Conformation of a Furanose Carbohydrate: an *X*-Ray Crystallographic Study of Methyl 1,2,3,5-Tetra-*O*-acetyl-β-D-galactofuranuronate

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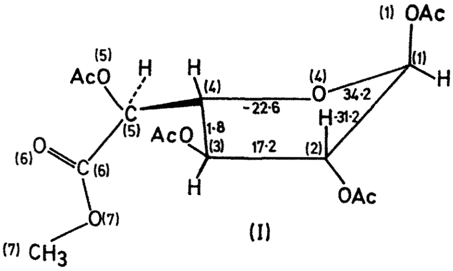
Summary The five-membered ring in the title compound has been shown to be a near envelope in which C-1 is the out-of-plane atom.

METHYL 1,2,3,5-TETRA-*O*-ACETYL-β-D-GALACTOFURANURONATE (I) was isolated by chromatography over silicic acid of the products of acetylation (with sodium acetate and acetic anhydride) of the methyl ester of galacturonic acid. Crystallization from aqueous acetone gave rectangular prisms, m.p. 105—106°, $[\alpha]_{\mathrm{D}}^{22}$ −56·5° (*c* 0·93 in $CHCl_3$).[1] The space group for (I) was determined from systematic absences as $P2_1$; unit-cell dimensions are $a = 7{\cdot}346(3)$, $b = 16{\cdot}254(8)$, $c = 8{\cdot}606(4)$ Å, and $\beta = 114{\cdot}33 \pm 0{\cdot}06°$.

The intensity data and unit-cell dimensions were obtained with a Siemens automatic single crystal diffractometer with Cu-K_α radiation and nickel attenuators. The integrated intensities were recorded using the five-value method.[2] The scanning procedure utilized the moving crystal-moving detector method ($\theta/2\theta$-scan)[3] with the scan range varying between 1·0° at low 2θ to 2·8° at high 2θ. A total of 1840 independent intensities were recorded with θ values less than 70°. The structure was solved using direct phasing methods and refined to a final discrepancy (*R*) factor of 0·060.

Torsional angles about the ring bonds are given in the Figure. The small value of the torsional angle about bond C(3)–C(4) shows that ring atoms C(2), C(3), C(4), and O(4) are close to planarity and C(1) is displaced from this plane in the direction indicated in the Figure. This displacement is 0·47 Å from the least-squares plane of C(2), C(3), C(4), and O(4). Calculation of the displacement of C(1) and O(4) from the plane of C(2), C(3), and C(4) gave values of 0·43 Å and 0·04 Å, respectively, on opposite sides of that plane, showing that the ring is distorted only slightly from an envelope conformation. This finding is in contrast to observations on the conformations of a variety of other furanose carbohydrates in which either C(2) or C(3) (or both) have been shown to be the out-of-plane ring atoms.[4] It agrees well, however, with the conformation suggested earlier[5] (for the configurationally related α-D-arabinofuranose case) on the basis of ^1H n.m.r. studies.



(I)

FIGURE

Three observations on the orientations of the substituent groups are of interest. Firstly, in keeping with earlier findings on the planarity of ester groupings,[6] for each of the acetoxy-groups, the five atoms in the C–O–(CO)–C grouping are close to coplanarity with the carbonyl group eclipsing the O–C group (an *s-cis*-conformation[7]). Secondly, these groups are oriented in such a way that the carbonyl group is rotated about 40° out of eclipsing with the carbinol C–H group for the C(2), C(3), and C(5) acetoxy-groups and about 2° for the C(1) acetoxy-group. This is of some interest in connection with the explanation put forward[8] for the origin of the "acylation shift" in n.m.r. spectroscopy. Thirdly, in the α-acetoxy methyl ester side-chain, the six atoms (C(5), O(5), C(6), O(6), C(7), and O(7) are close to coplanarity. In this case, oxygen atom O(5) also is coplanar with the five methyl ester group atoms.

We note that the conformation of the five-membered ring in (I) places O(1) in a position relative to O(4) so as to produce a most favourable "anomeric effect" which apparently offsets the torsional strains arising from near eclipsing of groups attached to C(3) and C(4) [which would be relieved if C(2) or C(3), or both, were out-of-plane atoms].

(*Received, October* 26*th*, 1970; *Com.* 1836.)

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[5] J. D. Stevens and H. G. Fletcher, jun., *J. Org. Chem.*, 1968, **33**, 1799.
[6] See Ref. 8 for references to the planarity of ester groups.
[7] See: E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Interscience, New York, 1965, pp. 19—22.
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