The Crystal Structure and Absolute Stereochemistry of Laurinterol. The Absolute Stereochemistry of Aplysin

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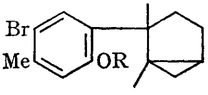
IN a previous Communication[1] we reported the detailed stereochemistry of an unusual naturally occurring bromo-compound laurencin[2] from *L. glandulifera*. A further search of Laurencia species has led to the isolation of another naturally occurring bromo-compound, a sesquiterpene, laurinterol[3] $C_{15}H_{19}OBr$, from *L. intermedia*. After chemical and spectroscopic studies Irie and his co-workers were able to deduce the structure of laurinterol as (I; R = H) but were unable to determine the stereochemistry at the asymmetric centres.

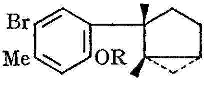
Professor Irie kindly sent us some beautiful needle-shaped crystals of laurinterol acetate (I; R = Ac) and our three-dimensional *X*-ray analysis confirms the suggested structure and provides details of the absolute stereochemistry as shown in (II).

A fundamental step in the chemical elucidation of the structure was the discovery that by treatment with toluene-*p*-sulphonic acid in acetic acid, laurinterol could be converted into aplysin (III).[4] Aplysin must therefore have the absolute stereochemistry indicated in (IV; $R^1 = R^2 = H$) with the tertiary methyl groups *cis*. The absolute stereochemistry of the related alcohol aplysinol[4] must be as shown in (IV; $R^1 = H$, $R^2 = OH$ or $R^1 = OH$, $R^2 = H$). The correct deduction that the tertiary methyl and CH_2OH groups were *cis* had been made previously.[4]

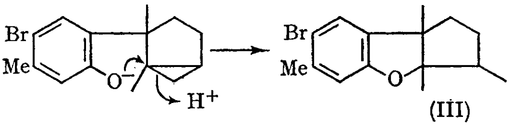
The structure and stereochemistry of the hydrocarbon laurene (V) from *L. glandulifera* have also been determined by Irie and his co-workers; the methyl groups are suggested to be *trans* on n.m.r. evidence.[5]



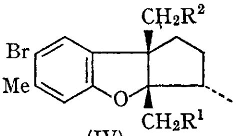
(I)



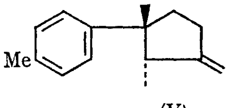
(II)



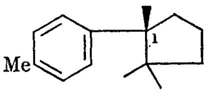
(III)



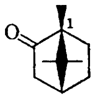
(IV)



(V)



(VI)



(VII)

The sesquiterpenoid hydrocarbon cuparene (VI) has been shown[6] to have the same stereochemistry at position (1) as (+)-camphor, which itself has been shown[7] to have the absolute stereochemistry (VII). Laurene itself has been converted[8] into (+)-cuparene and must therefore have identical stereochemistry at C(1) as the latter. That laurinterol and aplysin have the same absolute stereochemistry at C(1) as laurene and cuparene almost certainly indicates that they share a common biological precursor.

Crystals of laurinterol acetate are monoclinic, space group $P2_1$ with two molecules of $C_{17}H_{21}O_2Br$ in a cell of dimensions $a = 10{\cdot}26$, $b = 7{\cdot}28$, $c = 12{\cdot}22$ Å, $\beta = 114{\cdot}1°$. Some 1100 intensity data were obtained from a small crystal rotating about *b* on our Hilger & Watts linear diffractometer. The detailed crystal and molecular structure was determined from these data by the heavy-atom method. The analysis was somewhat complicated initially by the inevitable presence of pseudo-mirror symmetry in the first (heavy-atom-phased) electron-density distribution. This was overcome by careful selection of atomic sites from this distribution, and the structure was completely revealed in the second round of calculations. A Mo-K_α precession photograph of the $1kl$ reciprocal lattice net showed differences in intensity in 27 Bijvoet[9] pairs of reflexions and allowed the stereochemistry to be determined absolutely. The conformation of the molecule in the crystal is shown in the Figure, which also shows the absolute stereochemistry. *R* is now 10%; refinement of the atomic parameters is continuing by least-squares methods.

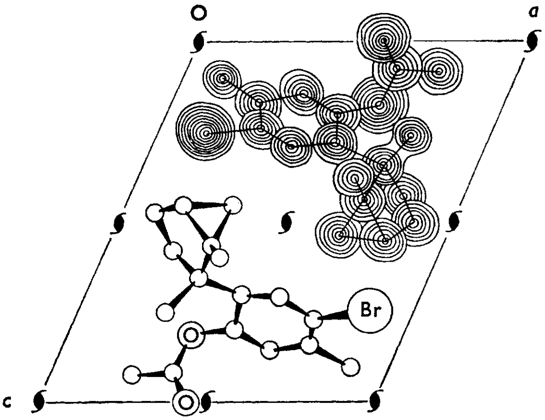


FIGURE. *A view down* b *of the two molecules in a unit cell of laurinterol acetate. The contours of the superimposed electron-density sections start at the* 1 e$Å^{-3}$ *level and continue at* 1 e$Å^{-3}$ *intervals except around the bromine atom where they are at* 4 e$Å^{-3}$.

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[5] T. Irie, Y. Yasunari, T. Suzuki, N. Imai, E. Kurosawa, and T. Masamune, *Tetrahedron Letters*, 1965, 3619.

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[8] T. Irie, 1966, personal communication.

[9] J. M. Bijvoet, *Proc. k. ned. Akad. Wetenschap.*, 1949, **52**, 313. See also S. Ramaseshan in "Advanced Methods of Crystallography", Academic Press, London, 1964, pp. 67—95.