

## A New Diterpene with a Novel Carbon Skeleton from a Marine Alga<sup>1</sup>

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A new diterpene (**1**) possessing a novel carbon skeleton has been isolated from a brown alga *Dictyota* sp. and its structure determined by X-ray crystallography.

Brown algae of the genus *Dictyota* (order *Dictyotaceae*) are common inhabitants of shallow water and intertidal communities, particularly in subtropical and tropical areas. Extracts of a variety of *Dictyota* species have been shown to exhibit cytotoxic,<sup>2</sup> antibacterial,<sup>3</sup> and antiviral activities.<sup>4</sup>

During a search for the biologically active constituents of marine algae of the Canary Islands, we have examined the antibiotic extracts of an alga of the genus *Dictyota* and have characterized the unusual new diterpenoid  $\alpha$ -dictalediol monoacetate, (**1**), in addition to the previously reported pachydictyol-A,<sup>5</sup> dictyol-B,<sup>6</sup> dictyoxide,<sup>7</sup> and dictyol-E.<sup>8</sup> The algae were collected off Güimar, Tenerife, during the summer of 1981. Extraction of the fresh material gave a diethyl ether-soluble portion which, after extensive chromatography, afforded (**1**) in 0.94% yield of the crude extract.

$\alpha$ -Dictalediol monoacetate (**1**),<sup>†</sup> m.p. 156–158 °C,  $[\alpha]_D -1.8^\circ$  (*c* 0.4, CHCl<sub>3</sub>) was shown to have the formula C<sub>22</sub>H<sub>36</sub>O<sub>3</sub> by mass spectrometry; i.r. (KBr) 3500, 1710, 1450, 1370, 1250, 1020, 990, and 790 cm<sup>-1</sup>; <sup>1</sup>H n.m.r. (CDCl<sub>3</sub>)  $\delta$  0.87 (d, *J* 7 Hz, 6H), 0.98, 1.38, 1.73, 2.10 (s, 3H each), 2.55 (m, 1H), 4.57 (br. s, *w*<sub>1</sub> 4.5 Hz, 1H), and 5.41 (br. s, *w*<sub>1</sub> 10 Hz, 1H). The <sup>13</sup>C n.m.r. (CDCl<sub>3</sub>) data for (**1**), assisted by off-resonance and selective proton-noise decoupling techniques, showed the presence of five methyls ( $\delta$  27.7, 22.3, 21.4, 21.3, and 20.8 p.p.m.), five methylenes ( $\delta$  37.5, 32.3, 26.3, 24.8, and 17.0 p.p.m.), seven methines ( $\delta$  122.4, 78.1, 47.4, 45.5, 39.7, 32.3, and 23.0 p.p.m.), and four fully-substituted carbon atoms ( $\delta$  170.6, 137.4, 73.6, and 40.4 p.p.m.).

Because of the limited availability and stability of (**1**) and

failure to correlate its skeletal structure with any known diterpenoid, an X-ray crystallographic study was carried out.

*Crystal data* for (**1**): C<sub>22</sub>H<sub>36</sub>O<sub>3</sub>, *M* = 348, monoclinic, *a* = 9.142(2), *b* = 11.910(2), *c* = 9.643(2) Å,  $\beta$  = 98.09(5)°, space group *P*2<sub>1</sub>, *U* = 1050 Å<sup>3</sup>, *D*<sub>m</sub> = 1.15 g cm<sup>-3</sup>, *Z* = 2, *D*<sub>c</sub> = 1.11 g cm<sup>-3</sup>, *F*(000) = 382. All unique diffraction maxima with  $2\theta < 114^\circ$  were collected on a four-circle diffractometer using 1°  $\omega$ -scans and graphite monochromated Cu-K $\alpha$  radiation ( $\lambda$  = 1.54178 Å). Of 1507 unique reflections, 1327 were treated as observed and corrected for Lorentz, polarization, and background effects. The programs described in ref. 9 were used to solve the structure. A phasing model was generated from a multiresolution tangent formula approach and phase refinements and electron density syntheses revealed the non-hydrogen framework. Hydrogens were located on a difference synthesis after refinement. Block-diagonal least-squares refinement with anisotropic non-hydrogens and fixed isotropic hydrogens gave *R* = 0.086.‡ The structure is shown in Figure 1. The absolute configuration was not determined. The cyclohexane rings are in the chair conformation and the cyclohexene ring is half-chair.

$\alpha$ -Dictalediol is the first representative of a new class of compound containing a *cis-cisoid-cis* perhydrophenanthrene ring system. The biosynthesis of such a compound is not straightforward. We suggest that (**1**) is terpene-derived and this can be accomplished formally by a single carbon-carbon bond shift of a unique cyclization of a geranyl-geranyl residue as illustrated in (**2**). Other related diterpenoids have been extracted from the alga and will be discussed elsewhere.

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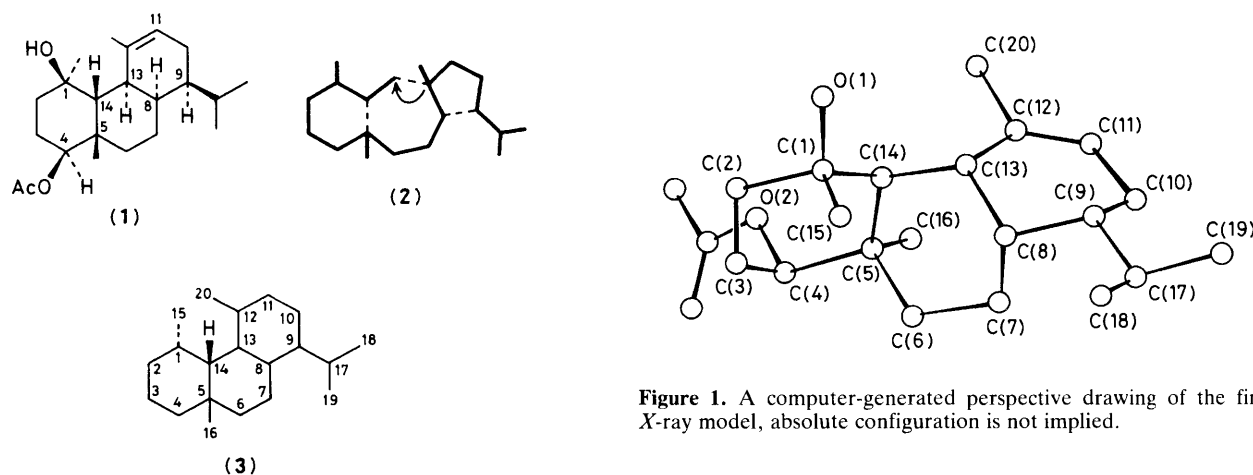


Figure 1. A computer-generated perspective drawing of the final X-ray model, absolute configuration is not implied.

† We suggest the trivial name dictalane for the basic skeleton of this new class of diterpenes, numbered as illustrated in structure (**3**). Thus,  $\alpha$ -dictalediol monoacetate (**1**) is named (1*R*\*,4*S*\*)-4-acetoxy-1-hydroxydictal-11-ene.

‡ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

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