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1,5-Anhydro-2,3-*O*-isopropylidene-L-lyxofuranose [(1*S*,4*S*,5*S*,6*R*)-5,6-*O*-isopropylidene-2,7-dioxabicyclo[2.2.1]heptane-5,6-diol]

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Key indicators

Single-crystal X-ray study
T = 150 K
Mean σ(C–C) = 0.003 Å
R factor = 0.031
wR factor = 0.031
Data-to-parameter ratio = 7.7

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

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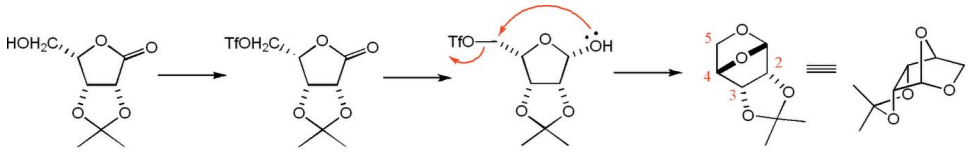
The tricyclic title compound, $C_8H_{12}O_4$, was formed in the reduction by diisobutylaluminium hydride of a 5-*O*-trifluromethanesulfonyl lactone and is likely to be useful as a chiral intermediate for the synthesis of bioactive compounds. The absolute configuration was determined by the use of 2,3-*O*-isopropylidene-L-lyxono-1,4-lactone as the starting material.

Comment

Branched sugar lactones may be useful as versatile intermediates in the synthesis of novel branched biologically important molecules and biopolymeric materials (Asano *et al.*, 2000; Ichikawa & Igarashi, 1995; Ichikawa *et al.*, 1998; Soengas *et al.*, 2005; Hotchkiss *et al.*, 2004, 2006). The Ho crossed-aldol reaction (Ho, 1979, 1985) of lactols with formaldehyde is one of the most powerful strategies for the synthesis of these compounds. In the course of the synthesis of a branched sugar lactone by a Ho procedure (Simone *et al.*, 2005), the trifluoromethanesulfonate, (2), derived from the 2,3-*O*-isopropylidene-L-lyxono-1,4-lactone, (1) (Simone *et al.*, 2005), was treated with diisobutylaluminium hydride (DIBAL-H). A rationalization for the formation of the title compound, (4), is that initial reduction afforded the β-lyxose, (3), which spontaneously cyclized to (4) by S_N2 displacement of the trifluoromethanesulfonate. The value of such highly oxygenated bicyclic intermediates as (4) is well established (Cossy *et al.*, 1995; Pechy *et al.*, 1993), and the unexpected formation of (4) may provide another valuable chiron.



(1) (2) (3) (4)

The structure of (4) has been determined by X-ray diffraction (Fig. 1), which showed that it is formed by a six-membered ring fused to a five-membered ring (the acetonide protecting group). The five-membered ring adopts an envelope conformation. The six-membered ring is a $B_{2,5}$-type conformationally constrained structure, due to the existence of the oxygen bridge linking the 1- and 4-positions.

Experimental

1,5-Anhydro-2,3-*O*-isopropylidene-L-lyxofuranose, (4), was obtained in 28% yield upon overnight reduction of the trifluoromethane-

sulfonate (2) with DIBAL-H in tetrahydrofuran at low concentration (16 mg ml^{-1}). The title material, (4), isolated as a crystalline but volatile product, was recrystallized *via* solvent evaporation (ethyl acetate–cyclohexane) (R_f 0.57; m.p. 338–339 K). HRMS (FI$^+$), found: 172.0732 $[M]^+$; $C_8H_{12}O_4$ requires: 172.0736; $[\alpha]_D^{21}$ 106.8 (*c*, 0.72 in methanol); IR (thin film, ν_{max}, cm^{-1}): 2992, 2955, 2906 (*s*, C—H), 1378 (–O—CO—CH), 1291 (C—O); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.34, 1.60 [2 × 3H, 2 × *s*, $C(CH_3)_2$], 3.55 (1H, *ddd*, $J_{H5,H5'}$ = 6.6 Hz, $J_{H5,H4}$ = 3.5 Hz, $J_{H5,H3}$ = 1.3 Hz, H5), 4.31 (1H, *a–d*, *J* = 6.8 Hz, H5′), 4.45 (1H, *a–dd*, *J* = 8.2 and 2.3 Hz, H2), 4.64 (1H, *dd*, $J_{H3,H2}$ = 8.1 Hz, $J_{H3,H4}$ = 4.6 Hz, H3), 4.72–4.77 (1H, *m*, H4), 5.45 (1H, *d*, $J_{H1,H2}$ = 2.2 Hz, H1); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 25.6, 26.1 [$C(CH_3)_2$], 63.7 (C5), 76.5 (C3), 78.8 (C4), 81.6 (C2), 100.1 (C1), 119.7 [$C(CH_3)_2$].

Crystal data

$C_8H_{12}O_4$
M_r = 172.18
Orthorhombic, $P2_12_12_1$
a = 8.1279 (3) Å
b = 9.4993 (4) Å
c = 10.8126 (4) Å
V = 834.83 (6) Å^3
Z = 4
D_x = 1.370 Mg m^{-3}
Mo *K*α radiation
μ = 0.11 mm^{-1}
T = 150 K
Fragment, colourless
0.38 × 0.32 × 0.14 mm

Data collection

Nonius KappaCCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*DENZO* and *SCALEPACK*; Otwinowski & Minor, 1997)
T_{min} = 0.96, T_{max} = 0.98
5825 measured reflections
1111 independent reflections
834 reflections with $I > 3\sigma(I)$
R_{int} = 0.037
θ_{max} = 27.4°

Refinement

Refinement on *F*
$R[F^2 > 2\sigma(F^2)]$ = 0.031
$wR(F^2)$ = 0.031
S = 1.15
834 reflections
109 parameters
H-atom parameters constrained
$w = [1 - (F_o - F_c)^2/36\sigma^2(F)]^2/[0.275T_0(x) + 0.0396T_1(x) + 0.0219T_2(x)]$ where T_i are Chebychev polynomials and $x = F_c/F_{max}$ (Prince, 1982; Watkin, 1994)
$(\Delta/\sigma)_{max}$ = 0.005
$\Delta\rho_{max}$ = 0.14 e Å^{-3}
$\Delta\rho_{min}$ = −0.14 e Å^{-3}

A large single-crystal was cut to give a small fragment. This was mounted on a glass fibre using perfluoropolyether oil and cooled rapidly to 150 K in a stream of cold N_2 using an Oxford Cryosystems CRYOSTREAM unit. H atoms were positioned geometrically after each cycle of refinement, with C—H = 1.00 Å and U_{iso}(H) = 1.2U_{eq}(C).

Data collection: *COLLECT* (Nonius, 2000); cell refinement: *DENZO* (Otwinowski & Minor, 1997); data reduction: *DENZO*and *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*.

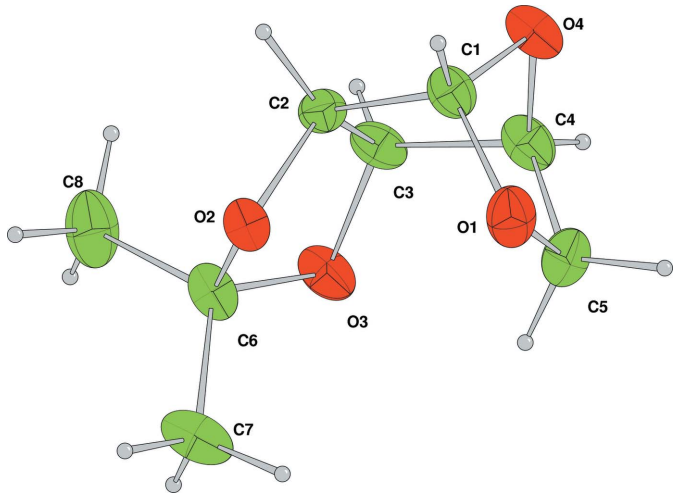


Figure 1
The molecular structure of the title compound, with displacement ellipsoids drawn at the 50% probability level. H atoms are shown as spheres of arbitary radius.

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Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 5825 reflections
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$\mu = 0.11$ mm^{-1}
$T = 150$ K
Fragment, colourless
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1111 independent reflections
834 reflections with $I > 3\sigma(I)$
$R_{int} = 0.037$
$\theta_{max} = 27.4°$, $\theta_{min} = 5.3°$
$h = -10 \rightarrow 10$
$k = -12 \rightarrow 12$
$l = -14 \rightarrow 14$

Refinement

Refinement on F
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.031$
$wR(F^2) = 0.031$
$S = 1.15$
834 reflections
109 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
Method, *P*art 1, Chebychev polynomial (Watkin, 1994; *P*rince, 1982) [*w*eight] = 1.0/[A_0*T_0(x) + A_1*T_1(x) ··· + A_{n-1}]*T_{n-1}(x)], where A_i are the Chebychev coefficients listed below and x = F /Fmax A_i are: 0.275 0.396E-01 0.219E-01. *P*art 2 robust *w*eighting (*P*rince, 1982) W = [*w*eight]*[1-(δF/6*σF)^2]^2
$(\Delta/\sigma)_{max} = 0.005$
$\Delta\rho_{max} = 0.14$ e Å^{-3}
$\Delta\rho_{min} = -0.14$ e Å^{-3}

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.1736 (3)	0.6521 (2)	0.62753 (19)	0.0262

C2	0.3607 (2)	0.6634 (2)	0.64715 (18)	0.0235
C3	0.3853 (3)	0.5599 (2)	0.75558 (18)	0.0264
C4	0.2093 (3)	0.5067 (2)	0.77520 (19)	0.0298
C5	0.1561 (3)	0.4181 (2)	0.6659 (2)	0.0358
O1	0.13420 (19)	0.52285 (17)	0.56943 (13)	0.0325
O2	0.45774 (16)	0.60634 (15)	0.54954 (12)	0.0246
O3	0.49639 (19)	0.45713 (16)	0.71003 (12)	0.0306
O4	0.11892 (18)	0.63636 (16)	0.75191 (13)	0.0316
C6	0.5795 (2)	0.5186 (2)	0.60626 (18)	0.0268
C7	0.6269 (3)	0.4035 (3)	0.5179 (2)	0.0431
C8	0.7237 (3)	0.6058 (3)	0.6504 (2)	0.0447
H11	0.1273	0.7317	0.5781	0.0314*
H21	0.3938	0.7642	0.6568	0.0282*
H31	0.4319	0.5955	0.8352	0.0317*
H41	0.1953	0.4551	0.8551	0.0358*
H51	0.0508	0.3676	0.6837	0.0429*
H52	0.2429	0.3483	0.6429	0.0429*
H71	0.7120	0.3419	0.5571	0.0517*
H72	0.6727	0.4460	0.4406	0.0517*
H73	0.5276	0.3460	0.4972	0.0517*
H81	0.8073	0.5429	0.6897	0.0536*
H82	0.6846	0.6765	0.7123	0.0536*
H83	0.7744	0.6557	0.5785	0.0536*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0237 (10)	0.0306 (11)	0.0243 (10)	0.0031 (9)	0.0010 (8)	0.0031 (10)
C2	0.0241 (10)	0.0220 (9)	0.0243 (10)	0.0003 (9)	−0.0012 (8)	−0.0025 (8)
C3	0.0275 (10)	0.0338 (11)	0.0178 (9)	0.0083 (9)	−0.0009 (9)	−0.0026 (9)
C4	0.0298 (11)	0.0348 (12)	0.0248 (10)	0.0072 (10)	0.0047 (8)	0.0073 (10)
C5	0.0346 (12)	0.0297 (12)	0.0430 (13)	−0.0075 (10)	0.0055 (11)	0.0029 (10)
O1	0.0265 (8)	0.0433 (9)	0.0277 (8)	−0.0068 (8)	−0.0028 (6)	−0.0017 (7)
O2	0.0215 (7)	0.0308 (7)	0.0215 (7)	0.0012 (6)	−0.0001 (6)	0.0031 (6)
O3	0.0313 (7)	0.0344 (8)	0.0259 (7)	0.0118 (7)	0.0052 (6)	0.0080 (7)
O4	0.0293 (7)	0.0390 (9)	0.0265 (7)	0.0094 (7)	0.0047 (7)	0.0008 (7)
C6	0.0225 (10)	0.0370 (12)	0.0209 (9)	0.0048 (9)	0.0004 (7)	0.0060 (10)
C7	0.0461 (14)	0.0475 (14)	0.0358 (13)	0.0176 (13)	0.0073 (12)	−0.0046 (12)
C8	0.0236 (11)	0.0646 (18)	0.0457 (14)	−0.0058 (12)	−0.0070 (10)	0.0042 (15)

Geometric parameters (Å, º)

C1—C2	1.539 (3)	C5—O1	1.453 (3)
C1—O1	1.416 (3)	C5—H51	1.000
C1—O4	1.424 (2)	C5—H52	1.000
C1—H11	1.000	O2—C6	1.432 (2)
C2—C3	1.543 (3)	O3—C6	1.434 (2)
C2—O2	1.425 (2)	C6—C7	1.503 (3)

C2—H21	1.000	C6—C8	1.512 (3)
C3—C4	1.532 (3)	C7—H71	1.000
C3—O3	1.418 (2)	C7—H72	1.000
C3—H31	1.000	C7—H73	1.000
C4—C5	1.514 (3)	C8—H81	1.000
C4—O4	1.456 (3)	C8—H82	1.000
C4—H41	1.000	C8—H83	1.000
C2—C1—O1	110.19 (17)	O1—C5—H51	111.212
C2—C1—O4	100.70 (16)	C4—C5—H52	111.212
O1—C1—O4	104.89 (17)	O1—C5—H52	111.211
C2—C1—H11	113.145	H51—C5—H52	109.466
O1—C1—H11	109.473	C1—O1—C5	104.34 (15)
O4—C1—H11	117.841	C2—O2—C6	106.66 (14)
C1—C2—C3	100.84 (17)	C3—O3—C6	106.94 (15)
C1—C2—O2	114.72 (17)	C1—O4—C4	95.43 (15)
C3—C2—O2	104.40 (15)	O2—C6—O3	104.26 (15)
C1—C2—H21	110.280	O2—C6—C7	109.17 (17)
C3—C2—H21	119.725	O3—C6—C7	108.77 (18)
O2—C2—H21	107.052	O2—C6—C8	110.63 (18)
C2—C3—C4	101.21 (16)	O3—C6—C8	109.94 (17)
C2—C3—O3	104.90 (15)	C7—C6—C8	113.64 (19)
C4—C3—O3	114.58 (17)	C6—C7—H71	109.467
C2—C3—H31	119.186	C6—C7—H72	109.467
C4—C3—H31	110.269	H71—C7—H72	109.476
O3—C3—H31	106.897	C6—C7—H73	109.467
C3—C4—C5	109.99 (17)	H71—C7—H73	109.476
C3—C4—O4	99.71 (16)	H72—C7—H73	109.476
C5—C4—O4	101.03 (16)	C6—C8—H81	109.467
C3—C4—H41	112.794	C6—C8—H82	109.467
C5—C4—H41	111.682	H81—C8—H82	109.476
O4—C4—H41	120.440	C6—C8—H83	109.467
C4—C5—O1	102.39 (16)	H81—C8—H83	109.475
C4—C5—H51	111.212	H82—C8—H83	109.475