Tetrahedron Letters No. 8, pp 585 - 588, 1976. Pergamon Press. Printed in Great Britain.

SESQUITERPENOID ALCOHOLS FROM THE HAWAIIAN MARINE ALGA LAURENCIA NIDIFICA. III.

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(Received in USA 13 November 1975; received in UK for publication 15 January 1976)

The Hawaiian marine alga Laurencia nidifica has been shown to consist of at least two varieties which elaborate quite different halogenated sesquiterpenoids.[1] We have now identified a third variety of this alga whose secondary metabolite content is entirely different from the two varieties of alga previously described, indicating that it, too, may be more properly classed as distinct species of Laurencia. We describe herein the structure of two sesquiterpenoid alcohols isolated from this third variety of L. nidifica. Its C_{15} halogenated components will be the subject of a future communication.

Collections of the alga were made in January and June, 1975, at Diamondhead and Black Point reefs on the island of Oahu, Hawaii. The alga is green in color and grows in patches on the reef where the wave action is substantial. Although its color and habitat are different from the two varieties of L. nidifica described previously, this alga has been classified as the same species.[2]

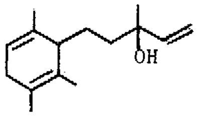
Silica gel column chromatography of the ether extract of the air-dried alga afforded an ether eluate, which, upon molecular distillation, yielded a colorless oil (5% of original extract). Tlc fractionation (hexane:dichloromethane, 1:3) of this oil gave 0.02% component A and 0.01% component B (dry weight of alga).

Component A analyzed for $C_{15}H_{24}O$ by mass spectroscopy m/e M^+ 220; high resolution m/e 220.18282 (calcd for $C_{15}H_{24}O$, 220.18271). Its ir spectrum (CCl_4) displayed OH absorption at 3600 and 3470 cm^{-1} and vinyl absorption at 3080, 1640, and 910 cm^{-1}. The pmr spectrum ($CDCl_3$) showed a methyl singlet at 1.27 δ ($CH_3-\overset{|}{\underset{|}{C}}-O-$) and a broad singlet at 1.68 δ assigned to three vinyl methyl groups. A three proton singlet (broad) at 2.60 δ was ascribed to doubly allylic hydrogens. The olefinic region of the spectrum gave a well resolved AMX pattern, the multiplets centered at 5.07 δ (dd, J = 10, 2 Hz), 5.20 δ (dd, J = 17, 2 Hz), and 5.95 δ (dd, J = 17, 10 Hz). A fourth olefinic proton appeared as an unresolved multiplet at 5.57 δ.

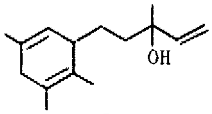
The cmr spectrum ($CDCl_3$) showed four methyl carbons (16.75, 18.64, 21.36, 23.83 ppm), three methylene carbons (27.67, 33.88, 35.77 ppm), one methine carbon (45.24 ppm), an oxygen-bearing quaternary carbon (73.15 ppm), a terminal vinylic carbon (111.49 ppm), and five additional vinylic carbons (121.05, 124.16, 125.42, 133.96, 145.18 ppm).

When allowed to stand at 25° for several days, component A was converted into component B. Component B analyzed for $C_{15}H_{22}O$ by mass spectroscopy m/e M^+ 218; high resolution m/e 218.16819 (calcd for $C_{15}H_{22}O$, 218.16706). The ir (CCl_4) showed OH (3600, 3470 cm^{-1}) and vinyl (1640, 920 cm^{-1}) absorptions. As in component A, the pmr spectrum ($CDCl_3$) of B retained the methyl singlet at 1.32 δ ($CH_3-\overset{|}{\underset{|}{C}}-O-$) and the three proton AMX pattern in the olefinic region with multiplets centered at 5.09 δ (dd, J = 10, 2 Hz), 5.26 δ (dd, J = 17, 2 Hz), and 6.01 δ (dd, J = 17, 10 Hz). However, the three vinyl methyl signals of component A were replaced by three aromatic methyl singlets at 2.18, 2.23, and 2.25 δ; the one proton olefinic signal and the three proton doubly allylic signal of A were replaced by a two proton aromatic singlet at 6.75 δ. In addition, two methylene multiplets (1.42-1.70, $-CH_2-$; 2.50-2.80, $Ar-CH_2-$) became evident in the spectrum of component B. The uv spectrum $\left(\lambda_{max}^{EtOH}\ 220\ m\mu,\ \epsilon = 7{,}500\right)$ also indicated that component B was aromatic.

On the basis of this data, two possible structures can be written for component A (1 and 2) and two for component B (3 and 4):



1



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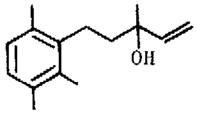

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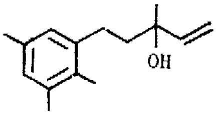

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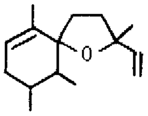
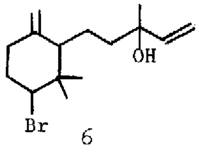
The choice in favor of structures 1 and 3 for the algal constituents is made from the infrared spectrum of the aromatic compound. In CS_2, compound B exhibited a strong sharp absorption at 800 cm^{-1} (and none in the 900-860 and 750-700 cm^{-1} regions) as expected for a 1,2,3,4-tetra substituted aromatic system.[3]

Component A (1) is closely related in structure to dactyloxene-B (5), a sesquiterpenoid isolated from the sea hare Aplysia dactylomela,[4] and snyderol (6) a monocyclic sesquiterpenoid isolated from Laurencia snyderae.[5]



5



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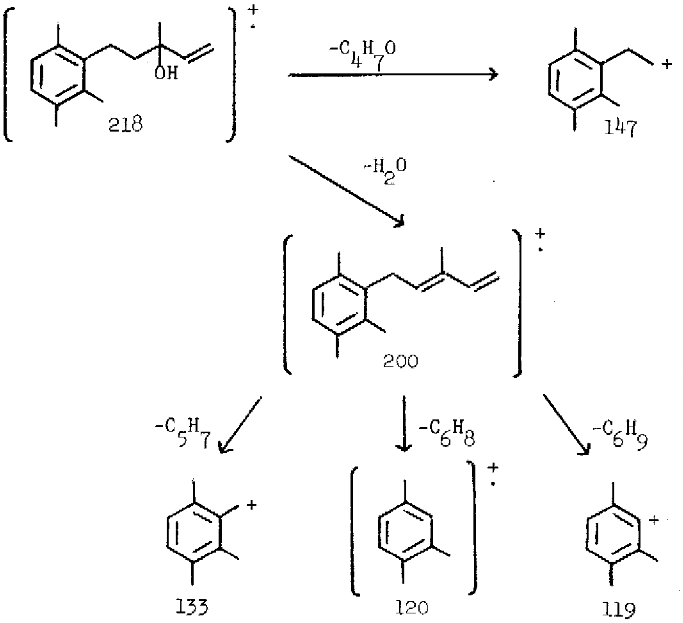
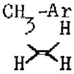
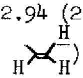
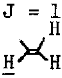
The mass spectrum of component B (3) showed major peaks at m/e 200, 147, 133, 120, and 119 which can be rationalized by the following fragmentation pattern:



Trimethylsilylation of component A (1) afforded the TMS derivative of component B (3) identified by its mass spectrum, M^+ 290, base peak 143 () and pmr spectrum (C_6D_6), δ 0.20 (9H, s, $(CH_3)_3$-Si-), 1.31 (3H, s, CH_3-C-O-), 1.48-1.80 (2H, m, -CH_2-), 2.18 (6H, s, CH_3-Ar), 2.32 (3H, s, CH_3-Ar), 2.65-2.94 (2H, m, -CH_2-Ar), 5.02 (1H, dd, J = 10, 2 Hz, ), 5.17 (1H, dd, J = 17, 2 Hz, ), 5.92 (1H, dd, J = 17, 10 Hz, ), and 7.00 (2H, s, ArH).

Since 1 is so readily converted to 3, the natural occurrence of the latter in the alga cannot be assumed.

Acknowledgements

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, Max Serraon, and Demetries 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 facility at the Massachusetts Institute of Technology supported by Grant RR0317 (Principal Investigator Professor K. Biemann) from the Biotechnology Research Branch, Division of Research Resources. The cmr spectra were provided by New England Area NMR Research Resource Laboratory at the University of Connecticut Health Center supported by Grant RR00639 (Principal Investigator J. Glasel).

References

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2. Y. Saito, Pacific Science, XXIII, 148 (1969).
3. L. J. Bellamy, The Infra-red Spectra of Complex Molecules, John Wiley & Sons, Inc., New York, 1958, pp. 78-79. Compare, for example, the spectra of 1,2,3,4- and 1,2,3,5-tetramethylbenzenes, Card Numbers 21121 and 269, Documentation of Molecular Spectroscopy, Butterworth & Co., Ltd., London.
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