

## The Crystal Structure of Humulene Bromohydrin

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THE monocyclic sesquiterpene, humulene (I), has been shown<sup>1</sup> to be readily convertible to a tricyclic bromohydrin, thought to be (IIa), which in turn is equally easily convertible into ( $\pm$ )-caryophyllene (III) or back into humulene (I). The ease and stereospecificity of these reactions, together with

the uncertainties as to the stereochemistry of (II), have led us to determine its structure by a three-dimensional X-ray-crystallographic study.

The crystals are monoclinic,  $P2_1/n$ ,  $a = 6.07$ ,  $b = 19.54$ ,  $c = 12.39 \text{ \AA}$ ,  $\beta = 93.47^\circ$ ,  $U = 1467 \text{ \AA}^3$ ,  $D_x = 1.36 \text{ g. cm.}^{-3}$ ,  $D_c = 1.37 \text{ g. cm.}^{-3}$  for  $Z = 4$

molecules per cell (2 of which are *L*, and 2 are *D*). ( $C_{15}H_{25}OBr$ ;  $M = 301.3$ .)

2116 reflections were estimated visually from Weissenberg photographs taken using  $Cu-K\alpha$  radiation. The elucidation and refinement of the structure were straightforward;  $R$  is now 0.122. Figure 1 shows a projection of the structure.

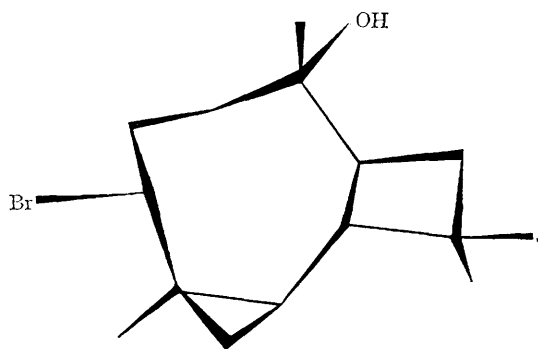


FIGURE 1

The *X*-ray work revises the constitution from (IIa) to (IIb), and thereby reveals that the attack on the C-1-C-2 double bond is *cis*, but is as expected *trans* for the other two.

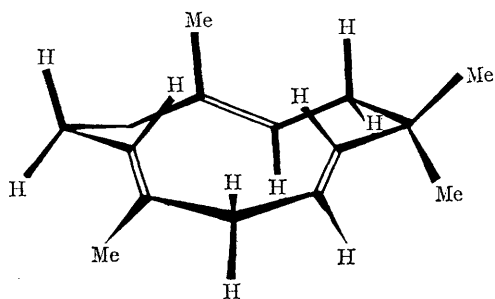


FIGURE 2a

The proposed *trans*-fusion of the cyclobutane ring is confirmed, and it has exactly the same mode of fusion relative to the larger ring as was found earlier in *X*-ray studies of caryophyllene hydrochloride<sup>2</sup> and caryophyllene chlorohydrin.<sup>3</sup> Indeed the buckling of the cyclobutane ring follows the same pattern as in those two molecules even though this time it is fused on to an eight- rather than a seven-membered ring.

In view of the stereospecific reconstitution of the all-*trans*-triene ring of humulene and the ease with which these reactions proceed in either

direction, it is instructive to note the close similarity between the conformation of the bromohydrin (Figure 2b) and that adopted by humulene

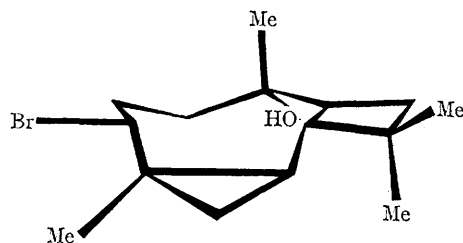
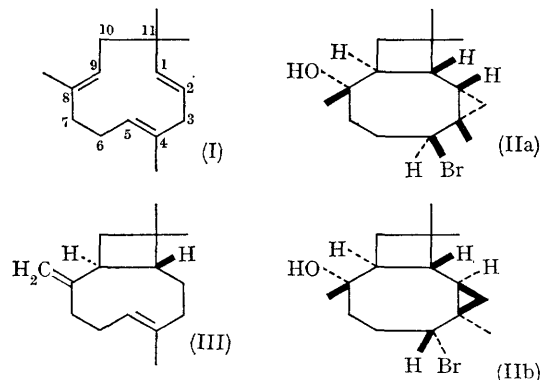


FIGURE 2b

(Figure 2a) in the silver nitrate adduct as found from an *X*-ray study by McPhail and Sim.<sup>4</sup> They found that the planes of all three ethylenic groups lay nearly perpendicular to the "plane" of the 11-membered ring. One might have expected such a large ring to have a very mobile shape especially in solution, and might therefore have been tempted to attribute the rather peculiar geometry they found to the influence of the  $Ag^+$  ions and packing requirements. Such a conformation must, however, have immediately preceded the ring closures when forming (IIb) (formed in 20% yield), for none of the 11 atoms has moved very far in doing so, and this suggests that the conformation found by McPhail and Sim is no mere accident, but represents a fairly stable configuration.



Although this structure determination has made the stereochemistry of the reactions clearer, it leaves largely unresolved interesting questions concerning the sequences and mechanisms involved.

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<sup>1</sup> J. M. Greenwood, J. K. Sutherland, and A. Torre, *Chem. Comm.*, 1965, 410.

<sup>2</sup> J. M. Robertson and G. Todd, *J. Chem. Soc.*, 1955, 1254.

<sup>3</sup> D. Rogers and Mazhar-ul-Haque, *Proc. Chem. Soc.*, 1963, 371.

<sup>4</sup> A. T. McPhail and G. A. Sim, *J. Chem. Soc. (B)*, 1966, 112.