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DICTYOPTERENE A, AN ODORIFEROUS CONSTITUENT FROM ALGAE OF THE GENUS DICTYOPTERIS*

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We wish to report the isolation and characterization of a novel hydrocarbon, dictyopterene A (1), from the essential oil of algae of the genus Dictyopteris (1, 2, 3).

Two species of Dictyopteris, viz. D. plagiogramma (Montagne) Vickers and D. australis Sonder, grow abundantly at times on the reefs of Waikiki, Honolulu. The fresh wet algae (unseparated) were placed in a large vacuum desiccator and the essential oil was trapped on the finger of a dry ice condenser. The volatile organic material was extracted with carbon disulfide, the carbon disulfide removed by fractional distillation, and the essential oil obtained in 0.005% yield by a short-path distillation, b.p. 90-150°. Separation of the components of the volatile oil was accomplished by preparative gas chromatography on a 10' x 3/8" column of 10% SE-30 on Aeropak 30. The first major compound to emerge from the gas chromatograph (Varian Aerograph Autoprep Model 705 with hydrogen flame ionization detector) was dictyopterene A: $[\alpha]_D^{21}$ + 77° ± 5° (C 0.5, EtOH); mol wt 150 which corresponds to the empirical formula $C_{11}H_{18}$ by mass spectrometry; λ_{max}^{EtOH} 206 mu (ϵ 16,000).

A complete analysis of its nmr spectrum, achieved only with the aid of several double resonance experiments, led us to the conclusion that dictyopterene A is trans-1-(trans-1-hexenyl)-2-vinylcyclopropane (1)

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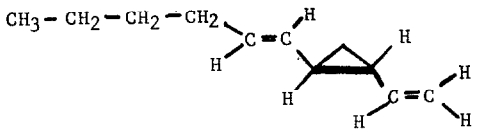
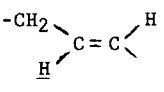
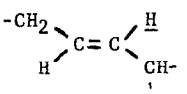
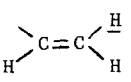
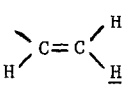
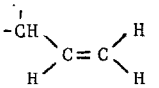


1

The nmr spectral data is summarized in Table I.

TABLE I

Nmr Spectral Data of Dictyopterene A

Description of signal	No. of protons	Chemical shift[a]	Coupling constant[b]	Assignment
Broad 1:3:3:1 quartet[c,d]	2	1.95	7	$-CH_2-\underline{CH_2}-CH=$
Doublet of triplets[e]	1	5.45	15.5[f], 7	
Doublet of doublets of triplets[g]	1	4.99	15.5, 6, 1.2	
Doublet of doublets	1	4.98	17[f], 2.5[h]	
Doublet of doublets	1	4.81	10[i], 2.5	
Doublet of doublets	1	5.37	17, 10, 6	
Triplet[k]	3	0.77	7	$\underline{CH_3}-CH_2-$
Multiplet	6	ca. 1.25		$-\underline{CH_2}-\underline{CH_2}-$ and 
Triplet[k,l]	2	0.87	7	

[a]Determined on a Varian HA-100 instrument in deuteriochloroform and reported as δ units relative to TMS (δ = 0).

[b]In cps.

[c]Collapses to a broad triplet (J = 7 cps) when irradiated at 5.45 ppm and to an unresolved doublet (J = 7 cps) when irradiated at 1.25 ppm.

[d]The signal is broad due to virtual coupling [see J. I. Musher and E. J. Corey, Tetrahedron, 18, 791 (1962)] to the ϵ-methylene protons and long-range coupling (J = 1.2 cps) to the α-methine proton of the hexenyl group.

[e]Collapses to a doublet (J = 15.5 cps) when irradiated at 1.95 ppm.

[f]J_{trans}.

[g]Collapses to a doublet of doublets (J = 15.5 and 6 cps) when irradiated at 1.95 ppm and to a doublet of triplets (J = 15.5 and 1.2 cps) when irradiated at 1.25 ppm.

[h]J_{gem}.

[i]J_{cis}.

[j]Collapses to a doublet of doublets (J = 17 and 10 cps) when irradiated at 1.25 ppm.

[k]Collapses to a singlet when irradiated at 1.25 ppm.

[l]The coincidence of chemical shifts for the two methylene protons establishes the trans configuration for the disubstituted cyclopropane ring.

Osmium tetroxide-periodate oxidation (4) of dictyopterene A yielded formaldehyde, n-valeraldehyde, and trans-1,2-cyclopropanedicarboxaldehyde that were converted to the corresponding 2,4-dinitrophenylhydrazones and separated by preparative thin layer chromatography on deactivated silica gel (1:1 isooctane-benzene). The DNP derivatives of formaldehyde and n-valeraldehyde were identical with authentic samples (mass spectra, R_f-values, and melting points). The bis-DNP of the cyclopropane dialdehyde was not obtained entirely pure, but had the expected molecular weight by mass spectrometry.

Treatment of dictyopterene A with osmium tetroxide followed by periodate-permanganate oxidation (5) afforded formic acid, n-valeric acid, and (+)-trans-1,2-cyclopropane dicarboxylic acid (6). Formic and valeric acids were identified by paper chromatography.

These data establish structure 1 unequivocally for dictyopterene A.

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