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Absolute configuration of the newly formed asymmetric centre in (1*R*,5*R*,8*S*)-8-benzyloxy-2,6-dioxabicyclo[3.2.1]octan-3-one

Marian Koman,[a]* Matej Babjak,[b] Tibor Gracza[b] and Tadeusz Glowiak[c]

[a]Department of Inorganic Chemistry, Slovak Technical University, Radlinského 9, 812 37 Bratislava, Slovakia, [b]Department of Organic Chemistry, Slovak Technical University, Radlinského 9, 812 37 Bratislava, Slovakia, and [c]Faculty of Chemistry, University of Wroclaw, 14 F. Joliot-Curie Street, 50-383 Wroclaw, Poland

Correspondence e-mail: koman@cvtstu.cvt.stuba.sk

Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.003 Å
R factor = 0.033
wR factor = 0.088
Data-to-parameter ratio = 10.7

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

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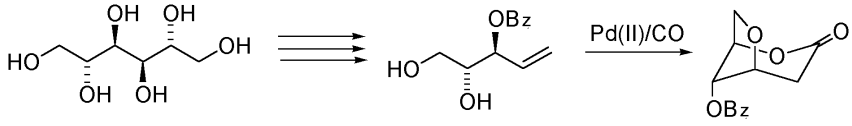
The absolute configuration of the asymmetric centre (8*S*) formed during Pd^{II}-catalyzed oxycarbonylation was established by X-ray analysis of the title compound (alternatively 3,6-anhydro-2-deoxy-D-*lyxo*-1,5-hexonolactone), $C_{13}H_{14}O_4$.

Comment

The title compound (alternative name: 3,6-anhydro-2-deoxy-D-*lyxo*-1,5-hexonolactone), (1), was prepared by palladium(II)-catalyzed oxycarbonylation (Gracza *et al.*, 1991) of (2*R*,3*S*)-3-*O*-benzylpent-4-ene-1,2,3-triol (Fürfsner *et al.*, 1991; Babjak, 1999). The molecular structure of the title compound with the atom-numbering scheme is shown in Fig. 1, and bond distances and angles are listed in Table 1. The *S* configuration of the newly formed asymmetric centre at the C8 atom determined by the refinement of the Flack parameter [*x* = −0.03 (19); Flack, 1983] was confirmed by a comparison of the configuration of the chiral centres at the C1 and C5 atoms (1*R* and 5*R*) with the known configurations of the corresponding atoms in the starting compounds, commercially available D-mannose, as determined in Fürfsner *et al.* (1991) and Babjak (1999).



D-mannitol (1)

Experimental

The title compound was prepared from 3-*O*-benzylated triol by Pd^{II}-bicyclization. A 50-ml flask, purged with CO and connected to a balloon with CO, was charged with $PdCl_2$ (18 mg, 0.1 mmol, 0.1 equivalent), $CuCl_2$ (anhydrous, 402 mg, 3 mmol, 3 equivalent), NaOAc (anhydrous, 246 mg, 3mmol, 3 equivalents), (2*R*,3*S*)-3-*O*-benzyl-pent-4-ene-1,2,3-triol (208 mg, 1 mmol), and AcOH (10 ml). The mixture was stirred at room temperature for 16 h. The crude product was purified by column chromatography on silica gel and recrystallized from ethyl acetate/hexane (m.p. 365–366 K, ?tpbgc=^st_head3_bgcolour]>$[\alpha]_D^{20}$ = −49, *c* = 0.15, $CHCl_3$).

Crystal data

$C_{13}H_{14}O_4$
M_r = 234.24
Orthorhombic, $P2_12_12_1$
a = 5.729 (1) Å
b = 10.079 (2) Å
c = 19.622 (4) Å
V = 1133.0 (4) Å^3
Z = 4
D_x = 1.373 Mg m^{-3}
Cu *Kα* radiation
Cell parameters from 25 reflections
θ = 5.2–15.2°
μ = 0.85 mm^{-1}
T = 293 (2) K
Rectangular plate, colourless
0.45 × 0.35 × 0.20 mm

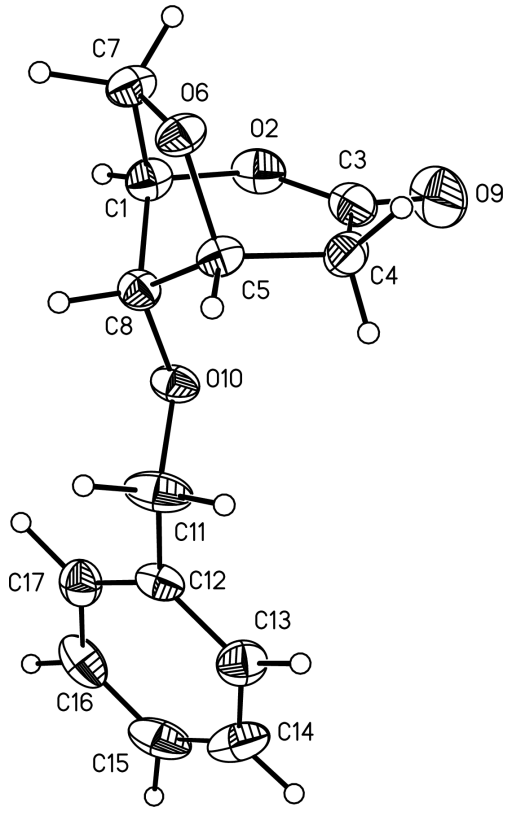


Figure 1
The molecular structure of (1*R*,5*R*,8*S*)-8-benzyloxy-2,6-dioxabicyclo[3.2.1]octan-3-one with the atom numbering and 30% probability displacement ellipsoids. H atoms are shown as spheres of arbitrary radii.

Data collection

Syntex $P2_1$ diffractometer
$\theta/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.656, T_{max} = 0.845
2583 measured reflections
2259 independent reflections
1969 reflections with $I > 2\sigma(I)$

R_{int} = 0.056
θ_{max} = 80.1°
$h = 0 \rightarrow 7$
$k = 0 \rightarrow 12$
$l = -25 \rightarrow 25$
2 standard reflections
every 100 reflections
intensity decay: 15%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.033
$wR(F^2)$ = 0.088
S = 1.13
2259 reflections
211 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0559P)^2 + 0.0550P]$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.19 e Å^{-3}
$\Delta\rho_{min}$ = −0.26 e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0083 (9)
Absolute structure: (Flack, 1983), no Friedel pairs
Flack parameter = −0.03 (19)

Table 1
Selected geometric parameters (Å, °).

C1—O2	1.445 (2)	C8—O10	1.4060 (17)
C1—C7	1.510 (2)	O10—C11	1.4338 (19)
C1—C8	1.507 (2)	C11—C12	1.501 (2)
O2—C3	1.350 (3)	C12—C13	1.375 (3)
C3—C4	1.501 (3)	C12—C17	1.378 (3)
C3—O9	1.200 (2)	C13—C14	1.385 (3)
C4—C5	1.507 (3)	C14—C15	1.368 (4)
C5—O6	1.4334 (17)	C15—C16	1.372 (4)
C5—C8	1.527 (2)	C16—C17	1.386 (3)
O6—C7	1.4402 (19)		
O2—C1—C7	111.55 (14)	O10—C8—C1	112.43 (13)
O2—C1—C8	110.74 (14)	O10—C8—C5	115.50 (13)
C8—C1—C7	101.19 (12)	C1—C8—C5	97.79 (11)
C3—O2—C1	119.21 (12)	C8—O10—C11	111.11 (12)
O9—C3—O2	117.1 (2)	O10—C11—C12	109.48 (13)
O9—C3—C4	123.4 (2)	C13—C12—C17	119.68 (16)
O2—C3—C4	119.43 (15)	C13—C12—C11	119.94 (18)
C3—C4—C5	114.46 (15)	C17—C12—C11	120.37 (19)
O6—C5—C4	110.34 (12)	C12—C13—C14	120.01 (19)
O6—C5—C8	103.25 (12)	C15—C14—C13	120.4 (2)
C4—C5—C8	108.49 (13)	C14—C15—C16	119.77 (18)
C5—O6—C7	108.07 (11)	C15—C16—C17	120.3 (2)
O6—C7—C1	105.31 (12)	C12—C17—C16	119.9 (2)

Data collection: $P2_1$ *Software* (Syntex, 1973); cell refinement: $P2_1$ *Software*; data reduction: *XP*21 (Pavelčík, 1993); program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP* (Johnson, 1965); software used to prepare material for publication: *SHELXL*97.

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