The Crystal Structure of Loganin Penta-acetate Monomethyl Ether Bromide

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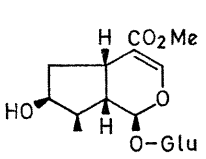
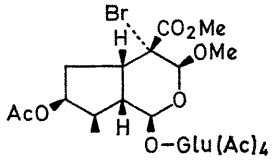
Summary The crystal structure of a derivative of loganin confirms the chemically determined structure.

LOGANIN (I) is a monoterpene β-D-glucoside first isolated from the fruit of *Strychnos nux vomica*.[1] Because of its involvement as a key intermediate in the biosynthesis of certain plant indole alkaloids,[2] its structure and stereochemistry have been the subjects of chemical study culminating in several recent reports of the chemically determined structure.[3] We report on the absolute configuration of a derivative of loganin, the penta-acetate monomethyl ether bromide (II), determined by *X*-ray crystallographic analysis.



(I)



(II)

The crystals are triclinic with $a = 7{\cdot}28 \pm 0{\cdot}02$, $b = 11{\cdot}04 \pm 0{\cdot}02$, $c = 11{\cdot}02 \pm 0{\cdot}02$ Å, $\alpha = 97{\cdot}65 \pm 0{\cdot}05°$, $\beta = 92{\cdot}70 \pm 0{\cdot}05°$, $\gamma = 102{\cdot}1 \pm 0{\cdot}1°$. The space group is $P\bar{1}$ with one molecule of $C_{28}O_{16}H_{39}Br$, M 711·5 per unit cell. The calculated density is 1·381 g./cm.^{3} and that observed by flotation in an ethanol–bromobenzene mixture is 1·396 g./cm.^{3}. The crystals are transparent white flat plates, but after about 50 hr. of *X*-irradiation (34kv, 40 mA) begin to turn light brown, and after 100 hr. become brown, almost opaque, and soft so that they cannot be readily re-mounted. Because of this decay problem two crystals were needed for the data collection.

A total of 3044 independent reflections were observed with Cu-K_α radiation using general-inclination Weissenberg photography about the three principal crystal axes. The intensities were estimated visually by comparison with an intensity scale prepared from one of the data crystals. The structure was solved by the heavy-atom technique and refined by Fourier and full-matrix least-squares methods to a current residual of 14·3%. Anisotropic temperature factors were applied to the bromine and isotropic factors to all the other non-hydrogen atoms.

The stereochemistry of the *X*-ray-determined structure is consistent with the recently published reports in all respects.

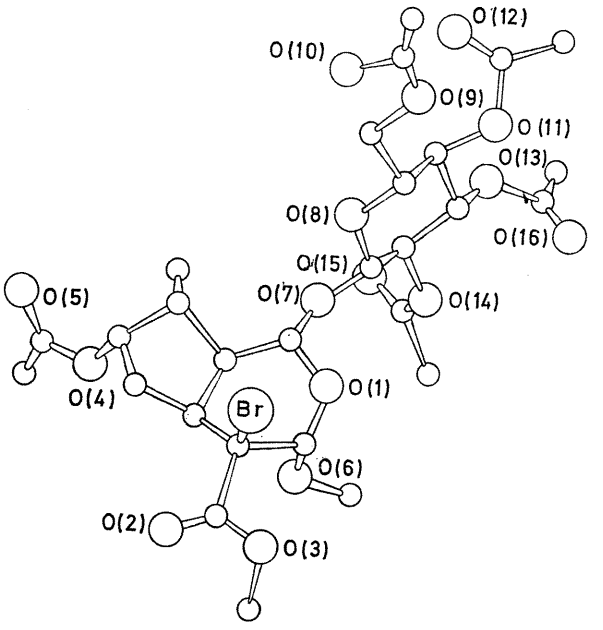


FIGURE. *View of the molecule looking down the* c *axis.*

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[1] W. R. Dunstan and F. W. Short, *Pharm. J. and Trans.*, 1883, **14**, 3.
[2] A. R. Battersby and B. Gregory, *Chem. Comm.*, 1968, 134; P. Loew and D. Arigoni, *ibid.*, p. 137.
[3] A. R. Battersby, R. S. Kapil, and R. Southgate, *Chem. Comm.*, 1968, 131; H. Inouye, T. Yoshida, and S. Tobita, *Tetrahedron Letters*, 1968, 2945; A. R. Battersby, E. S. Hall, and R. Southgate, *J. Chem. Soc.* (*C*), 1969, 721.