

Phenyl 2,3-O-isopropylidene-1-thio- α -D-rhamnopyranoside

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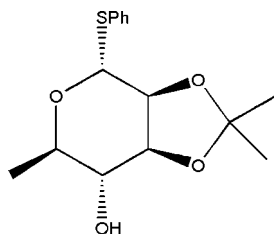
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Key indicators: single-crystal X-ray study; $T = 295$ K; mean $\sigma(\text{C}-\text{C}) = 0.004$ Å; disorder in main residue; R factor = 0.039; wR factor = 0.144; data-to-parameter ratio = 16.3.

In the title compound, $\text{C}_{15}\text{H}_{20}\text{O}_4\text{S}$, a dioxolane ring is fused to the pyran ring of the sugar which carries a thiophenyl substituent on the anomeric C atom. The dioxolane ring adopts an envelope conformation and the pyran ring system a distorted ${}^4\text{C}_1$ chair. The structure is stabilized by $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds, forming centrosymmetric dimers that generate an $R_2^2(10)$ ring motif. Additional $\text{C}-\text{H}\cdots\text{O}$ interactions form an extended network. Two C atoms of the phenyl ring are disordered over two positions; the site occupancy factors are *ca.* 0.7 and 0.3.

Related literature

For the background to angucyline antibiotics, see: Carreno & Urbano (2005); Toshima (2003); Krohn & Rohr (1997); Rohr & Thiericke (1992). For previous reports of the title compound, see: Kerekgyarto *et al.*, (1993); Yu & Wang, (2002). For related structures, see, for example: Yang *et al.* (2003); Wehlan *et al.* (2004). For ring puckering analysis, see: Cremer & Pople (1975). For graph-set analysis of hydrogen bonding, see: Bernstein *et al.* (1995).



Experimental

Crystal data

$\text{C}_{15}\text{H}_{20}\text{O}_4\text{S}$	$V = 1545.66$ (15) Å ³
$M_r = 296.37$	$Z = 4$
Monoclinic, $C2$	Mo $K\alpha$ radiation
$a = 24.3029$ (12) Å	$\mu = 0.22$ mm ⁻¹
$b = 5.3048$ (3) Å	$T = 295$ (2) K
$c = 12.0795$ (7) Å	$0.37 \times 0.30 \times 0.08$ mm
$\beta = 97.014$ (3)°	

Data collection

Bruker APEXII CCD diffractometer	17181 measured reflections
Absorption correction: multi-scan (SADABS; Bruker, 2004)	3318 independent reflections
$T_{\min} = 0.723$, $T_{\max} = 0.983$	2560 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.060$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.039$	H-atom parameters constrained
$wR(F^2) = 0.144$	$\Delta\rho_{\text{max}} = 0.33$ e Å ⁻³
$S = 1.03$	$\Delta\rho_{\text{min}} = -0.37$ e Å ⁻³
3318 reflections	Absolute structure: Flack (1983)
204 parameters	1392 Friedel pairs
1 restraint	Flack parameter: 0.03 (10)

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{O4}-\text{H4A}\cdots\text{O3}^{\text{i}}$	0.82	2.05	2.861 (2)	169
$\text{C8}-\text{H8A}\cdots\text{O3}^{\text{ii}}$	0.96	2.61	3.224 (3)	122
$\text{C14}-\text{H14}\cdots\text{O2}^{\text{iii}}$	0.93	2.62	3.524 (4)	164

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

Data collection: APEX2 (Bruker, 2004); cell refinement: SAINT (Bruker, 2004); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997) and TITAN2000 (Hunter & Simpson, 1999); molecular graphics: ORTEP-3 (Farrugia, 1997) and Mercury (Macrae *et al.*, 2006); software used to prepare material for publication: SHELXL97 and enCIFer (Allen *et al.*, 2004).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: NG2385).

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supplementary materials

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Phenyl 2,3-*O*-isopropylidene-1-thio- α -D-rhamnopyranoside

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Comment

In a sequence aimed at synthesizing 2,6-dideoxy-*D*-arabinopyranosides for use as glycosyl donors for the preparation of C-glycosides related to the angucycline antibiotics (Carreno & Urbano, 2005; Toshima, 2003; Krohn & Rohr, 1997; Rohr & Thiericke, 1992) we reduced tosylate (1) with lithium aluminium hydride to furnish the title compound (2), a known *D*-rhamnoside, (Kerekgyarto *et al.*, 1993; Yu & Wang, 2002) in 63% yield (Scheme 1). An unexpected by-product (3), where reduction of the isopropylidene group had occurred, was also isolated in 14% yield.

In (2), Fig. 1, the C2, C3, O2, C7, O3 dioxolane ring is fused to the pyran C1...C5, O1 ring of the sugar which carries a thiophenyl substituent on the anomeric C1 atom. The dioxolane ring adopts an envelope conformation with C2 0.600 (3) Å from the meanplane through C3, O2, C7, O3. The pyran ring system is in a distorted 4C_1 chair conformation with O1 and C3 0.609 (4) and -0.514 (4) Å from the meanplane through C1, C2, C4, C5 and $\theta = 17.9$ (3)° (Cremer & Pople, 1975).

In the crystal, adjacent molecules form inversion related dimers through O4—H4A...O3ⁱ hydrogen bonds ($i = -x, y, -z + 1$, Table 1, Fig. 2) in an $R_2^2(10)$ ring motif (Bernstein *et al.*, 1995). C—H...O hydrogen bonds stabilize the structure further, forming an extended network (Fig. 3).

Experimental

LiAlH₄ (0.590 g, 15.6 mmol) was carefully added to a solution of tosylate (1) (2.00 g, 4.30 mmol) in diethyl ether (100 ml) cooled in an ice-salt bath. The ice bath was removed and the mixture was stirred under nitrogen for 12 h. The reaction was cooled in ice and quenched by the addition of 1M sodium hydroxide (5 ml). The mixture was extracted with diethyl ether, the organic layer washed with brine (50 ml) and water (2 x 100 mL). After drying over anhydrous magnesium sulfate the solvent was removed *in vacuo*. Purification of the residue by silica gel column chromatography [hexane/diethyl ether 1:1 to 2:1 as eluant] afforded two fractions. The higher R_F fraction gave the title compound (2) (0.800 g, 63%) as a white crystalline solid. m.p. 76° C; $[\alpha]_D = +199.3$ (c 0.6, CH₂Cl₂); ν_{\max} (KBr): 3597, 2938, 2923, 1603, 1382, 1214, 1062 cm⁻¹; δ_H (300 MHz, CDCl₃): 1.26 (3H, d, J = 6.0 Hz, H-6), 1.39 (3H, s, CH₃), 1.56 (3H, s, CH₃), 2.2 (1H, OH), 3.50 (1H, m, H-5), 4.10 (1H, d, J = 6.4 Hz, H-2), 4.17 (1H, t, J = 7.1 Hz, H-4), 4.37 (2H, d, J = 0.9 Hz, H-3), 5.76 (1H, s, H-1), 7.32–7.50 (5H, m, PhH); δ_C (125 MHz, CDCl₃): 17.13, 26.47, 28.22, 67.02, 75.32, 76.66, 77.50, 78.41, 88.31, 109.84, 127.67, 129.11, 131.93, 133.47; Found: C, 60.57; H, 6.80, S, 10.65%. C₁₅H₂₀O₄S requires C, 60.79; H, 6.80; S, 10.82%.

Refinement

The C11 and C12 atoms of the thiophenyl ring were disordered over two conformations. The occupancy factor for the major component refined to 0.66 (3). H-atoms were positioned geometrically and refined using a riding model with d(C—H) =

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0.93 Å, $U_{\text{iso}}=1.2U_{\text{eq}}$ (C) for aromatic 0.98 Å, $U_{\text{iso}} = 1.2U_{\text{eq}}$ (C) for CH, 0.96 Å, $U_{\text{iso}} = 1.5U_{\text{eq}}$ (C) for CH₃ and 0.82 Å, $U_{\text{iso}} = 1.5U_{\text{eq}}$ (O) for the OH group.

Figures

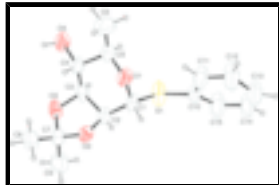


Fig. 1. The structure of (2) showing the atom numbering with thermal ellipsoids drawn at the 30% probability level. H atoms are drawn as circles with arbitrary radii. For clarity, only the major disorder component of the disordered benzene ring is shown.

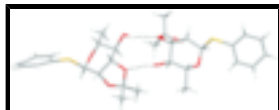


Fig. 2. Dimers of (2) formed by O4—H4A...O3 hydrogen-bonds, drawn as dashed lines showing only the major disorder component.

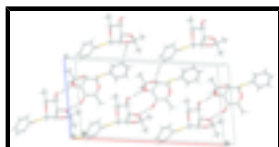


Fig. 3. Part of the crystal structure of (2) with hydrogen-bonds drawn as dashed lines and showing only the major disorder component.



Fig. 4. The formation of the title compound.

Phenyl 2,3-O-isopropylidene-1-thio- α -D-rhamnopyranoside

Crystal data

$C_{15}H_{20}O_4S$

$M_r = 296.37$

Monoclinic, $C2$

Hall symbol: $C\ 2y$

$a = 24.3029$ (12) Å

$b = 5.3048$ (3) Å

$c = 12.0795$ (7) Å

$\beta = 97.014$ (3)°

$V = 1545.66$ (15) Å³

$Z = 4$

$F_{000} = 632$

$D_x = 1.274$ Mg m⁻³

Mo $K\alpha$ radiation

$\lambda = 0.71073$ Å

Cell parameters from 4464 reflections

$\theta = 5.1$ – 53.9 °

$\mu = 0.22$ mm⁻¹

$T = 295$ (2) K

Irregular fragment, colourless

$0.37 \times 0.30 \times 0.08$ mm

Data collection

Bruker APEXII CCD
diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 295$ (2) K

φ & ω scans

Absorption correction: multi-scan

3318 independent reflections

2560 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.060$

$\theta_{\text{max}} = 27.1$ °

$\theta_{\text{min}} = 1.7$ °

$h = -30 \rightarrow 30$

(SADABS; Bruker, 2004)

$T_{\min} = 0.723$, $T_{\max} = 0.983$

17181 measured reflections

$k = -6 \rightarrow 6$

$l = -15 \rightarrow 15$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.039$

$wR(F^2) = 0.144$

$S = 1.04$

3318 reflections

204 parameters

1 restraint

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.1017P)^2 +]$$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.002$

$\Delta\rho_{\max} = 0.33 \text{ e } \text{\AA}^{-3}$

$\Delta\rho_{\min} = -0.37 \text{ e } \text{\AA}^{-3}$

Extinction correction: none

Absolute structure: Flack (1983) 1392 Friedel pairs

Flack parameter: 0.03 (10)

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
O1	0.18083 (7)	0.4599 (4)	0.64558 (13)	0.0532 (4)	
C1	0.17180 (10)	0.3676 (5)	0.75001 (19)	0.0463 (6)	
H1	0.1818	0.5016	0.8046	0.056*	
C2	0.11178 (10)	0.2973 (5)	0.7572 (2)	0.0463 (6)	
H2	0.1093	0.1902	0.8225	0.056*	
C3	0.08248 (9)	0.1708 (5)	0.6530 (2)	0.0496 (6)	
H3	0.0887	-0.0116	0.6565	0.060*	
C4	0.09941 (10)	0.2762 (5)	0.5457 (2)	0.0533 (6)	
H4	0.0827	0.4433	0.5321	0.064*	
O4	0.08181 (8)	0.1174 (5)	0.45401 (18)	0.0823 (8)	
H4A	0.0497	0.1512	0.4298	0.123*	
C5	0.16240 (11)	0.2999 (7)	0.5535 (2)	0.0642 (8)	
H5	0.1796	0.1333	0.5644	0.077*	

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C6	0.18068 (16)	0.4260 (13)	0.4507 (3)	0.1080 (17)	
H6A	0.1657	0.5935	0.4437	0.162*	
H6B	0.1674	0.3300	0.3855	0.162*	
H6C	0.2204	0.4338	0.4581	0.162*	
O2	0.07846 (7)	0.5178 (3)	0.76344 (14)	0.0476 (4)	
O3	0.02550 (7)	0.2257 (3)	0.66139 (16)	0.0527 (4)	
C7	0.02277 (10)	0.4350 (5)	0.7378 (2)	0.0474 (5)	
C8	-0.01126 (11)	0.6449 (5)	0.6803 (2)	0.0570 (7)	
H8A	-0.0087	0.7914	0.7273	0.085*	
H8B	-0.0493	0.5927	0.6657	0.085*	
H8C	0.0025	0.6846	0.6111	0.085*	
C9	-0.00051 (14)	0.3396 (9)	0.8398 (3)	0.0822 (10)	
H9A	0.0235	0.2116	0.8751	0.123*	
H9B	-0.0367	0.2698	0.8185	0.123*	
H9C	-0.0031	0.4764	0.8909	0.123*	
S1	0.21316 (3)	0.08767 (14)	0.79616 (7)	0.0730 (3)	
C10	0.27881 (10)	0.2165 (5)	0.8419 (2)	0.0494 (6)	
C11	0.3053 (4)	0.385 (3)	0.7765 (10)	0.077 (3)	0.66 (3)
H11	0.2869	0.4429	0.7094	0.092*	0.66 (3)
C12	0.3583 (4)	0.464 (3)	0.8110 (13)	0.100 (5)	0.66 (3)
H12	0.3765	0.5692	0.7659	0.120*	0.66 (3)
C11A	0.2958 (5)	0.456 (3)	0.8190 (18)	0.058 (4)	0.34 (3)
H11A	0.2721	0.5644	0.7752	0.070*	0.34 (3)
C12A	0.3488 (6)	0.534 (3)	0.8621 (19)	0.073 (4)	0.34 (3)
H12A	0.3587	0.7016	0.8523	0.088*	0.34 (3)
C13	0.38489 (15)	0.3843 (9)	0.9152 (3)	0.0866 (11)	
H13	0.4178	0.4591	0.9460	0.104*	
C14	0.36232 (13)	0.2024 (11)	0.9680 (3)	0.1015 (17)	
H14	0.3821	0.1311	1.0310	0.122*	
C15	0.30916 (13)	0.1145 (11)	0.9312 (3)	0.0966 (15)	
H15	0.2944	-0.0170	0.9691	0.116*	

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0429 (9)	0.0662 (11)	0.0483 (10)	-0.0123 (8)	-0.0041 (7)	0.0024 (8)
C1	0.0379 (13)	0.0511 (13)	0.0457 (13)	-0.0075 (10)	-0.0115 (10)	0.0022 (10)
C2	0.0382 (12)	0.0517 (13)	0.0467 (13)	-0.0039 (10)	-0.0041 (10)	0.0062 (10)
C3	0.0297 (10)	0.0385 (11)	0.0767 (18)	-0.0033 (8)	-0.0093 (10)	-0.0065 (10)
C4	0.0415 (13)	0.0636 (15)	0.0507 (15)	0.0054 (12)	-0.0106 (10)	-0.0165 (12)
O4	0.0537 (11)	0.1026 (19)	0.0830 (14)	0.0181 (12)	-0.0224 (10)	-0.0498 (14)
C5	0.0432 (14)	0.091 (2)	0.0564 (16)	0.0000 (14)	-0.0021 (12)	-0.0170 (15)
C6	0.077 (2)	0.192 (5)	0.0571 (19)	-0.017 (3)	0.0178 (17)	-0.007 (3)
O2	0.0397 (9)	0.0506 (10)	0.0503 (9)	-0.0060 (6)	-0.0029 (7)	-0.0082 (7)
O3	0.0337 (8)	0.0411 (9)	0.0796 (12)	-0.0055 (6)	-0.0078 (8)	-0.0083 (8)
C7	0.0386 (12)	0.0497 (12)	0.0528 (14)	-0.0065 (10)	0.0007 (10)	-0.0012 (10)
C8	0.0496 (15)	0.0457 (14)	0.0727 (18)	0.0014 (10)	-0.0040 (12)	-0.0037 (11)
C9	0.0603 (19)	0.111 (3)	0.077 (2)	-0.0063 (18)	0.0179 (16)	0.020 (2)

S1	0.0472 (4)	0.0536 (4)	0.1102 (6)	-0.0067 (3)	-0.0231 (4)	0.0170 (4)
C10	0.0322 (11)	0.0581 (15)	0.0554 (15)	0.0026 (10)	-0.0045 (10)	0.0056 (11)
C11	0.053 (4)	0.113 (7)	0.060 (5)	-0.021 (4)	-0.014 (3)	0.036 (5)
C12	0.050 (4)	0.151 (10)	0.093 (7)	-0.025 (5)	-0.016 (4)	0.063 (7)
C11A	0.031 (4)	0.072 (6)	0.070 (9)	0.014 (4)	0.006 (5)	-0.005 (6)
C12A	0.044 (6)	0.076 (7)	0.102 (11)	-0.020 (4)	0.021 (7)	-0.025 (7)
C13	0.0476 (17)	0.116 (3)	0.090 (2)	-0.0140 (19)	-0.0161 (16)	0.012 (2)
C14	0.0487 (17)	0.180 (5)	0.070 (2)	-0.007 (2)	-0.0170 (15)	0.045 (3)
C15	0.0522 (16)	0.158 (4)	0.075 (2)	-0.017 (2)	-0.0119 (14)	0.057 (3)

Geometric parameters (Å, °)

O1—C1	1.395 (3)	C8—H8A	0.9600
O1—C5	1.427 (3)	C8—H8B	0.9600
C1—C2	1.518 (3)	C8—H8C	0.9600
C1—S1	1.841 (3)	C9—H9A	0.9600
C1—H1	0.9800	C9—H9B	0.9600
C2—O2	1.429 (3)	C9—H9C	0.9600
C2—C3	1.525 (3)	S1—C10	1.762 (3)
C2—H2	0.9800	C10—C15	1.344 (4)
C3—O3	1.431 (3)	C10—C11	1.400 (8)
C3—C4	1.514 (4)	C10—C11A	1.374 (15)
C3—H3	0.9800	C11—C12	1.369 (10)
C4—O4	1.415 (3)	C11—H11	0.9300
C4—C5	1.527 (4)	C12—C13	1.407 (9)
C4—H4	0.9800	C12—H12	0.9300
O4—H4A	0.8200	C11A—C12A	1.394 (19)
C5—C6	1.524 (5)	C11A—H11A	0.9300
C5—H5	0.9800	C12A—C13	1.295 (18)
C6—H6A	0.9600	C12A—H12A	0.9300
C6—H6B	0.9600	C13—C14	1.313 (6)
C6—H6C	0.9600	C13—H13	0.9300
O2—C7	1.421 (3)	C14—C15	1.394 (5)
O3—C7	1.450 (3)	C14—H14	0.9300
C7—C9	1.506 (4)	C15—H15	0.9300
C7—C8	1.505 (3)		
C1—O1—C5	115.3 (2)	O3—C7—C8	109.76 (19)
O1—C1—C2	113.34 (19)	C9—C7—C8	112.7 (3)
O1—C1—S1	114.62 (18)	C7—C8—H8A	109.5
C2—C1—S1	106.12 (17)	C7—C8—H8B	109.5
O1—C1—H1	107.5	H8A—C8—H8B	109.5
C2—C1—H1	107.5	C7—C8—H8C	109.5
S1—C1—H1	107.5	H8A—C8—H8C	109.5
O2—C2—C1	110.9 (2)	H8B—C8—H8C	109.5
O2—C2—C3	101.14 (19)	C7—C9—H9A	109.5
C1—C2—C3	114.6 (2)	C7—C9—H9B	109.5
O2—C2—H2	110.0	H9A—C9—H9B	109.5
C1—C2—H2	110.0	C7—C9—H9C	109.5
C3—C2—H2	110.0	H9A—C9—H9C	109.5

supplementary materials

O3—C3—C4	110.6 (2)	H9B—C9—H9C	109.5
O3—C3—C2	102.1 (2)	C10—S1—C1	102.83 (12)
C4—C3—C2	113.3 (2)	C15—C10—C11	117.7 (4)
O3—C3—H3	110.2	C15—C10—C11A	112.7 (8)
C4—C3—H3	110.2	C15—C10—S1	118.9 (3)
C2—C3—H3	110.2	C11—C10—S1	122.1 (3)
O4—C4—C3	111.2 (2)	C11A—C10—S1	125.3 (6)
O4—C4—C5	107.6 (2)	C12—C11—C10	120.2 (6)
C3—C4—C5	110.6 (2)	C12—C11—H11	119.9
O4—C4—H4	109.1	C10—C11—H11	119.9
C3—C4—H4	109.1	C11—C12—C13	119.5 (6)
C5—C4—H4	109.1	C11—C12—H12	120.2
C4—O4—H4A	109.5	C13—C12—H12	120.2
O1—C5—C4	108.3 (2)	C10—C11A—C12A	119.1 (11)
O1—C5—C6	106.2 (3)	C10—C11A—H11A	120.4
C4—C5—C6	112.0 (3)	C12A—C11A—H11A	120.4
O1—C5—H5	110.1	C13—C12A—C11A	122.8 (12)
C4—C5—H5	110.1	C13—C12A—H12A	118.6
C6—C5—H5	110.1	C11A—C12A—H12A	118.6
C5—C6—H6A	109.5	C14—C13—C12A	113.2 (8)
C5—C6—H6B	109.5	C14—C13—C12	118.7 (5)
H6A—C6—H6B	109.5	C14—C13—H13	120.6
C5—C6—H6C	109.5	C12A—C13—H13	115.7
H6A—C6—H6C	109.5	C12—C13—H13	120.6
H6B—C6—H6C	109.5	C13—C14—C15	121.1 (3)
C7—O2—C2	105.45 (18)	C13—C14—H14	119.4
C3—O3—C7	108.72 (17)	C15—C14—H14	119.4
O2—C7—O3	105.01 (18)	C10—C15—C14	121.2 (4)
O2—C7—C9	111.6 (2)	C10—C15—H15	119.4
O3—C7—C9	108.3 (3)	C14—C15—H15	119.4
O2—C7—C8	109.1 (2)		

Hydrogen-bond geometry (\AA , $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O4—H4A \cdots O3 ⁱ	0.82	2.05	2.861 (2)	169
C8—H8A \cdots O3 ⁱⁱ	0.96	2.61	3.224 (3)	122
C14—H14 \cdots O2 ⁱⁱⁱ	0.93	2.62	3.524 (4)	164

Symmetry codes: (i) $-x, y, -z+1$; (ii) $x, y+1, z$; (iii) $-x+1/2, y-1/2, -z+2$.

Fig. 1

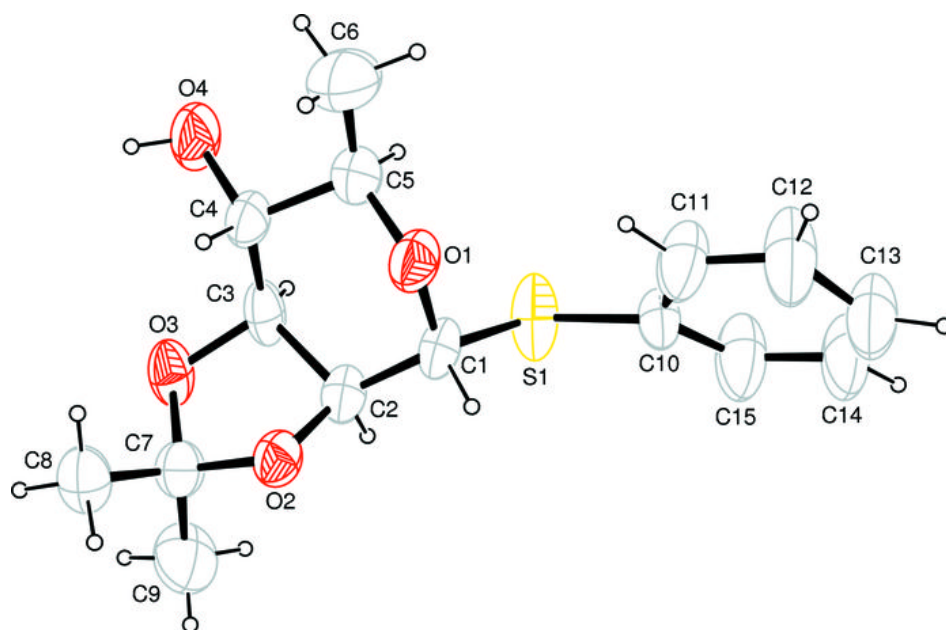


Fig. 2

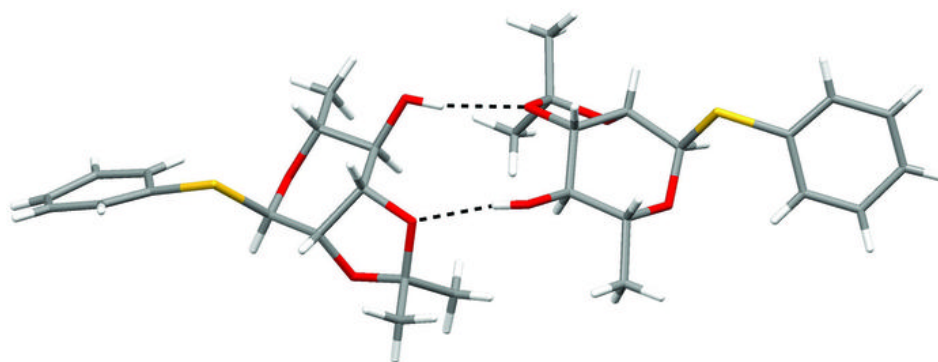


Fig. 3

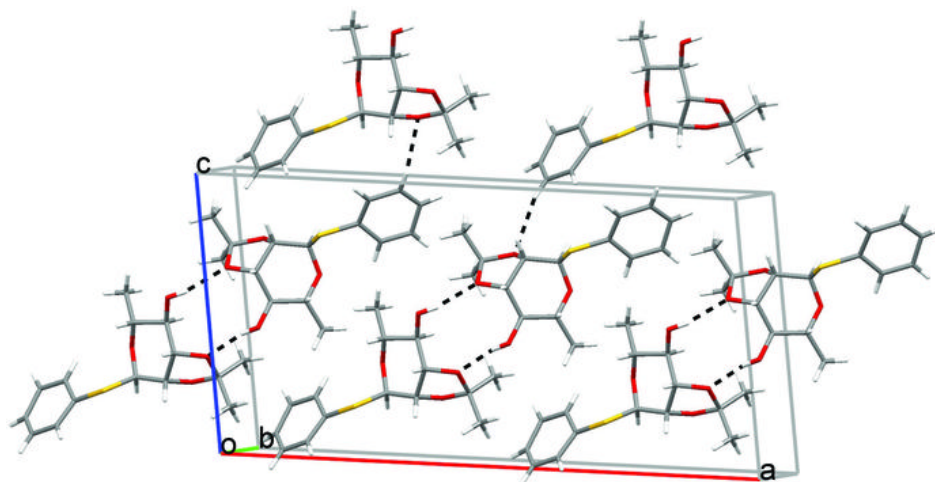


Fig. 4

