Isolation and Structure of Dictyoprolene, a Possible Precursor of Various Undecanes in Brown Algae from *Dictyopteris prolifera*

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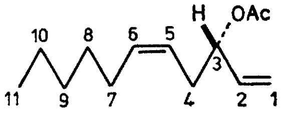
Summary The isolation and structure elucidation (including the absolute stereochemistry) of (+)-dictyoprolene (**1**) a constituent of *Dictyopteris prolifera*, together with the synthesis of (**1**) in optically active form indicate that (**1**) is the acetate of one of three undec-1-en-3-ols postulated to be key biosynthetic intermediates leading to various novel C_{11} hydrocarbons in *Dictyopteris*.

A variety of novel C_{11} hydrocarbons, including those important in reproduction, has been isolated from brown algae (*Dictyopteris, Ectocarpus*, and *Cutleria*).[1] Many related compounds possessing a C_{11} unit have also been isolated from brown algae (*e.g.*, sulphur-containing compounds).[2] Moore assumed that three kinds of undec-1-en-3-ols derived from oleic, linoleic, and linolenic acid, respectively, were precursors in the biogenesis of these various C_{11} hydrocarbons,[3,4] although they have not so far been detected in brown seaweeds.



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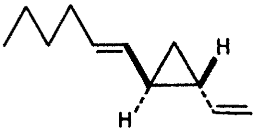

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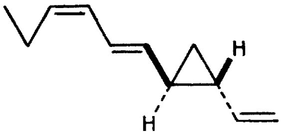

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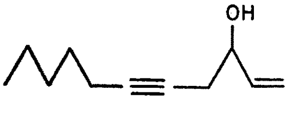
We herein describe the isolation and structure determination of (+)-dictyoprolene (**1**), the acetate of one of the undec-1-en-3-ols postulated[3,4] to be key biosynthetic intermediates leading to many C_{11} hydrocarbons, from *Dictyopteris prolifera*. A hexane-soluble fraction of the acetone extract of fresh *Dictyopteris prolifera* was chromatographed on silica gel with chloroform, and gave four major fractions (I—IV). Further separation of fraction I by preparative t.l.c. on silica gel with hexane afforded dictyopterene A (**2**),[1a,1e] $[\alpha]_D^{21}$ +59° (*c* 1·97, $CHCl_3$) (0·003%) and dictyopterene B (**3**).[1b,c] $[\alpha]_D^{21}$ −32° (*c* 0·84, $CHCl_3$) (0·001%). Fraction II was separated by repeated preparative t.l.c. on silica gel with hexane–chloroform–benzene (9 : 3 : 1), to yield (+)-dictyoprolene (**1**),† $C_{13}H_{22}O$ (0·0003%) as a colourless liquid, $[\alpha]_D^{27}$ +13° (*c* 1·30, $CHCl_3$). The structure of dictyoprolene, except for the stereochemistry of the disubstituted double bond, was deduced to be (**1**) on the basis of its spectral data and was confirmed by synthesis.

Dictyoprolene (**1**) showed characteristic i.r. bands (CCl_4) at 3020 (olefinic ν_{C-H}), 1740 (acetate C=O), and 1238 (acetate C–O) cm^{-1} and ^1H n.m.r. signals (100 MHz, $CDCl_3$) at δ 0·89 (3H, br.t, *J* 6·0 Hz, H-11), 1·30 (6H, m, H-8, H-9, and H-10), 2·02 (2H, m, H-7), 2·04 (3H, s, OAc), 2·41 (2H, dd, *J* 6·0 and 6·0 Hz, H-4), 5·1—5·6 (5H, complex pattern, H-1, H-3, H-5, and H-6), and 5·83 (1H, ddd, *J* 17·0, 10·0, and 6·0 Hz, H-2). The ^{13}C n.m.r. spectrum (20 MHz, $CDCl_3$) of (**1**) showed 13 carbon signals: δ 14·1 (q), 21·2 (q, -OCO*Me*), 22·5 (t), 27·4 (t), 29·2 (t), 31·5 (t), 32·2 (t), 74·3 (d), 116·6 (t), 123·4 (d), 133·1 (d), 136·1 (d), and 170·2 p.p.m. (s, -O*C*OMe). Prominent peaks were observed at *m/e* 150 (M^+ − AcOH) and 99 (M^+ − $Me[CH_2]_4CH{=}CHCH_2$) in the mass spectrum of (**1**).



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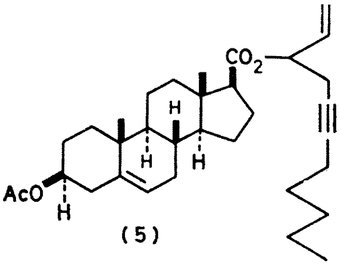

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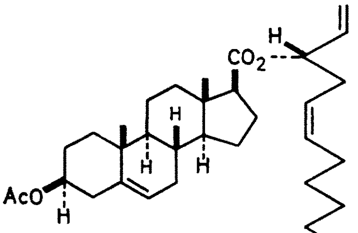

(6a)

The synthesis of optically active (**1**) was performed as follows. Acrolein was condensed with 1-bromo-oct-2-yne[5] in the presence of activated zinc [tetrahydrofuran (THF), 40—60 °C, 40 min] to give undec-1-en-5-yn-3-ol (**4**)†§ (17%). For optical resolution, the alcohol (**4**) was esterified with 3β-acetoxy-5-androstene-17β-carboxylic acid chloride[6,7] (*NN*-dimethylaminopyridine, toluene, 50 °C, 36 h) to give a diastereomeric mixture of the ester (**5**), which was separated by preparative t.l.c. on silica gel impregnated with silver nitrate with benzene affording the two diastereomers, (**5a**)†§ (38%) and (**5b**)†§ (39%). Both isomers were differentiated by ^1H n.m.r. spectroscopy [δ ($CDCl_3$) 0·70 (3H, s, H-18 of the steroid part) for (**5a**) and δ 0·72 for (**5b**)]. The diastereomer (**5a**) was hydrogenated in the presence of Lindlar's catalyst (Pd–$CaCO_3$, benzene–quinoline, room temp., 1·5 h) yielding the *cis*-olefinic ester (**6a**)†§ (90%). Reduction of (**6a**) with

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† Satisfactory elemental analyses or exact mass spectral data were obtained.

§ This compound had i.r., ^1H n.m.r., and mass spectra in agreement with the structure assigned.

lithium aluminium hydride (THF, 0 °C, 1 h) followed by acetylation (Ac_2O–pyridine, room temp., 13 h) and subsequent purification by preparative t.l.c. on silica gel with chloroform gave (+)-dictyoprolene (**1**),†§ $[\alpha]_D^{25}$ +11° (*c* 1·17, $CHCl_3$) (77% overall yield) spectroscopically (i.r., ^{1}H n.m.r., and mass) and chromatographically identical with a natural specimen. The absolute configuration of (+)-dictyoprolene (**1**) was determined as follows. Catalytic hydrogenation of (+)-(**1**) (PtO_2, EtOH, room temp., 1 h) afforded (+)-3-acetoxyundecane {$[\alpha]_D^{25}$ +11° (*c* 0·98, EtOH)}, which on methanolysis (NaOMe–MeOH, room temp., 14 h) yielded (−)-(3*R*)-undecan-3-ol,[8] $[\alpha]_D^{28}$ −9° (*c* 0·62, EtOH). Thus the absolute configuration at C-3 of (+)-dictyoprolene (**1**) was shown to be *S*, proving the validity of Moore's assumption[3] that the undec-1-en-3-ols, the hypothetical precursors of various dictyopterenes, would have *S* absolute stereochemistry at C-3.

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