The Structure of Aplysin-20

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Two naturally occurring bromo-compounds, aplysin and aplysinol, were isolated from *Aplysia kurodai*, whose structures have already been established.[1] We have now isolated a small amount of a third bromo-compound, aplysin-20, from the same source. Recrystallization from methanol gave colourless needles of aplysin-20 [m.p. 146—147°; $C_{20}H_{35}O_2Br$; $[\alpha]_D^{15}$ −78·1° (*c* 1, MeOH); ν_{max}(KBr) 3500—3300 (OH) and 1675 cm.$^{-1}$ (double bond); n.m.r. spectrum:† 0·96 (3H, s), 1·00 (3H, s), 1·08 (3H, s), 1·16 (3H, s), 1·70 (3H, s), 1·30—2·20 (16H, br), 3·85 (1H, q, J = 3·1, 8·5 c./sec.), 4·16 (2H, d, J = 7·0 c./sec.) and 5·41 (1H, t, J = 7·0 c./sec.)]. Aplysin-20 was treated with acetic anhydride–pyridine to give a monoacetate (m.p. 59—62°; *m/e* 430 and 428 (M^+); ν_{max}(KBr) 3520, 1730 sh, 1713, 1675, and 1260 cm.$^{-1}$), which could be converted into the starting material with methanolic potassium hydroxide. In a comparison of the n.m.r. spectra of aplysin-20 and its monoacetate, the doublet at 4·16 p.p.m. (2H, J = 7·0 c./sec.) and the triplet at 5·41 p.p.m. (1H, J = 7·0 c./sec.) are shifted to the doublet at 4·60 p.p.m. (2H, J = 7·0 c./sec.) and the triplet at 5·60 p.p.m. (1H, J = 7·0 c./sec.), respectively. The remaining signals are nearly identical in both compounds. The above fact indicates the presence of the partial structure (I). Furthermore, when considered in the light of the partial structure (I) and the presence of two hydroxyl groups in aplysin-20, the appearance of a pair of strong peaks (*m/e* 272 and 270) coupled with the strongest peak at (*m/e* 272 and 270) coupled with the strongest peak at *m/e* 191 in the mass spectrum suggests the presence of the partial structure (II).

$$-CMe{=}CH{-}CH_2OH \quad (I)$$

$$-CH_2{-}CH_2{-}CMe{=}CH{-}CH_2OH \quad (II)$$

† Chemical shifts of all n.m.r. spectra are given in p.p.m. from an internal Me_4Si standard using $CDCl_3$ as a solvent.

Aplysin-20 crystallises in space group $C2$ with $a = 34{\cdot}68$, $b = 8{\cdot}43$, $c = 7{\cdot}43$ Å, $\beta = 110{\cdot}8°$, and $Z = 4$. Using the multiple-film technique and Ni-filtered Cu-K_α radiation, relative intensities were estimated visually for equi-inclination Weissenberg photographs taken about the b and c axes. From these intensities 1167 structure factors on the absolute scale were derived by Wilson's method. The position of the bromine atom was determined from the sharpened Patterson function and those of other atoms were found from the three-dimensional minimum function as well as heavy-atom methods. These atomic co-ordinates were then refined, assuming anisotropic thermal motion, the R factor so far reached is 0·119 (observed data only). The molecular shape viewed along the b axis is shown in the Figure. The spectral and chemical evidence for the structure of aplysin-20 are in agreement with the result of the present X-ray analysis.

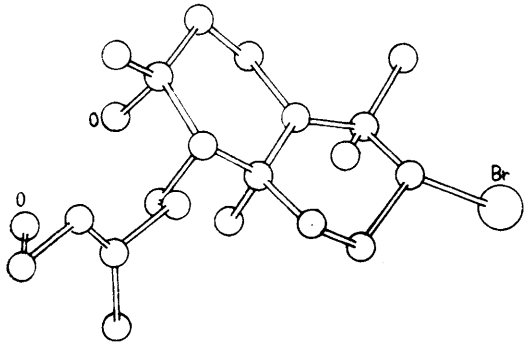

FIGURE. *Molecular structure projected along the* b-*axis.*

The most interesting point is that aplysin-20 has an axial hydroxyl group at C-8 and an equatorial bromine atom located at C-3.‡

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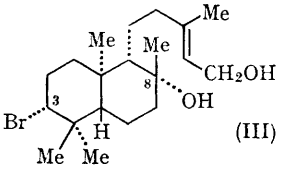

(III)

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‡ To the best of our knowledge aplysin-20 is the first bicyclic diterpene which has the axial hydroxyl group at C-8.

[1] S. Yamamura and Y. Hirata, *Tetrahedron*, 1963, **19**, 1485.