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Structure of a 2,3,4-Tri-*O*-acetyl-*β*-D-glucopyranosuronic Acid Derivative

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Abstract. Methyl {1-[(1′*R*)-1′-methoxybutyl]-2,3,4-tri-*O*-acetyl-*β*-D-glucopyranosid}uronate, $C_{18}H_{28}O_{11}$, $M_r = 420{\cdot}41$, orthorhombic, $P2_12_12_1$, $a = 8{\cdot}604$ (3), $b = 13{\cdot}500$ (2), $c = 18{\cdot}664$ (4) Å, $V = 2167{\cdot}9$ Å^3, $Z = 4$, $D_x = 1{\cdot}288$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 0{\cdot}10$ mm^{-1}, $F(000) = 896$, $T = 298$ K, $R = 0{\cdot}055$ for 1592 observed reflections. The structure was investigated to determine the relative configuration, which could not be established unambiguously by NMR. The endocyclic acetal bond is longer than the exocyclic by 0·045 (7) Å.

Introduction. In a series of papers (Jones, Sheldrick, Kirby & Glenn, 1982*a*,*b*; Edwards, Jones & Kirby, 1986; Allen & Kirby, 1984; Briggs, Glenn, Jones, Kirby & Ramaswamy, 1984; Jones & Kirby, 1984) a large number of organic compounds containing C—O single bonds were investigated to derive crystal structure–reactivity correlations in acetals and glucosides. In general the length of the bond R_1—OR_2 increases with increasing $+I$ and $+M$ effects of the group R_1, and with increasing electron withdrawal by the group OR_2. The lengths of the C—O bonds vary over a range of more than 0·1 Å (Allen & Kirby, 1984). We report here the crystal structure determination of the title compound (see Fig. 1).

Experimental. Crystal size 0·6 × 0·5 × 0·4 mm. Intensity data were collected on a Stoe–Siemens four-circle diffractometer with monochromated Mo *Kα* radiation using the profile-fitting mode involving variable scan width and speed (Clegg, 1981). 2173 reflections were measured with $2\theta_{\max}$ 50°, $+h+k+l$ and three check reflections with no significant intensity change. 2173 unique reflections were recorded, of which 1592 with $F > 4\sigma(F)$ were used for all calculations (*SHELXS*86, Sheldrick, 1985; *SHELX*76, Sheldrick, 1976). Cell constants were refined from $\pm 2\theta$ values of 44 reflec-

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tions in the range 20–25°. Absorption correction was not necessary. The structure was solved by direct methods and refined on F to $R = 0{\cdot}055$, $wR = 0{\cdot}060$ with all non-H atoms anisotropic. H atoms were included using a riding model [C—H 0·96 Å, U(H) = 0·08 Å^2, except for methyl protons U(H) = 0·12 Å^2]. We refined 262 parameters ($S = 1{\cdot}66$) with the weighting scheme $w^{-1} = \sigma^2(F) + 0{\cdot}0005F^2$ which led to a featureless analysis of variance in terms of $\sin\theta$ and F_o, max. $\Delta/\sigma = 0{\cdot}003$, max. and min. height in final $\Delta\rho$ synthesis 0·21 and −0·24 e Å^{-3} respectively. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974). Final atomic parameters are given in Table 1 and bond lengths and angles in Table 2.*

Discussion. The title compound fits in well with the bond length trends in previously investigated β-D-glucosides (Briggs *et al.*, 1984; Lindberg, 1976). They showed that the endocyclic C(1)—O bond varies from 1·426 (7) Å (for the peracetylated glucoside) to 1·431 (5) Å (for the methyl glucoside) [*cf.* 1·426 (4) Å here] whereas the exocyclic C(1)—O(1) bond varies from 1·408 (8) to 1·385 (5) Å [*cf.* 1·381 (5) Å here]. The corresponding O—C(1)—O(1) bond angle varies from 105·8 to 107·3° [*cf.* 107·5 (3)° here] and the C(1)—O(1)—C(1′) bond angle from 117·5 to 112·6° [*cf.* 115·0 (3)°]. The exocyclic C(1′)—O(1*A*) bond in the current structure [1·390 (6) Å] is comparable to the exocyclic C(1)—O(1) bond [1·381 (5) Å] and significantly shorter than the third exocyclic acetal bond C(1′)—O(1) [1·442 (6) Å], revealing an alternating

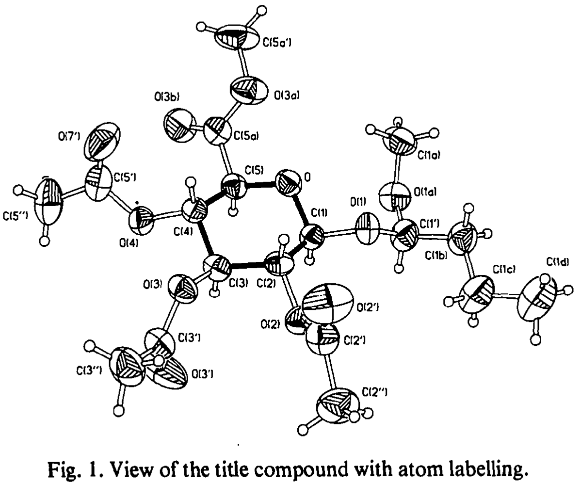

Fig. 1. View of the title compound with atom labelling.

Table 1. *Atomic coordinates* (× 10^4) *and equivalent isotropic displacement parameters* (Å^2 × 10^3)

	x	y	z	U_{eq}*
O	8343 (3)	2837 (2)	11 (1)	45 (1)
C(1)	7906 (5)	1963 (3)	391 (2)	40 (1)
O(1)	8596 (3)	1168 (2)	52 (1)	45 (1)
C(2)	8558 (5)	2057 (3)	1142 (2)	39 (1)
O(2)	8061 (3)	1216 (2)	1554 (1)	47 (1)
C(3)	7915 (6)	2973 (3)	1503 (2)	42 (1)
O(3)	8649 (4)	3080 (2)	2185 (1)	46 (1)
C(4)	8223 (5)	3893 (3)	1055 (2)	40 (1)
O(4)	7375 (4)	4685 (2)	1381 (2)	47 (1)
C(5)	7641 (5)	3705 (3)	292 (2)	40 (1)
C(5*A*)	7943 (6)	4570 (3)	−213 (2)	50 (2)
C(5′)	8140 (7)	5570 (3)	1442 (3)	59 (2)
O(7′)	9407 (5)	5707 (3)	1246 (3)	91 (2)
C(5″)	7074 (8)	6303 (4)	1810 (3)	86 (2)
C(2′)	9150 (7)	631 (4)	1855 (3)	57 (2)
O(2′)	10502 (5)	747 (3)	1774 (2)	88 (2)
C(2″)	8384 (8)	−145 (4)	2311 (3)	78 (2)
C(5*A*′)	9390 (8)	5134 (4)	−1203 (3)	91 (2)
C(3′)	7785 (7)	2939 (4)	2776 (3)	58 (2)
O(3′)	6419 (5)	2810 (4)	2763 (2)	96 (2)
C(3″)	8745 (8)	2965 (4)	3438 (2)	72 (2)
C(1′)	7616 (7)	651 (4)	−452 (2)	56 (2)
O(1*A*)	7188 (4)	1258 (3)	−1021 (2)	57 (1)
C(1*A*)	8411 (7)	1659 (5)	−1440 (3)	70 (2)
C(1*B*)	8424 (7)	−297 (3)	−628 (3)	60 (2)
C(1*C*)	8341 (9)	−1044 (4)	−26 (3)	81 (2)
C(1*D*)	9241 (11)	−1981 (4)	−154 (4)	103 (3)
O(3*A*)	9079 (5)	4367 (3)	−675 (2)	69 (1)
O(3*B*)	7267 (6)	5330 (3)	−182 (2)	80 (2)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 2. *Bond lengths* (Å) *and angles* (°)

O—C(1)	1·426 (4)	O—C(5)	1·420 (5)
C(1)—O(1)	1·381 (5)	C(1)—C(2)	1·515 (5)
O(1)—C(1′)	1·442 (6)	C(2)—O(2)	1·436 (5)
C(2)—C(3)	1·512 (6)	O(2)—C(2′)	1·348 (6)
C(3)—O(3)	1·428 (5)	C(3)—C(4)	1·520 (6)
O(3)—C(3′)	1·344 (6)	C(4)—O(4)	1·430 (5)
C(4)—C(5)	1·531 (6)	O(4)—C(5′)	1·368 (6)
C(5)—C(5*A*)	1·523 (6)	C(5*A*)—O(3*A*)	1·333 (6)
C(5*A*)—O(3*B*)	1·180 (6)	C(5′)—O(7′)	1·165 (7)
C(5′)—C(5″)	1·513 (8)	C(2′)—O(2′)	1·183 (7)
C(2′)—C(2″)	1·502 (8)	C(5*A*′)—O(3*A*)	1·455 (7)
C(3′)—O(3′)	1·188 (7)	C(3′)—C(3″)	1·487 (7)
C(1′)—O(1*A*)	1·390 (6)	C(1′)—C(1*B*)	1·494 (7)
O(1*A*)—C(1*A*)	1·419 (7)	C(1*B*)—C(1*C*)	1·511 (7)
C(1*C*)—C(1*D*)	1·502 (9)		

C(1)—O—C(5)	112·7 (3)	O—C(1)—O(1)	107·5 (3)
O—C(1)—C(2)	107·0 (3)	O(1)—C(1)—C(2)	109·2 (3)
C(1)—O(1)—C(1′)	115·0 (3)	C(1)—C(2)—O(2)	108·6 (3)
C(1)—C(2)—C(3)	110·2 (3)	O(2)—C(2)—C(3)	107·4 (3)
C(2)—O(2)—C(2′)	118·6 (4)	C(2)—C(3)—O(3)	108·6 (3)
C(2)—C(3)—C(4)	111·1 (3)	O(3)—C(3)—C(4)	109·2 (3)
C(3)—O(3)—C(3′)	118·2 (4)	C(3)—C(4)—O(4)	106·8 (3)
C(3)—C(4)—C(5)	108·6 (3)	O(4)—C(4)—C(5)	110·6 (3)
C(4)—O(4)—C(5′)	116·3 (4)	O—C(5)—C(4)	110·0 (3)
O—C(5)—C(5*A*)	109·4 (3)	C(4)—C(5)—C(5*A*)	113·1 (3)
C(5)—C(5*A*)—O(3*A*)	111·6 (4)	C(5)—C(5*A*)—O(3*B*)	123·6 (4)
O(3*A*)—C(5*A*)—O(3*B*)	124·8 (5)	O(4)—C(5′)—O(7′)	124·3 (5)
O(4)—C(5′)—C(5″)	108·5 (4)	O(7′)—C(5′)—C(5″)	127·2 (5)
O(2)—C(2′)—O(2′)	123·5 (5)	O(2)—C(2′)—C(2″)	109·9 (5)
O(2′)—C(2′)—C(2″)	126·6 (5)	O(3)—C(3′)—O(3′)	123·4 (5)
O(3)—C(3′)—C(3″)	111·8 (5)	O(3′)—C(3′)—C(3″)	124·8 (5)
O(1)—(1′)—O(1*A*)	111·6 (4)	O(1)—C(1′)—C(1*B*)	106·6 (4)
O(1*A*)—C(1′)—C(1*B*)	117·4 (4)	C(1′)—O(1*A*)—C(1*A*)	116·7 (4)
C(1′)—C(1*B*)—C(1*C*)	112·7 (4)	C(1*B*)—C(1*C*)—C(1*D*)	114·8 (5)
C(5*A*)—O(3*A*)—C(5*A*′)	115·3 (4)		

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* Lists of structure factors, anisotropic thermal parameters, torsion angles and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51250 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

pattern of shortened and lengthened ether bonds. As is evident from Fig. 1, the pyranose ring adopts the expected $^4C_1$ conformation. The ring torsion angles, from 52 to 65° (Table 6 of the deposited data) lie within the range for strain-free pyranose rings (Jeffrey, 1973).

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Study of Short Hydrogen Bonds. II.[*] Structure of Piperidinium Hydrogen Bis(*p*-bromobenzoate)

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Abstract. $C_5H_{12}N^+.C_{14}H_9Br_2O_4^-$, $M_r = 487{\cdot}19$, triclinic, $P\bar{1}$, $a = 12{\cdot}264\ (3)$, $b = 12{\cdot}252\ (3)$, $c = 7{\cdot}367\ (1)$ Å, $\alpha = 106{\cdot}78\ (2)$, $\beta = 93{\cdot}71\ (2)$, $\gamma = 67{\cdot}67\ (2)°$, $V = 979{\cdot}1\ (4)$ Å^3, $Z = 2$, $D_x = 1{\cdot}653$ Mg m^{-3}, $\lambda(\mathrm{Cu}\ K\alpha) = 1{\cdot}5418$ Å, $\mu = 5{\cdot}5$ mm^{-1}, $F(000) = 488$, $T = 291$ K, final $R = 0{\cdot}048$ for 3112 unique reflections. In the crystal there are two kinds of hydrogen bis(*p*-bromobenzoate) anions having $\bar{1}$ symmetry. Two benzoate residues in each are linked by short O···H···O hydrogen bonds with O···O 2·451 (6) and 2·460 (8) Å, respectively. The KKM effect was clearly observed in the former hydrogen bond. The center of gravity of the piperidinium cation lies nearly on $(\frac{1}{4},0,\frac{1}{2})$. The cations and anions related by a pseudo glide plane parallel to $(01\bar{2})$ are linked by two kinds of N—H···O hydrogen bonds to form a ribbon along **a**.

Introduction. In the present work the structure of the title compound has been determined in order to see the effect of the *p*-bromo substituent on the mode of the hydrogen bonds and the crystal structure compared with piperidinium hydrogen bis(*p*-methylbenzoate) (Misaki, Kashino & Haisa, 1986).

Experimental. The compound was prepared by a procedure reported previously (Kashino, Kanei & Hasegawa, 1972). Crystals grown by slow evaporation from benzene solution were plates developed along {010}. Twinned crystals grew frequently as hexagonal prisms elongated along an axis corresponding to the *a* axis of the single crystal. A specimen, 0·20 × 0·18 × 0·23 mm, was cut from a large single crystal. Lattice parameters were determined with 20 reflections in the range $16 < 2\theta < 39°$. The intensities were collected on a Rigaku AFC-5 four-circle diffractometer equipped with a rotating anode using Ni-filtered Cu $K\alpha$ ($\lambda = 1{\cdot}5418$ Å) with ω–2θ scan method (scan speed 6° min^{-1} in ω, scan range $1{\cdot}2° + 0{\cdot}15°\tan\theta$ in ω, $2\theta_{\max} = 125°$). Background was measured for 4 s on either side of peak. Three standard reflections were recorded after every 57 reflections; their fluctuation was within 2·5% in F. Lorentz and polarization corrections were applied, but no absorption correction. Number of unique reflections 3112, of which 3019 were $> 1{\cdot}0\sigma(F_o)$; $R_{\rm int} = 0{\cdot}014$ for 165 $h0l$ reflections. All the unique reflections (ranging over $h = -14$ to 14, $k = 0$ to 14, $l = -8$ to 8) were used for the refinement. The structure was solved by the Patterson heavy-atom method, and refined by full-matrix least squares. The non-H atoms were refined anisotropically and the H atoms iso-

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[*] Part I: Misaki, Kashino & Haisa (1986).

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