Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

3-Deoxy-1,2-*O*-isopropylidene-3-*C*-methyl-5-*O*-(*p*-tolylsulfonyl)-D-ribofuranose

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.004 Å
R factor = 0.036
wR factor = 0.105
Data-to-parameter ratio = 9.9

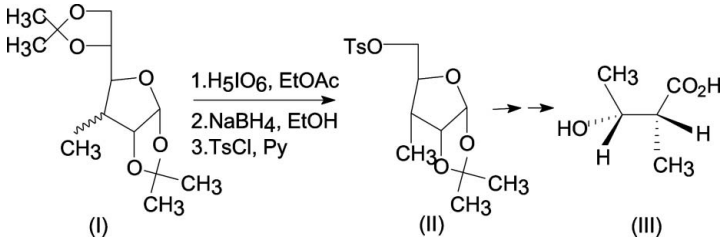
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Received 23 March 2007
Accepted 14 April 2007

In the title compound [alternative name: (2,2,6*R*-trimethyltetrahydrofuro[2*R*,3*R*-*d*][1,3]dioxol-5*S*-yl)methyl 4-methylbenzenesulfonate], $C_{16}H_{22}O_6S$, the *ribo*-pentofuranose ring is in the *T* (twisted) conformation, with atom C3 *exo* and atom C4 *endo*. The isopropylidene ring is in an envelope conformation. The crystal structure is stabilized by means of van der Waals interactions and weak C—H···O interactions.

Comment

As part of an ongoing research programme in our laboratory, there is a need to obtain all four stereoisomers of 3-hydroxy-2-methylbutanoic acid. The 3*R*,2*R* isomer, (III), can be obtained from 1,2,5,6-di-*O*-isopropylidene-D-glucofuranose *via* its conversion to the 3-deoxy-3-*C*-methyl-*allo*- and -*gluco*-compounds, (I) (Martin *et al.*, 1983; Dang *et al.*, 2000). Both epimers can be separated by chromatography, but this is rather difficult for a larger scale preparation. However, a single stereoisomer at C3, *viz.* (II), could be easily obtained after degradation of the C5,6 side chain (Robins *et al.*, 2000; Xie *et al.*, 1996), followed by conventional tosylation, as shown in the scheme. In order to assure the correct stereochemistry of the final compound, (III), it is necessary to establish the absolute configuration of the intermediate title compound, (II), in particular the firm confirmation of the configuration at atom C3. Therefore, compound (II) was subjected to an X-ray crystallographic analysis.



In the crystal structure of (II), the puckering parameters (Cremer & Pople, 1975) for the *ribo*-pentofuranose ring (O1/C1/C2/C3/C4) are q_2 = 0.362 (3) Å and φ = 306.5 (4)°, and for the isopropylidene ring (O2/C2/C1/O3/C9), q_2 = 0.253 (3) Å and φ = 175.7 (6)°. The *ribo*-pentofuranose ring is in the *T* form (twisted), with atom C3 *exo* and atom C4 *endo*. The pseudorotation parameters (Rao *et al.*, 1981) for this ring are *P* = 38.9 (3)° and τ_m = 38.2 (2)° for the reference bond C2—C3. The configurations at atoms C1, C2, C3, C4 are *R*, *R*, *R*, *S*, respectively. The H atoms at C1 and C2 are in a bisecting orientation, while those at C3 and C4 are in an axial orientation. In this ring, the O1—C1 bond is significantly shorter than the O1—C4 bond, as is found in most 1,2-*O*-isopropyl-

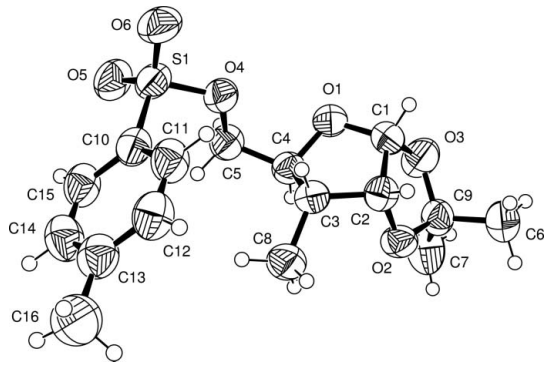


Figure 1
The molecular structure of (II), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are represented by circles of arbitrary size.

idene-3,4-disubstituted furanoid rings (Phillips & Trotter, 1977). The isopropylidene ring conformation can be described as an envelope, with O2 as the flap atom, with pseudorotation parameters P = 264.1 (3)° and τ_m = 28.5 (1)° for the reference bond C1—O3.

Since no electron-donor groups are present to form classical hydrogen bonds, the crystal structure of (II) is stabilized by means of weak C—H···O interactions, along with van der Waals interactions.

Experimental

The details of the synthesis of (II) and its further transformation to the target compound, (III), will be published elsewhere. Compound (II), as a pure *ribo* isomer, was obtained in 54% yield starting from (I). Suitable crystals were obtained by slow evaporation of a solution in ethyl acetate (m.p. 393–396 K). Spectroscopic analysis: ^{1}H NMR (300 MHz, $CDCl_3$, δ, p.p.m.): 7.88 (*d*, J = 8.2 Hz, 2H, aromatic), 7.34 (*d*, J = 8.2 Hz, 2H, aromatic), 5.69 (*d*, J_{12} = 3.5 Hz, 1H, H1), 4.52 (*t*, $J_{12} = J_{23}$ = 4.1 Hz, 1H, H2), 4.23 (*dd*, J_{45} = 2.5 Hz, $J_{55'}$ = 11.1 Hz, 1H, H5), 4.07 (*dd*, $J_{5'4}$ = 3.9 Hz, $J_{5'5}$ = 11.1 Hz, 1H, H5′), 3.86 (*dt*, J_{43} = 10.3 Hz, $J_{45} = J_{45'}$ = 3.2 Hz, 1H, H4), 2.45 (*s*, 3H, Me), 2.02 (*ddq*, J_{32} = 4.5 Hz, J_{34} = 10.0 Hz, $J_{3\text{-Me}}$ = 7.5 Hz, 1H, H3), 1.46 and 1.31 (two *s*, 3H each, isopropylidene), 1.03 (*d*, $J_{\text{Me-3}}$ = 6.8 Hz, 3H, Me). Exact mass calculated for $C_{16}H_{22}O_6S$ + Na = 365.10295; found: 365.10166.

Crystal data

$C_{16}H_{22}O_6S$
M_r = 342.40
Orthorhombic, $P2_12_12_1$
a = 7.7521 (3) Å
b = 11.6202 (4) Å
c = 19.0242 (11) Å
V = 1713.72 (13) Å^3
Z = 4
Cu $K\alpha$ radiation
μ = 1.93 mm^{-1}
T = 293 K
0.61 × 0.40 × 0.27 mm

Data collection

Siemens *P*4 four-circle diffractometer
Absorption correction: ψ scan [(North *et al.*, 1968) and *XEMP* (Siemens, 1989)]
T_{min} = 0.441, T_{max} = 0.595
2295 measured reflections
2113 independent reflections
2049 reflections with $I > 2\sigma(I)$
R_{int} = 0.041
3 standard reflections
every 100 reflections
intensity decay: none

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.036
$wR(F^2)$ = 0.105
S = 1.11
2113 reflections
213 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.14 e Å^{-3}
$\Delta\rho_{min}$ = −0.26 e Å^{-3}
Absolute structure: Flack (1983), with 210 Friedel pairs
Flack parameter: 0.00 (2)

Table 1
Selected geometric parameters (Å, °).

S1—O6	1.421 (2)	O2—C9	1.418 (3)
S1—O5	1.422 (2)	O2—C2	1.423 (3)
S1—O4	1.5740 (19)	O3—C1	1.400 (4)
S1—C10	1.743 (3)	O3—C9	1.420 (4)
O1—C1	1.406 (3)	O4—C5	1.456 (3)
O1—C4	1.443 (3)		
C10—S1—O4—C5	73.1 (2)	C8—C3—C4—C5	76.8 (3)
S1—O4—C5—C4	−153.96 (18)		

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

D—H···A	D—H	H···A	D···A	D—H···A
C3—H3···O4	0.98	2.56	2.964 (3)	105
C4—H4···O6^{i}	0.98	2.53	3.496 (3)	168
C15—H15···O5	0.93	2.56	2.923 (4)	104
C15—H15···O3^{ii}	0.93	2.55	3.309 (4)	139

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

All H atoms, apart from those of the methyl groups, were placed in geometrically idealized positions and constrained to ride on their parent atoms, with C—H = 0.93 Å and U_{iso}(H) = 1.25U_{eq}(C). The methyl H atoms were then constrained to an ideal geometry, with C—H = 0.98 Å and U_{iso}(H) = 1.2U_{eq}(C), but each group was allowed to rotate freely about its C—C bond.

Data collection: *XSCANS* (Siemens, 1996); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Bergerhoff, 1996); software used to prepare material for publication: *PLATON* (Spek, 2003).

HNA is grateful to the Faculty of Pharmaceutical Sciences (Katholieke Universiteit Leuven, Belgium) for funding.

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