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A NEW DITERPENE FROM *APLYSIA DACTYLOMELA*[1)]

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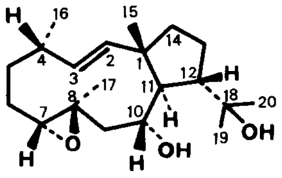
Summary: From the digestive gland of the sea hare Aplysia dactylomela a new trioxygenated diterpene possessing the dolabellane skeleton was isolated. The structure was solved by spectral properties and X-ray diffraction analysis.

The major components of the digestive gland of the mollusc *Aplysia dactylomela* collected off Playa de Las Américas, Tenerife, Canary Islands, during November 1980, are a series of polyhydroxylated diterpenes possessing antimicrobial activity against gram-positive and gram-negative organisms. Florisil chromatography of the acetone extracts of homogenized digestive glands resulted in the isolation of three diterpenes, the less polar of which crystallized from n-hexane, mp 171-2 °C; $\{\alpha\}_D$ +11 (c, 0.33, $CHCl_3$). The molecular formula was determined as $C_{20}H_{34}O_3$ by elemental analysis and mass spectrometry, M^+ at m/z 322, further peaks at m/z 307, 304, 289 and 286. IR, $\nu_{max}^{CHCl_3}$ 3410, 2960, 2870, 1460, 1385, 1110 and 985 cm^{-1}. ^1H-NMR ($CDCl_3$): 1.01 (*s*, 3H); 1.03 (*d*, *J*= 7 Hz, 3H); 1.25, 1.28, 1.40 (*s*, 3H each); 2.83 (*d*, *J*= 9 Hz, 1H); 3,12 (*m*, 1H); 3.61 (*dt*,*J*= 11,2,2Hz,1H); 5.25 (*d*, *J*= 17 Hz, 1H); 5.61 (*dd*, *J*= 17, 6 Hz, 1H). The structure was determined as (*1S**, *2E* , *4S**, *7R**, *8R**, *10R**, *11R**, *12S**)-10,18-dihydroxy- 7,8 -epoxy-dolabella-2-ene (1) by single-crystal X-ray diffraction analysis.



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Preliminary X-ray photographs showed orthorhombic symmetry and accurate lattice parameters of a = 9.565(3), b = 11.295(3) and c = 11.006(5) Å were determined from diffractometer measured 2θ-values. The systematic extinctions, presence of chirality and density were uniquely accommodated by space group $P2_12_12_1$ with one molecule of $C_{20}H_{34}O_3$ forming the asymmetric unit. All unique diffraction maxima with $2\theta \leq 55°$ were surveyed using graphite monochromated Mo$K\bar{\alpha}$ radiation (0.71069 Å) and a variable speed ω-scan. Of the 1478 reflections examined, 1087 (74%) were judged observed ($|F_o| \geq 3\sigma(F_o)$) after correction for Lorentz, polarization and background effects.

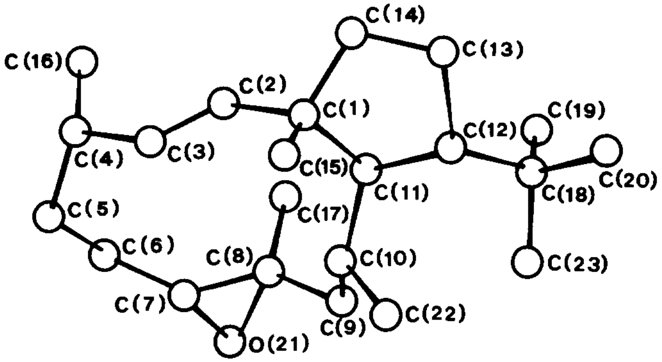

Figure 1. A computer generated perspective drawing of 1. Hydrogens are not shown, and no absolute stereochemistry is implied.

A phasing model was achieved using a multisolution weighted tangent formula approach2). Full-matrix least-squares refinements with anisotropic nonhydrogen atoms and isotropic hydrogens have converged to a standard crystallographic residual of 0.0603). Figure 1 is a computer generated perspective drawing of the final X-ray model less hydrogens. The enantiomer shown is an arbitrary choice and the stereochemical designators are C-1 (S*), C-4 (S*), C-7 (R*), C-8 (R*), C-10 (R*), C-11 (R*) and C-12 (S*). The C-2 - C-3 double bond is trans.

Compounds of this type had been originally isolated from the herbivorous mollusc *Dolabella californica*4) and successively from the brown alga *Glossophora galapagensis*5) and *Dictyota dichotoma*6) upon which the mollusc probably feeds.

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