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2-Azido-(*R*)-3,5-*O*-benzylidene-2-deoxy-2-*C*-methyl-D-xylono-1,4-lactone [(2*S*,4a*R*,7*R*,7a*R*)-7-azido-7-methyl-2-phenyldihydro-4*H*-furo[3,2-*d*][1,3]dioxin-6(4a*H*)-one]

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The unknown relative configurations in the title compound, $C_{13}H_{13}N_3O_4$, of the acetal carbon and of the quaternary carbon bearing the azide were determined by X-ray crystallographic analysis; the absolute configuration was defined by the use of 2-*C*-methyl-D-lyxonolactone as a starting material. There are two molecules in the asymmetric unit ($Z' = 2$).

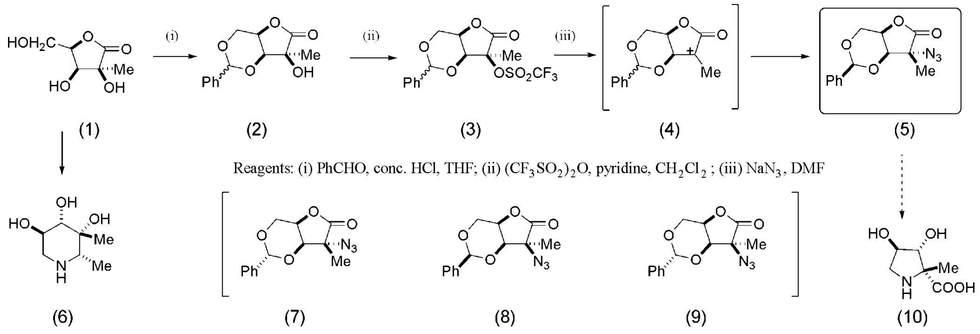
Key indicators

Single-crystal X-ray study
T = 150 K
Mean σ(C–C) = 0.005 Å
R factor = 0.044
wR factor = 0.119
Data-to-parameter ratio = 9.3

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

The isomerization of aldoses to 2-*C*-methyl aldonic acids (Hotchkiss *et al.*, 2006) has provided the first easily available carbohydrates with a branched carbon chain. Such branched carbohydrate scaffolds may be exploited in the synthesis of sugar mimics and of highly functionalized heterocycles; thus 2-*C*-methyl-D-lyxono-1,4-lactone, (1) (Punzo *et al.*, 2006), obtained by isomerization of D-galactose (Hotchkiss, Soengas *et al.*, 2007), may readily be converted to the complex piperidine (6) (Hotchkiss, Kato *et al.*, 2007). This paper reports that (1) may also be transformed into the azidolactone (5), an intermediate for the preparation of pyrrolidines containing a quaternary centre, such as the proline (10); the crystal structure removes the ambiguities of the configuration at two chiral centres.



Reagents: (i) PhCHO, conc. HCl, THF; (ii) $(CF_3SO_2)_2O$, pyridine, CH_2Cl_2 ; (iii) NaN_3, DMF

The carbon-branched lyxonolactone (1) on treatment with benzaldehyde and hydrochloric acid gave a benzylidene acetal (2) in which the stereochemistry at the acetal carbon was unknown. Subsequent triflation of the tertiary alcohol at C2 in (2), followed by reaction with sodium azide in DMF, resulted in the formation of an azide in good yield (Fleet & Hotchkiss, 2007). Since the nucleophilic displacement most likely proceeded *via* an S_N1 pathway, the carbocation (4) could potentially be attacked from either face, giving any of the diastereomers (5), (7), (8) or (9). The crystal structure determination shows unequivocally that the molecular structure of the product is (5) (Fig. 1), resolving the ambiguities at both the acetal and the quaternary carbon atoms; the absolute config-

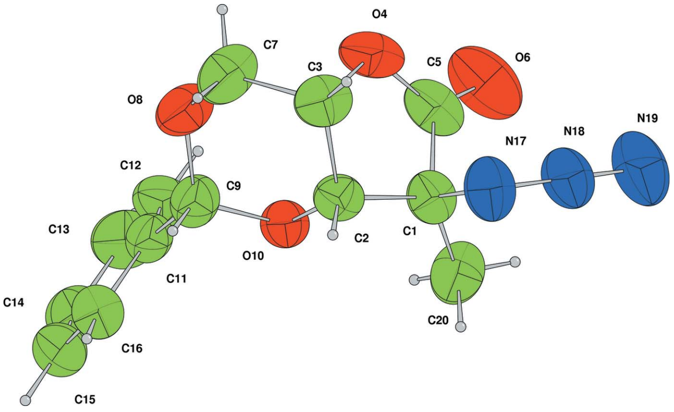


Figure 1
The molecular structure of one of the independent molecules of (5), with displacement ellipsoids drawn at the 50% probability level. H atoms are shown as spheres of arbitary radius.

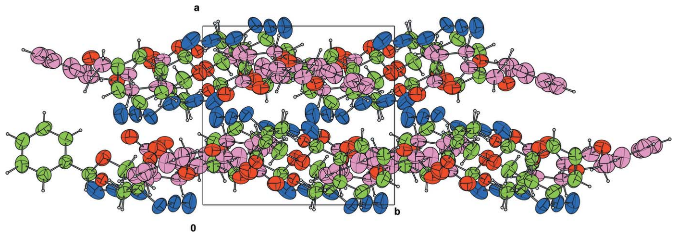


Figure 2
The packing of the title compound, projected along the *c* axis. The crystal adopts interlocking bilayers lying parallel to *b*.

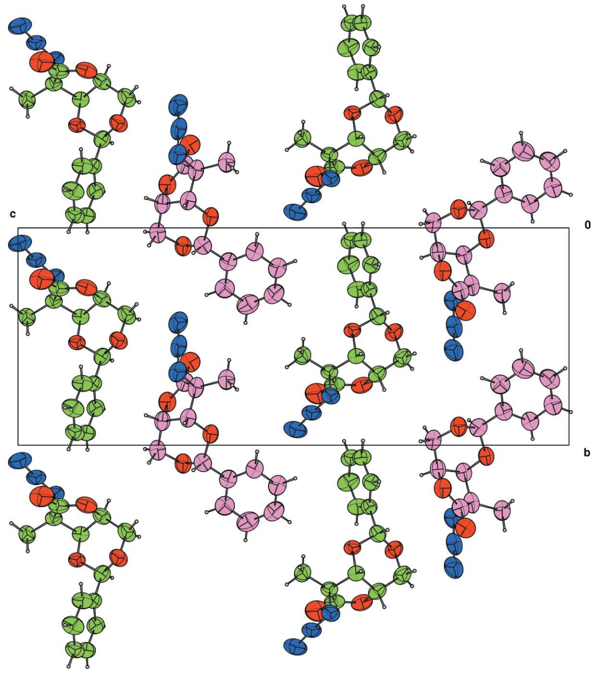


Figure 3
The packing of the title compound projected along the *a* axis. The sheets are made up of alternate rows of molecule 1 (green C atoms) and molecule 2 (pink C atoms).

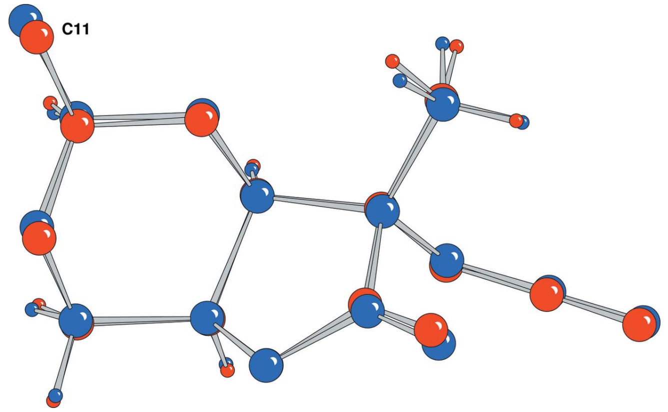


Figure 4
Overlay of the two molecules in the asymmetric unit, with the phenyl group omitted, where C11 is the quaternary aromatic carbon.

uration of the azide (5) was defined by the use of 2-*C*-methyl-D-lyxonolactone (1) as the starting material.

The crystal structure shows sheets of molecules with interlocking azide functionalities (Fig. 2). Each sheet consists of alternate rows of molecule 1 and molecule 2 (Fig. 3). The main difference between the two independent molecules is in the orientation of the phenyl groups [torsion angles O10—C9—C11—C12 = −70.983° and O110—C109—C111—C116 = −167.451°]. The main residues are very similar (Fig. 4). After least-squares fitting of the residues against each other, the r.m.s. positional discrepancy is 0.156 Å, the r.m.s. bond-length discrepancy is 0.018Å, and the r.m.s. torsion angle deviation is 6.02°. As is common with these materials (Chesterton *et al.*, 2006), the azide group is nonlinear [N17—N18—N19 = 173.1 (4)°; *Mogul* average (Bruno *et al.*, 2004) 172 (1)°] with the anisotropic atomic displacement parameter of the central atom lowered with respect to its neighbours.

Experimental

The branched azido-xylonolactone (5) was crystallized from a diethyl ether/petroleum ether mixture by slow evaporation until crystals appeared (m.p. 341–344 K); $[\alpha]_D^{22}$ +138.5 (*c*, 1.4 in acetone).

Crystal data

$C_{13}H_{13}N_3O_4$
$M_r = 275.26$
Orthorhombic, $P2_12_12_1$
$a = 9.7507$ (2) Å
$b = 10.4263$ (2) Å
$c = 26.4090$ (5) Å
$V = 2684.84$ (9) Å^3
$Z = 8$
Mo $K\alpha$ radiation
$\mu = 0.10$ mm^{-1}
$T = 150$ K
0.40 × 0.40 × 0.10 mm

Data collection

Nonius KappaCCD diffractometer
Absorption correction: multi-scan (*DENZO*/*SCALEPACK*; Otwinowski & Minor, 1997)
$T_{\min} = 0.69$, $T_{\max} = 0.99$
12730 measured reflections
3360 independent reflections
2414 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.055$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.044$
$wR(F^2) = 0.119$
$S = 0.87$
3360 reflections
362 parameters
H-atom parameters constrained
$\Delta\rho_{\max} = 0.21$ e Å^{-3}
$\Delta\rho_{\min} = -0.18$ e Å^{-3}

Acta Cryst. (2007). E**63**, o2168–o2170 Hotchkiss *et al.* • $C_{13}H_{13}N_3O_4$ **o2169**

In the absence of significant anomalous scattering, Friedel pairs were merged and the absolute configuration was assigned from the starting material.

The relatively large ratio of minimum to maximum corrections applied in the multi-scan process (1:1.45) reflects changes in the illuminated volume of the crystal. These were kept to a minimum, and were taken into account (Görbitz, 1999) by the multi-scan inter-frame scaling (*DENZO*/*SCALEPACK*; Otwinowski & Minor, 1997).

The H atoms were all located in a difference map, but those attached to C atoms were repositioned geometrically. The H atoms were initially refined with soft restraints on the bond lengths and angles to regularize their geometry (C—H = 0.93–0.98 Å and O—H = 0.82 Å) and $U_{\rm iso}$(H) values (in the range 1.2–1.5$U_{\rm eq}$ of the parent atom), after which the positions were refined with riding constraints.

Data collection: *COLLECT* (Nonius, 2001); cell refinement: *DENZO*/*SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO*/*SCALEPACK*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *CRYSTALS* (Betteridge *et al.*, 2003); molecular graphics: *CAMERON* (Watkin *et al.*, 1996); software used to prepare material for publication: *CRYSTALS*.

References

Altomare, A., Cascarano, G., Giacovazzo, G., Guagliardi, A., Burla, M. C., Polidori, G. & Camalli, M. (1994). *J. Appl. Cryst.* **27**, 435.

Betteridge, P. W., Carruthers, J. R., Cooper, R. I., Prout, K. & Watkin, D. J. (2003). *J. Appl. Cryst.* **36**, 1487.

Bruno,I. J., Cole, J. C., Kessler, M., Luo, J., Motherwell, W. D. S., Purkis, L. H., Smith, B. R., Taylor, R., Cooper, R. I., Harris S. E. & Orpen, A. G. (2004). *J. Chem. Inf. Comput. Sci.* **44**, 2133–2144.

Chesterton, A. K. S., Jenkinson, S. F., Jones, N. A., Fleet, G. W. J. & Watkin, D. J. (2006). *Acta Cryst.* E**62**, o2983–o2985.

Fleet, G. W. J. & Hotchkiss, D. J. (2007). In preparation.

Görbitz, C. H. (1999). *Acta Cryst.* B**55**, 1090–1098.

Hotchkiss, D. J., Jenkinson, S. F., Storer, R., Heinz, T. & Fleet, G. W. J. (2006). *Tetrahedron Lett.* **47**, 315–318.

Hotchkiss, D. J., Kato, A., Odell, B., Claridge, T. D. W. & Fleet, G. W. J. (2007). *Tetrahedron Asymmetry* **18**. Accepted.

Hotchkiss, D. J., Soengas, R., Booth, K. V., Weymouth-Wilson, A. C., Eastwick-Field, V. & Fleet, G. W. J. (2007). *Tetrahedron Lett.* **48**, 517–520.

Nonius (2001). *COLLECT*. Nonius BV, Delft, The Netherlands.

Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.

Punzo, F., Watkin, D. J., Hotchkiss, D. & Fleet, G. W. J. (2006). *Acta Cryst.* E**62**, o98–o100.

Watkin, D. J., Prout, C. K. & Pearce, L. J. (1996). *CAMERON*. Chemical Crystallography Laboratory, Oxford, England.

o2170 Hotchkiss *et al.* • $C_{13}H_{13}N_3O_4$ *Acta Cryst.* (2007). E**63**, o2168–o2170