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# DACTYLOMELOL, A NEW CLASS OF DITERPENE FROM THE SEA HARE APLYSIA DACTYLOMELA

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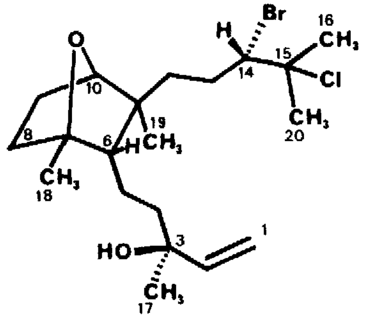
SUMMARY: A new bicyclic diterpene, dactylomelol, has been isolated from the shell-less mollusc Aplysia dactylomela and its structure was determined by the single crystal X-ray diffraction method together with assignments of $^1$H- and $^{13}$C-NMR data for dactylomelol.

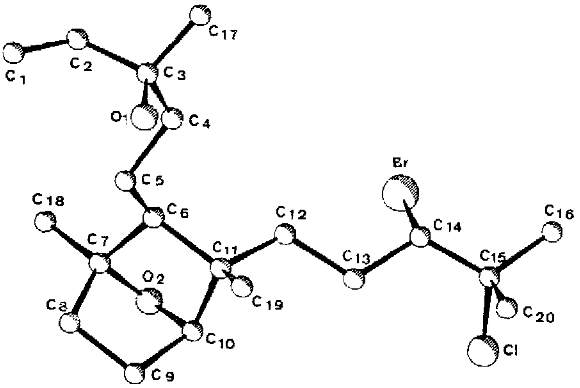
As a part of a program aimed at studying predator-prey relationships in the marine environment,[1] it was found that the shell-less mollusc Aplysia dactylomela contains a potentially useful defensive substance which we have named dactylomelol (1). In this note, we report on the isolation and structural elucidation of 1 by the single-crystal X-ray diffraction method together with assignments of $^1$H- and $^{13}$C-NMR spectra.



DACTYLOMELOL (1)

Specimens of A. dactylomela were carefully dissected and the digestive glands extracted with acetone. After evaporating the solvent, the residual brown solid was purified by column chromatography on silica gel (n-hexane-ethyl acetate) to afford dactylomelol (1) as crystals (12.5 mg, $3\times10^{-3}$ % yield): mp 85-86° ; $(\alpha)_D^{20}$ -31.3° (c=0.7, $CHCl_3$); $C_{20}H_{34}BrClO_2$ (M+ obsd. m/z 422.1394, calcd. for $C_{20}H_{34}{}^{81}Br^{35}ClO_2$ 422.1409). The $^1$H- and $^{13}$C-NMR data for 1 were assigned[2] from $^1$H-$^1$H COSY, $^{13}$C-$^1$H COSY spectra and proton spin decoupling experiments.

In order to clarify the entire structure, an X-ray crystallographic analysis was carried out using a single crystal of 1 recrystallized from methylene chloride-n-hexane. Crystals of 1 belonged to the orthorhombic space group $P2_12_12_1$ with a=9.577(1), b=10.616(4), c=21.213(9)Å, V=2156.7(12)Å$^3$, Z=4. Data were measured on a Siemens AED diffractometer with Cu-K$\alpha$ radiation (graphite monochromator), using the $\omega$:$\theta$ scan technique. 1825 Intensities were measured in the range $3.0° \leq 2\theta \leq 120°$ and 1743 were taken as observed by application of the condition $I \geq 2.5\sigma(I)$. The intensity data were corrected for Lp and absorption (after isotropic refinement, correction range 0.743 to 1.228) with the DIFABS program. The structure was solved by means of the DIRDIF system based upon the Br-atom coordinates obtained from the Patterson synthesis (SHELX-76 computer program). The final R-value is 0.049 ($R_W$=0.0592, $w=(\sigma^2|F| +0.00076\,|F|^2)^{-1}$). The absolute configuration was determined by comparison of 138 Bijvoet pairs with $F_o > 10\sigma(F_o)$, which are in the ranges $5 < F_o < 50$. and $0.15 \sin\theta/\lambda < 0.4$. The averaged Bijvoet differences are 1.190 for the correct enantiomer vs. 2.300 for the wrong one.[3] The structure of this compound differs from those of other marine halogenated diterpenes, in that the $C_{20}$ isoprenoid precursor (geranyllinalool) has cyclized on the two internal double bonds to form a carbocyclic ring.[4]



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## REFERENCES AND NOTES

1. M.L. Rodríguez, J.D. Martín and D. Estrada, Acta Cryst. C 45, 306-308 (1989).
2. Chemical shifts are expressed in ppm using TMS as internal standard: $^1$H NMR ($CDCl_3$)$\delta$5.91 (1H, dd, J=17.3, 10.7 Hz, $C_2$H), 5.21 (1H, dd, J=17.3, 1.3 Hz, $C_1$H), 5.08 (1H, dd, J=10.7, 1,3 Hz, $C_1$H), 4.03 (1H, dd, J=7.3, 0.5 Hz, $C_{14}$H), 3.99 (1H, s, $C_{10}$H), 1.79 (3H, s, $C_{16}$H), 1.67 (3H, s, $C_{20}$H), 1.39 (3H, s, $C_{18}$H), 1.29 (3H, s, $C_{17}$H), 0.87 (3H, s, $C_{19}$H); $^{13}$C-NMR ($CDCl_3$) 112.0 (C1), 144.9 (C2), 72.4 (C3), 42.1 (C4), 30.0 (C5), 56.0 (C6), 87.9 (C7), 29.1 (C8), 26.6 (C9), 84.1 (C10), 45.1 (C11), 42.8 (C12), 21.2(C13), 66.6 (C14), 73.2 (C15), 33.3 (C16), 27.8 (C17), 21.7(C18), 17.1 (C19), 27.0 (C20).
3. Crystallographic parameters have been deposited with the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge, CB2 1EW, U.K.
4. D. J. Faulkner, Nat. Prod. Rep., 4, 539-576 (1987) and references quoted therein.

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