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3-*O*-*tert*-Butyldimethylsilyl-2,2′:5,6-di-*O*-isopropylidene-2-*C*-hydroxymethyl-D-1,4-gluconolactone

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The title compound, $C_{19}H_{34}O_7Si$, is derived from the minor component of a Kiliani reaction on D-fructose. Its crystal structure has been determined in order to confirm its structure and stereochemistry.

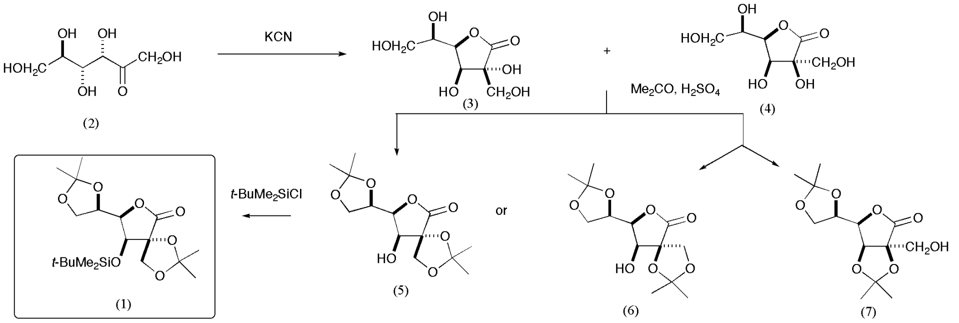
Key indicators

Single-crystal X-ray study
T = 150 K
Mean σ(C–C) = 0.003 Å
R factor = 0.037
wR factor = 0.040
Data-to-parameter ratio = 16.4

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

Comment

Carbohydrates provide the most diverse set of building blocks for the synthesis of enantiomerically pure compounds (Bols, 1996). At present, all these scaffolds have linear carbon chains and there are no accessible branched sugar chirons (Hanessian, 1983). Such materials, if readily and cheaply available, are likely to have many uses. In particular, they will provide efficient access to highly functionalized compounds containing non-linear carbon chains. While the carbon linear extension of an aldose with cyanide to provide a higher sugar (the Kiliani ascension) has long been developed as an industrial process (Hudson, 1945), the cyanohydrin reaction with ketoses is barely reported. The Kiliani reaction of cyanide with D-fructose was first studied long ago (Kiliani, 1885, 1928) but has only been reported subsequently very rarely (Gorin & Perlin, 1958). In practice, the Kiliani reaction of D-fructose (2) proceeds in good yield to give a mixture of the two diastereomers (3) and (4) which cannot easily be separated. However, direct treatment of this crude material produced the diacetonide (7) as the major product, which crystallized relatively easily. A second diacetonide was also isolated which could have been either of the diacetonides (5) or (6). This unknown product was converted to a crystalline *tert*-butyldimethylsilyl ether (1), the structure and stereochemistry of which were unequivocally determined by X-ray crystallographic analysis. This firmly established that the minor component in the acetonation reaction was the *gluco*-diacectonide (5).



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Experimental

The diacetonide (1) was prepared from fructose (2) (Hotchkiss *et al.*, 2004). The title material was crystallized from methanol as colourless plates.

Crystal data

$C_{19}H_{34}O_7Si$
$M_r = 402.56$
Orthorhombic, $P2_12_12_1$
$a = 6.4765$ (2) Å
$b = 13.2189$ (2) Å
$c = 25.7075$ (6) Å
$V = 2200.88$ (9) Å^3
$Z = 4$
$D_x = 1.215$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 12716 reflections
$\theta = 5$–28°
$\mu = 0.14$ mm^{-1}
$T = 150$ K
Fragment, colourless
0.40 × 0.20 × 0.20 mm

Data collection

Nonius KappaCCD diffractometer
ω scans
Absorption correction: multi-scan (*DENZO*/*SCALEPACK*; Otwinowski & Minor, 1997)
$T_{\min} = 0.95$, $T_{\max} = 0.97$
12716 measured reflections

4801 independent reflections
4025 reflections with $I > 3$ s(I)
$R_{\rm int} = 0.051$
$\theta_{\max} = 27.5°$
$h = -8 \rightarrow 8$
$k = -17 \rightarrow 17$
$l = -33 \rightarrow 33$

Refinement

Refinement on F
$R = 0.037$
R = missing
$wR = 0.040$
$S = 1.11$
4025 reflections
245 parameters
H-atom parameters not refined

Weighting scheme: see text
$(\Delta/\sigma)_{\max} = 0.002$
$\Delta\rho_{\max} = 0.45$ e Å^{-3}
$\Delta\rho_{\min} = -0.29$ e Å^{-3}
Absolute structure: Flack (1983), 1960 Friedel pairs
Flack parameter = 0.04 (12)

The weighting scheme used a Chebychev polynomial (Watkin, 1994, Prince, 1982): $w = \{1 - [(F_o - F_c)/6\sigma(F)]^2\}^2/[0.682T_0(x) + 0.0517T_1(x) + 0.322T_2(x)]$, where $x = F_c/F_{\max}$. All H atoms were positioned geometrically (C—H = 1.0 Å), and refined as riding, with $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(parent atom).

Data collection: *COLLECT* (Nonius, 2000); cell refinement: *COLLECT* and *DENZO* (Otwinowski & Minor, 1997); data reduction: *COLLECT* and *DENZO*; program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994); program(s) used to refine structure: *CRYSTALS* (Betteridge *et al.*, 2003); molecular graphics: *ATOMS for Windows* (Shape Software, 2002); software used to prepare material for publication: *CRYSTALS*.

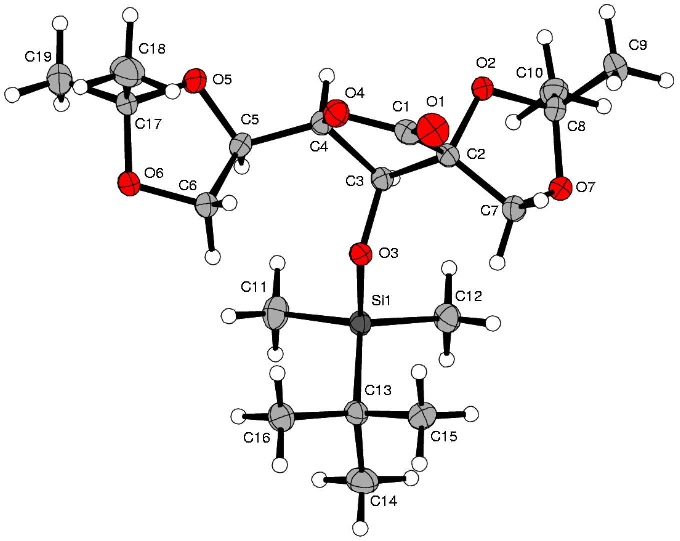

Figure 1
View of the title molecule, showing displacement ellipsoids at the 40% probability level. H atoms are shown as spheres of arbitrary radius.

References

Altomare, A., Cascarano, G., Giacovazzo, C., 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.
Bols, M. (1996). *Carbohydrate Building Blocks*. New York: John Wiley and Sons.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Gorin, P. A. J. & Perlin, A. S. (1958). *Can. J. Chem.* **36**, 480–485.
Hanessian, S. (1983). *The Total Synthesis of Natural Products. The Chiron Approach*. New York: Pergamon Press.
Hotchkiss, D., Soengas, R., Simone, M. I., van Ameijde, J., Hunter, S., Cowley, A. R. & Fleet, G. W. J. (2004). *Tetrahedron Lett.* **45**. Accepted.
Hudson, C. S. (1945). *Adv. Carbohydr. Chem.* **1**, 2–36.
Kiliani, H. (1885). *Ber. Dtsch Chem. Ges.* **18**, 3066–3074.
Kiliani, H. (1928). *Ber. Dtsch Chem. Ges.* **61**, 1155–1169.
Nonius (2000). *COLLECT* Software. 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 and R. M. Sweet, pp. 307–326. New York: Academic Press.
Prince, E. (1982). *Mathematical Techniques in Crystallography and Materials Science*. New York: Springer-Verlag.
Shape Software (2002). *ATOMS for Windows*. Version 6.0. Shape Software, 521 Hidden Valley Road, Kingsport, TN 37663, USA.
Watkin, D. J. (1994). *Acta Cryst.* A**50**, 411–437.