

**Isolation of *S*-(3-Oxoundecyl) Thioacetate, Bis-(3-oxoundecyl) Disulphide, (-)-3-Hexyl-4,5-dithiacycloheptanone, and *S*-(*trans*-3-Oxoundec-4-enyl) Thioacetate from *Dictyopteris***

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**Summary** *S*-(3-Oxoundecyl) thioacetate (VIII), bis-(3-oxoundecyl) disulphide (XII), (-)-3-hexyl-4,5-dithiacycloheptanone (XIII), and *S*-(*trans*-3-oxoundec-4-enyl) thioacetate (XIV) are four new lipids containing sulphur from *Dictyopteris*.

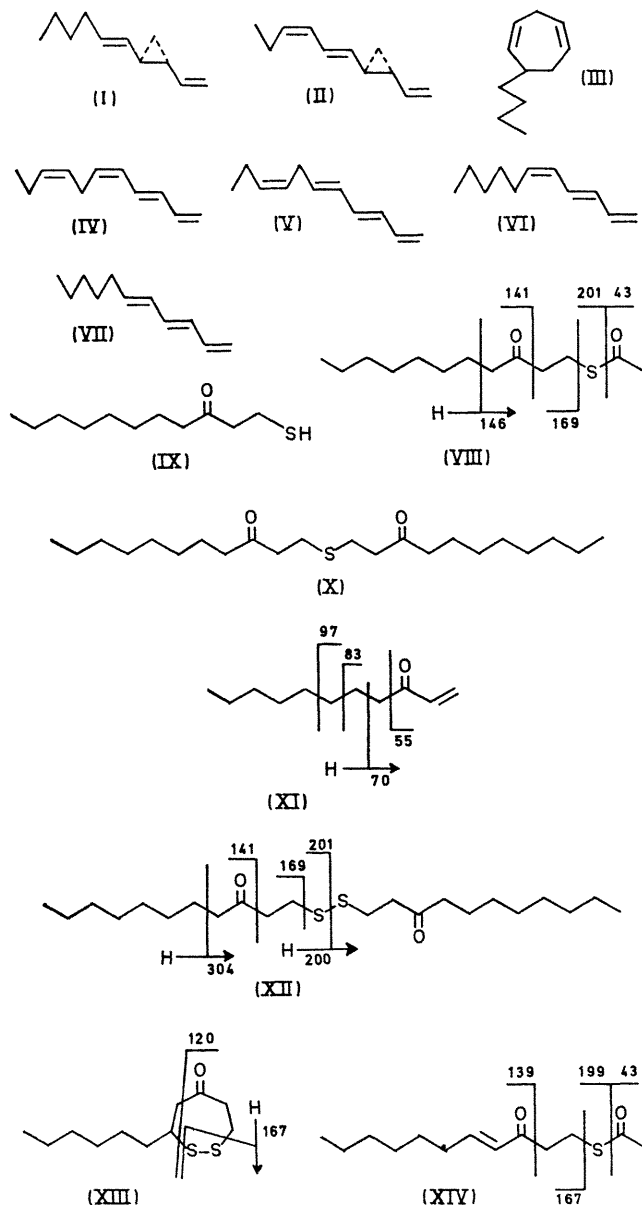
THE genus *Dictyopteris* is one of the few genera of seaweed possessing odour<sup>1</sup> and its essential oil, about 40% of the lipid content, is composed of C<sub>11</sub> hydrocarbons. The major constituents are (+)-dictyopterene A (I)<sup>2</sup> and (-)-dictyopterene B (II)<sup>3</sup> with smaller amounts of (-)-dictyopterene C' (III),<sup>4</sup> *trans,cis,cis*-undeca-1,3,5,8-tetraene (IV),<sup>3</sup> *trans,trans,cis*-undeca-1,3,5,8-tetraene (V),<sup>4</sup> *trans,cis*-undeca-1,3,5-triene (VI)<sup>4</sup>, and *trans,trans*-undeca-1,3,5-triene (VII).<sup>4</sup> We report the isolation of four lipids containing sulphur from *Dictyopteris* which may be precursors of these hydrocarbons.

The lipids were separated by column chromatography of the chloroform-methanol extract of *Dictyopteris plagiogramma* on Permutit Decalso or silica gel with 1-5% ether-hexane followed by gel filtration of the various fractions on Sephadex LH-20 with 50%chloroform-methanol and/or t.l.c. on silica gel with benzene.

From one of the earlier fractions was obtained a pale yellow oil, b.p. 80-85° (5 × 10<sup>-4</sup> mmHg), having the molecular formula C<sub>13</sub>H<sub>24</sub>O<sub>2</sub>S by high resolution mass spectrometry.† The oil was identified as *S*-(3-oxoundecyl) thioacetate (VIII) on the basis of the following data. The mass spectrum of (VIII) showed characteristic fragment ions at *m/e* 201, 169, 146, 141, and 43 (base peak), n.m.r. (CDCl<sub>3</sub>) δ 3.05 (t, *J* 7 Hz, 2H), 2.75 (t, *J* 7 Hz, 2H), 2.38 (t, *J* 7 Hz, 2H), 2.31 (s, 3H), 1.56 (quintet, *J* 7 Hz, 2H), 1.28 (br, 10H), and 0.88 (t, *J* 7 Hz, 3H) and the i.r. spectrum (neat) showed two carbonyl absorptions at 1690 and 1715 cm<sup>-1</sup>. Hydrolysis of (VIII) under acidic conditions (14%

† High resolution mass measurements were obtained by the Battelle High Resolution Mass Spectrometry Center under the auspices of the National Institutes of Health, Division of Research Resources.

$\text{BF}_3$  in MeOH) produced 1-mercaptoundecan-3-one (IX) [n.m.r. spectrum in  $\text{C}_6\text{D}_6$ :  $\delta$  1.40 (t,  $J$  7 Hz, SH)] whereas hydrolysis under basic conditions (neutral alumina) resulted in bis-(3-oxoundecyl) sulphide (X) [molecular ion  $m/e$  370] and not the vinyl ketone (XI) as expected.



From a later fraction was obtained a white crystalline solid, m.p. 67–67.5°, which was shown to be bis-(3-oxoundecyl) disulphide (XII). Compound (XII) had a molecular weight of 402 by mass spectrometry and showed

characteristic fragment ions at  $m/e$  304, 201, 200, 169, and 141 (base peak). Its n.m.r. spectrum ( $\text{C}_6\text{D}_6$ ) exhibited signals at  $\delta$  2.75 (t,  $J$  7 Hz, 4H), 2.40 (t,  $J$  7 Hz, 4H), 2.00 (t,  $J$  7 Hz, 4H), 1.48 (quintet,  $J$  7 Hz, 4H), 1.21 (br, 20H), and 0.91 (t,  $J$  7 Hz, 6H), and its i.r. spectrum showed a single carbonyl band at  $1705\text{ cm}^{-1}$ . More conclusively naturally occurring (XII) was identical with the product resulting from air oxidation of (IX) and could be converted into (VIII) on treatment with Zn, AcOH, and  $\text{Ac}_2\text{O}$ .

Also obtained from the earlier fraction was a small amount of a colourless, optically active oil,  $[\alpha]_D^{25}$  ( $\text{CCl}_4$ )  $-65^\circ$ , which we have concluded to be 3-hexyl-4,5-dithia-cycloheptanone (XIII). The mass spectrum of (XIII) exhibited a molecular ion at  $m/e$  232 and fragment ions at  $m/e$  167 and 120 and the i.r. spectrum gave a single carbonyl band at  $1712\text{ cm}^{-1}$ . Its n.m.r. spectrum ( $\text{C}_6\text{D}_6$ ) showed a perturbed multiplet, essentially a quartet of triplets, at  $\delta$  2.70 for a methine proton attached to sulphur and coupled equivalently to a methylene absorbing in a broad 10H multiplet at 1.0–1.4 p.p.m. and non-equivalently to a methylene at ca. 2.45 p.p.m. Also in the n.m.r. spectrum was a sharp 4H singlet at 2.37 p.p.m. (a complex m in  $\text{C}_6\text{D}_5\text{N}$ ,  $\text{CD}_3\text{COCD}_3$ , and  $\text{CCl}_4$ ) assigned to two adjacent methylenes flanked by a carbonyl group and sulphur and a 3H triplet at 0.86 p.p.m. for the methyl protons of a hexyl side chain.

In even smaller amount was obtained a colourless oil from a fraction eluted between those containing (VIII) and (XII) which was characterized as *S*-(*trans*-3-oxoundec-4-enyl) thioacetate (XIV). The mass spectrum of (XIV) showed a molecular ion at  $m/e$  242 and fragment ions at  $m/e$  199, 167, and 139. Its n.m.r. spectrum ( $\text{CCl}_4$ ) had signals at  $\delta$  5.98 [dt,  $J$  1.5, 16 Hz C-(4)H], 6.75 [dt,  $J$  7, 16 Hz C-(5)H], 2.26 [broad q, C-(6) methylene], 2.85 [t, C-(2) methylene], 3.11 [t, C-(1) methylene] and 2.31 (s,  $\text{COCH}_3$ ).

All the fractions contained an unstable oil which polymerized rapidly. This compound was concluded to be undec-1-en-3-one (XI) on the basis of its mass spectrum [ $m/e$  168 (molecular ion), 97, 83, 70 (base peak), and 55] and n.m.r. spectrum  $\delta$  2.47 [t,  $J$  7 Hz, C-(4) methylene] 5.68 [q,  $J$  10 and 2 Hz, C-(1) H *trans* to C-(3) carbonyl] and 6.18 (m,  $J$  18, 10, and 2, C-(2) H and C-(1) H *cis* to C-(3) carbonyl]. Addition of thioacetic acid to (XI) in the presence of triethylamine gave (VIII). Compound (XI) is suspected to be an artifact formed during the chromatography as the mass spectrum of the essential oil shows no  $m/e$  168 ion. Small peaks, however, are observed at  $m/e$  162 and 164 in the mass spectrum of the essential oil and may indicate the presence of undecatrien-3-ones and undecatetraen-3-ones in *Dictyopterus*.

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<sup>1</sup> Besides our work dimethyl sulphide has been the only odoriferous substance to be identified from wet, undecomposed algae. P. Haas, *Biochem. J.*, 1935, **29**, 1297; R. Bywood and F. Challenger, 1953, **53**, xxvi; F. Challenger and M. I. Simpson, *J. Chem. Soc.*, 1948, 1591; F. Challenger, R. Bywood, P. Thomas, and B. J. Hayward, *Arch. Biochem. Biophys.*, 1957, **69**, 514; R. C. Greene, *J. Biol. Chem.*, 1962, **237**, 2251. For a review of this work see F. Schlenk, *Fortschr. Chem. Org. Naturstoffe*, 1965, **23**, 61.

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<sup>3</sup> J. A. Pettus, jun. and R. E. Moore, *Chem. Comm.*, 1970, 1093.

<sup>4</sup> J. A. Pettus, jun. and R. E. Moore, Abstracts, 161st National Meeting of the American Chemical Society, Los Angeles, Calif., March 1971.