Dihydrotropones from *Dictyopteris*

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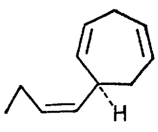
Summary (+)-(*R*)-4-Butylcyclohepta-2,6-dienone and (+)-6-butylcyclohepta-2,4-dienone are minor constituents of the essential oil of two species of Hawaiian *Dictyopteris*.

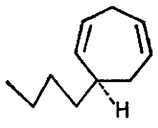
DICTYOPTERENE D′ (I), a constituent of the essential oil of two species of Hawaiian *Dictyopteris*,[1] *viz. D. plagiogramma* and *D. australis*, is identical with the sperm attractant (gamone) produced by the female gametes of another brown seaweed *Ectocarpus siliculosus*.[2] The mode of action and metabolic fate of the gamone in the reproduction of *Ectocarpus* are at present unknown. We report[3] here the isolation and identification of two dihydrotropones from *D. plagiogramma* and *D. australis* which are metabolites of the structurally related[1] dictyopterene C′ (II).

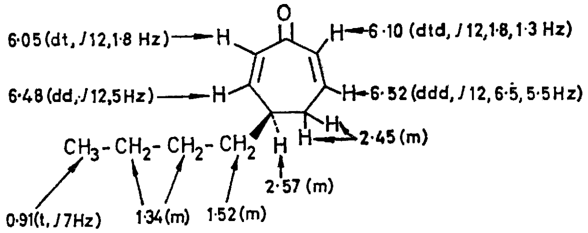
Initial separation of the chloroform–methanol extract of the seaweed was achieved by chromatography on silica gel with 1—5% ether–hexane. The dihydrotropone (III) was found in a fraction containing *S*-(*trans*-3-oxoundec-4-enyl) thioacetate[4] while (IV) was eluted before *S*-(3-oxoundecyl) thioacetate.[4] Further separation and final purification of each compound resulted from gel filtration on Sephadex LH-20 with 50% chloroform–methanol followed by molecular distillation at 70—75° (5×10^{-3} mm Hg).

Compound (III), an odoriferous oil, $[\alpha]_D$ +96° (isooctane–MeOH), exhibited eleven carbon signals in its proton noise decoupled 25·15 MHz carbon-13 n.m.r. spectrum in $CDCl_3$. The off-resonance c.w. decoupled spectrum allowed the assignments of a carbonyl (192·7), four olefinic methines

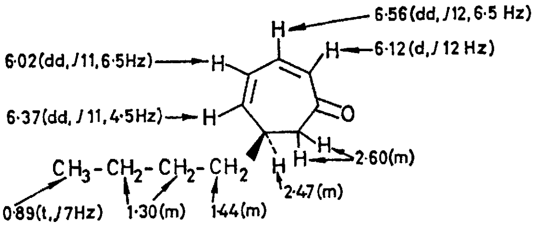
(132·4, 133·6, 142·8, 149·2), a saturated methine (38·0), four saturated methylenes (22·7, 29·4, 32·9, 34·6), and a methyl group (14·0, relative to Me_4Si). The electron-impact mass spectrum of (III) showed virtually no molecular ion but characteristic fragment ions were found at *m/e* 108, 79, 57, and 55; the high resolution chemical ionization spectrum (isobutane), however, exhibited an intense peak at *m/e* 165·1277 ($M + 1$) for (III) having the molecular formula $C_{11}H_{16}O$. I.r. bands at 1616 and 1651 cm^{-1} and a u.v. absorption peak at 224 nm (ε 7400) in pentane showed (III) to be an αβ-unsaturated ketone. Complete characterization of (III) followed from a detailed analysis of the 300 MHz ^1H n.m.r. spectrum in $(CD_3)_2CO$. Proton assignments were confirmed by the appropriate spin–spin decoupling experiments. Particularly revealing were the long range couplings of the C-2 and C-7 protons not only to the C-4 methine and C-5 methylene protons, respectively, but to each other (**W**-coupling). Finally, (III) was shown to be the *R*-enantiomer by selenium dioxide oxidation[5] of (II) → (III); the optical rotations and c.d. curves of the natural and synthetic products were identical.


(I)


(II)



(III)



(IV)

Compound (IV) was also strong smelling and possessed a high optical rotation, $[\alpha]_D$ +1120° (pentane). Its carbon-13 n.m.r. spectrum suggested that (IV) was isomeric with (III), showing eleven signals at 200·7 (C=O), 146·2 (CH), 137·6 (CH), 131·3 (CH), 124·7 (CH), 47·4 (CH_2), 33·4 (CH), 33·1 (CH_2), 29·1 (CH_2), 22·7 (CH_2), and 14·0 (CH_3). The presence of a carbonyl was confirmed by the i.r. band at 1660 cm^{-1} and the u.v. spectrum [λ_{max} 279 nm (ε 5900)] was consistent with that of a dienone. The electron-impact mass spectrum of (IV) showed a molecular ion peak at *m/e* 164 and fragment ions at *m/e* 136, 108, 107, and 79 (base peak). The structure of (IV) was completed from analysis of its 300 MHz ^1H n.m.r. spectrum in $CDCl_3$. Finally, by analogy the absolute configuration of C-6 is thought to be *R*.

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[1] J. A. Pettus, jun., and R. E. Moore, *J. Amer. Chem. Soc.*, 1971, **93**, 3087.

[2] D. G. Müller, L. Jaenicke, M. Donike, and T. Akintori, *Science*, 1971, **171**, 815; the optical rotation of the gamone has been found to be identical with that of dictyopterene D′, L. Jaenicke, personal communication.

[3] Presented in part at the 166th National Meeting of the American Chemical Society, Chicago, Illinois, September, 1973, Abstract No. AGFD 065.

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

[5] P. Radlick, *J. Org. Chem.*, 1964, **29**, 960.