(−)-Bis-(3-acetoxyundec-5-enyl) Disulphide and *S*-(−)-3-Acetoxyundec-5-enyl Thioacetate, Possible Precursors to Undeca-1,3,5-trienes in *Dictyopteris*

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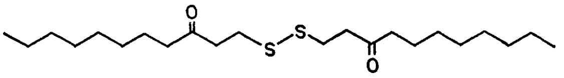
Summary (−)-Bis-(3-acetoxyundec-5-enyl) disulphide and *S*-(−)-3-acetoxyundec-5-enyl thioacetate are two new sulphur compounds from Hawaiian *Dictyopteris* and may be precursors to undeca-1,3,5-trienes found in the essential oil.

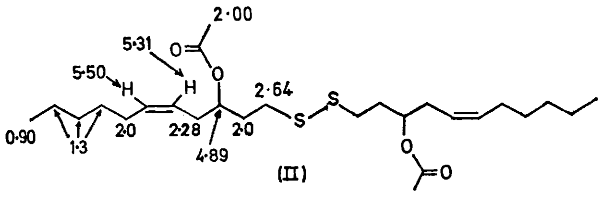
Hawaiian species of seaweed belonging to the genus *Dictyopteris* are rich in C_{11} hydrocarbons.[1,2] Recently, six organic sulphur compounds have been found in *Dictyopteris* which may be precursors of the hydrocarbons.[3] One of these, bis-(3-oxoundecyl) disulphide (I), is accompanied by a mixture of bis-(3-oxoundecyl) polysulphides and a small amount of another sulphur compound which we have now characterized as (−)-bis-(3-acetoxyundec-5-enyl) disulphide (II). We found that (II) could not be completely separated from (I) by either fractional recrystallization, gel filtration, or t.l.c. To achieve separation the mixture of (I) and (II) was first reductively acetylated with Zn, AcOH, and Ac_2O and the resulting mixture of (III) and (IV) was separated by repeated gel filtration on Sephadex with 50% $CHCl_3$–MeOH and t.l.c. on silica gel with 2% EtOAc–cyclohexane. Compound (IV) moved faster than (III) on Sephadex and slower than (III) on silica gel. Compound (II) was finally regenerated by treating (IV) with neutral alumina in n-hexane. Compound (IV) is also a constituent of *Dictyopteris*, appearing in the fraction eluted immediately after (III) from silica gel column chromatography of the $CHCl_3$–MeOH extract of *D. plagiogramma* and *D. australis*.

Disulphide (II), a low-melting, white solid, having a negative optical rotation, was characterized by mass and n.m.r. spectroscopy.

Thioacetate (IV), a liquid, $[\alpha]_D$ $-25 \pm 10°$ (CCl_4), exhibited a n.m.r. spectrum in CCl_4 similar to that of (III), except for an additional singlet at δ 2·30 for the thioacetate protons. The C-2 protons, however, could not be clearly seen as a doublet of triplets at δ 1·76 (J 6·5 and 7 Hz) and double resonance experiments confirmed the interaction of the C-2 hydrogens with the C-1 and C-3 protons. Double resonance experiments also supported the assignment of a multiplet obscured by the thioacetate signal to C-4 CH_2 since irradiation at 2·35 p.p.m. caused a collapse of the quintet at 4·84 p.p.m. (C-3 methine) to a triplet and the doublet of triplets at 5·31 p.p.m. (C-5 olefinic H) to a doublet (J = 11 Hz for *cis*-geometry of the Δ^5 double bond). The mass spectrum of (IV) showed no molecular ion and exhibited only one intense peak at *m/e* 150 ascribed to loss of acetic acid and thioacetic *S*-acid from the molecular ion to give a undeca-1,3,5-triene ion.



(I)



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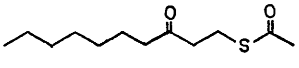

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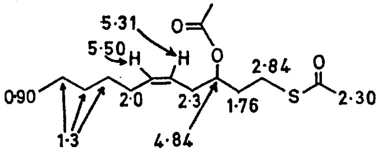
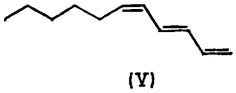
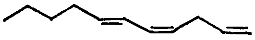


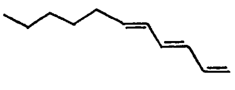
(IV)



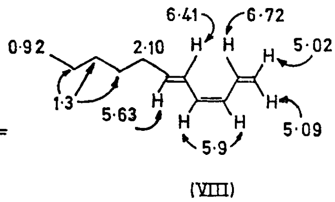
(V)



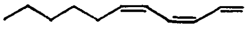
(VI)



(VII)



(VIII)



(IX)

Elimination of acetic acid and thioacetic *S*-acid from (IV) may occur enzymatically in the seaweed to give *trans,-cis*-undeca-1,3,5-triene (V), one of the constituents of the essential oil of *Dictyopteris*. Another possible route to (V) is a 1,5 sigmatropic proton migration from C-3 to C-7 in an intermediate *cis,trans*-undeca-1,4,6-triene (VI).[4]

Fraction 1 from chromatography of the essential oil of *Dictyopteris* on 25% $AgNO_3$–silica gel[2] is roughly a 20:10:1 mixture of (V), *trans,trans*-undeca-1,3,5-triene (VII), and *cis,trans*-undeca-1,3,5-triene (VIII), respectively. The trienes were separated by preparative g.l.c. Trienes (V) and (VII) were identical in all respects with authentic samples.[5] Triene (VIII), which had the longest retention time, was identical with a sample produced from photoisomerization of (V) or (VII); the van der Waals deshielding of the C-2 and C-5 protons in its n.m.r. spectrum shows *cis*-geometry for the Δ^3-double bond. The C-2 and C-5 protons of trienes (V) and (VII) resonate at higher field.

Trienes (VII) and (VIII) are most probably formed from the photosensitized isomerization of (V) in the plant, possibly with chlorophyll as the sensitizer.[6] Photoisomerization occurs readily in n-pentane with u.v. light (3660 Å) in the presence of benzophenone or chlorophyll a. Isomerization is more favoured around the terminal Δ^5 double bond of the undeca-1,3,5-triene than around the central Δ^3 double bond[7] and at the photostationary state the *cis*-Δ^3-trienes (VIII) and (IX) are found in smallest amounts, especially at high triene concentration or in the presence of a quencher such as azulene.[8]

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[1] R. E. Moore, J. A. Pettus, jun., and M. S. Doty, *Tetrahedron Letters*, 1968, 4787; J. A. Pettus, jun. and R. E. Moore, 161st National Meeting of the American Chemical Society, Los Angeles, California, March 1971, Abstract No. ORGN 113; J. A. Pettus, jun. and R. E. Moore, *J. Amer. Chem. Soc.*, 1971, **93**, 3087.

[2] J. A. Pettus, jun. and R. E. Moore, *Chem. Comm.*, 1970, 1093.

[3] P. Roller, K. Au, and R. E. Moore, *Chem. Comm.*, 1971, 503; R. E. Moore, *ibid.*, 1971, 1168.

[4] The rearrangement of *cis*-β-ocimene to *trans,cis*-allo-ocimene proceeds readily at 190° (G. Ohloff, J. Seibl, and E. Kovats, *Annalen*, 1964, **675**, 83; T. Sasaki, S. Eguchi, and H. Yamada, *Tetrahedron Letters*, 1971, 99); *trans*-β-ocimene is thermally stable at 190°, even for a short period at 450° (J. Wolinsky, B. Chollar, and M. D. Baird, *J. Amer. Chem. Soc.*, 1962, **84**, 2775).

[5] Authentic samples were kindly provided by Dr. W. I. Taylor, International Flavors and Fragrances. Undeca-1,3,5-trienes are constituents of Galbanum (Y.-R. Naves, *Bull. Soc. Chim. France*, 1967, 3152; Y. Christien-Bessiere, J. Garnero, L. Benezet, and L. Peyron, *ibid.*, 1967, 97).

[6] E. H. White and C. C. Wei, *Biochem. Biophys. Res. Comm.*, 1970, **39**, 1219.

[7] R. S. H. Liu and Y. Butt, *J. Amer. Chem. Soc.*, 1971, **93**, 1532.

[8] At high triene concentration or in the presence of a quencher, the *c,c* and *c,t* isomers of allo-ocimene are found in trace amounts at the photostationary state (R. S. H. Liu, *Pure Appl. Chem.*, 1971, **1** (Supplement), 335.