

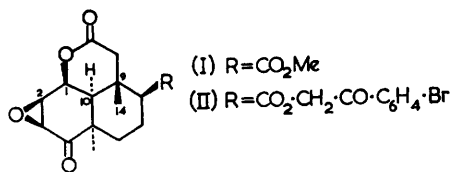
Configuration of the Epoxide in Palmarin: a Case of Immoderate Conformational Distortion

By K. M. S. ISLAM, G. FERGUSON, K. H. OVERTON, and D. W. MELVILLE

(Chemistry Department, The University, Glasgow, W.2)

In an attempt¹ to interpret the n.m.r. spectrum of the palmarin derivative (I) and in particular to account for the observed coupling constants $J_{1,2} = 3.6$ c./sec. and $J_{1,10} = 9$ c./sec., we were compelled to postulate an upward rotation of C(1) so as to reduce $\theta_{H(1), H(10)}$ to approximately 25° , whereupon $\theta_{H(1), H(2)}$ becomes approximately 35° . A convincing cause for such a distortion exists in (I) if the 2,3-epoxide has the β -configuration but not if it has the α -configuration and mainly on this basis we tentatively assigned the β -epoxide configuration in (I) and hence in palmarin.

In order to establish the extent of the postulated conformational distortion and incidentally to confirm the β -epoxide configuration in palmarin we undertook an X-ray examination of the *p*-bromophenacyl derivative (II).



The results of this analysis, depicted in the Figure, appear to us of interest in that they reveal a degree of conformational distortion that might appear unreasonable from an examination of Dreiding models.

The extent of distortion of ring-A is best characterized by comparing the C(14) \cdots C(2) distance of 3.57 Å with the C(9) \cdots C(1) distance of 2.61 Å. [The C(1) \cdots C(3) distance in a cyclohexane chair is 2.53 Å]. The most important factor responsible

for this must be interaction between the C(14) methyl group and the epoxide oxygen and this is reflected in the separation of these centres by 2.92 Å.

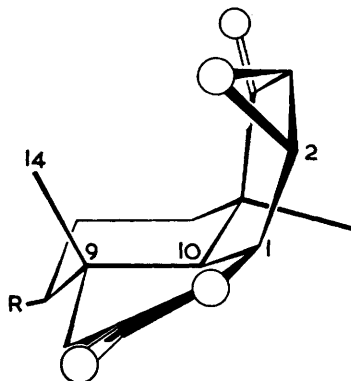


FIGURE. A view of the derivative (II) showing the distortion induced by the methyl group C(14), and the epoxide ring. The circles represent oxygen atoms.

Crystals of the *p*-bromophenacyl derivative (II) are orthorhombic with 4 molecules of $\text{C}_{23}\text{H}_{23}\text{O}_7\text{Br}$ in a cell of dimensions: $a = 10.76$, $b = 8.95$, $c = 21.79$ Å. Systematic absences and Harker sections uniquely determine the space group as $P2_12_12_1$. Some 1900 intensity data were measured visually from equi-inclination Weissenberg photographs taken with a crystal rotating about a and the structure was solved by the heavy-atom method. Because the heavy-atom y co-ordinate is close to $1/4$ the first electron-density distribution derived

from the observed data and the heavy-atom phases was complicated by the presence of pseudo-mirror planes. By careful selection of atomic sites from this map and from consideration of intermolecular contacts, the complete structure was revealed.

Refinement of the structure proceeded by further electron-density calculations and then by least-squares methods.² *R* is now 0·078.

(Received, December 28th, 1966; Com. 1046.)

¹ K. H. Overton, N. G. Weir and A. Wylie, *J. Chem. Soc. (C)*, 1966, 1482.

² Using programs devised by the Glasgow Group: Fourier program: Dr. J. G. Sime; least-squares program: Professor D. W. J. Cruickshank and J. G. F. Smith.