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2-*C*-Benzyloxymethyl-2,3:5,6-di-*O*-isopropylidene-D-allono-1,4-lactone

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The crystal structure of the title benzyl ether, $C_{20}H_{26}O_7$, establishes the stereochemistry of the major diacetonide product from the Kiliani reaction of D-psicose. There are two independent molecules in the cell related by a pseudo-twofold screw axis. There are no suitable donors for strong hydrogen bonds: the molecules are simply in van der Waals contact.

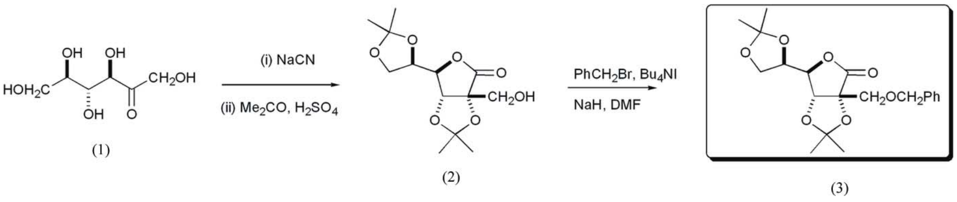
Key indicators

Single-crystal X-ray study
T = 190 K
Mean σ(C–C) = 0.004 Å
R factor = 0.049
wR factor = 0.097
Data-to-parameter ratio = 11.6

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

Comment

Almost all of the readily available carbohydrate building blocks have linear carbon chains (Bols, 1996; Lichtenthaler & Peters, 2004). However, the Kiliani reaction on ketohexoses provides branched sugar lactones bearing a hydroxymethyl substituent at C-2. Acetonation of the crude mixtures of the resulting lactones gives reasonable yields of crystalline diacetonides (Hotchkiss *et al.*, 2004) which are suitable chiral starting materials for the synthesis of branched sugar mimics (Simone *et al.*, 2005). Ambiguities in the structures of the acetonides arise from (i) the stereochemistry at the quaternary carbon and (ii) the ring size of the ketal protecting groups. The structures of diacetonides derived from three of the four diastereomeric ketohexoses [D-fructose (Cowley *et al.*, 2004; van Ameijde *et al.*, 2004), L-sorbose (Anderson *et al.*, 1977) and D-tagatose (Harding *et al.*, 2005; Shallard-Brown *et al.*, 2004)] have been firmly established by X-ray crystallographic analysis. The fourth diastereomeric ketohexose D-psicose (1) is available from equilibration of D-fructose by D-tagatose 3-epimerase (Granstrom *et al.*, 2004; Izumori, 2002; Takeshita *et al.*, 2000; Itoh & Izumori, 1996).



The sequential treatment of D-psicose (1) with sodium cyanide, followed by extraction of the crude lactones with acetone in the presence of sulfuric acid gave, as the major product (Soengas *et al.*, 2005), a diacetonide tentatively assigned as structure (2); although the *cis*-fused diacetonide (2) was easily crystallized, the crystals were not suitable for X-ray crystallographic analysis. However, reaction of (2) with benzyl bromide and sodium hydride in the presence of tetra-n-butylammonium iodide in dimethylformamide afforded the corresponding benzyl ether (3), which formed crystals for X-;ray suitable analysis. This paper reports the crystal structure of (3) (Fig. 1) which unequivocally establishes the stereochemistry of the major lactone product (2) from the Kiliani–acetonation sequence on D-psicose.

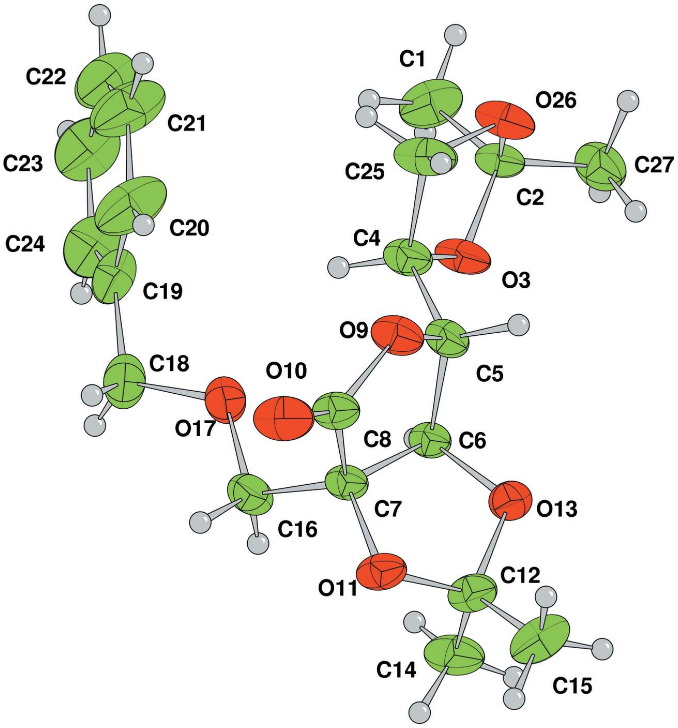


Figure 1
View of one of the two independent molecules in the asymmetric unit, with atomic displacement ellipsoids drawn at the 50% probability level. H-atom radii are arbitary.

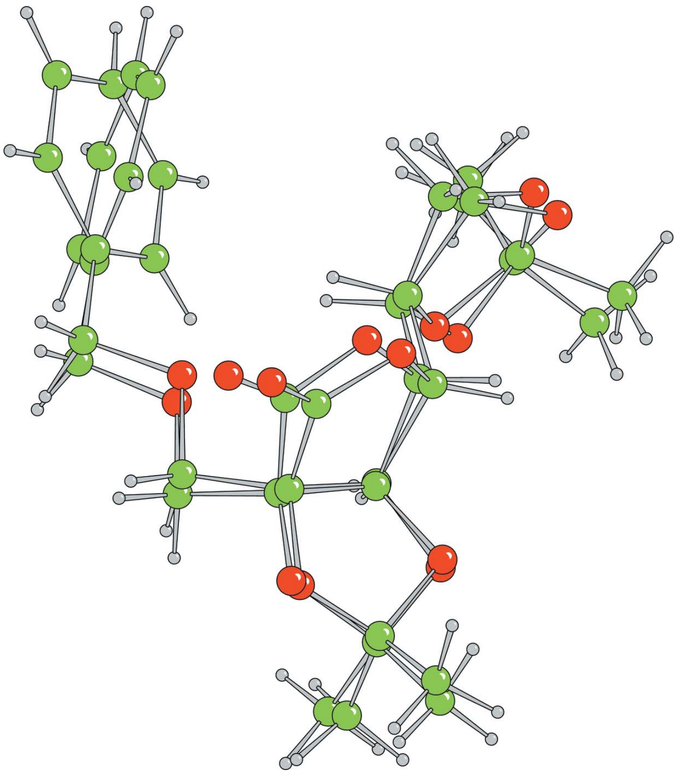


Figure 2
View of the two independent molecules superimposed to give the least-squares best fit between the atom coordinates.

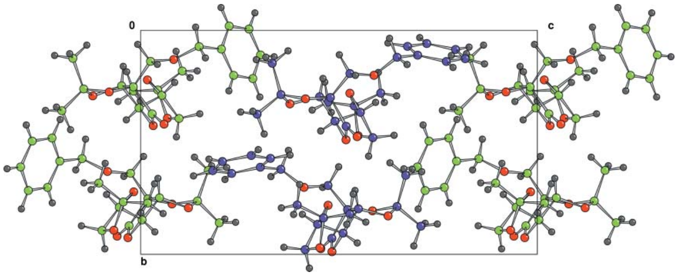


Figure 3
An *a* axis projection of the title compound. The C atoms in one of the independent molecules are coloured green, those in the other blue.

The crystals were in the form of large fragile prisms which crushed easily. A long sample was eventually selected and mounted on a nylon loop using perfluoropolyether oil so that the damaged end of the crystal was outside the X-ray beam. By mounting the crystal approximately parallel to the φ axis, the changes in illuminated volume were kept to a minimum, and were taken into account (Görbitz, 1999) by the multi-scan inter-frame scaling (*DENZO*/*SCALEPACK*, Otwinowski & Minor, 1997).

There are two independent molecules in the asymmetric unit related by a pseudo-twofold screw axis ($0.51 - x$, $0.46 + y$, $1.50 - z$). The molecules differ mainly in the orientation of the phenyl group (Fig. 2). The structure contains no hydrogen bonds and consists of layers loosely packed perpendicular to the *c* axis (Fig. 3). Alternate layers contain only molecules of one type.

Experimental

The benzyl ether (3) was crystallized from ethyl acetate–cyclohexane (m.p. 345–346 K); $[\alpha]^{\rm D}_{22} - 30.0$ (*c*, 1.06 in chloroform); $\nu_{\rm max}$ (NaCl): 1781 (–C═O) cm-1; ^{1}H NMR ($CDCl_3$): δ 1.27, 1.40, 1.46 [3 × *s*, 12 H, 2 × $-C(CH_3)_2$], 3.73 (*d*, 1H, $J_{2',2''}$ 9.0 Hz, H2′), 3.92–3.97 (*m*, 3H, H6, H6?, H4), 4.12–4.15 (*m*, 1 H, H5), 4.29 (*d*, 1H, $J_{2',2''}$ 9.0 Hz, H2″), 4.57 (*s*, 2H, $-OCH_2Ph$), 4.85 (*s*, 1H, H3); ^{13}C NMR ($CDCl_3$): δ 24.60, 26.07, 26.60, 26.63 [2 × $-C(CH_3)_2$], 66.47 (C2’), 69.34 (C6), 73.37 (C5), 73.99 ($-OCH_2Ph$), 80.05 (C3), 83.13 (C4), 83.70 (C2), 109.91, 113.33 [2 × $-C(CH_3)_2$], 127.76, 127.91, 128.29 (–CHAr), 136.70 (–CAr) 174.56 (C1); *m*/*z* (NH_3, ES+): 401 $(M + Na)^+$.

Crystal data

$C_{20}H_{26}O_7$
$M_r = 378.42$
Monoclinic, $P2_1$
$a = 10.3839$ (2) Å
$b = 10.4574$ (2) Å
$c = 19.0310$ (5) Å
$\beta = 103.8061$ (9)°
$V = 2006.84$ (8) Å^3
$Z = 4$
$D_x = 1.252$ Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 3433 reflections
$\theta = 1$–30°
$\mu = 0.09$ mm^{-1}
$T = 190$ K
Prism, colourless
1.20 × 0.75 × 0.45 mm

Data collection

Nonius Kappa CCD diffractometer
ω scans
Absorption correction: multi-scan (*DENZO*/*SCALEPACK*; Otwinowski & Minor, 1997)
$T_{\rm min} = 0.81$, $T_{\rm max} = 0.96$
11499 measured reflections
5664 independent reflections
5635 reflections with $I > -3\sigma(I)$
$R_{\rm int} = 0.027$
$\theta_{\rm max} = 30.1$°
$h = -14 \rightarrow 14$
$k = -7 \rightarrow 14$
$l = -26 \rightarrow 26$

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Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.049$
$wR(F^2) = 0.097$
$S = 0.95$
5635 reflections
487 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F^2) + (0.03P)^2 + 0.6P]$
where $P = [\max(F_o^2,0) + 2F_c^2]/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.23$ e Å^{-3}
$\Delta\rho_{\min} = -0.17$ e Å^{-3}

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 = 0.93–98 Å) and isotropic displacement parameters [$U_{\rm iso}({\rm H}) = 1.2$–$1.5U_{\rm eq}({\rm C})$], after which they were refined with riding constraints. In the absence of significant anomalous dispersion effects, Friedel pairs were averaged.

Data collection: *COLLECT* (Nonius, 2001); cell refinement: *DENZO*/*SCALEPACK*; data reduction: *DENZO*/*SCALEPACK* (Otwinowski & Minor, 1997); 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*.

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References

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

Ameijde, J. van, Cowley, A. R., Fleet, G. W. J., Nash, R. J, Simone, M. I. & Soengas, R. (2004). *Acta Cryst.* E**60**, o2140–o2141.

Anderson, R. A., Einstein, F. W. B., Hoge, R. & Slessor, K. N. (1977). *Acta Cryst.* B**33**, 2780–2783.

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

Bols, M. (1996). *Carbohydrate Building Blocks*. New York: John Wiley & Sons.

Cowley, A. R., Fleet, G. W. J., Simone, M. I. & Soengas, R. (2004). *Acta Cryst.* E**60**, o2142–o2143.

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

Granstrom, T. B., Takata, G., Tokuda, M. & Izumori, K. (2004). *J. Biosci. Bioeng.* **97**, 89–94.

Harding, C. C., Watkin, D. J., Cowley, A. R., Soengas, R., Skytte, U. P. & Fleet, G. W. J. (2005). *Acta Cryst.* E**61**, o250–o252.

Hotchkiss, D., Soengas, R., Simone, M. I., van Ameijde, J., Hunter, S., Cowley, A. R. & Fleet, G. W. J. (2004). *Tetrahedron Lett.* **45**, 9461–9464.

Itoh, H. & Izumori, K. (1996). *J. Ferment. Bioeng.* **81**, 351–353.

Izumori, K. (2002). *Naturwissenschaften,* **89**, 120–124.

Lichtenthaler, F. W. & Peters, S. (2004). *Compt. Rend. Chim.* **7**, 65–90.

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.

Shallard-Brown, H. A., Harding, C. C., Watkin, D. J., Soengas, R., Skytte, U. P. & Fleet G. W. J. (2004). *Acta Cryst.* E**60**, o2163–o2164.

Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.

Simone, M. I., Soengas, R., Newton, C. R., Watkin, D. J. & Fleet, G. W. J. (2005). *Tetrahedron Lett.* **46**, 5761–5765.

Soengas, R., Izumori, K., Simone, M. I., Watkin, D. J., Skytte, U. P., Soetaert, W. & Fleet, G. W. J. (2005). *Tetrahedron Lett.* **46**, 5755–5759.

Takeshita, K., Suga, A., Takada, G. & Izumori, K. (2000). *J. Biosci. Bioeng.* **90**, 453–455.

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

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