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Preliminary communication

The crystal structures of galactitol diarsenite and D-mannitol diarsenite

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In 1961, Wolfrom and Holm reported[1] the preparation of several alditol arsenites by a general procedure involving an acid-catalysed reaction between an alditol and arsenious trioxide. Crystalline esters were obtained from glycerol, galactitol, and D-mannitol, but the points of attachment of the arsenic atoms to the hexitol residues have never been ascertained. We now report on the X-ray crystallographic structures of the two hexitol diarsenites.

Weissenberg data were collected photographically and intensities were automatically measured with the facility at the S.R.C. Laboratory, Daresbury. Both structures were solved by the Patterson method, using the Shellx routines with full-matrix least-squares refinement.

Galactitol diarsenite. Prepared as described[1], this ester had m.p. 266° (sublimes); lit.[1], m.p. 266–267°. Crystal data: space group C2/c; $Z = 4$; $a = 15.35$ Å, $b = 6.78$ Å, $c = 9.63$ Å; $\beta = 121.25°$; 335 unique reflexions were measured with $R = 0.053$. After refinement with anisotropic As atoms, the F(calc) and F(obs) agreement index was $R = 0.070$.

Fig. 1 is a computer-generated diagram of the centrally symmetric molecule. One arsenic atom is attached to O-1, O-2, and O-4; the other is attached to O-3, O-5, and O-6. Atoms C-2, C-3, C-4, and C-5 lie in one plane, and atoms C-1 and C-6 are displaced equally (0.929 Å) to opposite sides of this plane. Atoms O-3, C-3, C-4, and O-4 lie in another plane, and the [4.4.0]bicyclo ring-system formed by the fusion of the rings described by As-1, O-2, C-2, C-3, C-4, and O-4, and by As-2, O-3, C-3, C-4, C-5 and O-5 is essentially a heterocyclic analogue of that found in the chair–chair form of *trans*-decalin.

D-*Mannitol diarsenite.* Prepared as described[1], this ester had m.p. 231–235°; lit.[1], m.p. 225–226°. Crystal data: space group B2; $Z = 8$; $a = 21.88$ Å, $b = 15.64$ Å, $c = 6.02$ Å; $\gamma = 119.2°$; 887 unique reflexions were measured with $R = 0.057$. After refinement with anisotropic As atoms, the final agreement index was $R = 0.081$.

There are two similar (but not crystallographically identical) types of molecule in the unit cell, the perspective drawing of one of which is shown in Fig. 2. As in the galactitol derivative, one arsenic atom is attached to O-1, O-2, and O-4 and the other is at-

tached to O-3, O-5, and O-6; in the D-mannitol derivative, the dihedral angle defined by C-2 and C-5 with respect to the C-3–C-4 bond is ~167° and C-1 and C-6 are both displaced to the same side of the mean plane through C-2, C-3, C-4, and C-5. These displacements are of magnitude ~0.96 Å. The dihedral angle defined by O-3 and O-4 with respect to the C-3–C-4 bond is ~75°, and the two six-membered rings formed by As-1, O-2, C-2, C-3, C-4, and O-4 and by As-2, O-3, C-3, C-4, C-5, and O-5 form a heterocyclic, [4.4.0]bicyclo ring-system with a conformation bearing a resemblance to that found in the chair–chair form of *cis*-decalin.

In both compounds, the measured As–O bond-lengths lie in the range 1.72–1.87 Å.

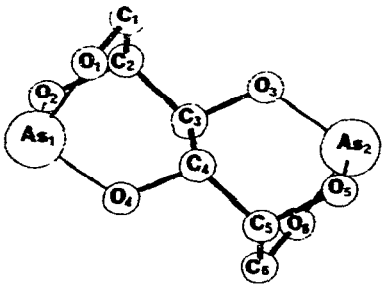

Fig. 1. Computer-generated perspective of galactitol diarsenite, showing the points of attachment of the arsenic atoms.

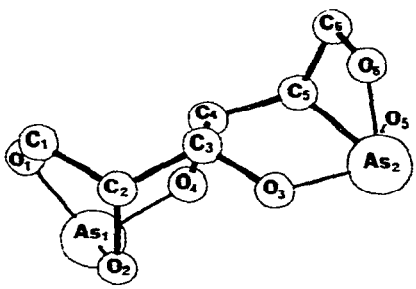

Fig 2. Computer-generated perspective of D-mannitol diarsenite.

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REFERENCE

1 M. L. Wolfrom and M. J Holm, *J. Org. Chem.*, 26 (1961) 273–274.