organic papers

2-C-Methyl-D-lyxono-1,4-lactone

Francesco Punzo,[a]*‡ David J. Watkin,[b] David Hotchkiss[c] and George W. J. Fleet[c]

[a]Dipartimento di Scienze Chimiche, Facoltà di Farmacia, Università di Catania, Viale A. Doria 6, 95125 Catania, Italy, [b]Department of Chemical Crystallography, Chemical Research Laboratory, Mansfield Road, Oxford OX1 3TA, England, and [c]Department of Organic Chemistry, Chemical Research Laboratory, Mansfield Road, Oxford OX1 3TA, England

‡ Visiting Scientist at the Department of Chemical Crystallography, Chemical Research Laboratory, Mansfield Road, Oxford OX1 3TA England

Correspondence e-mail: fpunzo@unict.it

The title compound, $C_6H_{10}O_5$, has been crystallized for the first time, allowing the stereochemistry at C-2 and the ring size of the lactone to be firmly established.

Comment

The Kiliani ascension of ketoses (Hotchkiss *et al.*, 2004; Soengas *et al.*, 2005) provides ready access to a new class of branched carbohydrate scaffolds (Lichtenthaler & Peters, 2004; Bols, 1996) with branched carbon chains. Although saccharinic acids, which are 2-*C*-methyl aldonic acids, are formed in very low yields from treatment of aldoses or ketoses with aqueous calcium hydroxide (Whistler & BeMiller, 1963), it has been shown that significantly higher yields may be obtained from the reaction of lime with ketoses (Hotchkiss *et al.*, 2006) derived from the Amadori rearrangement (Hodge, 1955). D-Galactose reacted with dibenzylamine to form the Amadori ketose, (2) (Grunnagel & Haas, 1969), in which the α-configuration at the anomeric position of the pyranose ring has been proved by X-ray crystallographic analysis (Harding *et al.*, 2005). Treatment of (2) with aqueous calcium hydroxide allowed the isolation of a mixture of two epimeric lactones.
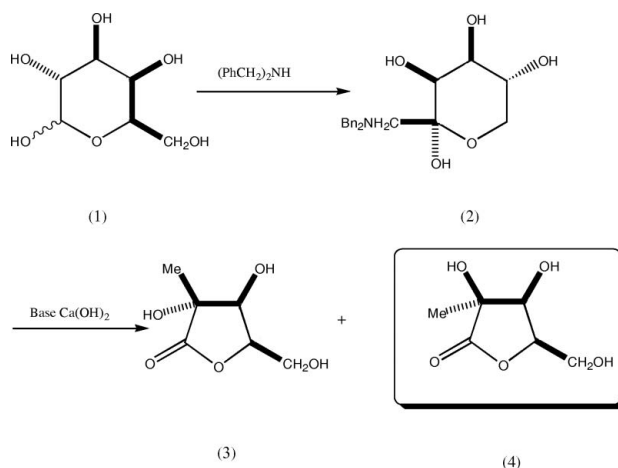
The structure of the minor isomer was confirmed as 2-*C*-methyl-D-xylono-1,4-lactone, (3), by an X-ray structure of its 3,5-acetonide (Watkin *et al.*, 2005). The major product, 2-*C*-methyl-D-lyxono-1,4-lactone, (4), initially isolated as an oil, slowly crystallized, allowing the relative configuration at C-2 and the ring size of the lyxonolactone to be unambiguously assigned by X-ray crystallographic analysis.

Racemic lactone (4) has only been obtained as an oil (Lopez *et al.*, 1984); the enantiomer of (4) has been prepared in low yield from L-sorbose (Ishizu *et al.*, 1972). The absolute configuration of (4) was determined from the use of D-galactose (1) as the starting material.

Experimental

The lactone (4) {m.p. 379–380K, $[\alpha]_D^{23}$ +70.4 (c 0.87 in acetone)} was crystallized by dissolving it in acetone and allowing the slow evaporation of the solvent until colourless block-shaped crystals formed. The multi-scan technique was used to correct for changes in the illuminated volume.

Crystal data

$C_6H_{10}O_5$
$M_r = 162.14$
Monoclinic, $C2$
$a = 18.6680 (5)$ Å
$b = 5.8280 (2)$ Å
$c = 6.3943 (2)$ Å
$\beta = 92.2219 (14)°$
$V = 695.16 (4)$ Å^3
$Z = 4$

$D_x = 1.549$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 1011
  reflections
$\theta = 5–30°$
$\mu = 0.14$ mm^{-1}
$T = 120$ K
Block, colourless
$0.70 \times 0.60 \times 0.50$ mm

Data collection

Nonius KappaCCD area-detector
  diffractometer
ω scans
Absorption correction: multi-scan
  (DENZO and SCALEPACK;
  Otwinowski & Minor, 1997)
  $T_{min} = 0.92$, $T_{max} = 0.93$
1943 measured reflections

1087 independent reflections
1073 reflections with $I > 2\sigma(I)$
$R_{int} = 0.010$
$\theta_{max} = 30.0°$
$h = -25 \rightarrow 26$
$k = -7 \rightarrow 8$
$l = -8 \rightarrow 9$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.024$
$wR(F^2) = 0.061$
$S = 1.04$
1087 reflections
101 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F^2) + (0.03P)^2 + 0.33P]$
  where $P = (F_o^2,0) + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.22$ e Å^{-3}
$\Delta\rho_{min} = -0.16$ e Å^{-3}
Extinction correction: Larson
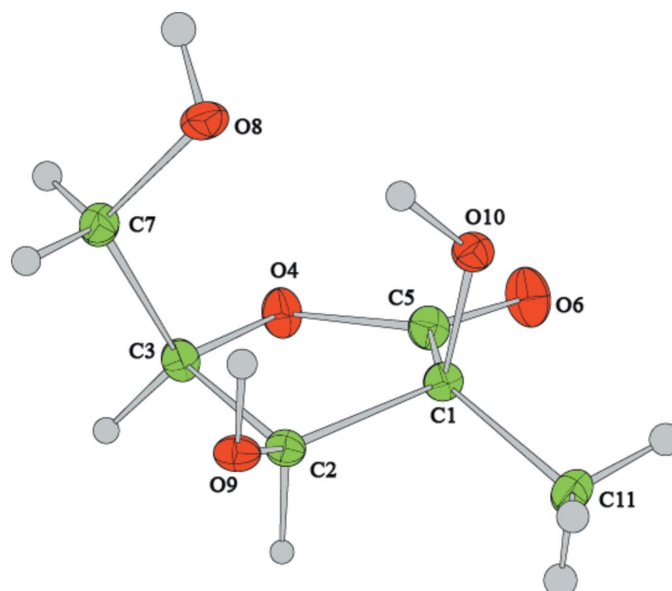 (1970), equation 22
Extinction coefficient: 4.90 (3) $\times 10^2$

Figure 1
The molecular structure of (4), with displacement ellipsoids drawn at the 50% probability level. H-atom radii are arbitrary.

Table 1
Selected geometric parameters (Å, °).

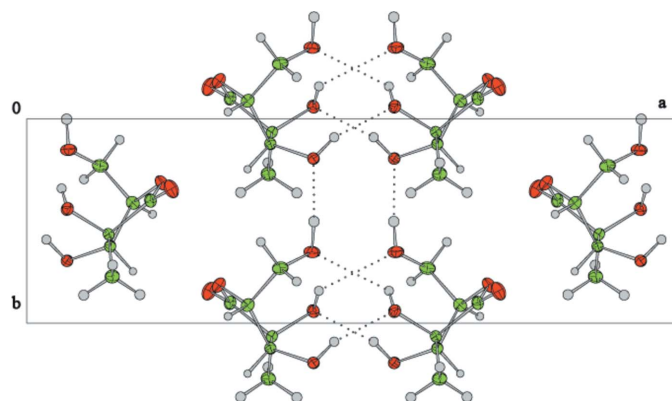|			
C1—C2	1.5382 (16)	C3—O4	1.4652 (15)
C1—C5	1.5342 (17)	C3—C7	1.5098 (18)
C1—O10	1.4329 (14)	O4—C5	1.3553 (15)
C1—C11	1.5150 (18)	C5—O6	1.2027 (15)
C2—C3	1.5448 (19)	C7—O8	1.4327 (16)
C2—O9	1.4163 (14)		
C2—C1—C5	100.95 (9)	C2—C3—O4	103.36 (9)
C2—C1—O10	112.80 (9)	C2—C3—C7	117.44 (10)
C5—C1—O10	107.55 (10)	O4—C3—C7	109.87 (11)
C2—C1—C11	114.56 (10)	C3—O4—C5	112.01 (10)
C5—C1—C11	113.52 (10)	C1—C5—O4	110.53 (10)
O10—C1—C11	107.29 (9)	C1—C5—O6	128.09 (11)
C1—C2—C3	104.94 (10)	O4—C5—O6	121.36 (12)
C1—C2—O9	115.82 (10)	C3—C7—O8	110.46 (10)
C3—C2—O9	114.94 (10)		

Figure 2
Packing diagram of (4), viewed down the c axis. Hydrogen bonds are displayed with dashed lines.

In the absence of significant anomalous scattering, Friedel pairs were merged. H atoms were located in a difference density map. Those attached to C atoms were repositioned geometrically. 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 isotropic displacement parameters [U_{iso}(H) = 1.2–1.5U_{eq}(parent atom)], after which their positions were refined with riding constraints.

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

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O10—H10···O8	0.81	1.90	2.6770 (13)	159
O8—H8···O9^{i}	0.88	1.82	2.6906 (14)	172
O9—H9···O10^{ii}	0.86	1.93	2.7547 (13)	160

Symmetry codes: (i) $x, y + 1, z$; (ii) $-x + 1, y, -z + 1$.

organic papers

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.

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

Grunnagel, R. & Haas, H. J. (1969). *Annalen*, **721**, 234–235.

Harding, C. C., Cowley, A. R., Watkin, D. J., Punzo, F., Hotchkiss, D. J. & Fleet, G. W. J. (2005). *Acta Cryst.* E**61**, o1475–o1477.

Hodge, J. E. (1955). *Adv. Carbohydr. Chem.* **10**, 169–205.

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

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.

Ishizu, A., Yoshida, K. & Yamazaki, N. (1972). *Carbohydr. Res.* **23**, 23–29.

Larson, A. C. (1970). *Crystallographic Computing*, edited by F. R. Ahmed, S. R. Hall & C. P. Huber, pp. 291–294. Copenhagen: Munksgaard.

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

Lopez, A. F. J., Izquierdo, C. I. & Portal, A. M. D. (1984). *Carbohydr. Res.* **129**, 99–109.

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

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

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.

Watkin, D. J., Parry, L. L., Hotchkiss, D. J., Eastwick-Field, V. & Fleet, G. W. J. (2005). *Acta Cryst.* E**61**, o3302–o3303.

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

Whistler, R. L. & BeMiller, J. N. (1963). *Methods Carbohydr. Chem.* **2**, 484–485.