Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

Methyl (2′*R*,3′*R*)-6-deoxy-3,4-*O*-(2′,3′-dimethoxybutane-2′,3′-diyl)-2-*O*-toluene-*p*-sulfonyl-α-L-mannopyranoside

John C. Barnes,[a]* John S. Brimacombe,[b] Lisa M. C. Connolly[b] and Alexander P. Dix[b]

[a]Carnelley Building, University of Dundee, Perth Road, Dundee DD1 4HN, Scotland, and [b]Division of Biological Chemistry and Molecular Microbiology, The School of Life Sciences, University of Dundee, Dundee DD1 5EH, Scotland

Correspondence e-mail: j.c.barnes@dundee.ac.uk

Key indicators

Single-crystal X-ray study
T = 150 K
Mean σ(C–C) = 0.005 Å
R factor = 0.069
wR factor = 0.122
Data-to-parameter ratio = 18.6

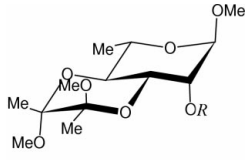
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Received 11 December 2001
Accepted 30 January 2002
Online 8 February 2002

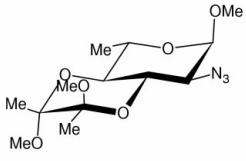
In the title compound, $C_{20}H_{30}O_9S$, (III), both six-membered rings adopt chair conformations, placing H3 and the 2-sulfonyloxy group in the antiperiplanar arrangement required for an *E*2 reaction. However, unlike other α-mannopyranoside-2-sulfonates, the 2-*O*-trifluoromethylsulfonyl (trifluoromethanesulfonate) derivative, (II), underwent an S_N2 displacement with an azide ion to give methyl (2′*R*,3′*R*)-2-azido-2,6-dideoxy-3,4-*O*-(2′,3′-dimethoxybutane-2′,3′-diyl)-α-L-glucopyranoside, (IV), in preference to the *E*2 reaction.

Comment

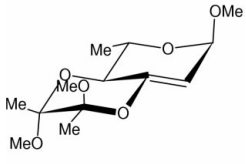
Bimolecular nucleophilic (S_N2) displacements on α-hexopyranoside 2-sulfonates are notoriously difficult to effect with charged nucleophiles (Richardson, 1969). Elimination reactions tend to be favoured with α-mannopyranoside 2-sulfonates (Binkley & Binkley, 1997) and are sometimes accompanied by more deep-seated rearrangements (Vos *et al.*, 1984; Barnes *et al.*, 1996).



(I) R = H
(II) R = SO_2CF_3
(III) R = $SO_2C_6H_4Me$-*p*



(IV)



(V)

We reasoned that S_N2 displacements on a bicyclic 2-sulfonate, such as (II), stood a much better chance of success since the incipient 2,3-double bond at the ring junction would introduce appreciable torsional strain in the transition state of the competing *E*2 reaction. The butane-3,4-diacetal, (I), is

accessible through the seminal work of Ley's group (Hense *et al.*, 1997; Ley *et al.*, 1997) and is readily transformed into the 2-sulfonates (II) and (III). Sulfonate (II), an oil, reacted readily with sodium azide in dimethylformamide at 343 K to give, principally, the azide (IV). An extremely labile (minor) product of this reaction was identified as the 2,3-unsaturated sugar, (V), by ^{1}H NMR spectroscopy. (III) and (IV) are crystalline. The structure of (III) is reported here; that of (IV) is given in the following paper (Barnes *et al.*, 2002).

(III) did not react with sodium azide in DMF, even at 423 K. The *p*-toluenesulfonate group at C2 would be much less reactive than the OSO_2CF_3 group in (II). In addition, there will be some stabilization of (III) from the close approach of the methyl H atom H16*c* to the centroid of the phenyl ring (3.237 Å). The presence of the sulfonate group made it possible to determine the absolute configuration of (III) by Flack's method (Flack, 1983). Fig. 1 shows that, as expected, (III) retains the configuration of (I). The same is presumably true of (II). Comparison with the structure of (IV) (Barnes *et al.*, 2002) shows that in (IV) the original configuration is preserved at all centres except for inversion of the configuration at the reaction centre C2. Thus the hoped for S_N2 displacement had occurred. In (III), the torsion angle O2—C2—C3—H3 is 172.6(1)°, only slightly displaced from the ideal antiperiplanar arrangement favoured by *E*2 eliminations (Eliel & Wilen, 1994). In (IV), the torsion angles N11—C2—C3—H3 are 61.02(4) and 62.64(4)°, showing the change in configuration at C2. There are no unusual bond lengths or angles in either structure.

Experimental

(III) was prepared conventionally from (I). Analysis of (III), found: C 53.69, H 6.74, S 7.31%; calculated: C 53.80, H 6.77, S 7.18%. $[\alpha]_D$ −121° (*c* = 1, MeOH). Crystals from diethyl ether/hexane.

Crystal data

$C_{20}H_{30}O_9S$
M_r = 446.50
Orthorhombic, $P2_12_12_1$
a = 8.7709 (3) Å
b = 14.0181 (10) Å
c = 18.1744 (13) Å
V = 2234.6 (2) Å^3
Z = 4
D_x = 1.327 Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 9970 reflections
θ = 3.0–28.3°
μ = 0.19 mm^{-1}
T = 150 (2) K
Needle, colourless
0.25 × 0.10 × 0.05 mm

Data collection

Nonius KappaCCD area-detector diffractometer
φ and ω scans
9970 measured reflections
5177 independent reflections
3591 reflections with $I > 2\sigma(I)$
R_{int} = 0.058
θ_{max} = 28.3°
h = −9 → 9
k = −18 → 18
l = −24 → 24

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.069
$wR(F^2)$ = 0.122
S = 1.09
5177 reflections
278 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0139P)^2 + 2.7542P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.007
$\Delta\rho_{max}$ = 0.31 e Å^{-3}
$\Delta\rho_{min}$ = −0.33 e Å^{-3}
Absolute structure: Flack (1983)
Flack parameter = 0.00 (12)

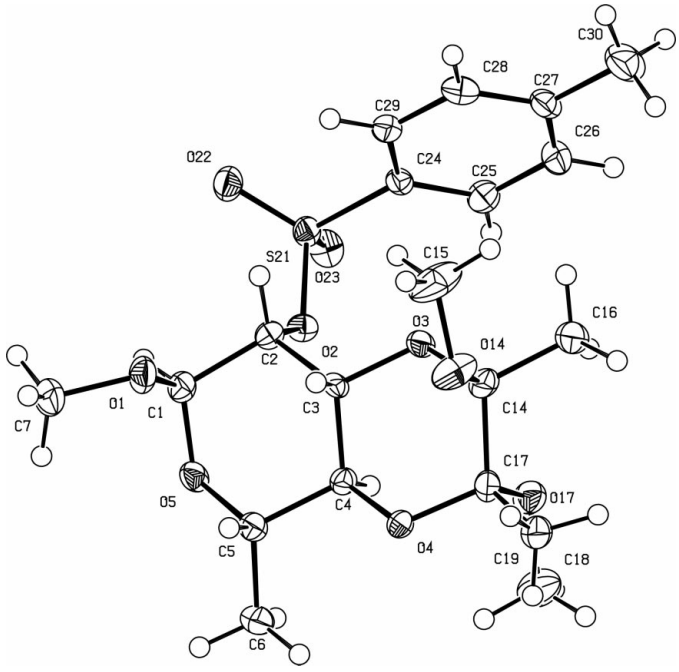


Figure 1
The structure of (III), showing 50% probability displacement ellipsoids.

All H atoms were introduced at calculated positions as riding atoms (C—H = 0.97–0.98 Å), with a displacement parameter equal to 1.2 (CH) or 1.5 (CH_3) times that of the parent atom. On the basis of 2259 Friedel pairs, final refinement allowed the fraction contribution of the inverted enantiomer to vary (Bernardinelli & Flack, 1985; Flack, 1983), the absolute structure parameter quoted being the refined value of this contribution.

Data collection: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT* (Hooft, 1998); cell refinement: *DENZO* and *COLLECT*; data reduction: *DENZO* and *COLLECT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLUTON*92 (Spek, 1992) and *PLATON*92 (Spek, 1992); software used to prepare material for publication: *SHELXL*97.

We thank the EPSRC X-ray Crystallographic Service and Professor M. B. Hursthouse for the data collection. APD thanks the BBSRC for a studentship.

References

Barnes, J. C., Brimacombe, J. S., Connolly, L. M. C. & Dix, A. P. (2002). *Acta Cryst.* E**58**, o227–o228
Barnes, J. C., Brimacombe, J. S. & Kabir, A. K. M. S. (1996). *Acta Cryst.* C**52**, 416–418.
Bernardinelli, G. & Flack, H. D. (1985). *Acta Cryst.* A**41**, 500–511.
Binkley, E. R. & Binkley, R. W. (1997). *Preparative Carbohydrate Chemistry*, edited by S. Hanessian, p. 95. New York: Marcel Decker.
Eliel, E. L. & Wilen, S. H. (1994). Stereochemistry of Organic Compounds, p.723. New York: John Wiley.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Hense, A., Ley, S. V., Osborn, H. M. I., Owen, D. R., Poisson, J.-F., Warriner, S. L. & Wesson, K. E. (1997). *J. Chem. Soc. Perkin Trans.* 1, pp. 2023–2031.
Hooft, R. (1998). *COLLECT*. Nonius BV, Delft, The Netherlands.

Ley, S. V., Owen, D. R. & Wesson, K. E. (1997). *J. Chem. Soc. Perkin Trans.* **1**, pp. 2805–2806.
Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, Macromolecular Crystallography, Part A, edited by C. W. Carter and R. M. Sweet, pp. 307–326. London: Academic Press.
Richardson, A. C. (1969). *Carbohydr. Res.* **10**, 395–402.
Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.
Spek, A. L. (1992). *PLATON*92 and *PLUTON*92. University of Utrecht, The Netherlands.
Vos, J. N., van Boom, J. H., van Boeckel, C. A. A. & Beetz, T. (1984). *J. Carbohydrate Chem.* **3**, 117–124.