

Structure and Absolute Configuration of Aplysiapyranoid B, a New Polyhalogenated Pyranoid Monoterpene from *Aplysia kurodai*

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The structure and absolute configuration of aplysiapyranoid B, a new polyhalogenated pyranoid monoterpene isolated from *Aplysia kurodai*, were determined by an X-ray crystal analysis.

Sea hares possess a chemical defence mechanism, whereby they accumulate selected algae metabolites in the digestive gland. The metabolites are distasteful and are slowly released to prevent potential predators.¹ Recently we isolated four new polyhalogenated pyranoid monoterpenes from the midgut gland of *Aplysia kurodai*, collected at Shimoda, Izu (Japan).² Of these, aplysiapyranoid A and B (**1**) showed complicated coupling patterns in their n.m.r. spectra, suggesting confor-

mational mobility in solution. Their stereochemistry could not be determined by the usual techniques of nuclear Overhauser enhancement or low temperature n.m.r. analysis. In this communication we report the structure and absolute configuration of aplysiapyranoid B (**1**) by a single crystal X-ray analysis.

Aplysiapyranoid B (**1**) was recrystallized from ethanol, m.p. 46–49 °C.† The asymmetric unit contains two independent molecules. The conformations of both molecules are similar to each other, one of which is shown in Figure 1.‡ The

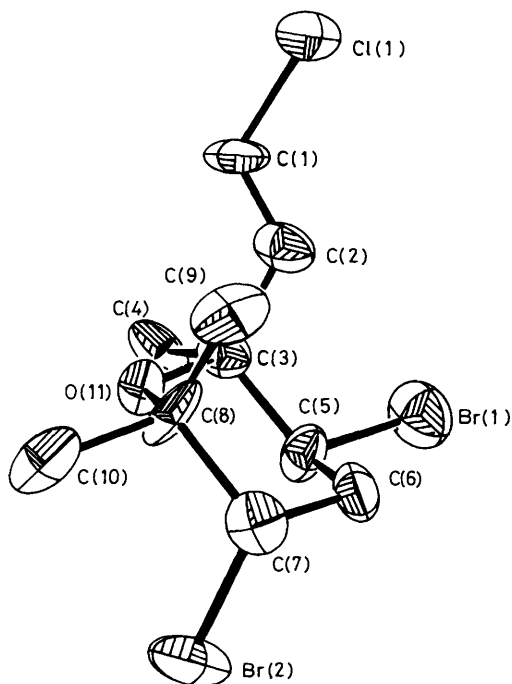


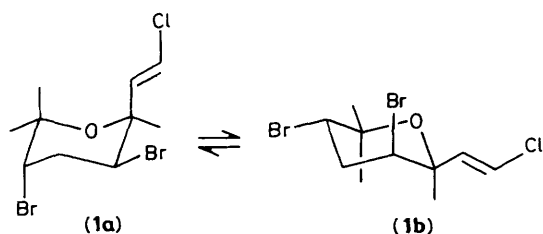
Figure 1. An ORTEP projection of (**1**). Non-hydrogen atoms are depicted as 50% probability ellipsoids.

† Selected spectroscopic data for (**1**): $C_{10}H_{15}OBr_2Cl$ ($M^+ - Cl$) 308.9466, calc. 308.9490; ν_{max} (CCl₄) 2950, 1120, and 930 cm^{-1} ; 1H n.m.r. (C₆D₆, 90 MHz) δ 1.02(3H, s), 1.07(3H, s), 1.13(3H, s), 2.14(2H, t, J 6 Hz), 3.89(1H, t, J 6 Hz), 3.92(1H, t, J 6 Hz), 5.97(1H, d, J 13.3 Hz), and 6.14(1H, d, J 13.3 Hz); ^{13}C n.m.r. (C₆D₆, 22.5 MHz) δ 28.0(q), 28.6(q), 29.1(q), 37.1(t), 54.4(d), 56.3(d), 75.5(s), 76.1(s), 121.0(d), and 137.6(d).

‡ Crystal data: (**1**) monoclinic, space group $P2_1$, $a = 20.683(3)$, $b = 7.937(1)$, $c = 8.210(2)$ Å, $\beta = 110.02(1)^\circ$, $Z = 4$, $D_m = 1.75$ $g\ cm^{-3}$. Intensity data were collected on a Rigaku automated four-circle diffractometer with graphite monochromated Mo- K_α radiation, $2\theta \leq 48^\circ$. Considerable crystal damage was observed (20% decay in 2 days exposure) and consequently three crystals were used during data collection. The data were corrected for Lorentz, polarization effects, and crystal damage but not for absorption. The structure was solved by the direct method (MULTAN 80)³ to give the positions of four bromine atoms and subsequently the other non-hydrogen atoms were revealed on difference Fourier maps. The atomic parameters were refined by the full matrix least-squares method (REFINE 2)⁴ with anisotropic temperature factors under $\Delta f'' = 0.0$ to reduce the R value to 0.057 for 1635 observed reflections [$|F_o| \geq 3\sigma(F_o)$].

The Bijvoet pairs of 29 reflections having the S value, $S = [|F_c(hkl)| - |F_c(-h-k-l)|]/\sigma(F_o)$, larger than ± 5.0 calculated using above atomic parameters including $\Delta f''$, were measured. The mean D value⁵ was found to be 1.024 [$\sigma(D) = 0.125$] and the absolute configuration of aplysiapyranoid B was determined as shown in (**1**). Refinement including $\Delta f''$ led to the R value to 0.056 ($R_w = 0.076$).

Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.



chlorovinyl group is oriented in an axial position. One bromine atom is in an axial position, the other is equatorial. However, the conformation in the crystalline state is not in agreement with the n.m.r. data for (1) in solution; the coupling pattern of the $-\text{CHBr}-\text{CH}_2-\text{CHBr}-$ moiety does not include the expected axial-axial coupling (typically J 12 Hz)⁶ for the proton attached to the carbon bearing the equatorial bromine atom [H-C(5)]. If rapid equilibration between two conformers, (1a) \rightleftharpoons (1b), is assumed in solution, the intermediate value (J 6 Hz) of the coupling constant and the

magnetic equivalence of the two methylene protons at C(6) can be reasonably explained.

Aplysiapyranoid A is thought to be a stereoisomer of (1).

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