Molecular Structure Corporation (1991). *MSC/AFC Diffractometer Control Software.* MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Pirkle, W. H., Burke, J. A. & Wilson, S. R. (1989). *J. Am. Chem. Soc.* **111**, 9222–9223.

Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.

Acta Cryst. (1997). C**53**, 1939–1941

Two Tosylated 1,2-*O*-Isopropylidene-α-D-xylofuranoses

PHILIP J. COX,[a] R. ALAN HOWIE,[b] HELENA RUFINO[b] AND JAMES L. WARDELL[b]

[a]*School of Pharmacy, The Robert Gordon University, Schoolhill, Aberdeen AB10 1FR, Scotland, and* [b]*Department of Chemistry, University of Aberdeen, Meston Walk, Old Aberdeen AB9 1UE, Scotland. E-mail: paspjc@pharmacy.rgu.ac.uk*

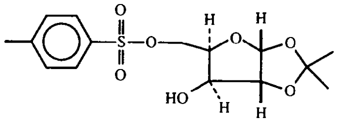
(*Received 18 February 1997; accepted 1 August 1997*)

Abstract

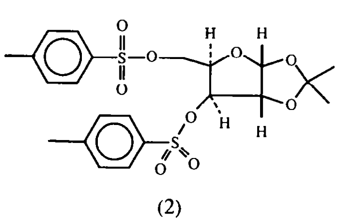
The tosyl side-chain orientation in 1,2-*O*-isopropylidene-5-*O*-*p*-tosyl-α-D-xylofuranose, $C_{15}H_{20}O_7S$, and in 1,2-*O*-isopropylidene-3,5-di-*O*-*p*-tosyl-α-D-xylofuranose, $C_{22}H_{26}O_9S_2$, is influenced by ring substitution and intermolecular hydrogen bonding.

Comment

As part of a continuing study involving novel functionally substituted carbohydrate molecules (Armishaw *et al.*, 1996), we have prepared two tosylated xylofuranoses, namely, 1,2-*O*-isopropylidene-5-*O*-*p*-tosyl-α-D-xylofuranose, (1), and 1,2-*O*-isopropylidene-3,5-di-*O*-*p*-tosyl-α-D-xylofuranose, (2).



(1)



(2)

Intermolecular –OH···O=C hydrogen bonding is present in (1) but absent in (2). In (1), O4···O1(−1 + *x*, *y*, *z*) is 2.868 (7), O4—H4 is 0.820 (11), H4···O1 is 2.061 (11) Å and the angle at H4 is 168 (4)°. In both carbohydrates, the groups attached to C3 and C4 are *syn* with similar O4—C3—C4—C8 torsion angles of −37.3 (6)° in (1) and −40.9 (8)° in (2). However, the orientation of the tosyl group which is common to both molecules differs, with the torsion angle S1—O5—C8—C4 having values of 95.0 (5)° in (1) and 156.3 (5)° in (2). This is due to the different substituents at C3, the only feature not common to both molecules.

The puckering parameters (Cremer & Pople, 1975) in (1) for the furanose ring are q_2 = 0.350 (5) Å and φ_2 = 294.2 (8)°, and for the isopropylidene ring, q_2 = 0.259 (5) Å and φ_2 = 265.7 (11)°. Similarly, in (2), for the furanose ring, q_2 = 0.346 (8) Å and φ_2 = 321.8 (14)°, and for the isopropylidene ring, q_2 = 0.269 (8) Å and φ_2 = 314.9 (17)°.

To date, 14 X-ray structures of tosylated carbohydrates have been reported (Allen & Kennard, 1993). Of these, the most similar compound to those reported

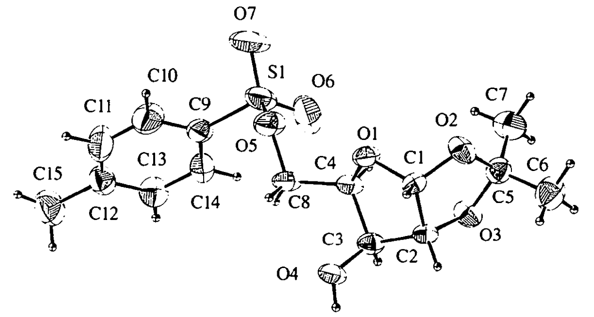


Fig. 1. The atomic arrangement in molecule (1). Displacement ellipsoids are shown at the 50% probability level.

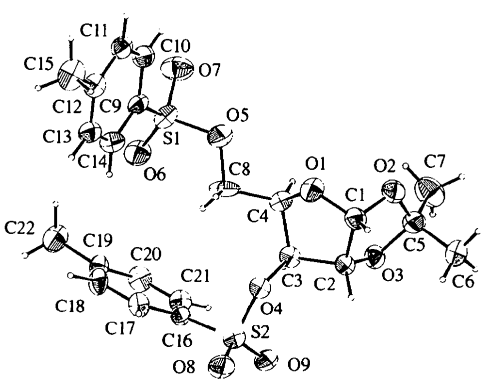


Fig. 2. The atomic arrangement in the molecule (2). Displacement ellipsoids are shown at the 50% probability level.

here is 6-(5-amino-4-cyano-5-oxo-3-aza-2-oxapent-3-enyl)-2,3-(*O*,*O*-isopropylidene)-4,6-(*O*,*O*-di-*p*-tosyl)xylofuranoside (Banert *et al.*, 1990).

Experimental

Compound (1) was prepared according to the method of Levene & Raymond (1933). Compound (2) was prepared according to the procedure of Hughes & Speakman (1966). In each case, the recrystallization solvent was diethyl ether.

Compound (1)

Crystal data

$C_{15}H_{20}O_7S$
$M_r = 344.37$
Orthorhombic
$P2_12_12_1$
$a = 5.717\,(10)$ Å
$b = 10.051\,(13)$ Å
$c = 29.07\,(3)$ Å
$V = 1670\,(4)$ Å^3
$Z = 4$
$D_x = 1.370$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 14 reflections
$\theta = 10.9–16.9°$
$\mu = 0.226$ mm^{-1}
$T = 293\,(2)$ K
Block
0.50 × 0.26 × 0.14 mm
Colourless

Data collection

Nicolet *P*3 diffractometer
ω scans
Absorption correction: none
1737 measured reflections
1737 independent reflections
1110 reflections with $I > 2\sigma(I)$

$\theta_{\max} = 24.99°$
$h = 0 \rightarrow 6$
$k = 0 \rightarrow 11$
$l = 0 \rightarrow 34$
2 standard reflections every 50 reflections intensity variation: 2.4%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.057$
$wR(F^2) = 0.148$
$S = 1.014$
1736 reflections
211 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.053P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.002$

$\Delta\rho_{\max} = 0.21$ e Å^{-3}
$\Delta\rho_{\min} = -0.21$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute configuration: Flack (1983)
Flack parameter = −0.6 (2) (not reliably determined)

Table 1. *Selected geometric parameters (Å, °) for (1)*

S1—O7	1.410 (5)	S1—O5	1.579 (5)
S1—O6	1.430 (5)	S1—C9	1.738 (6)
O7—S1—O6	120.2 (4)	O7—S1—C9	109.4 (3)
O7—S1—O5	103.5 (4)	O6—S1—C9	109.1 (3)
O6—S1—O5	109.0 (3)	O5—S1—C9	104.4 (3)
O4—C3—C4—C8	−37.3 (6)	S1—O5—C8—C4	95.0 (5)

Compound (2)

Crystal data

$C_{22}H_{26}O_9S_2$
$M_r = 498.55$
Monoclinic
$P2_1$
$a = 6.391$ (6) Å
$b = 13.795$ (6) Å
$c = 13.967$ (8) Å
$\beta = 100.17$ (6)°
$V = 1212.0$ (14) Å^3
$Z = 2$
$D_x = 1.366$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 14 reflections
$\theta = 11.8–19.0°$
$\mu = 0.268$ mm^{-1}
$T = 293$ (2) K
Plate
0.5 × 0.4 × 0.2 mm
Colourless

Data collection

Nicolet *P*3 diffractometer
θ–2θ scans
Absorption correction: none
2449 measured reflections
2252 independent reflections
1178 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.056$

$\theta_{\max} = 25.06°$
$h = 0 \rightarrow 7$
$k = 0 \rightarrow 16$
$l = -16 \rightarrow 16$
2 standard reflections every 50 reflections intensity variation: 2.2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.061$
$wR(F^2) = 0.115$
$S = 0.968$
2252 reflections
304 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0398P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = -0.005$

$\Delta\rho_{\max} = 0.20$ e Å^{-3}
$\Delta\rho_{\min} = -0.21$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute configuration: Flack (1983)
Flack parameter = −0.09 (15)

Table 2. *Selected geometric parameters (Å, °) for (2)*

S1—O6	1.389 (6)	S2—O9	1.419 (6)
S1—O7	1.432 (6)	S2—O8	1.426 (5)
S1—O5	1.577 (6)	S2—O4	1.595 (5)
S1—C9	1.762 (9)	S2—C16	1.737 (8)
O4—C3—C4—C8	−40.9 (8)	S1—O5—C8—C4	156.3 (5)

In each case, the absolute structure was assigned from the known asymmetric centres in the sugar moiety. H atoms were initially placed in calculated positions and then allowed to ride on their attached atoms with common isotropic displacement parameters of 0.058 (5) (non-methyl) and 0.092 (8) Å^2 (methyl) for (1), and 0.071 (6) (non-methyl) and 0.135 (12) Å^2 (methyl) for (2). The hydroxyl H atom was located using the circular Fourier method with refined torsion angle (*AFIX* 147) as described in *SHELXL*93 (Sheldrick, 1993).

For both compounds, program(s) used to solve structures: *SHELXS*86 (Sheldrick, 1990); program(s) used to refine structures: *SHELXL*93; molecular graphics: *ZORTEP* (Zsolnai, 1996).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1152). Services for accessing these data are described at the back of the journal.

References

Allen, F. H. & Kennard, O. (1993). *Chem. Des. Autom. News*, **8**, 131–136.

Armishaw, O. A., Cox, P. J., Hassan, A. K. & Wardell, J. L. (1996). *J. Chem. Cryst.* **26**, 701–705.
Banert, K., Reissaus, E., Deiseroth, H.-J., Kluge, C. P. & Peters, E.-M. (1990). *Angew. Chem. Int. Ed. Engl.* **29**, 1164–1166.
Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Hughes, N. A. & Speakman, P. R. H. (1966). *Carbohydr. Res.* **1**, 341–348.
Levene, P. A. & Raymond, A. L. (1933). *J. Biol. Chem.* **102**, 317–330.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.
Zsolnai, L. (1996). *ZORTEP. Interactive Graphics Program.* University of Heidelberg, Germany.

Acta Cryst. (1997). C**53**, 1941-1943

(5*R*/5*S*)-2,5-Diphenyl-7-[*trans*-(1*R*/1*S*,2*S*/2*R*)-2-phenylcyclohexyloxy]-2,3,5,8-tetrahydro-1*H*-1,2,4-triazolo[1,2-*a*]pyridazine-1,3-dione–Water (1/1): a Face-Selective Diels–Alder Reaction of 2-Alkoxy-1,3-butadiene

Santiago García-Granda,[a] Rafael Santiago-García,[a] Angel Suárez-Sobrino[b] and Luis Angel López[b]

[a]*Departamento de Química Física y Analítica, Facultad de Química, Universidad de Oviedo, Avda. Julián Clavería 8, 33071 Oviedo, Spain, and* [b]*Instituto Universitario de Química Organometálica Enrique Moles, Unidad Asociada al CSIC, Universidad de Oviedo, Avda. Julián Clavería 8, 33071 Oviedo, Spain. E-mail: sgg@sauron.quimica.uniovi.es*

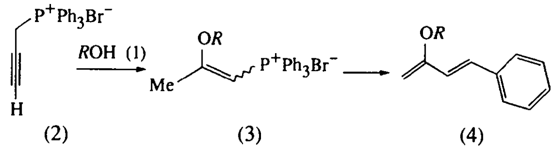
(*Received 13 March 1997; accepted 27 May 1997*)

Abstract

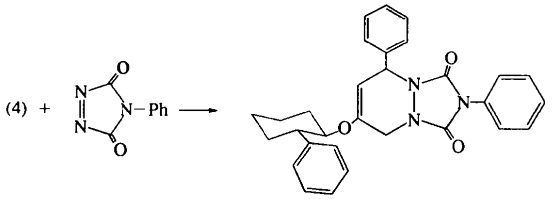
The title compound, $C_{30}H_{29}N_3O_3.H_2O$, is the final product in the Diels–Alder reaction between a 2-alkoxydiene and a reactive dienophile such as phenyltriazolinedione after recrystallization from methanol. The water molecule forms a hydrogen bond with a carbonyl O atom in one dione molecule and a weaker interaction with an N atom in a symmetry-related molecule, forming dimers linked by the water molecule. Atoms in the five-membered ring stemming from the dienophile molecule are related by a non-crystallographic C_2 axis through an N atom.

Comment

Chiral 2-substituted dienes are useful in Diels–Alder reactions. The role of chiral 2-alkoxy-1,3-butadienes in face-selective Diels–Alder reactions has recently been studied. The synthesis of substituted dienes has been reported as well as their [4+2] cycloaddition to hetero and carbo-dienophiles (Barluenga, Tomás, Suárez-Sobrino & López, 1995). The [4+2] cycloaddition of the racemic diene (4) (see reaction scheme below) to phenyltriazolinedione (PTAD) results in the formation of a new compound, (5), which is stable at room temperature. Knowledge of the structure of this Diels–Alder cycloadduct is a key for determining the stereochemical assignment of the other adducts in the cited work. The compound was crystallized from a methanol solution in the form of colourless crystals by slow evaporation.



(1) = (1*R*,2*S*/1*S*,2*R*)-*trans*-2-phenylcyclohexanol



(5)

In the title structure, most bond parameters are in the expected range. The O(3)—C(3) bond distance is shorter than the O(3)—C(13) distance due to conjugation with the double bond in the six-membered ring between atoms C(2) and C(3). The six-membered ring [C(1)–C(4), N(1) and N(2)] shows a half-chair conformation [$^6H_5$ in the notation of Boeyens (1978)]. The Cremer & Pople (1975) ring-puckering parameters are q_2 = 0.307 (3), q_3 = −0.284 (4), Q = 0.418 (3), φ = 92.5 (8)° and θ = 132.8 (3)°. The five-membered ring [N(1), N(2), C(6), C(5), N(3)] is almost planar. The sum of the bond angles is 538.2 (15)° and the maximum deviation from the least-squares plane is 0.069 (4) A, for C(5). A careful inspection of the internal Cartesian coordinates of the ring atoms shows that atoms C(6) and N(2) are related to C(5) and N(1), respectively, by *C*2 symmetry. The Cremer & Pople (1975) ring-puckering parameters for this ring are q_2 = 0.119 (3) and φ = 94 (1)°. The triply bonded N(3) atom is in a planar environment, the sum of the bond angles being 359.9 (9)°. The flattening is due to conjugation with the two carbonyl groups in the five-membered ring. Conjugation with the phenyl group is less important because of the unfavourable geometry. The dihedral angle between the least-squares planes formed by atoms C(25)–C(30) and the plane formed by atoms N(3), C(5), C(6), O(1) and O(2) is 45.06 (16)°. The maximum deviations from these two planes are C(27) 0.010 (5) and C(5) 0.040 (4) Å.

The six-membered ring formed by atoms C(13)–C(18) shows a chair conformation [$^1C_4$ in the notation of