

Dictyotetraene, a New Diterpenoid from a *Dictyota* sp. (Chromophycota, Dictyotaceae) of the North Brittany Sea

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Homonuclear spin decouplings of the non-first order 500 MHz ^1H n.m.r. spectrum, proton shift-correlated 2D (COSY) n.m.r. experiments, and mass spectra suggest for the title compound the novel benz[e]azulene structure (1), or its enantiomer, formally derived by cyclization of a prenylated guaiane.

Chromophycota of the family Dictyotaceae have given a wide variety of novel diterpenoids which can formally be assumed to be derived by prenylation at an isopropylidene appendage of sesquiterpenoids of known skeleton. There are a few exceptions to this rule,¹ and the present case of dictyotetraene, isolate from a *Dictyota* sp.,[†] and which is suggested from spectroscopic data to have structure (1), is a further example of an exception.

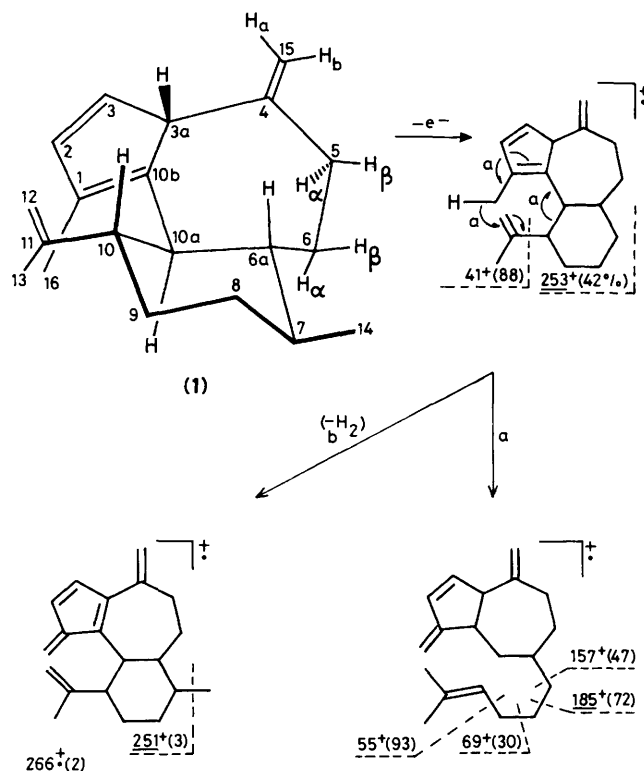
Dictyotetraene is a volatile oil showing $\Delta\epsilon$ (266 nm) = -4.8 and $\Delta\epsilon$ (217 nm) = -7.3 in cyclohexane, as for a fused cyclopentadiene.² The molecular formula $\text{C}_{20}\text{H}_{28}$ was derived by accurate mass measurements (M^{++} : found, m/z 268.212 \pm 0.01; calc. 268.2191), and the compound must be tricyclic as ^{13}C n.m.r. signals for only four double bonds could be detected.[‡]

The protons at δ 6.20 (H-2), 6.09 (H-3), 3.88 (H-3a), and 1.78 (3H-16) show the coupling pattern[‡] expected for a methylcyclopentadiene.³ Also, the δ 3.88 resonance, at unusually low field for a proton at an sp^3 cyclopentadiene carbon atom,³ suggests a triply allylic position for H-3a in structure (1). This is fully supported by both double-resonance and COSY (Figure 1) experiments.

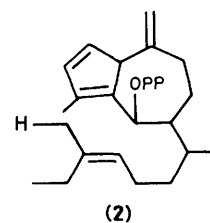
The n.m.r. spectra[‡] also reveal both an isopropylidene and a methyl group which double-resonance (500 MHz) and COSY⁴ (Figure 1) experiments suggest are in the C(12)–

[†] ca. 0.003% Yield from 0.5 kg (dry wt.) on ethanol extraction of a fresh *Dictyota* sp., followed by extensive h.p.l.c. The *Dictyota* sp. was collected at low tide, as a floating specimen, at the Ile de Callot, Brittany, in August 1982 and preliminarily identified by Dr. J. Cabioch as *D. dichotoma* (Hudson) Lamouroux var. *intricata* (C. Ag.) Greville. Neither *D. dichotoma*, simultaneously collected in the same place and identified by Dr. J. Cabioch, nor *D. dichotoma*, *D. dichotoma* var. *intricata*, and *D. letteracea* Boud. (unpublished), collected near Banyuls-Sur-Mer, East Pyrenean, in August 1983, and identified by Prof. C. F. Bouduresque, proved to contain dictyotetraene.

[‡] ^{13}C N.m.r. (C_6D_6 , 20 MHz, multiplicities from off-resonance decoupling) δ 149.1 (s, C-11), 147.6 (s, C-4), 144.5 (s, C-10b), 137.0 (s, C-1), 136.2 (d, C-2 or C-3), 136.0 (d, C-3 or C-2), 111.9 (t, C-15), 110.6 (t, C-12), 59.7 (d, C-3a), 53.3 (d, C-10a), 49.7 (d, C-10), 44.9 (d, C-6a), 37.3 (d, C-7), 36.7 (t, C-5), 32.8 (t, C-8), 29.4 (t, C-9), 28.2 (t, C-6), 22.2 (q, C-14), 20.8 (q, C-13), and 13.7 (q, C-16). ^1H N.m.r. (C_6D_6 , J in Hz, 500 MHz) 6.20 (dd, $J_{2,3}$ 5.2, $J_{2,3a}$ 1.4, H-2), 6.09 (dd, $J_{3,2}$ 5.2, $J_{3,3a}$ 1.9, H-3), 5.07 (dd, J_{gem} 1.9, $J_{15a,3a}$ 1.0, H_a -15), 4.91 (br. s, H_b -15), 4.73 and 4.66 (2 \times br. s, 2H-12), 3.88 (br. s, H-3a), 2.26 (dd, $J_{10a,6a} = J_{10a,10}$ 10.5, H-10a), 1.97 (m, H-10 and H_β -5), 1.82 [m (the high-field part lies under the 1.78 d), H_α -5 and H_β -6], 1.78 (d, $J_{16,3a}$ 1.4, 3H-16), 1.66 (m, H_{eq} -8 and H_{eq} -9), 1.60 [br. ddd (the low-field part of these four absorptions lines under the 1.66 m), $J_{6a,10a}$ 10.5, $J_{6a,7} = J_{6a,6a} = 10.0$, whilst $J_{6a,6\beta}$ proved to be small and insufficiently resolved, H-6a], 1.53 (br. s, 3H-13), 1.50 [br. ddd (the low-field one of the four principal absorptions lies under the 1.53 br. s), J_{gem} 13.5, $J_{\text{ax}9,\text{ax}8} = J_{\text{ax}9,10} = 10.0$, $J_{\text{ax}9,\text{eq}8}$ 3, H_{ax} -9], 1.10 (m, H-7 and H_{ax} -8), 1.00 (m, H_α -6), and 0.90 (d, J 5.1, 3H-14).



Scheme 1



C(11)–C(10)–C(10a)–C(6a)–C(7)–C(14) fragment in structure (1). In fact, on irradiation at the isolated δ 2.26 dd signal (H-10a) both the low-field part of the δ 1.97 multiplet, attributable to H-6a, were simplified by loss of couplings of ca. 10 Hz, suggesting a *trans*-diaxial relationship for these protons. This is further supported by irradiation at either the δ 1.60 br. ddd (H-6a) or the δ 1.97 m (H-10) signals, whereby the double doublet for H-10a became a doublet with loss of 10.5 Hz coupling. Furthermore, on irradiation at δ 1.10 (m, H-7 and H_{ax} -8) the C(14) methyl doublet became a singlet, while the H-6a br. ddd signal became a br. double doublet with loss of 10 Hz coupling, indicating a *trans*-diaxial relationship between H-6a and H-7 and, consequently, establishing the equatorial

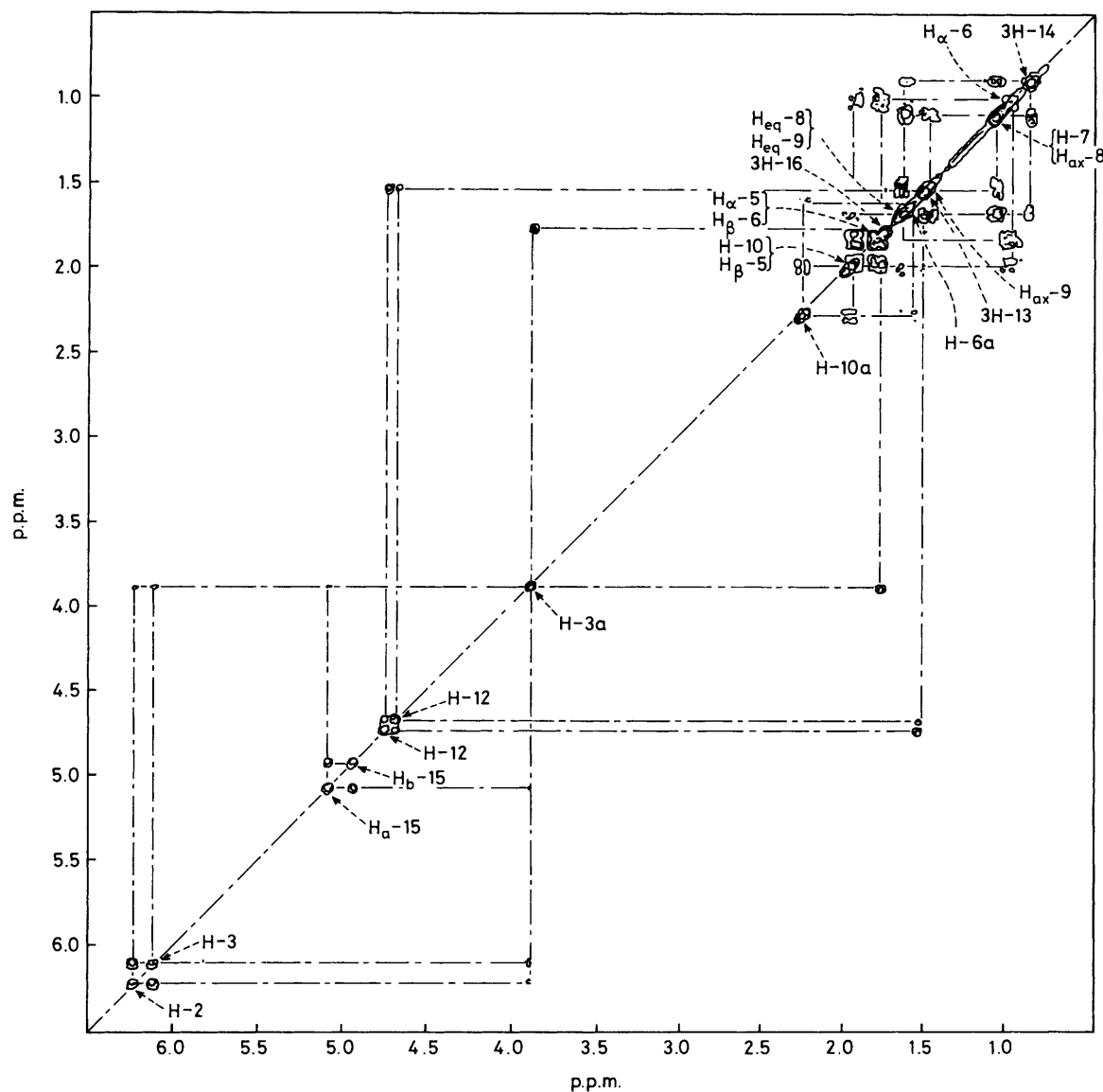


Figure 1. COSY contour plot for dictyotetraene (1) (400 MHz in C_6D_6).

position for the C(14) methyl group.[§] In addition, a small allylic coupling between H-12 (δ 4.73) and H-10 locates the isopropylidene group at C(10), which is also suggested by both the low-field resonance for H-10 \ddagger and biogenetic considerations. All these carbon connectivities, except C(11)–C(10), are also revealed by the COSY experiment (Figure 1), although, disappointingly, signals superimposed in 1D 500 MHz spectra, such as those for H-7 and H_{ax}-8, \ddagger find their equivalent in partly superimposed contours in the 400 MHz COSY (Figure 1) spectra.

Similar decoupling experiments also revealed the C(15)–C(4)–C(5)–C(6)–C(6a) fragment. On irradiation at δ 1.00

[§] The small 4J coupling between equatorial 3H-14 and H_{eq}-8 (M. Barfield, A. M. Dean, C. J. Fallick, R. J. Spear, S. Sternell, and P. W. Westerman, *J. Am. Chem. Soc.*, 1975, **97**, 1482) may well account for the COSY correlation among these protons (Figure 1). The equatorial position for the C-14 methyl is also expected on biogenetic grounds. In fact, the relative configurations at C-7 and C-6 in structure (1) are the same as in the putative prenylated guaiane precursors of (1) which have been isolated from members of the genus *Dictyota*, \S including the present one.

(H_{ax}-6) and H-6a br. ddd signal became a br. double doublet with loss of 10 Hz coupling, indicating a *trans*-diaxial relationship between these two protons. Also, on irradiation at δ 1.82 m (H_{ax}-5 and H_β-6) the δ 1.60 br. ddd signal for H-6a sharpened while a doublet with J 2.5 Hz, attributable to H_β-5, became apparent from the δ 1.97 m (H_β-5) signal. Finally, and most importantly, irradiation at δ 4.91 (H_b-15) brought about a simplification, by losses of 0.8 Hz couplings, of the low-field portion of the δ 1.82 multiplet, which must be then attributed to H_{ax}-5, thus establishing the connectivity across the C(4)–C(5) bond. This is not revealed by the COSY experiment (Figure 1), perhaps owing to the threshold being too high during plotting. In this respect we note that it is common with COSY plots for a low threshold to produce symmetrical contours as artefacts on COSY maps corresponding to strong signals. Two cases in point are ghost contours in Figure 1 for the unrealistic 3H-16–H_a-15 and 3H-13–3H-16 correlations.

The connectivity of the C(10)–C(9)–C(8)–C(7) fragment is supported by the fact that irradiation of the δ 1.97 multiplet due to H-10 affected both the δ 1.50 br. ddd (H_{ax}-9) and the δ 1.66 multiplet (H_{eq}-9) signals.

To complete the picture, the relative configuration at C(10) and C(3a) is supported by a 3% nuclear Overhauser effect (n.O.e.) difference spectrum, whereby H-10 was observed as a ddd, J 10.5, 10.5, and 2.5 Hz, as expected for structure (1), on irradiation at H-3a. (This also produced a series of signals at δ 1.5–1.7, although we were unable to identify a clear pattern for an n.O.e. with H-6a probably owing to the presence of strong resonances in this region.) This n.O.e. result also suggests a boat conformation for the seven-membered ring as in (1).

Mass spectral fragmentation data (Scheme 1) further support the above conclusions, although the linked-scan (underlined) fragments at m/z 185 and 251 cannot represent primary processes and must be the result of rapid processes occurring in the ion source.

In an attempt to provide chemical proof for the structure assignment, reaction of the last 1 mg of dictyotetraene available with freshly oxidised phenylurazole at room temperature did not proceed cleanly. Continuous search in 1984 for this *Dictyota* sp. was fruitless (it is not obtainable every year), so for the moment the structure of dictyotetraene must rest on spectroscopic data alone.

We propose that (1) is derived biogenetically from GGPP via the 6-hydroxyguaiane derivative (2). A C-6 hydroxy group, as in (2), is a common feature of prenylated guaianes

isolated from members of the genus *Dictyota*, including the present one.¶

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¶ Pachidictyol-A, dictyol-A acetate, and dictyol-C (D. J. Faulkner, B. N. Ravi, J. Finer, and J. Clardy, *Phytochemistry*, 1977, **16**, 991) have been isolated from our *Dictyota* sp.