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18-HYDROXY-3,7-DOLABELLADIENE FROM THE BROWN ALGA, *DICTYOTA DICHOTOMA*

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Key Word Index—*Dictyota dichotoma*; Dictyotaceae; brown algae; diterpenoids; 18-hydroxy-3,7-dolabelladiene.

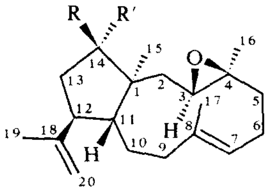
INTRODUCTION

A previous report from this laboratory [1] describes the isolation from an unnamed variety of *Dicytota dichotoma* (Dictyotaceae) of several diterpenoids based on the dolabellane skeleton, i.e. the four new ones **1**–**4**, besides **5**–**7** found earlier in the opistobranch *Dolabella californica* [2, 3]. The antibiotic properties of this class of natural compounds [1] prompted us to investigate the minor constituents of the alga.

This paper describes the isolation of 18-hydroxy-3,7-dolabelladiene from *Dictyota dichotoma.*

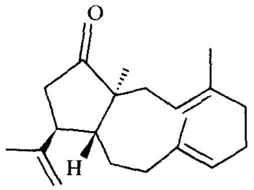
RESULTS AND DISCUSSION

A chloroform extract of *Dictyota dichotoma* was repeatedly chromatographed to give **8** as a viscous liquid, $[\alpha]_D$ +27.5°. Mass spectral analysis established the molecular formula $C_{20}H_{34}O$. The ^{1}H NMR spectrum (80 MHz, $CDCl_3$) is strongly reminiscent of that of **5**, the main difference being the replacement of a methyl doublet (δ 0.92) by the signal of a vinyl methyl at δ 1.56. Extensive double resonance experiments led to the following assignments of protons consistent with structure **8**: δ 4.95 (1H, *bd*, J = 6 Hz, H-3), 4.85 (1H, *bd*, J = 6 Hz, H-7),



1  = =O

2 R = OH, R' = H
3 R = R' = H



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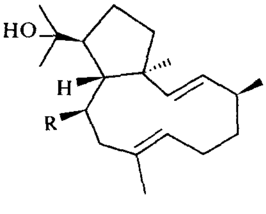
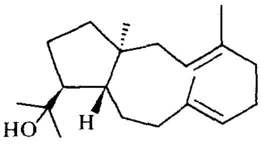
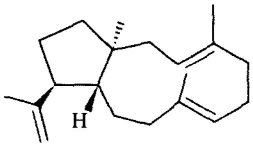


5 R = H
6 R = OAc
7 R = OH



8



9

2.00–2.10 (8H, *m*, H-2, H-5, H-6 and H-9), 1.56 (6H, *s*, 4-Me and 8-Me), 1.25 and 1.23 (3H each, *s*, 18-Mes), 0.99 (3H, *s*, 1-Me). Definite proof of the structure of **8** was provided by its dehydration to triene **9** which was found identical ($[\alpha]_D$, IR, ^{1}H NMR, GLC, MS) with a semisynthetic sample obtained from **3** by treatment with zinc–copper couple. This result also determines the stereochemistry of all the chiral centres in **8** and at the same time establishes the configuration of the C-3 double bond as *E*, since the analogous reduction performed earlier [1] on **1** has been shown to give only the diastereomer **4** with the newly generated double bond *trans* with respect to the continuous chain of carbons.

EXPERIMENTAL

Extraction and isolation of **8**. Thalli of *D. dichotoma* were collected in July 1979 at Acicastello near Catania, Sicily, Italy. A voucher specimen has been retained in the Herbarium of the Institute of Botany, Catania. The freeze-dried and ground alga (200 g) was extracted 3 × with $CHCl_3$ at room temp. The combined extracts were concd. *in vacuo* and the residue chromatographed on a Si gel column (2 × 100 cm) using increasing concentrations of Et_2O in hexane as the eluent. Fractions containing **8**, which eluted between **3** and **5**, were pooled and rechromatographed on a column (1 × 80 cm) of Si gel (C_6H_6) to give **8** (40 mg, 0.02% dry wt) $[\alpha]_D$ +27.5° (*c* 1, $CHCl_3$); IR 3550 cm^{-1}; mass measurement observed *m/e* 290.2645, $C_{20}H_{34}O$; requires *m/e* 290.2609.

Zn–Cu *couple reduction of* **3** *to produce* **9**. The procedure described by Kupchan and Maruyama [4] was essentially followed. Compound **3** (80 mg) was dissolved in EtOH (2 ml), Zn–Cu couple (2.5 g) prepared according to Templeton and Wie [5] was added with stirring and the mixture was refluxed for 4 days. The ppt. was filtered off and the soln was evaporated. The residue was purified by CC (hexane) to give 50 mg of **9**, oily, $[\alpha]_D$ +62.7°; M^+ *m/e* 272; IR ν_{max} cm^{-1}: 1640, 890; ^{1}H NMR (80 MHz, $CDCl_3$): δ 5.15 (1H, *dd*, $J = 4.5$ and 11 Hz, H-3), 4.86 (1H, *bd*, H-7), 4.83 (1H, *bs*, H-20), 4.67 (1H, *bs*, H-20′), 1.72 (3H, *bs*, 18-Me), 1.53 (6H, *bs*, 4-Me and 8-Me), 1.07 (3H, *s*, 1-Me).

Dehydration of **8** *to produce* **9**. **8** (30 mg) in pyridine (1 ml) was treated with $POCl_3$ (0.5 ml), at 0°. After 20 min the mixture was added to H_2O (10 ml) and extracted with Et_2O (3 × 10 ml). The combined extracts were dried and the solvent removed leaving a residue which was purified by argentation chromatography to give a product (10 mg) identical in all respects with that obtained by reduction of **4**.

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