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Structure of an α-Methylene-γ-lactone Sugar Derivative

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Abstract. 3-*O*-Benzyl-6,7-dideoxy-1,2-*O*-isopropylidene-7-*C*-methylene-β-D-*ido*-octofuranurono-8,5-lactone, $C_{19}H_{22}O_6$, $M_r = 346.4$, $[\alpha]_D^{25°C} = -46.2°$, orthorhombic, $P2_12_12_1$, $a = 11.1786\ (9)$, $b = 12.471\ (1)$, $c = 13.158\ (1)$ Å, $V = 1834.4\ (3)$ Å^3, $Z = 4$, $D_x = 1.254$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 0.87$ cm^{-1}, $F(000) = 736$, room temperature, $R = 0.054$, $wR = 0.065$ for 1832 unique observed reflections with $F_o \geq 3\sigma F_o$. The absolute configuration of the title compound was assigned by ^{1}H NMR spectroscopy. The furanoid ring adopts a C(4)-*exo* envelope conformation (E_4) with a pseudorotation phase angle P of 48.7°. Atom C(4) deviates 0.557 (3) Å from the plane defined by the other four atoms in the ring. The dihedral angle between the planes defined by atoms C(1), C(2), C(3), O(4) and C(1), C(2), O(1), O(2) is 116.4 (2)°. The isopropylidene ring has an unsymmetrical twist conformation with a major O(2)-*exo* and minor C(6)-*endo* puckered $^2T_6$ conformation. Atoms O(2) and C(6) deviate 0.199 (3) and 0.069 (5) Å from the plane defined by the other three atoms in the ring. The benzyloxy side chain is linked axially at C(3) to the furanoid ring with a *gauche–trans–gauche* conformation. The side chain has an *anti* orientation relative to the isopropylidene ring.

Experimental. Synthesis of the title compound was accomplished by the Reformatsky reaction of 3-*O*-benzyl-1,2-*O*-isopropylidene-α-D-*xylo*-pentodialdo-1,4-furanose with ethyl bromomethylacrylic ester and zinc (Rauter, Figueiredo, Ismael, Pais, Gonzalez, Diaz & Barrera, 1987). The compound was purified by column chromatography with silica gel (230–400 mesh) using ethyl acetate/toluene (1:5) as eluent, and recrystallized from benzene. Parallelepipedic-shaped crystal of dimensions 0.8 × 0.7 × 0.4 mm. Unit-cell parameters refined from 25 centred reflections in the range $10.1 \leq \theta \leq 20.3°$. Enraf–Nonius CAD-4 diffractometer, graphite-monochromated Mo $K\alpha$ radiation. 3036 independent *hkl* intensities measured using the $\omega/2\theta$ scan mode, with $1.5 \leq \theta \leq 30°$, for one octant of the reflection sphere, h from 0 to 15, k from 0 to 17, l from 0 to 18. Three standard reflections $3\bar{3}5$, 424 and $50\bar{3}$ monitored every 100 reflections and their intensities showed no decay during data collection. Data corrected for Lorentz and polarization effects but not for absorption. 1834 reflections with $F_o \geq 3\sigma F_o$ used in the solution and refinement of the structure. Structure solved by direct methods with *SHELXS*86 (Sheldrick, 1985) from 588 reflections phased with $E \geq 1.2$. Least-squares refinements (on F) made with *SHELX*76 (Sheldrick, 1976). Refinement with isotropic temperature factors for all non-hydrogen atoms gave $R = 0.127$. Anisotropic refinement reduced R to 0.094. Hydrogen atoms located from difference Fourier maps and refined isotropically with global temperature factors. Two strong reflections, 110 and 022, with high $|F_o - F_c|$ differences, possibly affected by extinction, removed from the data set. Weighting scheme $w = K/[\sigma^2(F_o) + |g|F_o^2]$ refined to $K = 1.8712$ and $g = 0.001437$. Final refinements converged at $R = 0.054$ and $wR = 0.065$ in final cycle of refinement, maximum shift/e.s.d. = 0.067 on refined coordinates. Final difference Fourier maps showed a maximum value of 0.19 and a minimum value of -0.24 e Å^{-3} for electron density. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV). Illustrations drawn with *ORTEP* (Johnson, 1976). Fig. 1 shows the structure of the molecule with the numbering scheme and Fig. 2 a stereoview of the unit-cell contents. Table 1 gives final atomic parameters.* Table 2 gives bond lengths, angles and

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54366 (7 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Fractional atomic coordinates* ($\times 10^4$) *and equivalent isotropic temperature factors,* U_{eq} ($Å^2 \times 10^3$), *with e.s.d.'s in parentheses*

$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i . \mathbf{a}_j$.

	x	y	z	U_{eq}
C(1)	881 (4)	734 (3)	3282 (3)	51 (1)
C(2)	1788 (4)	566 (4)	2425 (3)	54 (1)
C(3)	2729 (3)	−175 (3)	2883 (3)	44 (1)
C(4)	1994 (3)	−749 (3)	3694 (3)	39 (1)
C(5)	2738 (3)	−1231 (3)	4538 (3)	45 (1)
C(6)	−113 (4)	110 (4)	1850 (3)	65 (2)
C(7)	−679 (8)	−974 (8)	1717 (8)	124 (3)
C(8)	−637 (6)	967 (8)	1196 (6)	116 (3)
C(9)	3540 (4)	−2131 (3)	4182 (3)	52 (1)
C(10)	3336 (3)	−2995 (3)	4948 (3)	49 (1)
C(11)	2292 (3)	−2688 (3)	5571 (3)	47 (1)
C(12)	3928 (5)	−3891 (4)	5094 (5)	76 (2)
C(13)	4608 (4)	680 (4)	2727 (3)	64 (2)
C(14)	5440 (4)	1417 (3)	3295 (3)	52 (1)
C(15)	6606 (4)	1137 (4)	3490 (4)	68 (1)
C(16)	7353 (5)	1826 (5)	4002 (5)	83 (2)
C(17)	6941 (5)	2793 (4)	4338 (4)	73 (2)
C(18)	5797 (5)	3078 (4)	4159 (4)	68 (2)
C(19)	5058 (5)	2406 (4)	3627 (4)	66 (1)
O(1)	−222 (3)	411 (3)	2882 (2)	73 (1)
O(2)	1143 (3)	13 (3)	1666 (2)	69 (1)
O(3)	3636 (2)	414 (2)	3376 (2)	53 (1)
O(4)	1231 (2)	68 (2)	4092 (2)	49 (1)
O(5)	1913 (2)	−1706 (2)	5281 (2)	50 (1)
O(6)	1805 (3)	−3161 (2)	6241 (2)	68 (1)

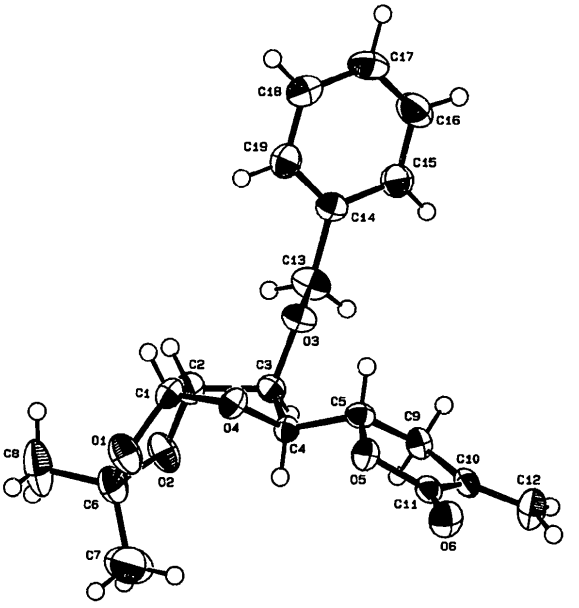

Fig. 1. The molecular structure of the title compound. 30% thermal ellipsoids are shown for non-hydrogen atoms.

selected endocyclic torsion angles for non-hydrogen atoms.

Related literature. Bond lengths and angles in the two fused rings are in agreement with those found in the other molecules with a similar central system (Giannousis, Hofmeister, McLaren & Nolan, 1987; Kashino, Inokawa, Haisa, Yasuoka & Kakudo, 1981; Sheldrick, Makie & Akrigg, 1988; Holzapfel, Kruger, van Dyk & Drijver, 1987).

Table 2. *Bond lengths* (Å), *bond angles* (°) *and selected endocyclic torsion angles* (°), *with e.s.d.'s in parentheses*

C(2)—C(1)	1.530 (8)	C(3)—C(2)	1.524 (7)
C(4)—C(3)	1.525 (7)	C(5)—C(4)	1.512 (7)
C(9)—C(5)	1.512 (8)	C(7)—C(6)	1.502 (12)
O(1)—C(1)	1.400 (6)	O(2)—C(2)	1.412 (6)
O(3)—C(3)	1.410 (5)	O(4)—C(1)	1.407 (5)
O(4)—C(4)	1.429 (5)	O(5)—C(5)	1.469 (5)
C(6)—O(1)	1.414 (6)	C(6)—O(2)	1.429 (6)
C(8)—C(6)	1.492 (9)	C(13)—O(3)	1.421 (6)
O(5)—C(11)	1.351 (5)	O(6)—C(11)	1.191 (6)
C(10)—C(9)	1.492 (7)	C(11)—C(10)	1.477 (7)
C(12)—C(10)	1.314 (7)	C(14)—C(13)	1.507 (8)
C(15)—C(14)	1.373 (7)	C(19)—C(14)	1.376 (7)
C(16)—C(15)	1.374 (8)	C(17)—C(16)	1.365 (9)
C(18)—C(17)	1.349 (8)	C(19)—C(18)	1.370 (8)

O(1)—C(1)—C(2)	105.5 (4)	O(4)—C(1)—C(2)	107.0 (4)
O(4)—C(1)—O(1)	111.1 (4)	C(3)—C(2)—C(1)	104.5 (4)
O(2)—C(2)—C(1)	104.5 (4)	O(2)—C(2)—C(3)	109.6 (4)
C(4)—C(3)—C(2)	100.9 (4)	O(3)—C(3)—C(2)	111.3 (4)
O(3)—C(3)—C(4)	108.1 (4)	O(4)—C(4)—C(3)	104.1 (4)
C(5)—C(4)—C(3)	113.8 (4)	C(5)—C(4)—O(4)	110.0 (4)
C(6)—O(1)—C(1)	111.2 (4)	C(6)—O(2)—C(2)	109.9 (4)
C(13)—O(3)—C(3)	113.2 (4)	C(4)—O(4)—C(1)	108.0 (3)
C(9)—C(5)—C(4)	113.2 (4)	O(5)—C(5)—C(4)	107.7 (4)
O(5)—C(5)—C(9)	106.2 (4)	O(2)—C(6)—O(1)	105.7 (4)
C(7)—C(6)—O(1)	108.2 (6)	C(7)—C(6)—O(2)	108.5 (6)
C(8)—C(6)—O(1)	109.3 (6)	C(8)—C(6)—O(2)	110.4 (5)
C(8)—C(6)—C(7)	114.3 (7)	C(10)—C(9)—C(5)	103.6 (4)
C(11)—C(10)—C(9)	108.0 (4)	C(12)—C(10)—C(9)	129.5 (5)
C(12)—C(10)—C(11)	122.5 (5)	O(5)—C(11)—C(10)	109.0 (4)
O(6)—C(11)—C(10)	130.1 (4)	O(6)—C(11)—O(5)	121.0 (5)
C(11)—O(5)—C(5)	110.9 (4)	C(14)—C(13)—O(3)	108.4 (4)
C(15)—C(14)—C(13)	121.6 (5)	C(19)—C(14)—C(13)	120.8 (5)
C(19)—C(14)—C(15)	117.6 (5)	C(16)—C(15)—C(14)	120.6 (6)
C(17)—C(16)—C(15)	120.4 (6)	C(18)—C(17)—C(16)	119.7 (6)
C(19)—C(18)—C(17)	120.0 (6)	C(18)—C(19)—C(14)	121.6 (6)

Furanoid ring

C(2)—C(1)—O(4)—C(4)	−20.1 (4)
O(4)—C(1)—C(2)—C(3)	−5.1 (4)
C(1)—C(2)—C(3)—C(4)	26.0 (4)
C(2)—C(3)—C(4)—O(4)	−38.5 (3)
C(3)—C(4)—O(4)—C(1)	37.5 (3)

Isopropylidene ring

C(2)—C(1)—O(1)—C(6)	−3.0 (4)
O(1)—C(1)—C(2)—O(2)	−8.4 (4)
C(1)—C(2)—O(2)—C(6)	16.8 (4)
C(2)—O(2)—C(6)—O(1)	−18.9 (4)
C(1)—O(1)—C(6)—O(2)	13.2 (4)

Exocyclic torsion angles

C(2)—C(3)—O(3)—C(13)	−90.4 (4)	C(3)—O(3)—C(13)—C(14)	173.2 (3)
O(3)—C(13)—C(14)—C(19)	−62.1 (5)	O(2)—C(2)—C(3)—O(3)	160.0 (3)

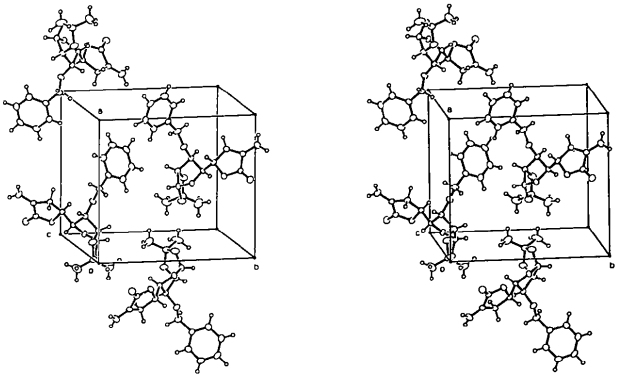

Fig. 2. Stereoscopic view of the crystal structure, with **b** horizontal and **a** vertical.

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References

GIANNOUSIS, P. P., HOFMEISTER, G. E., MCLAREN, K. L. & NOLAN, M. C. (1987). *Acta Cryst.* C**43**, 2104–2106.
HOLZAPFEL, C. W., KRUGER, G. J., VAN DYK, M. S. & DRIJVER, L. D. (1987). *Acta Cryst.* C**43**, 372–374.
JOHNSON, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
KASHINO, S., INOKAWA, S., HAISA, M., YASUOKA, N. & KAKUDO, M. (1981). *Acta Cryst.* B**37**, 1572–1575.
RAUTER, A. P., FIGUEIREDO, J. A., ISMAEL, I., PAIS, M. S., GONZALEZ, A. G., DIAZ, J. & BARRERA, J. B. (1987). *J. Carbohydr. Chem.* **6**(2), 259–272.
SHELDRICK, B., MAKIE, W. & AKRIGG, D. (1988). *Acta Cryst.* C**44**, 1687–1688.
SHELDRICK, G. M. (1976). *SHELX*76. Program for crystal structure determination. Univ. of Cambridge, England.
SHELDRICK, G. M. (1985). *SHELXS*86. *Crystallographic Computing* 3, edited by G. M. SHELDRICK, C. KRUGER & R. GODDARD, pp. 175–189. Oxford Univ. Press.

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Structure of 1-(4-Nitrophenyl)pyrrole, -imidazole, -pyrazole and -1,2,4-triazole Derivatives

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Abstract. Structures of seven related compounds were determined to assess the nonlinear optical properties of the crystals. Mo $K\alpha$, $\lambda = 0.71073$ Å. 2-Methyl-1-(4-nitrophenyl)imidazole (I), $C_{10}H_9N_3O_2$, $M_r = 203.2$, monoclinic, $P2_1/c$, $a = 17.513$ (3), $b = 7.405$ (1), $c = 16.819$ (3) Å, $\beta = 118.25$ (1)°, $V = 1921.4$ (6) Å^3, $Z = 8$, $D_x = 1.40$ Mg m^{-3}, Mo $K\alpha$, $\mu = 0.095$ mm^{-1}, $F(000) = 848$, $T = 300$ (1) K, $R = 0.049$ for 2172 reflections. 2,4-Dimethyl-1-(4-nitrophenyl)imidazole (II), $C_{11}H_{11}N_3O_2$, $M_r = 217.2$, orthorhombic, $P2_1ab$, $a = 11.808$ (3), $b = 22.132$ (7), $c = 3.999$ (1) Å, $V = 1045.1$ (5) Å^3, $Z = 4$, $D_x = 1.38$ Mg m^{-3}, Mo $K\alpha$, $\mu = 0.092$ mm^{-1}, $F(000) = 456$, $T = 297$ (1) K, $R = 0.064$ for 723 reflections. 2-Ethyl-1-(4-nitrophenyl)imidazole (III), $C_{11}H_{11}N_3O_2$, $M_r = 217.2$, orthorhombic, $Pca2_1$, $a = 24.159$ (5), $b = 4.033$ (1), $c = 10.658$ (2) Å, $V = 1038.4$ (4) Å^3, $Z = 4$, $D_m = 1.38$ (1), $D_x = 1.39$ Mg m^{-3}, $\mu = 0.093$ mm^{-1}, $F(000) = 456$, $T = 300$ (1) K, $R = 0.043$ for 926 reflections. 1-(4-Nitrophenyl)-2-phenylimidazole (IV), $C_{15}H_{11}N_3O_2$, $M_r = 265.3$, triclinic, $P\bar{1}$, $a = 9.350$ (2), $b = 11.893$ (3), $c = 12.658$ (3) Å, $\alpha = 103.73$ (2), $\beta = 103.68$ (2), $\gamma = 97.05$ (2)°, $V = 1304.6$ (6) Å^3, $Z = 4$, $D_x = 1.35$ Mg m^{-3}, Mo $K\alpha$, $\mu = 0.087$ mm^{-1}, $F(000) = 552$, $T = 297$ (1) K, $R = 0.043$ for 1804 reflections. 1-(4-Nitrophenyl)pyrazole (V), $C_9H_7N_3O_2$, $M_r = 189.2$, monoclinic, $P2_1/n$, $a = 11.519$ (2), $b = 10.342$ (2), $c = 7.077$ (1) Å, $\beta = 93.68$ (1)°, $V = 841.3$ (2) Å^3, $Z = 4$, $D_m = 1.49$ (1), $D_x = 1.49$ Mg m^{-3}, Mo $K\alpha$, $\mu = 0.103$ mm^{-1}, $F(000) = 392$, $T = 299$ (1) K, $R = 0.045$ for 1188 reflections. 3,5-Dichloro-1-(4-nitrophenyl)-1,2,4-triazole (VI), $C_8H_4N_4O_2Cl_2$, $M_r = 259.1$, monoclinic, $P2_1$, $a = 11.282$ (4), $b = 11.902$ (5), $c = 3.753$ (1) Å, $\beta = 92.81$ (3)°, $V = 503.3$ (3) Å^3, $Z = 2$, $D_x =$

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