Dictyol A and B, Two Novel Diterpene Alcohols from the Brown Alga *Dictyota dichotoma*

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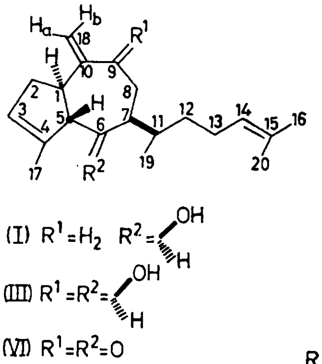
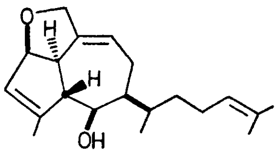
Summary From the brown alga *Dictyota dichotoma*, two diterpene alcohols with a hydroazulene skeleton, dictyol A (II) and B (III), have been isolated and their structures determined on the basis of spectroscopic and chemical evidence.

In 1973 Hirschfeld *et al.*[1] reported the isolation of the diterpene alcohol pachydictyol A (I) from the brown marine alga *Pachydictyon coriaceum* (Dictyotaceae). This compound, which possessed a mild antibiotic activity, was unique among diterpenes in having a hydroazulene skeleton.

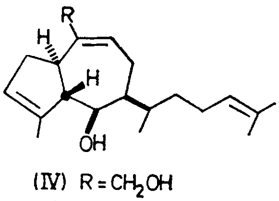
During a survey of Mediterranean seaweeds,[2] we observed that the allied species *Dictyota dichotoma* var. *implexa* (Desf.) J. Ag. contains two metabolites whose spectral properties are strongly reminiscent of those of pachydictyol A. These compounds, dictyol A (II) and B (III) were isolated (in *ca.* 0·042 and 0·034% yield of the fresh plant, respectively) from the chloroform extract of the alga by conventional column chromatography (silica gel; $CHCl_3$–MeOH 99:1).

Dictyol A (II), $[\alpha]_D$ + 86·2°, m.p. 85–86 °C, has the molecular formula $C_{20}H_{30}O_2$ (M^+, *m/e* 302·2249, calc. 302·2246). The i.r. spectrum (ν_{max} 3400 cm^{-1}) showed the presence of an OH group. The n.m.r. spectrum (90 MHz, $CDCl_3$) displayed signals at δ 0·99 (3H, d, *J* 6 Hz, 11-Me), 1·61 (3H, s, *trans*-15-Me), 1·68 (3H, s, *cis*-15-Me), 1·86 (3H, s, 4-Me), 2·85br (1H, d, 5-H), 3·13 br (1H, 1-H), 4·06 (1H, m, 6-H), 4·36br (2H, s, 18-H_2), 4·62br (1H, d, *J* 7 Hz, 2-H), 5·09br (1H, t, *J* 7 Hz, 14-H), and 5·46br (2H, 3- and 9-H). The mass spectrum showed prominent peaks at *m/e* 284, 273, 269, and 255. Reduction of (II) with Na–NH_3 in EtOH at −45 °C gave (IV) as the main product, $[\alpha]_D$ − 17·0°; m.p. 92—94 °C, ν_{max} 3320 cm^{-1} (OH), δ ($CDCl_3$) 0·97 (3H, d, *J* 6 Hz, 11-Me), 1·59 (3H, s, *trans*-15-Me), 1·67 (3H, s, *cis*-15-Me), 1·83 (3H, s, 4-Me), 3·81—4·20br (3H, 6-H and 18-H_2), 5·10br (1H, t, *J* 7·5 Hz, 14-H), 5·33 (1H, m, 3-H), and 5·66 (1H, m, 9-H); *m/e* 304, 286, 273, 271, 268, 255, and 253. In addition, small amounts of (V) {oil, $[\alpha]_D$ − 17·60°, M^+, *m/e* 288; ν_{max} 3500 cm^{-1} (OH), δ ($CDCl_3$) 0·96 (3H, d, *J* 6 Hz, 11-Me), 1·59 (3H, s, *trans*-15-Me), 1·68 (6H, s, 10-Me and *cis*-15-Me), 1·83 (3H, s, 4-Me), 3·87 (1H, m, 6-H), 5·06br (1H, t, 7 Hz, 14-H), 5·23—5·56br (2H, 3- and 9-H)} and pachydictyol A





(II)



(IV) R=CH_2OH
(V) R=Me

were also isolated. All the above data are consistent with structure (II) for dictyol A. The stereochemistry at C-2 was deduced from the fact that closure of the tetrahydrofuran ring requires a *cis* relationship between 1- and 2-H.

Dictyol B (III), $[\alpha]_D + 73{\cdot}5°$, m.p. 110—114 °C, has molecular formula $C_{20}H_{32}O_2$ (M^+, *m/e* 304·2400; $C_{20}H_{32}O_2$ requires 304·2402), i.r. absorptions at ν_{max} 3340 (OH), 3040, 1640, and 896 cm^{-1} ($>C{=}CH_2$); δ (CCl_4) 1·00 (3H, d, *J* 6 Hz, 11-Me), 1·59 (3H, s, *trans*-15-Me), 1·67 (3H, s, *cis*-15-Me), 1·75 (3H, s, 4-Me), 3·65—4·03br (2H, 6- and 9-H), 4·81br (1H, s, H_a), 5·05br (1H, t, *J* 7 Hz, 14-H), 5·08br (1H, s, H_b), and 5·21 (1H, m, 3-H); *m/e* 286 and 268. Reduction of dictyol B with Na–NH_3 in EtOH at −45 °C gave (V), while Jones' oxidation furnished the diketone (VI), as an oil, $[\alpha]_D - 6{\cdot}6°$, M^+, *m/e* 300; ν_{max} 1704 (seven-membered ring ketone) and 1692 cm^{-1} ($\alpha\beta$-unsaturated ketone); δ (CCl_4) 1·02 (3H, d, *J* 6 Hz, 11-Me), 1·53 (3H, s, *trans*-15-Me), 1·61 (3H, s, *cis*-15-Me), 1·71 (3H, s, 4-Me), 4·90br (1H, t, *J* 7 Hz, 14-H), 5·19br (1H, s, H_a), 5·40br (1H, s, 3-H), and 6·01br (1H, s, H_b).

From these data, structure (III) was deduced for dictyol B; the stereochemistry at C-9 has been tentatively assigned on the basis of further examination of the n.m.r. spectrum in the presence of variable amounts of $Eu(fod)_3$.

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