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D-Galactono-1,4-lactone: a case of wrong absolute configuration surviving three decades

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The title compound, $C_6H_{10}O_6$, had been previously characterized by X-ray analysis but was reported with the wrong absolute configuration [Jeffrey, Rosenstein & Vlasse (1967). *Acta Cryst.* **22**, 725–733]. This structure has now been redetermined at higher resolution and including precise positions for H atoms.

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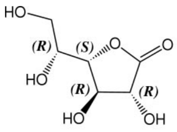
Key indicators

Single-crystal X-ray study
T = 296 K
Mean σ(C–C) = 0.001 Å
R factor = 0.027
wR factor = 0.076
Data-to-parameter ratio = 12.8

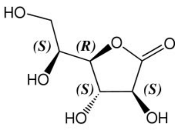
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

Galactono-1,4-lactone is a furanose which, as for many other sugar lactones, is of significant biological interest. For instance, L-galactono-1,4-lactone appears as a key intermediate in the biosynthesis of L-ascorbic acid by conversion of D-glucose, both in animals (Bánhegyi *et al.*, 1997) and in plants (Wheeler *et al.*, 1998). The enantiomer, D-galactono-1,4-lactone, was reported as an efficient inhibitor of β-galactosidases of *Escherichia coli* (Huber & Brockbank, 1987).



(I)



(II)

The crystal structure of D-galactono-1,4-lactone, (I), was determined more than 35 years ago (Jeffrey *et al.*, 1967) on the basis of Weissenberg photographs and was refined to R = 0.078, with a model including H atoms. The solid-state conformation was also established by single-crystal analysis for one diastereoisomer, D-gulono-1,4-lactone (Berman *et al.*, 1971) and for the derivative 2,3,6-tri-*O*-methyl-D-galactono-1,4-lactone (Sheldrick, 1973). Some conformational studies, using ^{1}H and ^{13}C NMR spectroscopy, were carried out for a series of D-hexono-1,4-lactones, including D-galactono-1,4-lactone (Wałaszek & Horton, 1982). These authors observed an equilibrium in solution between two envelope forms, $^3E(D)$ and $E_3(D)$, with a solvent-dependent equilibrium constant [^3E and E_3 are IUPAC notations for envelope conformations with C3 as flap atom; the former indicates C3 above the reference plane and the latter C3 below the reference plane (IUPAC, 1996*a*)]. More recently, these studies were extended to the L-series, with the crystal structure of L-mannono-1,4-lactone and to the closely related sugar lactone L-rhamnono-1,4-lactone (Shalaby *et al.*, 1994).

All these papers cite the 1967 publication reporting the X-ray structure of D-galactono-1,4-lactone. However, to the best of our knowledge, nobody realised that the atomic coordinates given in that paper describe the structure of the L-isomer, rather than the D-isomer [see scheme: (II) and (I),

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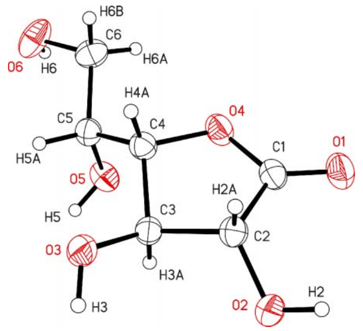

Figure 1
The structure of (I), with displacement ellipsoids drawn at the 50% probability level for non-H atoms. The complete labelling scheme is given.

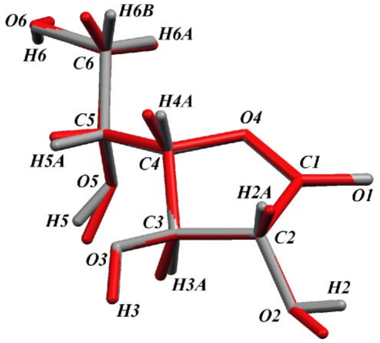

Figure 2
Least-squares fit between the present refinement of (I), represented with grey capped sticks, and the 1967 reported structure (Jeffrey *et al.*, 1967) after hand inversion, represented with red capped sticks. Atomic positions for the fitted molecules were computed using non-H atoms by means of *XP* in *SHELXTL-Plus* (Sheldrick, 1998) and plotted with *MERCURY* (Bruno *et al.*, 2002). Note the large deviations observed for atoms H2, H6*B* and H5.

respectively]. This inversion of configuration is reflected in the corresponding refcode of the Cambridge Structural Database (CSD, Version 5.25; Allen, 2002) (GALLAD); expected absolute configurations for chiral centres in D-galactono-1,4-lactone (I) are 2*R*, 3*R*, 4*S* and 5*R*, while the reported coordinates yield a 2*S*,3*S*,4*R*,5*S* absolute configuration, *i.e.* they describe enantiomer (II). This inversion is also confirmed by listing the torsion angle values involving atoms of the chiral centres: close absolute values are obtained for the 1967 and current structures, but with systematically opposite signs. Although it is difficult to trace a work performed 37 years ago, the most probable explanation is that Jeffrey *et al.* (1967) actually characterized a D-sample, since the absolute configuration may be easily checked, for example, by measuring the optical rotation of the sample. However, due to the lack of atoms with suitable anomalous contributions in the crystal under study, L and D samples were obviously indistinguishable from diffraction patterns. Thus, it seems that these authors failed in the checking of the final model, not in the experimental work. It is nevertheless surprising that this mistake apparently survived undetected for more than three decades.

We now report the X-ray structure of an authentic sample of D-galactono-1,4-lactone, (I), as a part of our current research dealing with the determination of thermodynamic properties of selected aldonolactones (Flores & Amador, 2004). The lactone ring and the exocyclic groups adopt the previously reported $E_3(D)$, $gg,g't'$ conformation (Fig. 1) with expected geometric parameters (Table 1) [*g* (*gauche*) and *t* (*trans*) are non-IUPAC synonyms for synclinal and antiperiplanar torsion angles, respectively (IUPAC, 1996*b*)]. With the exception of the inversion of configuration mentioned above, the geometry observed for this core is very close to that of the 1967 refinement. A fit between the present and the 1967 models, excluding H atoms, gives an r.m.s. deviation of 0.017 Å (Fig. 2). However, when including H atoms in the fit, the r.m.s. deviation increases to 0.201 Å, mainly because of the misplaced atoms H2 (deviation: 0.495 Å), H6*B* (deviation: 0.440 Å) and H5 (deviation: 0.342 Å) in the 1967 structure. These discrepancies for H-atom positions clearly arise from the higher resolution achieved with the current refinement when compared with the earlier work; s.u. values for C—C bond lengths which were in the range 0.006–0.010 Å are now greatly improved, with an average value of 0.0012 Å. As a consequence, the hydrogen-bonding scheme for (I) can now be more reliably described (Table 2), with all hydroxyl groups participating in a complex three-dimensional network. A comparison between the present hydrogen-bonding scheme and that calculated from the Jeffrey *et al.* (1967) coordinates gives differences for geometric parameters spanning the ranges 0–0.24 Å for $H\cdots A$ contacts and 1–44° for $D—H\cdots A$ angles.

In conclusion, we would like to comment on the current concern related to the correctness of structural data contained in the CSD; the well known problem of single-crystal structures reported in wrong space groups is a legitimate concern, but should not override other potential undetected inaccuracies, such as inversion of configuration for non-racemic chiral compounds, especially in the case of structures containing only light atoms. Fortunately, this occurrence is probably limited to a few subsets of the CSD, such as carbohydrates or steroids.

Experimental

The title compound, (I), was purchased from Aldrich and crystallized from ethanol. The absolute configuration was confirmed by measuring the specific optical rotation of the recrystallized sample, $[\alpha]_D^{20} = -74.99°$ (c 0.04 g ml^{-1}, H_2O).

Crystal data

$C_6H_{10}O_6$
$M_r = 178.14$
Orthorhombic, $P2_12_12_1$
$a = 6.4818$ (6) Å
$b = 10.6714$ (8) Å
$c = 10.9799$ (11) Å
$V = 759.48$ (12) Å^3
$Z = 4$
$D_x = 1.558$ Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 78 reflections
$\theta = 4.9–13.8°$
$\mu = 0.14$ mm^{-1}
$T = 296$ (1) K
Irregular, colourless
0.60 × 0.44 × 0.40 mm

Data collection

Bruker *P*4 diffractometer
ω scans
Absorption correction: none
13 164 measured reflections
1925 independent reflections
1826 reflections with $I > 2\sigma(I)$
$R_{int} = 0.032$
$\theta_{max} = 35.0°$
$h = -10 \rightarrow 10$
$k = -17 \rightarrow 17$
$l = -17 \rightarrow 17$
3 standard reflections every 97 reflections intensity decay: 3.9%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.027$
$wR(F^2) = 0.076$
$S = 1.04$
1925 reflections
150 parameters
All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0489P)^2 + 0.0364P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.25$ e Å^{-3}
$\Delta\rho_{\min} = -0.16$ e Å^{-3}
Extinction correction: *SHELXTL-Plus*
Extinction coefficient: 0.040 (5)

Table 1
Selected geometric parameters (Å, °).

C1—O1	1.2031 (11)	C3—C4	1.5274 (12)
C1—O4	1.3487 (11)	C4—O4	1.4581 (10)
C1—C2	1.5278 (12)	C4—C5	1.5196 (12)
C2—O2	1.4043 (11)	C5—O5	1.4221 (12)
C2—C3	1.5223 (12)	C5—C6	1.5217 (13)
C3—O3	1.4124 (10)	C6—O6	1.4221 (14)
O1—C1—O4	122.67 (8)	O4—C4—C5	109.46 (7)
O1—C1—C2	127.65 (9)	O4—C4—C3	103.84 (7)
O4—C1—C2	109.68 (7)	C5—C4—C3	116.80 (7)
O2—C2—C3	113.59 (7)	C1—O4—C4	109.25 (6)
O2—C2—C1	113.25 (7)	O5—C5—C4	111.30 (8)
C3—C2—C1	101.18 (6)	O5—C5—C6	109.91 (8)
O3—C3—C2	115.52 (7)	C4—C5—C6	110.57 (8)
O3—C3—C4	109.79 (7)	O6—C6—C5	111.97 (9)
C2—C3—C4	100.51 (7)		

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O2—H2$\cdots$O3$^{\rm i}$	0.89 (2)	1.84 (2)	2.7195 (10)	171.4 (18)
O3—H3$\cdots$O5$^{\rm ii}$	0.872 (17)	1.818 (17)	2.6807 (10)	169.3 (16)
O5—H5$\cdots$O6$^{\rm iii}$	0.86 (2)	1.84 (2)	2.6809 (11)	167 (2)
O6—H6$\cdots$O2$^{\rm iv}$	0.88 (2)	1.92 (2)	2.7923 (12)	176 (2)

Symmetry codes: (i) $\frac{1}{2} - x, 1 - y, z - \frac{1}{2}$; (ii) $1 - x, \frac{1}{2} + y, \frac{3}{2} - z$; (iii) $\frac{1}{2} + x, \frac{1}{2} - y, 2 - z$; (iv) $1 - x, y - \frac{1}{2}, \frac{3}{2} - z$.

A complete diffraction sphere was collected to 0.62 Å resolution and reflections were merged, including Friedel opposites, before refinement. H atoms were found in difference maps and were refined freely (coordinates and isotropic U parameters).

Data collection: *XSCANS* (Siemens, 1996); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXTL-Plus* (Sheldrick, 1998); program(s) used to refine structure: *SHELXTL-Plus*; molecular graphics: *SHELXTL-Plus* and *MERCURY* (Bruno *et al.*, 2002); software used to prepare material for publication: *SHELXTL-Plus*.

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