

***p*-Tolyl 2,3-anhydro-5,6-*O*-isopropylidene-1-thio- β -D-gulofuranoside**Yu Bai,^a Todd L. Lowary^a and Michael J. Ferguson^{b*}^aAlberta Ingenuity Centre for Carbohydrate Science, Department of Chemistry, University of Alberta, Edmonton, AB T6G 2G2, Canada, and ^bX-Ray Crystallography Laboratory, Department of Chemistry, University of Alberta, Edmonton, AB T6G 2G2, Canada

Correspondence e-mail: michael.ferguson@ualberta.ca

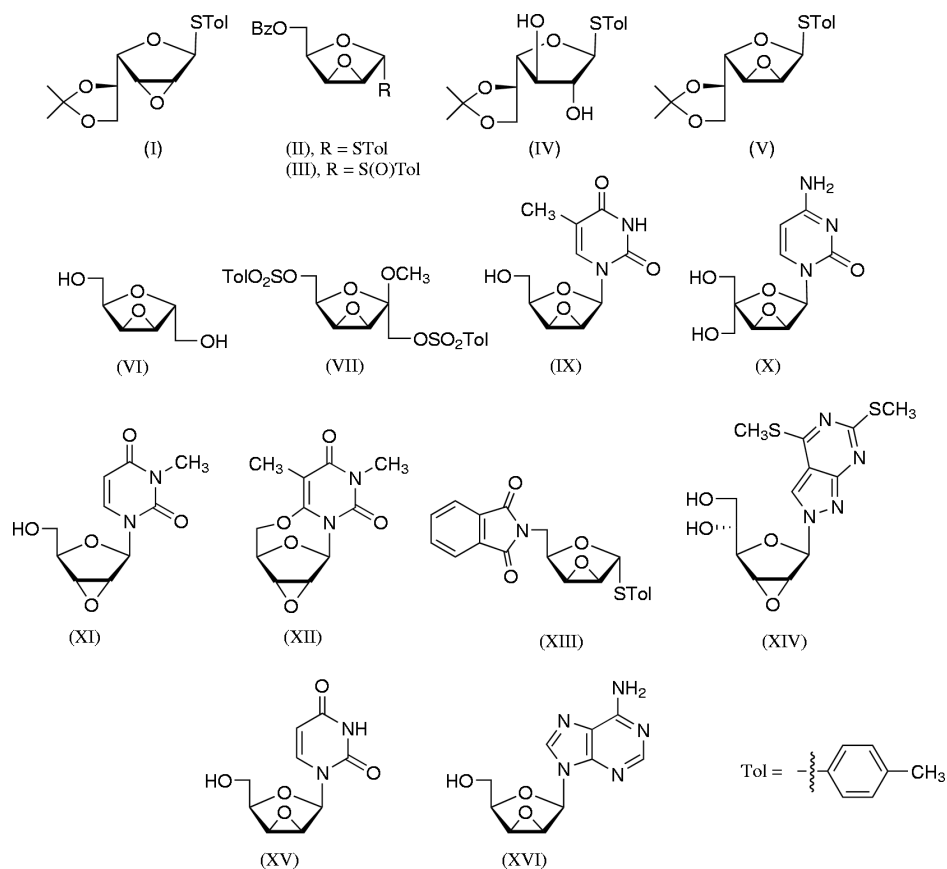
Key indicators

Single-crystal X-ray study
T = 193 K
Mean σ (C–C) = 0.003 Å
R factor = 0.033
wR factor = 0.079
Data-to-parameter ratio = 16.8For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

In the title compound, C₁₆H₂₀O₄S, the epoxide ring is *trans* to the *p*-tolyl group and *cis* to the dioxolane moiety. The furanose ring adopts a conformation in which the furanose and epoxide O atoms are on the same face of the molecule (*E_O*) and the *p*-tolyl group adopts the conformation favored by the *exo*-anomeric effect, *gauche* to the ring O atom and *anti* to the ring C atom.

Comment

We have recently developed a new method for the synthesis of glycosidic bonds that makes use of 2,3-anhydrosugar thio-glycosides and the corresponding sulfoxides [e.g. (II) and (III)] as the glycosylating agents (Callam *et al.*, 2003; Gadikota *et al.*, 2003).



In exploring the scope of this method, we sought to prepare additional 2,3-anhydrosugar thio-glycosides and, to that end, we reacted *p*-tolyl 5,6-*O*-isopropylidene-1-thio- β -D-galactofuranoside, (IV), with triphenylphosphine and diisopropyl

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azodicarboxylate. This reaction afforded a single compound, in 95% yield, in which the diol had been converted to an epoxide. However, from the NMR spectra obtained for the product, it was impossible to determine if (I) or its isomer (V) had been formed. Fortunately, the compound was crystalline and single-crystal X-ray diffraction allowed us to establish the structure of this product as (I).

The crystal structure of (I) is shown in Fig. 1, from which it is clear that the epoxide moiety is *trans* to the tolyl moiety at C1 and *cis* to the dioxolane group appended to the ring at C4. In (I), the epoxide and furanose ring O atoms are on the same face of the molecule, resulting in a 'boat-like' structure. The pseudorotational phase angle (P) of the furanose ring is 85.6° and the puckering amplitude (τ_m) is 31.6° (Altona & Sundaralingam, 1972). In this regard, this structure is similar to other 2,3-anhydrosugar-derived molecules for which crystal structures have been determined (VI)–(XIV) (Gurskaya *et al.*, 1990, 1996; Gallucci *et al.*, 2000; Garcia *et al.*, 1992; Guthrie *et al.*, 1981; Márton-Merész *et al.*, 1983; Biswas *et al.*, 1996) or for which molecular mechanics calculations have been carried out [(IX), (XV) and (XVI); Koole *et al.*, 1991]. Previous *ab initio* and density functional theory calculations on 2,3-anhydrosugar glycosides (Callam *et al.*, 2001) showed similar conformational features. In all cases, a 'boat-like' conformation is favored.

The dioxolane ring in (I) adopts an envelope conformation in which atoms O5, C5, C6 and C7 are essentially coplanar, while atom O6 is displaced out of the plane by $0.507(3) \text{ \AA}$. This conformation for the dioxolane ring places both methyl groups (C8 and C9) in pseudo-equatorial orientations, which is more favored than alternate envelope conformers in which one of these groups would be oriented pseudo-axial, thus introducing significant steric strain with other substituents on the ring. The molecule contains only three rotatable bonds. The C4–C5 bond adopts the *trans,gauche* (Bock & Duus, 1994) orientation, presumably because in the other two staggered rotamers, *gauche,gauche* and *gauche,trans*, there would be significant steric interactions between the dioxolane and furanose rings. The orientation about the C1–S bond is the one favored by the *exo*-anomeric effect (Lemieux & Koto, 1974), *i.e.* S is *anti* to C2 and *gauche* to the furanose ring O atom. The third rotatable bond, S–C10, is aligned such that the aromatic ring is roughly parallel to the C1–C2 bond; the C1–S–C10–C11 torsion angle is $-73.55(16)^\circ$.

Experimental

Diisopropyl azodicarboxylate (0.24 ml, 1.24 mmol) was added dropwise over 10 min to a solution of *p*-tolyl 5,6-*O*-isopropylidene-1-thio- β -D-galactofuranoside [(IV); 0.310 g, 0.95 mmol] and triphenylphosphine (0.324 g, 1.24 mmol) in tetrahydrofuran (5 ml) at 273 K. The reaction mixture was warmed to room temperature over a period of 30 min and the resulting mixture concentrated and diethyl ether added to precipitate triphenylphosphine oxide, which was subsequently removed by filtration. The resulting organic layer was concentrated and the residue purified by chromatography (6:1 hexanes–EtOAc) to yield (I) (0.277 g, 95%) as a white solid [R_F 0.46

(4:1 hexanes–EtOAc)]. Compound (I) was crystallized from methanol (m.p.: 349–351 K).

Crystal data

$C_{16}H_{20}O_4S$
 $M_r = 308.38$
 Orthorhombic, $P2_12_12_1$
 $a = 9.1248(7) \text{ \AA}$
 $b = 12.0366(10) \text{ \AA}$
 $c = 14.2666(11) \text{ \AA}$
 $V = 1566.9(2) \text{ \AA}^3$
 $Z = 4$
 $D_x = 1.307 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation
 Cell parameters from 5599 reflections
 $\theta = 2.2\text{--}25.8^\circ$
 $\mu = 0.22 \text{ mm}^{-1}$
 $T = 193(2) \text{ K}$
 Rod, colourless
 $0.61 \times 0.11 \times 0.10 \text{ mm}$

Data collection

Bruker PLATFORM/SMART 1000
 CCD area-detector diffractometer
 ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
 $T_{\min} = 0.878$, $T_{\max} = 0.978$
 12110 measured reflections

3202 independent reflections
 2780 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.032$
 $\theta_{\text{max}} = 26.4^\circ$
 $h = -11 \rightarrow 11$
 $k = -15 \rightarrow 14$
 $l = -17 \rightarrow 17$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.033$
 $wR(F^2) = 0.080$
 $S = 1.03$
 3202 reflections
 191 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0376P)^2 + 0.2041P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.23 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.13 \text{ e \AA}^{-3}$
 Absolute structure: Flack (1983),
 1359 Friedel pairs
 Flack parameter = 0.03 (7)

Table 1

Selected geometric parameters (\AA , $^\circ$).

S–C10	1.7697 (19)	O6–C6	1.433 (2)
S–C1	1.8217 (18)	C1–C2	1.502 (3)
O1–C1	1.419 (2)	C2–C3	1.458 (3)
O1–C4	1.440 (2)	C3–C4	1.503 (3)
O2–C2	1.435 (2)	C4–C5	1.518 (3)
O2–C3	1.437 (2)	C5–C6	1.525 (3)
O5–C5	1.422 (3)	C7–C9	1.494 (3)
O5–C7	1.428 (2)	C7–C8	1.517 (3)
O6–C7	1.417 (2)		
C10–S–C1	99.95 (8)	O1–C4–C5	107.44 (14)
C1–O1–C4	108.52 (13)	C3–C4–C5	119.51 (15)
C2–O2–C3	61.02 (11)	O5–C5–C4	107.78 (15)
C5–O5–C7	109.14 (14)	O5–C5–C6	104.29 (15)
C7–O6–C6	105.68 (15)	C4–C5–C6	115.52 (18)
O1–C1–C2	104.76 (14)	O6–C6–C5	102.58 (15)
O1–C1–S	112.84 (12)	O6–C7–O5	105.02 (14)
C2–C1–S	107.83 (13)	O6–C7–C9	109.05 (16)
O2–C2–C3	59.56 (11)	O5–C7–C9	108.36 (15)
O2–C2–C1	111.74 (16)	O6–C7–C8	111.11 (17)
C3–C2–C1	106.75 (16)	O5–C7–C8	110.09 (16)
O2–C3–C2	59.41 (11)	C9–C7–C8	112.88 (18)
O2–C3–C4	113.70 (15)	C11–C10–S	120.92 (15)
C2–C3–C4	106.56 (15)	C15–C10–S	120.55 (15)
O1–C4–C3	103.86 (15)		

H atoms were placed in idealized positions (according to the sp^2 or sp^3 geometries of their parent C atoms) and then refined using a riding model with fixed C–H distances (C–H = $0.95\text{--}1.00 \text{ \AA}$) and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Data collection: SMART (Bruker, 1997); cell refinement: SAINT (Bruker, 1997); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1990); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997a); molecular graphics:

SHELXTL (Sheldrick, 1997*b*); software used to prepare material for publication: *SHELXTL*.

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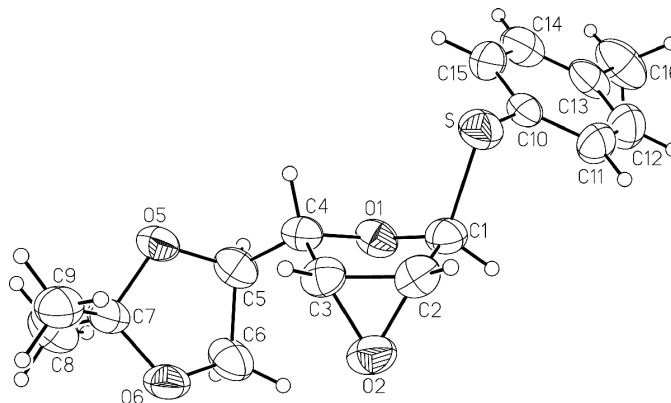


Figure 1
Perspective view of (I), showing the atom-labeling scheme. Non-H atoms are represented by ellipsoids at the 50% probability level. H atoms are shown with arbitrarily small radii.