

A NEW TRIOXYGENATED DITERPENE FROM THE  
MOLLUSK *APLYSIA DACTYLOMELA*

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Diterpenes with a dolabellane skeleton were initially isolated from the herbivorous sea hare *Dolabella californica* (1). They were later isolated from the brown algae of the family Dictyotaceae (2-4), from the sea whip *Eunicea calculata* (5), and from the mollusk *Aplysia dactylomela* Rang (Gasteropod, Opisthobranch) (6). From a new collection of *A. dactylomela*, a new diterpene having the dolabellane skeleton was isolated.

## RESULTS AND DISCUSSION

Compound **1** [ $\alpha$ ]<sub>D</sub><sup>25</sup> + 13° (*c* 0.06, CHCl<sub>3</sub>), had the molecular formula C<sub>24</sub>H<sub>38</sub>O<sub>5</sub> from the mass measurement of the parent ion, M<sup>+</sup>, at *m/z* 406. The presence of two methyl signals at  $\delta$  1.9 and 2.0, a band at 1730 cm<sup>-1</sup> in the ir spectrum, and signals in the <sup>13</sup>C-nmr spectrum at 69.9 (d) and 84.8 (s) ppm strongly suggested that **1** was a diacetate. From the rest of the spectroscopic data of this compound (see Experimental section), we inferred that it is bicyclic with the skeleton of dolabellane. The structure was chemically confirmed by base catalyzed hydrolysis to the previously isolated diol **2**, whose structure was rigorously determined by X-ray diffraction analysis (6). The stereochemis-

try of **1** was deduced from the following evidence. The NOESY spectrum exhibited the presence of nOes indicating that the bridgehead Me-15, H-3, and H-10 have a  $\beta$  orientation, while the Me-16, Me-17, H-2, and H-11 are  $\alpha$  (Figure 1).

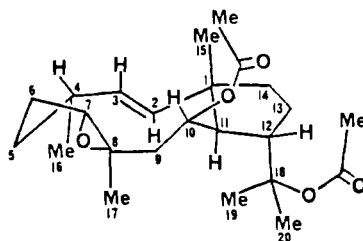
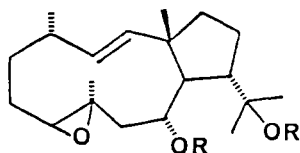


FIGURE 1

## EXPERIMENTAL

COLLECTION, EXTRACTION, AND CHROMATOGRAPHIC SEPARATION.—For general experimental procedures, see González *et al.* (7). In all, 35 specimens of *A. dactylomela* were collected in August 1983, at Los Cristianos, Tenerife, Canary Islands. A specimen of the animal was deposited at the Department of Zoology, University of La Laguna. The hepatopancreas of each animal was removed and stored in Me<sub>2</sub>CO for 2 days at 10°. The solvent was evaporated to leave a dark-green viscous oil (40 g). The crude extract was chromatographed on Si gel using a solvent gradient of increasing polarity from *n*-hexane to EtOAc. The fraction eluted with *n*-hexane-EtOAc (9:1) was rechromatographed with low pressure Si gel chromatography using *n*-hexane as eluent to obtain the diacetate **1** (20 mg) as an oil, [ $\alpha$ ]<sub>D</sub><sup>25</sup> + 13° (*c* 0.06, CHCl<sub>3</sub>); ir (CHCl<sub>3</sub>) 3000, 2960, 2920, 2850, 1730, 1450, 1250 cm<sup>-1</sup>; <sup>1</sup>H nmr (200 MHz,  $\delta$ , CDCl<sub>3</sub>) 0.80 (s, Me-15), 0.85 (m, H-14); 1.02 (d, Me-16, *J*=6.5 Hz), 1.23 (m, H-9 $\beta$ ), 1.37 (s, Me-20), 1.40 (s, Me-17), 1.5 (m, H-6), 1.5 (m, H-13), 1.63 (s, Me-19), 1.80 (m, H-11), 1.90 (m, H-5), 1.90 [s, Me(OAc)], 2.00 [s, Me(OAc)], 2.47 (dd, H-9 $\alpha$ , *J*=11.5 and 13 Hz), 2.5 (m, H-4), 3.07 (d, H-7, *J*=9 Hz), 3.18 (ddd, H-12, *J*=11.5 and 5 Hz), 4.97 (bd, H-10, *J*=9.3 Hz), 5.21 (dd, H-2,



- 1** R=Ac  
**2** R=H

$J=16.3$  and  $2$  Hz),  $5.69$  (dd, H-3,  $J=16.3$  and  $4.5$  Hz);  $^{13}\text{C}$ -nmr ( $\text{CDCl}_3$ )  $15.9$  (q),  $16.8$  (q),  $20.7$  (q),  $21.1$  (q),  $22.8$  (t),  $23.2$  (q),  $23.4$  (q),  $32.3$  (t),  $33.5$  (d),  $39.9$  (t),  $44.3$  (d),  $44.5$  (t),  $48.9$  (s),  $50.6$  (d),  $60.4$  (s),  $63.4$  (d),  $69.9$  (d),  $84.8$  (s),  $134.2$  (d),  $136$  (d),  $170.3$  (s); ms  $M^+$  at  $m/z$   $406$  (4),  $346$  (8),  $286$  (53),  $271$  (100),  $243$  (56),  $228$  (25).

**HYDROLYSIS OF DIACETATE 1.**—A mixture of the diacetate **1** ( $15$  mg,  $0.037$  mmol) and  $\text{K}_2\text{CO}_3$  ( $15$  mg) in  $\text{MeOH}$  ( $2$  ml) was allowed to stand at room temperature for  $24$  h. The mixture was neutralized with  $\text{HCl}$   $1$  N and extracted with  $\text{Et}_2\text{O}$  ( $3 \times 10$  ml). The  $\text{Et}_2\text{O}$  extracts were combined and dried over anhydrous  $\text{MgSO}_4$ . The solvent was evaporated to yield  $10$  mg of the diol **2**, identical (mp, tlc,  $^1\text{H}$ -nmr) with authentic material.

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