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SHORT COMMUNICATION

ZONARENE, A SESQUITERPENE FROM THE BROWN SEAWEED *DICTYOPTERIS ZONARIOIDES**

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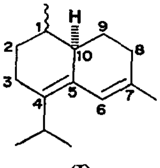
Abstract—The major hydrocarbon component of the brown seaweed *Dictyopteris zonarioides*, zonarene, has been isolated and identified as the first $C_{15}H_{24}$ conjugated diene sesquiterpene of the cadanane type.

INTRODUCTION

THE MAJOR hydrocarbon components of a number of species of *Dictyopteris* have been described. Those derived from *D. divaracata* were found to be sesquiterpenes of the cadanene type[2] while *D. plagiogramma* and *D. australis*[3] yielded an unusual array of non-isoprenoid molecules. We have extracted and identified the major hydrocarbon component of *D. zonaroiodes*, zonarene, I. Zonarene is the first example of a conjugated diene member of the cadanene hydrocarbons.[4]



(I)

RESULTS AND DISCUSSION

Hexane extraction and chromatographic separation of the essential oil of *D. zonarioides* results in the isolation of zonarene as the major (95% hydrocarbon content) hydrocarbon constituent. The structure of zonarene, $M^+ = 204$ ($C_{15}H_{24}$), was confirmed by its NMR

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* Part II in the series "Marine Natural Products". For Part I see Ref. 1.

[1] J. SIMS, W. FENICAL, R. WING and P. RADLICK, *J. Am. Chem. Soc.* **93**, 3774 (1971).

[2] E. KUROSAWA, M. IZAWA, K. YAMAMOTO, T. MASAMUNE and T. IRIE, *Bull. Chem. Soc. Japan* **37**, 1053 (1964).

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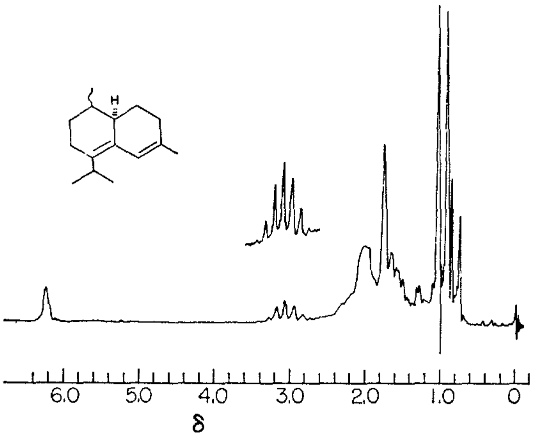

Fig. 1. NMR spectrum of zonarene, I, taken at 60 mHz (CCl_4).

spectrum shown in Fig. 1, and by its dehydrogenation to cadalene,[4,5] II, with dichlorodicyano-*p*-benzoquinone (DDQ) in refluxing benzene. The single allylic tertiary proton of the isopropyl group in I stands out as a heptet ($J = 6{\cdot}5$ Hz) in Fig. 1. The four coupled methyl groups are clearly visible with the 1-methyl group appearing as a doublet ($J = 6{\cdot}0$ Hz) at 0·8 ppm. The isopropyl and vinyl methyl groups are assigned to the intense doublet at 0·95 ppm and to the broad band at 1·75 ppm, respectively.

Zonarene showed UV absorptions (EtOH) at 241 (18,600), 248 (19,070) and 258 nm (13,020), closely resembling the absorptions of its closest relative δ-selinene.[6] The absolute stereochemistry of I has been partially defined, (C-10), by a comparison of its ORD spectrum (negative Cotton effect; $[\alpha]_D^{30}$ −217·8°, c, 0·46 cyclohexane) with that shown by (−) δ-selinene,[6,7] In addition, the indicated stereochemistry at C-10 is predicted by an evaluation of the chirality of the transoid diene system[8] as well as the conformation of its axial allylic hydrogens.[9] The prediction of the absolute stereochemistry of the 1-methyl group using the above methods require knowledge of the conformations of both cyclohexene rings. Molecular models reveal that the energy differences between the more stable conformations are too small to allow an accurate prediction to be made at present.

EXPERIMENTAL

Hexane extraction. 3·1 kg air dried *D. zonarioides* (whole plants, collected 3-27-71, Puerto Peñasco, Mexico) was powdered with a Wiley mill (1 mm screen). Extraction with 2 × 4 l. of warm hexane, followed by drying ($MgSO_4$) and solvent evaporation gave 14 g crude extract. Column chromatography (4 × 30 cm column, Davison grade 950 silica gel) eluting with hexane and 10% benzene in hexane gave five fractions of hydrocarbons which contained varying amounts of zonarene. These fractions were combined (2·2 g) and further purified as described below. Continued elution with varying amounts of Et_2O in benzene resulted in the liberation of a mixture of linoleic acid esters. One of these esters is the *bis*-ester of a $C_{21}H_{30}O_2$ hydroquinone which is under current investigation. Large quantities of this hydroquinone are obtained by chromatography of the methanol extract of *D. zonarioides*.

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[4] V. Herout and V. Sykora, *Tetrahedron* **4**, 246 (1958).

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Silver nitrate chromatography. The combined hydrocarbon fractions from above (2·2 g) were chromatographed on a 2·5 × 33 cm column of 10% $AgNO_3$ impregnated Davison grade 950 silica gel. 2·5% benzene in hexane gave a small amount of saturated hydrocarbons (total 35 mg). 10% benzene in hexane gave four fractions which were shown to be 95+% zonarene by GLC analysis on a 1·8 m × 8 mm 20% SF-96 on firebrick column at 240°. The combined yield of purified zonarene was 1·2 g. The IR spectrum of I showed characteristic absorptions at 1470, 1460, 1425, 1375, 1250, 1200, 1090, 866, 843 and 786 cm^{-1} (thin film). (*Anal.* Calcd. for $C_{15}H_{24}$: C, 88·17; H, 11·83. Found: C, 87·96; H, 11·97%.)

Dehydrogenation of zonarene. 150 mg zonarene, *ca.* 95% by GLC, was dissolved in 20 ml benzene and a 10 M excess dichlorodicyano-*p*-benzoquinone (DDQ) was added. The mixure was refluxed overnight, the benzene was removed and the solid residue was warmed into cyclohexane. Removal of solvent after drying MgSO$_4$) left 75 mg of a yellow oil shown by its NMR spectrum to contain 70% cadalene.[5]

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Key Word Index—Dictyopteris zonarioides; Phaeophyta; sesquiterpene; zonarene.