Bis-(3-oxoundecyl) Polysulphides in *Dictyopteris*

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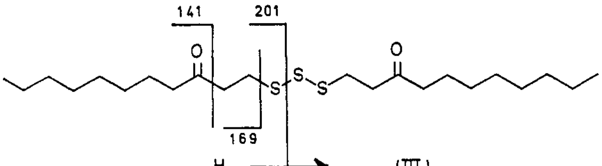
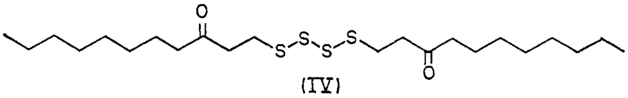
Summary Bis-(3-oxoundecyl) trisulphide and bis-(3-oxoundecyl) tetrasulphide from Hawaiian species of *Dictyopteris* are examples of naturally-occurring organic polysulphides.

ORGANIC sulphides and disulphides occur extensively in Nature, but hitherto only one polysulphide has been detected.[1] I report here the isolation of bis-(3-oxoundecyl) trisulphide (III) and bis-(3-oxoundecyl) tetrasulphide (IV) from the Hawaiian algae *Dictyopteris plagiogramma* and *D. australis*.



(III)

Column chromatography of the chloroform–methanol extract of *D. plagiogramma* and *D. australis* on Permutit Decalso or silica gel with 1—5% ether–hexane followed by gel filtration on Sephadex LH-20 with 50% chloroform–methanol gave a fraction which was predominately bis-(3-oxoundecyl) disulphide (II).[2] Crystallization from hexane gave pure (II), m.p. 67—67·5°, and the mother-liquors contained a mixture of polysulphides which could be separated from residual (II) by t.l.c. on silica gel HF with 1—4% ethyl acetate–cyclohexane.



(IV)

Trisulphide (III) crystallized from the mixture of polysulphides in n-pentane at 20° as colourless needles, m.p. 60·5—61° after recrystallization from methanol, and was characterized on the basis of the following data. The mass spectrum of (III) showed a molecular ion at *m/e* 434 with an $M + 2$ isotopic peak characteristic of a molecule containing three sulphur atoms (relative intensity 15% of the molecular ion) and fragment ions at *m/e* 402, 304, 201, 200, 169, and 141 (base peak). The u.v. spectrum of (III) exhibited a band at 200 nm (ϵ 5800) with a broad shoulder at 250 nm (ϵ 1800). The ^{1}H n.m.r. spectrum of (III) showed two triplets at δ 2·83 and 3·02 p.p.m. (J 7 Hz) for the C-1 and C-2 methylenes, respectively. In the Table the C-1 and C-2 proton chemical shifts of (III) are compared with those of bis-(3-oxoundecyl) sulphide (I)[2] [colourless needles from n-hexane, m.p. 80—82°] and (II); the paramagnetic shifts which increase with increasing sulphur chain-length are due to the anisotropic effects of the neighbouring sulphur atoms.[3,4] Finally, photolysis of (III) in n-pentane with u.v. light of 253·7 nm gave (II) as the major product.[5]

^{1}H *n.m.r. data for*

$CH_3[CH_2]_7{\cdot}CO{\cdot}CH_2{\cdot}CH_2S_nCH_2{\cdot}CH_2{\cdot}CO{\cdot}[CH_2]_7CH_3$

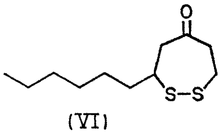
Compound	Sulphur chain length, n	Chemical shift,[a] p.p.m. from Me_4Si C-1	C-2	C-4	C-5	C-11
(I)	1	2·65	2·60	2·35	1·54	0·89
(II)	2	2·82	2·74	2·37	1·55	0·89
(III)	3	3·02	2·83	2·37	1·55	0·89
(IV)	4	3·10	2·85	2·38	1·56	0·89

[a] Determined at 100 MHz in carbon tetrachloride.

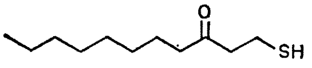
The remaining (III) in the polysulphide mixture was removed by rapid crystallization from methanol at 20°. The mother-liquors were then cooled to 0° and the tetrasulphide (IV), contaminated with some (III), separated as colourless needles, m.p. 32—33°. Prolonged standing of (IV) in methanol resulted in decomposition of (IV) to (III) and sulphur. The mass spectrum of (IV) showed a molecular ion peak at m/e 466 with an $M + 2$ isotopic peak corresponding to four sulphur atoms in the molecule. The n.m.r. spectrum of (IV) showed the expected chemical shifts for the C-1 and C-2 methylene protons (Table).

Compounds (III) and (IV) proved to be identical with products obtained from the triethylamine-catalysed reaction of (II) and sulphur in benzene (overnight reflux).

The bis-(3-oxoundecyl) polysulphides may be formed in the seaweed by the reaction of elemental sulphur[6,7] or dihydrogen disulphide[5] with (II) or 3-oxoundecanethiol (V) and may serve as precursors of the dictyopterenes[8] using intermediates such as 3-hexyl-4,5-dithiacycloheptanone (VI)[2] to introduce unsaturation into the C_{11} unit.



(VI)



(V)

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[1] Sporidesmin-E (D. Brewer, R. Rahman, S. Safe, and A. Taylor, *Chem. Comm.*, 1968, 1571) is an example of a naturally occurring trisulphide.

[2] P. Roller, K. Au, and R. E. Moore, *Chem. Comm.*, 1971, 503.

[3] J. R. VanWazer and D. Grant, *J. Amer. Chem. Soc.*, 1964, **86**, 1450; D. Grant and J. R. VanWazer, *ibid.*, p. 3012; D. J. Martin and R. H. Pearce, *Analyt. Chem.*, 1966, **38**, 1604.

[4] The sulphur chain of (III) should not be coplanar with either C-1 or C-2 and both the C-1 and C-2 methylenes may be relatively close to all of the sulphur atoms. See the crystal structure of 2,2′-di-iododiethyl trisulphide: J. Donohue, *J. Amer. Chem. Soc.*, 1950, **72**, 2701. X-Ray data suggests that the sulphur chain of organic polysulphides is linear and not branched.

[5] S. Safe and A. Taylor, *J. Chem. Soc.* (*C*), 1970, 432.

[6] K. C. Murdock and R. B. Angier, *Chem. Comm.*, 1970, 55.

[7] B. D. Vineyard, *J. Org. Chem.*, 1966, **31**, 601.

[8] Dictyopterene A: R. E. Moore, J. A. Pettus, jun., and M. S. Doty, *Tetrahedron Letters*, 1968, 4787. Dictyopterene B: J. A. Pettus, jun., and R. E. Moore, *Chem. Comm.*, 1970, 1093. Dictyopterenes C′ and D′: J. A. Pettus, jun., and R. E. Moore, *J. Amer. Chem. Soc.*, 1971, **93**, 3087.