Marine Natural Products.[1] Concinndiol, A Bromo-diterpene Alcohol from the Red Alga, *Laurencia concinna*

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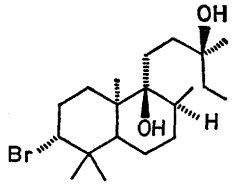
Summary A bromo-diterpene (1) has been isolated from *Laurencia concinna* and its structure determined by X-ray crystallography.

ONLY one bromo-diterpene† has ever been found to occur naturally: aplysin-20, isolated from the sea hare, *Aplysia kurodai*.[2] It was suggested that aplysin-20 was produced by a marine plant eaten by the sea hare. We have now isolated an isomer of aplysin-20 from a marine alga, *Lauren-*



(1)

† A chloro-diterpene, guierolide, was recently isolated from a composite herb.[5]

cia concinna, which was collected off the coast of New South Wales, Australia. Sea hares are known to eat red algae,[3] especially *Laurencia* species. It appears that the source of aplysin-20 [2] was a *Laurencia* species.

Concinndiol (**1**), crystallized from a hexane extract of the dry alga as colourless needles, m.p. 212°. High resolution m.s. established its formula as $C_{20}H_{35}O_2Br$. I.r. showed OH absorption, which was found to be due to two hydroxy-groups by a D_2O exchange n.m.r. experiment. The OH signals in the n.m.r. were sharp singlets and (**1**) could not be acylated with acetic anhydride in pyridine, thus indicating two tertiary hydroxy-groups in the molecule. Other signals in the n.m.r. (100 MHz, $CDCl_3$) are consistent with (**1**) as a possible structure for concinndiol.

The structure was confirmed by an *X*-ray crystal structure determination which also gave the absolute configuration of concinndiol. Concinndiol crystallizes in space group $P2_12_12_1$ with cell constants $a = 7{\cdot}995(5)$, $b = 9{\cdot}294(8)$, and $c = 26{\cdot}97(2)$ Å. Three-dimensional intensity data were collected on a Picker diffractometer with PDP-8/1 computer automation and monochromatic Mo-K_α radiation ($\lambda = 0{\cdot}71069$ Å).

The structure was solved by the heavy-atom method and refined by full-matrix least-squares calculations, using 691 observed reflections. The bromine atom was refined anisotropically, while other atoms were refined isotropically. When the weighted residue, wR, converged to 8·8%, the absolute configuration was confirmed using the anomalous dispersion effect of the Br atom (wR = 9·8% for the enantiomer).[4] Location of hydrogen atoms was not attempted. We thank the U.S. Department of Commerce Sea Grant for partial support of this research, Dr. H. B. S. Womersley, University of Adelaide for identifying the alga, and Mr. D. Flinn for experimental assistance.

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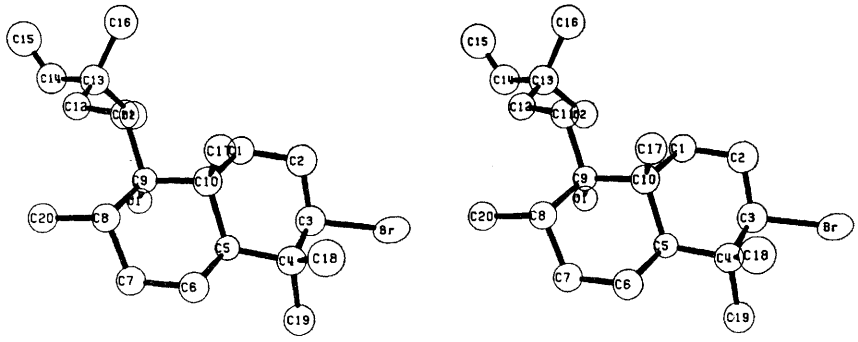

FIGURE. *A stereo view of concinndiol*

[1] For previous papers in this series see: *J. Amer. Chem. Soc.*, in the press.
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