# Isolation and Structure Determination of an Undeca-1,3,5,8-tetraene and Dictyopterene B from Algae of the Genus *Dictyopteris*

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*Summary* *trans,cis,cis*-Undeca-1,3,5,8-tetraene (II) and dictyopterene B (III) are two new hydrocarbons from *Dictyopteris*.

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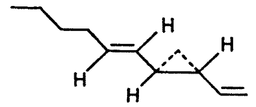
We describe the isolation and structure determination of two new hydrocarbons from the essential oil of *Dictyopteris*, an undeca-1,3,5,8-tetraene (II) and dictyopterene B (III).

Separation of the essential oil into five major fractions is accomplished by gradient chromatography on 25% silver nitrate–silica gel with 0—5% ether–pentane. Dictyopterene A(I),[1] the second major constituent of the essential oil (25%) is obtained from fraction 2.

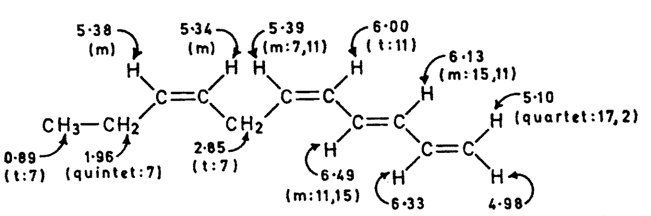
Fraction 4 (5% of the essential oil) is an optically inactive liquid [mass spectrum: molecular ion $m/e$ 148 (corresponds to the molecular formula $C_{11}H_{16}$); u.v. spectrum: $\lambda_{max}$ (EtOH) 257, 266, and 277 nm (conjugated triene)]. Its n.m.r. spectrum in $C_6D_6$ shows a triplet at 0·89 p.p.m. and a quintet at 1·96 p.p.m. ($J$ 7 Hz) for an ethyl group attached to an olefinic methine, a triplet at 2·85 p.p.m. ($J$ 7 Hz) for a methylene flanked by two olefinic methines, and quartets at 4·98 ($J$ 9·5 and 2 Hz) and 5·10 p.p.m. ($J$ 17 and 2 Hz) for the methylene protons of a vinyl group. These data are consistent with an undeca-1,4,6,8- or 1,3,5,8-tetraene. An unequivocal choice of the 1,3,5,8-structure is permitted from the following double-resonance experiments: irradiation at 5·3 p.p.m. reduces the quintet and triplet to a quartet and singlet, respectively, indicating three olefinic methines coupled to the two saturated methylenes absorbing in a complex multiplet at 5·2—5·5 p.p.m. The vinyl methine is located in a four-proton multiplet at 5·8—6·7 p.p.m., as irradiation at 6·33 p.p.m. reduces the vinyl methylene signals to two partially resolved doublets ($J$ 2 Hz).

We conclude that fraction 4 is *trans,cis,cis*-undeca-1,3,5,8-tetraene (II). The triplet of triplets at 6·00 p.p.m. assigned to the C-5 proton, shows long-range coupling to the C-7 methylene ($J$ 1·5 Hz), *cis*-coupling to the C-6 proton ($J$ 11 Hz), and coupling to the C-4 proton ($J$ 11 Hz). The long-range coupling in the latter signal is removed by irradiation of the C-7 protons. The C-4 proton, appearing essentially as a doublet of doublets at 6·49 p.p.m. due to van der Waals deshielding by the *cis*-C-7 methylene shows *trans*-coupling to the C-3 proton ($J$ 15 Hz) and coupling to the C-5 proton ($J$ 11 Hz). Finally, the geometry of the 8,9-double bond is most likely *cis* as the closest match of a calculated spectrum with the complex multiplet at 5·2—5·5 p.p.m. is obtained with $J$ 11 Hz for the C-8 and C-9 proton interaction.

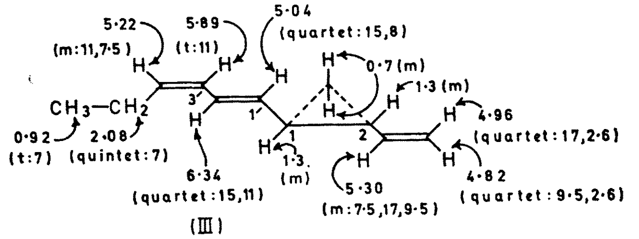
From fraction 5 is obtained the major constituent (50%) of the essential oil, dictyopterene B, $[\alpha]_D$ − 43°; $\lambda_{max}$ (EtOH) 247 nm. Its n.m.r. spectrum in $C_6D_6$ exhibits the familiar patterns for a vinyl group, an ethyl group attached to an olefinic methine, and a *trans*-disubstituted cyclopropane ring. The presence of a hexa-1′,3′-dienyl group attached to the cyclopropane ring is revealed from the following n.m.r. data: (1) a triplet of triplets at 5·89 p.p.m. ($J$ 1·3, 11, and 11 Hz) for the C-3′ proton showing long-range coupling to the C-5′ methylene, *cis*-coupling to the C-4′ proton, and coupling to the C-2′ proton, respectively; (2) a doublet of doublets at 6·34 p.p.m. ($J$ 11 and 15 Hz) for the C-2′ proton showing coupling with the C-3′ proton and *trans*-coupling with the C-1′ proton, respectively; and (3) a doublet of doublets at 5·04 p.p.m. ($J$ 8 and 15 Hz) for the C-1′ proton showing coupling to the C-1 proton of the cyclopropane ring and *trans*-coupling to the C-2′ proton, respectively. Dictyopterene B is therefore *trans*-1-(*trans*, *cis*-hexa-1′,3′-dienyl)-2-vinylcyclopropane (III). Lemieux oxidation[2] of (III) to (+)-*trans*-cyclopropane-1,2-dicarboxylic acid establishes the absolute configuration of the cyclopropane ring. Finally, heating (III) in benzene at 90° for several hours produces 6-(*cis*-but-1′-enyl)cyclohepta-1,4-diene (IV).



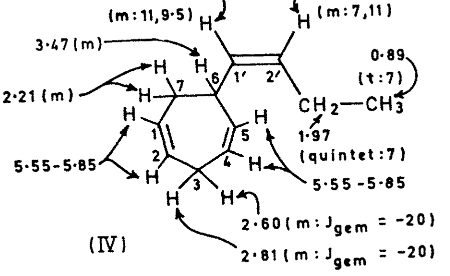
(I)



(II)

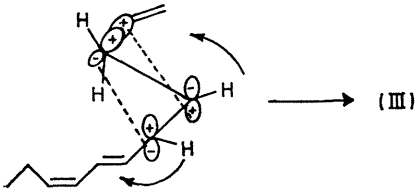


(III)



(IV)

The presence of (II) and other linear $C_{11}$ polyenes and no branched methyl compounds in the essential oil suggest that the optically active cyclopropane ring of the dictyopterenes may be formed by an enzymatically controlled and photochemically induced (with or without light[3]) di-π-methane rearrangement[4] of a polyunsaturated fatty acid followed by degradation to the hydrocarbon. Compounds (II) and (III) can be inter-related through a common intermediate *cis,trans,cis*-undeca-1,4,6,8-tetraene (V) where a thermally induced 1,5-sigmatropic proton shift in (V) from C-3 to C-7 results in (II) and a concerted,[5] photochemically induced di-$\pi$-methane rearrangement of (V) results in (III).



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