

(5) Bromination of the parent alkene 2-methyl-2-azabicyclo[2.2.2]oct-5-ene in CCl_4 followed by treatment of the resulting dibromo-*N*-bromine complex witlh acetone gave **5a**. Refluxing **5a** in acetone gave essentially complete conversion to the rearranged salt **6a**. A similar predominance of the [3.2.1] over the [2.2.2] ring system was noted by Huffman and coworkers[2a] with isoquinuclidones. Apparently, the bicyclo[3.2.1] skeleton is the more thermodynamically stable as is the case with the carbocyclic analog.[6] However, Büchi has observed[2e] that nitrogen migrations in certain iboga alkaloid intermediates favor the bicyclo[2.2.2] system. Ostensibly, other (probably steric) factors play a decisive role in determining the stability in these complex derivatives.

(6) P. v. R. Schleyer, K. R. Blanchard, and C. D. Woody, *J. Am. Chem. Soc.*, **85**, 1358 (1963).

(7) H. C. Brown and S. Krishnamurthy, *J. Am. Chem. Soc.*, **95**, 1669 (1973); S. Krishnamurthy, R. M. Schubert, and H. C. Brown, *ibid.*, **95**, 8486 (1973).

(8) An ir spectrum of authentic **9** was kindly supplied by Professor Grant Krow (Temple University); cf. P. G. Gassman and J. H. Dygos, *Tetrahedron Lett.*, 4745 (1970).

(9) H. Bohme and K. Osmers, *Chem. Ber.*, **105**, 2237 (1972), and references cited therein.

(10) The importance of bond allignment in rearrangements of bicyclic systems has recently been discussed; cf. A. Nickon and R. C. Weglein, *J. Am. Chem. Soc.*, **97**, 1271 (1975).

(11) NDEA Fellow, 1971–1974.

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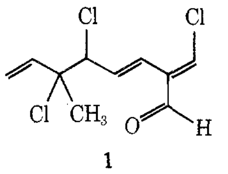
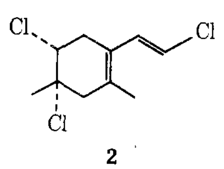
Plocamene B, a New Cyclic Monoterpene Skeleton from a Red Marine Alga

Summary: A nonisoprenoid trichloromonoterpene, plocamene B, has been isolated and characterized from Northern California collections of the red alga *Plocamium violaceum.*

Sir: Very recently we reported an acyclic polychlorinated monoterpene aldehyde 1 as a major component from the red alga *Plocamium cartilagineum.*[1] Our observation that semipurified extracts from this alga possess marked antiinsecticidal activity against mosquito larvae[2a] prompted us to examine a related, less common alga, *P. violaceum.* We report below the characterization of a major metabolite from this latter alga, plocamene B (**2**), which has a nonisoprenoid monoterpene skeleton and displays moderate toxicity to lab test fish.[2b]



1



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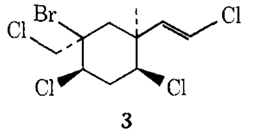
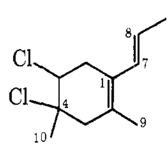


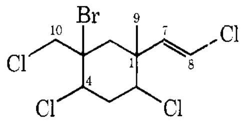
3

Collections were made of *P. violaceum* in the fall of 1974 [week of Sept 15] from several different intertidal locations north of Santa Cruz. Separate extractions ($CHCl_3$) of each batch of frozen thalli yielded about equal amounts of essential oils. Preliminary analysis of the crude, nonpolar fractions for halomonoterpenes by GC/MS showed (see

Table I
CMR Data at 25.1 MHz



2



3

Carbon	Ppm[a]	J (Hz)[b]	Pattern[c]	Carbon	Ppm	J (Hz)	Pattern
9	18.4	128.4	q	10	38.8	155.7	t
10	30.3	129.4	q	9	27.4	129.4	q
6	34.5	127.0	t	3	38.3	134.3	t
3	48.5	127.0	t	6	48.8	131.7	t
5	64.1	148.9	d	4	64.1	146.5	d
4	69.3		s	5	71.3		s
8	117.7	194.1, 9.8	dd	8	119.5	192.9, 9.8	dd
1,2	123.8		s	1	42.0		s
	129.8		s	2	59.0	146.5	d
7	130.3	162.1, 13.4	dd	7	135.4	156.1	br d

[a] Relative to TMS ($CDCl_3$ solvent). [b] Error, ±1 Hz. [c] From ^1H coupled spectra.[6]

paragraph at end of paper regarding supplementary material) that the relative levels of the major components varied significantly between collection locations. Although the origin of this effect is at present unclear, this observation was useful in facilitating our isolation work.

Chromatographic purification (silica gel column) of the oil from *P. violaceum* of Davenport Landing gave fractions which were further purified by HPLC (Porasil-A). This procedure enabled isolation of the two major components which were both crystalline. The major compound of shortest GC retention time (mp 100–101°, $[\alpha]D$ −48°) was unknown, and support of our assignment as structure **2** is presented below.[3] The longer retention time component had spectral properties[4] and mp 70–71° ($[\alpha]D$ −81°) identical with violacene (**3**) recently reported from *Plocamium*.[5]

The mass spectrum of plocamene B [m/e 238, 240, 242, 244; 203, 205, 207; 167 (base peak), 169; 131] required the formula $C_{10}H_{13}Cl_3$. The appearance of four vinyl carbons, including two quaternary ones, in the ^{13}C NMR of plocamene B (Table I) together with its molecular formula required a monocyclic constitution. Moreover, a substituted diene chrompohore was implied by its uv λ_{max} (EtOH) 245 nm (ϵ 16,000). Close inspection of its ^1H NMR at 100 MHz (Figure 1, benzene-d_6) confirmed the presence of 13 H's of the following subgroups: (a) quaternary CH_3 (δ 1.4); (b) allylic CH_3 (1.22); (c) isolated $-CH_2-$, AB quartet [1.8 and 2.3δ (J = 17 Hz)]; (d) a $-CHXCH_2-$ ABX pattern [1.6–2.6 and 3.35 (J = 20, 10.0, 5.5 Hz)]; and (e) an (*E*)-vinyl AB quartet [5.5 and 6.6 (J = 13.5 Hz)]. Further verification of the above interpretation for the region δ 1.6–2.6 as an overlapping AB and ABX pattern was achieved via a 300-MHz ^1H NMR spectrum. This spectral region was first order at that higher frequency, and J's could be determined by direct measurement. Finally, the distinct broadening observable for the allylic methyl relative to the quaternary methyl concurrent with enhanced half-width of the highfield AB doublet relative to the one at lower field must arise from long range coupling.

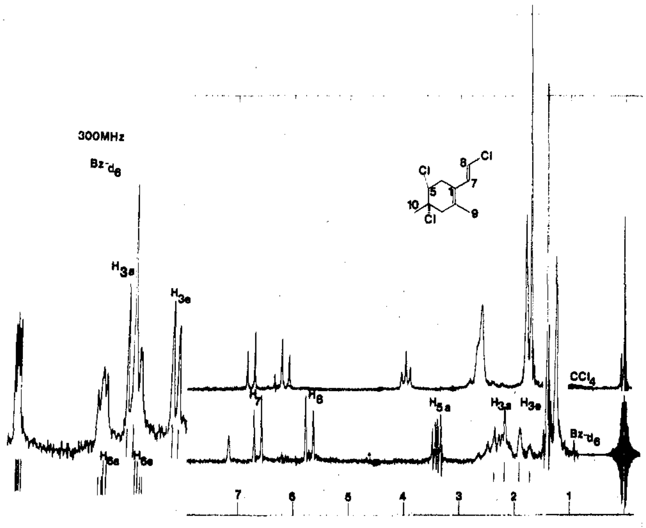
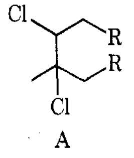


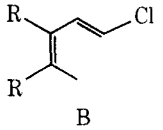
Figure 1. NMR spectra of plocamene B (**2**) at 100 and 300 MHz.

A full assignment of the ^{13}C NMR of plocamene B (Table I) was aided by considering both δ and J_{CH} values. The direct J_{CH} data in Table I were obtained by comparison of the broad-band ^1H CW decoupled spectra to the ^1H coupled spectra obtained via a pulse decoupling technique.[6] A knowledge of J_{CH} enables an unambiguous distinction of carbons of similar chemical shift and constitution, but of differing substituent electronegativity.[7] As an example, the (*E*)-vinyl double bond of **2** shows carbon resonances at 117.7 and 130.3 ppm which display J_{CH} = 194.1 and 162.1 Hz, respectively. Based on those observed J's, these peaks could be assigned as shown in the table. A reverse assignment, on the other hand, might have been predicted on the basis of chemical shifts and multiplicities alone.[8]

The carbon shifts of plocamene B (**2**) were remarkably similar to those observed for violacene (**3**). Consequently, the combined spectral data for **2** were most consistent with the two partial structures shown below as A and B. The structure elucidation now involved determination of both the regiochemistry of the ring connection between fragments A and B and the relative stereochemistry between the adjacent chiral centers in fragment A.



A



B

The NMR data provided a means for directly addressing each of these questions. Union of A and B to give a 1,3-

dimethyl orientation as in structure 2 provides a constitutional arrangement consistent with the long range coupling between the equatorial H_{3e} and the vinyl CH_3.[9] The *J*'s between H_5 and the adjacent $-CH_2-$ are consistent with an equatorial Cl at C_5. Carbon chemical shifts, especially in cyclohexane ring systems, are extremely sensitive to stereochemical factors.[8,10] Hence, in methylcyclohexane the axial methyl is shielded relative to the equatorial one by 6 ppm,[10a] and the methyl shielding in *cis*- and *trans*-9-methyldecalin differ by 12 ppm.[10b] The similarity of the shift position for the equatorial methyl in methylcyclohexane (24 ppm) and the equatorial quaternary methyl in **3** (27.4 ppm) vs. that of the quaternary methyl in **2** (30.3 ppm) suggests its stereochemistry to be equatorial.[11]

Chemical conformation of the proposed structure of **2** was provided by aromatization of **2** to (*E*)-1-chloro-2-(2,4-dimethylphenyl)ethylene (**4**) by 1,5-diazobicyclo[5.4.0]undec-5-ene (DBU) in THF. Compound **4** was treated with O_3 to yield 2,4-dimethylbenzaldehyde (**5**) which was in turn prepared directly from commercial 2,4-dimethylbenzoic acid (**6**).[12]

We have observed by GC/MS five isomers of formula $C_{10}H_{13}Cl_3$ from various collections of *P. violaceum*. Comparative mass spectral data [especially intense fragmentation to an aromatic nucleus $(C_{10}H_{11})^+$, *m/e* 131] indicates that four of the uncharacterized $C_{10}H_{13}Cl_3$ isomers probably have a trialkyl six-membered ring with no points of geminate alkyl substitution.[13] Thus, plocamene B may be just the first representative of a host of nonisoprenoid monoterpenes from red alga. Migration of methyl from C_1 or vinyl from C_2 are the simplest possibilities to link plocamene B to the isoprenoid biosynthetic manifold. The nucleus of the former precursor, however, represents an uncommon tail-to-tail isoprenoid arrangement, and there are, as yet, no literature examples of the carbon constitution of this envisioned precursor.[14]

Acknowledgment. We thank Professor I. Abbott (Hopkins Marine Station) for guidance in alga identification. Mr. Dennis Taylor (Finnigan Corp.) kindly provided GC/MS data, and Professor R. Wing (UCR) provided the 300-MHz NMR spectra. We also thank the UCSC Committee on Research for support of this research.

Supplementary Material Available. The GC/MS traces showing halomonoterpene distribution of *P. violaceum* from two different intertidal locations north of Santa Cruz will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Business Office, Books and Journals Division, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.00 for photocopy or $2.50 for microfiche, referring to code number JOC-75-2568.

References and Notes

(1) P. Crews and E. Kho, *J. Org. Chem.*, **39**, 3303 (1974).

(2) (a) These tests assay for a variety of insect growth effects, such as immediate mortality, growth inhibitory effects, juvenile hormone effects, and antimolting effects. This testing program is being carried out through a collaboration with Zoecon Corp. Research Division, Biology Department. We hope in the near future to present a detailed account of these results. (b) A bioassay using gold fish has been patterned after a literature description: G. J. Bakus and G. Green, *Science*, **185**, 951 (1974).

(3) Examples to date of halo monoterpenes from red marine algae include (a) ref 1; (b) ref 5; (c) N. Ichikawa, Y. Naya, and S. Enomoto, *Chem. Lett.*, 1333 (1974).

(4) We initially named this compound plocamene A and its ^1H NMR (δ) showed (in benzene-d_6, 100 MHz) (a) CH_3, s, 0.62 (1.25 in CCl_4); (b) $-CH_2-$, AB q, 1.34 and 1.57 (J = 15 Hz); (c) $-ClCHCH_2CHCl-$, ABX_2 m, H_{3e}, doubled t, 1.78 (J = 13, 4, 4 Hz), H_{3a}, q, 2.19 (J = 13, 12, 12 Hz), H_{2a} and H_{4a}, dd, 2.55 and 3.52 (J = 12 and 4 Hz); (d) $-CH_2-$, AB q, 2.85 and 3.40 (J = 10 Hz); (e) H_7 and H_8, AB q, 5.50 and 6.30 (J = 13 Hz) (note that many of these *J*'s are first order approximations). This spectrum is closely comparable with that of violacene (**3**)[5] at 300 MHZ (solvent unspecified).

(5) J. S. Mynderse and D. J. Faulkner, *J. Am. Chem. Soc.*, **96**, 6771 (1974).

(6) This methodology has been previously described: O. Ganson and W. Shittenhelm, *J. Am. Chem. Soc.*, **93**, 4294 (1972).

(7) Some examples of the variation of J_{CH} with substituent electronegativity are (a) G. E. Maciel and K. D. Summerhays, *J. Am. Chem. Soc.*, **93**, 520 (1971); (b) M. E. Freeburger and L. Spialter, *ibid.*, **93**, 1894 (1971); (c) J. B. Stothers, "Carbon-13 NMR Spectroscopy", Academic Press, New York, N.Y., 1972, Chapter 10.

(8) G. C. Levy and G. R. Nelson, "Carbon-13 Magnetic Resonance for Organic Chemists", Wiley-Interscience, New York, N.Y., 1972, Chapter 3.

(9) The ^1H NMR spectra of β-ionone (Varian Catalog, Vol. II, #617) and β-cyclocitral [prepared according to R. N. Gedge et al., *Can. J. Chem.*, **49**, 1764 (1971)] both show greatly broadened vinylic methyls. See P. Crews, *J. Am. Chem. Soc.*, **95**, 636 (1973), and references within for a discussion of long range *J*'s.

(10) (a) F. A. L. Anet, C. H. Bradley, and G. W. Buchanan, *J. Am. Chem. Soc.*, **93**, 258 (1971); (b) J. L. Gough, J. P. Guthrie, and J. B. Stothers, *Chem. Commun.*, 979 (1972); (c) J. B. Stothers and N. K. Wilson, *Top. Stereochem.*, **8**, 1 (1974).

(11) It would appear that only a small chemical shift difference should be observed for a CH_3 geminate to a vinyl vs. geminate to a Cl. Compare Tables 3.7 and 3.18 of ref 8.

(12) (a) Purchased from Aldrich Chemical Co. (b) The physical properties of **4** and **5** were consistent with their structures.

(13) Based upon comparison of the individual mass spectral data from our lab; however, see also ref 5.

(14) The biosynthesis of head-to-head terpenes has recently been investigated: (a) R. M. Coates and W. H. Robinson, *J. Am. Chem. Soc.*, **94**, 5921 (1972); (b) C. D. Poulter, O. J. Muscio, C. J. Spillner, and R. G. Goodfellow, *ibid.*, **94**, 5923 (1972).

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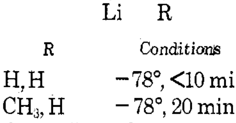
Organoselenium Chemistry. Synthetic Transformations Based on Allyl Selenide Anions[1]

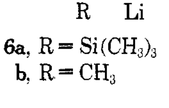
Summary: Enones and allyl alcohols are formed when substituted allyl selenides, prepared by alkylation or silylation of allyl selenide anions, are oxidized.

Sir: Lithium reagents derived from allyl sulfides,[2,3a] sulfoxides,[3] sulfones,[4] phosphonates,[5] ethers,[6a,b] and amines[6c,d] have been used to perform useful synthetic transformations. We have been exploring the chemistry of α-lithio selenoxides and selenides[7,8] and report here preliminary results on the deprotonation of a variety of allyl selenides, their reaction with representative electrophiles, and some transformations of these alkylation products. Alkyllithium reagents can rarely be used for the deprotonation of selenides or selenoxides since extensive cleavage reactions often occur.[7,8] We have found lithium diisopropylamide (LDA) in tetrahydrofuran a useful base for this purpose. In sterically hindered situations lithium diethylamide is superior.

The lithium reagents **1–5** are formed using LDA in tetrahydrofuran under the conditions indicated. β-Methylallyl phenyl selenide can also be deprotonated and the anion behaves quite similarly to **1**. Attempts to extend the procedure to α-substituted allyl anions (**6**) have been successful only for the α-trimethylsilyl derivative **6a**, which can be



	R	Conditions
1	H,H	−78°, <10 min
2	CH_3, H	−78°, 20 min
3	CH_3, CH_3	0°, 20 min
4	Ph, H	−78°, <5 min
5	CH_3, Cl	−78°, <5 min



6a, R = $Si(CH_3)_3$
b, R = CH_3