

**The Molecular and Crystal Structure of Bromomexicanin E**  
( $C_{14}H_{15}O_3Br$ )

C. N. CAUGHLAN and MAZHAR-UL-HAQUE

*(Department of Chemistry, Montana State University, Bozeman, Montana 59715)*

and MERLE T. EMERSON

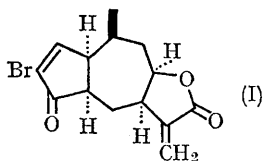
*(Department of Chemistry, Florida State University, Tallahassee, Florida)*

In addition to many chemical studies, structures based on X-ray diffraction have now been solved for bromoisotenulin by Rogers and Haque<sup>1</sup> and

for bromohelenalin by Emerson, Caughlan, and Herz.<sup>2</sup> These compounds exhibit different stereochemistry as well as showing biogenetically

abnormal structures. Structures of such compounds are of interest in regard to their origin and function in plants.

The norsesquiterpene mexicanin E was first isolated by A. Romo de Vivar and J. Romo<sup>3</sup> from *Helenium Mexicanum*. Further studies were made by Herz<sup>4</sup> and J. Romo *et al.*<sup>5,6</sup> An X-ray study of the compound was undertaken to confirm independently the structure and to supply the relative stereochemistry. Our findings are in accord with the chemical study. The constitution and relative stereochemistry as determined by X-ray study of bromomexicanin E is as shown in (I).



Bromomexicanin E ( $C_{14}H_{15}O_3Br$ ) crystallizes in the orthorhombic space group  $P 2_1 2_1 2_1$  with four molecules per unit cell. The lattice parameters are  $a = 6.12$ ,  $b = 12.21$ ,  $c = 18.09$  Å. The intensities

of 800 independent reflections were measured visually. The position of the bromine atom was evident from the three-dimensional Patterson map. The rest of the structure emerged gradually from five successive Fouriers. Refinement of positions and isotropic temperature factors using Busing, Martin, and Levy Least-Squares refinement programme (ORNL-TM-305) has reduced the  $R$ -factor to 0.17 for all observed reflections. Refinement is continuing, but bond lengths and angles are satisfactory for this stage of refinement and the stereochemistry is apparent.

In bromomexicanin-E both five-membered rings are *cis*-fused to the seven-membered ring, the two fusions being *cis-syn-cis*. The seven-membered ring is bent and is in a boat form.

It is interesting to compare this to other related compounds from *Helenium* species, *i.e.*, tenulin and helenalin. In tenulin, both five-membered rings are *trans*-fused to the seven-membered ring, while in helenalin, one five-membered ring is *trans*-fused to the seven-membered ring, while the other, the lactone junction is *cis*. All three compounds are appreciably folded.

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<sup>1</sup> D. Rogers and Mazhar-Ul-Haque, *Proc. Chem. Soc.*, 1963, 92.

<sup>2</sup> M. T. Emerson, C. N. Caughlan, and W. Herz, *Tetrahedron Letters*, 1964, 821.

<sup>3</sup> A. Romo de Vivar and J. Romo, *Ciencia*, 1961, 21, 33.

<sup>4</sup> W. Herz, *J. Org. Chem.*, 1962, 28, 4043.

<sup>5</sup> J. Romo and A. Romo de Vivar, *J. Amer. Chem. Soc.*, 1961, 83, 232.

<sup>6</sup> J. Romo, A. Romo de Vivar, and W. Herz, *Tetrahedron*, 1963, 19, 2317.