The Crystal and Molecular Structure of Methyl 6-*O*-Acetyl-*β*-D-galactopyranoside

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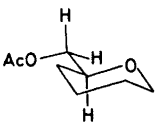
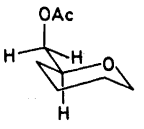
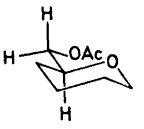
In the course of studies of the circular dichroism of *O*-acetylated glycopyranosides[1,2] differential dichroic absorption was observed for glycosides with an *O*-acetyl group in the 6-position. On the basis of NMR studies, Hall and Manville have concluded that, in solution, conformation A predominates for D-*threo*-hexopyranoses, while that of B predominates for D-*erythro*-hexopyranoses.[3] Lemieux and co-workers, on the basis of NMR studies as well as from studies of optical rotation, have concluded that at least for D-*erythro*-hexopyranoses, conformation C predominates in solution.[4,5]



A



B



C

It was therefore considered of interest to determine the conformation in the solid state of a 6-*O*-acetylhexopyranoside by means of X-ray crystallography in order to see if this conformation would correlate with the observed dichroism. Due to its crystalline properties, methyl 6-*O*-acetyl-*β*-D-galactopyranoside[6] was selected for the study.

The compound crystallized in space group $P2_12_12_1$, **a** = 26.230, **b** = 9.196, **c** = 4.718, Z = 4. The X-ray data were obtained

Table 1. Intramolecular nonhydrogen bond distances and angles. Estimated standard deviations are given in parentheses.

C(1)–C(2)	1.519 (6) Å	C(1)–O(2)–C(3)	111.0 (4)°
C(2)–C(3)	1.518 (6)	C(2)–C(3)–C(4)	109.9 (4)
C(3)–C(4)	1.523 (6)	C(3)–C(4)–C(5)	109.6 (4)
C(4)–C(5)	1.504 (7)	C(4)–C(5)–O(5)	110.9 (4)
C(5)–C(6)	1.518 (7)	C(5)–O(5)–C(1)	112.6 (3)
C(8)–C(9)	1.465 (10)	O(5)–C(1)–C(2)	110.3 (4)
C(1)–O(1)	1.374 (6)	C(4)–C(5)–C(6)	114.7 (4)
C(7)–O(1)	1.428 (7)	O(5)–C(5)–C(6)	105.1 (4)
C(2)–O(2)	1.421 (5)	C(5)–C(6)–O(6)	106.8 (5)
C(3)–O(3)	1.416 (5)	C(1)–O(1)–C(7)	114.4 (5)
C(4)–O(4)	1.431 (5)	C(6)–O(6)–C(8)	117.9 (4)
C(1)–O(5)	1.437 (5)	O(6)–C(8)–C(9)	114.5 (5)
C(5)–O(5)	1.427 (6)	O(6)–C(8)–O(7)	121.1 (5)
C(6)–O(6)	1.445 (7)	C(9)–C(8)–O(7)	124.1 (5)
C(8)–O(6)	1.285 (5)	O(1)–C(1)–O(5)	107.3 (4)
C(8)–O(7)	1.181 (8)	O(1)–C(1)–C(2)	108.7 (4)
		C(1)–C(2)–O(2)	109.9 (4)
		C(3)–C(2)–O(2)	110.0 (4)
		C(2)–C(3)–O(3)	113.7 (4)
		C(4)–C(3)–O(3)	111.4 (4)
		C(3)–C(4)–O(4)	109.5 (4)
		C(5)–C(4)–O(4)	109.9 (4)

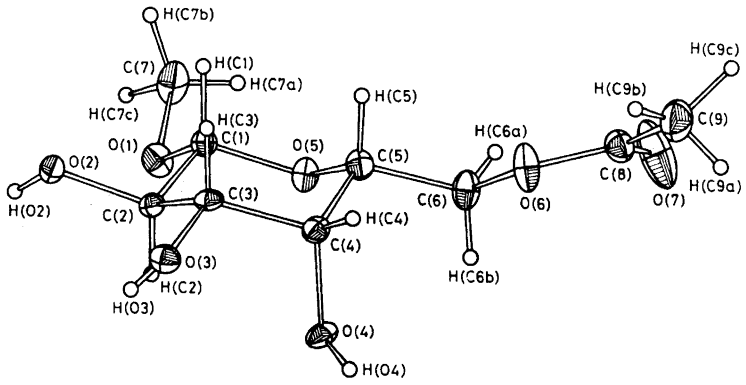
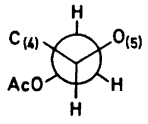


Fig. 1.

on a Philips PW 1100 computer-controlled single-crystal diffractometer with graphite monochromatized Cu$K\alpha$ radiation. The phase determinations were carried out by a computerized application of direct methods using the weighted phase-sum formula described by Norrestam.[7] Several cycles of full-matrix least-squares refinement (anisotropic nonhydrogen and fixed isotropic hydrogen temperature parameters) gave an R-value of 0.044. The molecular structure is shown in Fig. 1. Intramolecular distances and angles are listed in Table 1. Full details of the X-ray diffraction investigation will be published elsewhere.

The conformation found agrees with that suggested by Hall and Manville [3] for D-*threo*-hexopyranoses (A). In this conformation the acetoxy group and the ring oxygen are *trans*-oriented (D). As discussed elsewhere [1,2] the Cotton effect associated with an $n \rightarrow \pi^*$ transition of an acetoxy carbonyl group situated near a chiral centre in a pyranose ring most probably is determined by the dihedral angle of the acetoxy group and a neighbouring oxygen or oxymethylene function.



D

By this argument, D would not be expected to give rise to a Cotton effect. As discussed in another paper,[2] the CD band observed for the title compound most likely is caused by the presence, in solution, of molecules in conformation C.

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