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Preliminary communication

An X-ray crystallographic study of a carbohydrate orthoester: 3,4,6-tri-*O*-acetyl-1,2-*O*-(1-*exo*-ethoxyethylidene)-α-D-glucopyranose

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During the formation of 3,4,6-tri-*O*-acetyl-1,2-*O*-(1-ethoxyethylidene)-α-D-glucopyranose and other similar orthoacetates, a new asymmetric center is created at C-7, resulting in two isomeric compounds. The crystal structure of the major isomer (2), m.p. 96–98°, displaying an n.m.r. methyl singlet at $\delta = 1.71$ p.p.m. ($CDCl_3$), has been determined from low-temperature (approximately −193°) three-dimensional X-ray data obtained by the multiple-film, equi-inclination Weissenberg technique (CuKα radiation, $\lambda = 1.54182$ Å). The structure was solved by using Patterson search methods and tangent-formula recycling techniques, and the block-diagonal, anisotropic refinement (fixed hydrogen parameters obtained from difference maps) was terminated at a conventional R index of 0.068 for 1680 observed reflections. One formula unit ($C_{16}O_{10}H_{24}$) comprises the asymmetric unit in a monoclinic unit-cell having $a = 7.649(4)$, $b = 14.465(5)$, $c = 8.212(3)$ Å, $\beta = 96.26(7)°$ (En-293°) and space group $P2_1$. The atomic coordinates for carbon and oxygen atoms are given in Table I.

Considering the dioxolane ring as a plane of reference, this isomer was found to have a configuration in which the ethoxy group is *trans* (*exo*) to the glucopyranose ring (Fig. 1). The shape of the dioxolane ring can best be described as an envelope form, with four atoms approximately planar, and O-2 offset 0.46 Å toward the glucose side of the plane.

The D-glucopyranose ring approximates a $^3S_5$ skew conformation[1], but there is some flattening of the skew conformation in the vicinity of C-1 and C-2. This flattening can be considered a slight departure toward a $B^{3,0}$ boat conformation in this part of the pyranoid ring. A smaller departure toward a $B_{5,2}$ boat conformation appears to be present in the vicinity of C-5. The skew conformation of the pyranoid ring causes the C-3 acetoxyl group to be oriented axially. The C-4 acetoxyl group is quasi-axial (between axial and equatorial), and the C-5 substituent is equatorial.

Bond distances (standard deviations, 0.008 and 0.007 Å for carbon–carbon and carbon–oxygen bonds) in 1 are similar to those found in other α-glycosides[2]. Bond angles (standard deviation, 0.4°) in the pyranoid ring at C-1, C-2, and C-3 appear to be

TABLE I

FRACTIONAL ATOMIC COORDINATES FOR THE CARBON AND OXYGEN ATOMS IN **1**

Atom [a]	*Fractional atomic coordinates*		
	x	*y*	*z*
C-1	0.25214(68)	−0.05030(37)	0.44810(59
C-2	0.20814(66)	0.05309(39)	0.45552(57)
C-3	0.30494(74)	0.11323(37)	0.34276(62)
C-4	0.31588(72)	0.07209(38)	0.17265(61)
C-5	0.26364(72)	−0.03038(38)	0.16286(61)
O-5	0.33540(48)	−0.07372(26)	0.31032(41)
C-6	0.33647(78)	−0.07814(40)	0.02280(64)
O-1	0.08363(48)	−0.09381(25)	0.43832(42)
O-2	0.02686(46)	0.05801(25)	0.40180(41)
C-7	−0.04744(69)	−0.02541(37)	0.45080(62)
C-8	−0.21021(78)	−0.04787(40)	0.34233(65)
O-9	−0.07506(50)	−0.01205(27)	0.61541(41)
C-10	−0.13557(93)	−0.09116(46)	0.69917(73)
C-11	−0.18563(82)	−0.05993(50)	0.86013(72)
O-3	0.48273(47)	0.12381(27)	0.42020(41)
C-3′	0.51091(70)	0.19839(38)	0.51916(60)
C-3″	0.69666(76)	0.20102(42)	0.59360(67)
O-3′	0.39900(48)	0.25498(27)	0.53711(42)
O-4	0.19951(50)	0.12407(29)	0.05839(40)
C-4′	0.25554(79)	0.14971(38)	−0.08576(66)
C-4″	0.11986(78)	0.20223(42)	−0.18918(66)
O-4′	0.40108(52)	0.12888(34)	−0.12327(45)
O-6	0.25599(52)	−0.16823(27)	0.00512(43)
C-6′	0.31515(80)	−0.22367(43)	−0.10750(64)
C-6″	0.22569(81)	−0.31490(42)	−0.11609(71)
O-6′	0.42691(65)	−0.19973(33)	−0.19163(56)

[a] See Fig.1. Primed numbers refer to acetyl groups; doubly primed numbers refer to methyl groups of acetyl groups.

larger (3.3 σ, 2.8 σ, 2.8 σ) than the average values of 109.2, 110.5, and 110.5° reported by Arnott and Scott[2]. There is some structural difference between the O-1 and O-2 sides of the dioxolane ring. The angle at O-1 (109.2°) is significantly larger than the angle at O-2 (106.3°). There is a large difference (12.5 σ) between the value of 110.3° for O-1—C-7—O-9 and the value of 105.3° for O-2—C-7—O-9.

REFERENCES

1 For explanations of the conformational designation, see L. Hough and A. C. Richardson in *Rodd's Chemistry of Carbon Compounds*, S. Coffey, ed. 2nd ed. Vol. 1, part F, Amsterdam, Elsevier Publishing Co., 1967, p. 91.

2 S. Arnott and W. E. Scott, *J. Chem. Soc.*, (Perkin II), (1972) 324.

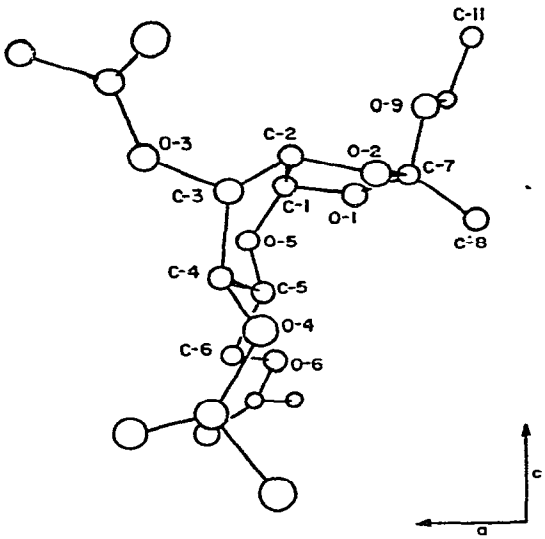

Fig. 1. Perspective view from the $+b$ direction, showing ring conformations and isomeric configuration in 1.