Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

Phenyl 2,3,4-tri-*O*-acetyl-1-thio-α-L-rhamnopyranoside: a glycosyl donor

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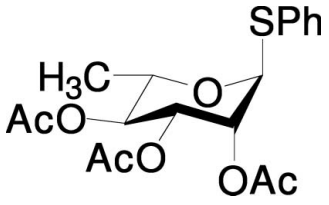
Received 27 June 2007; accepted 7 August 2007

Key indicators: single-crystal X-ray study; T = 295 K; mean σ(C–C) = 0.005 Å; R factor = 0.035; wR factor = 0.095; data-to-parameter ratio = 8.5.

The title compound, $C_{18}H_{22}O_7S$, is the product of the per-*O*-acetylation and thioglycosylation of the hexose L-(+)-rhamnopyranose. The structure has a chair conformation and the thiophenyl group on the anomeric carbon (C-1) is in an axial position.

Related literature

For related literature, see: Agnihotri *et al.* (2005); Bauer *et al.* (2006); Garegg (1997); Lang & Wullbrandt (1999); Leisinger & Margraff (1979); Norberg (1995).



Experimental

Crystal data

$C_{18}H_{22}O_7S$
M_r = 382.42
Monoclinic, $P2_1$
a = 9.3919 (11) Å
b = 11.6665 (13) Å
c = 9.5762 (9) Å
β = 108.336 (8)°
V = 996.00 (19) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.20 mm^{-1}
T = 295 (2) K
0.8 × 0.8 × 0.2 mm

Data collection

Bruker $P4$ diffractometer
Absorption correction: ψ-scan (North *et al.*, 1968)
T_{min} = 0.906, T_{max} = 1.000
(expected range = 0.871–0.961)
2399 measured reflections
2014 independent reflections
1726 reflections with $I > 2\sigma(I)$
R_{int} = 0.016
3 standard reflections
every 97 reflections
intensity decay: none

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.035
$wR(F^2)$ = 0.095
S = 1.06
2014 reflections
236 parameters
1 restraint
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.15 e Å^{-3}
$\Delta\rho_{min}$ = −0.15 e Å^{-3}
Absolute structure: Flack (1983), with 168 Friedel pairs
Flack parameter: 0.15 (11)

Data collection: *XSCANS* (Siemens, 1995); cell refinement: *XSCANS*; data reduction: *SHELXTL* (Bruker, 1997); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

The authors gratefully acknowledge financial support from both the National Science Council, Taiwan (grant No. NSC 95-2113-M-033-006), and the Project of Specific Research Fields, Chung Yuan Christian University, Taiwan (grant No. CYCU-95-CR-303020-3).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: TK2174).

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  doi:10.1107/S1600536807038974

supplementary materials

Acta Cryst. (2007). E**63**, o3772 [**doi:10.1107/S1600536807038974**]

Phenyl 2,3,4-tri-*O*-acetyl-1-thio-*α*-L-rhamnopyranoside: a glycosyl donor

Y.-F. Tsai, J.-T. Yang, J.-D. Chen and C.-H. Lin

Comment

Rhamnolipids comprise one of the most important classes of biosurfactants (Lang *et al.*, 1999) and exhibit diverse biological functions (Leisinger *et al.*, 1979). For the above reasons, the total synthesis of rhamnolipids has attracted considerable attention recently (Bauer *et al.*, 2006). Thioglycosides have been widely used as a glycosyl donor in synthetic carbohydrate chemistry (Garegg, 1997; Norberg, 1995). According to the literature (Agnihotri *et al.*, 2005), the title compound, $C_{18}H_{22}O_7S$ (I), was synthesized *via* one-pot two-step reaction of the commercially available optically pure *L*-(+)-rhamnopyranose as the starting material. As a part of our study on the total synthesis of rhamnolipids, the structure of (I) was investigated (Fig. 1). Notably, the thiophenyl group on anomeric carbon (C-1) is in an axial position.

Experimental

To a stirred suspension of *L*-(+)-rhamnopyranose ($[a]^{20}_D = +8.2°$) (0.846 g, 5.16 mmol) in acetic anhydride (Ac_2O) (2.0 ml, 21.29 mmol) was added $BF_3{\cdot}OEt_2$ (3.9 ml, 30.96 mmol) in one portion at 0°C. The mixture was stirred for 5 min at 0°C, and then was continuously stirred at room temperature for 15 min. After completion of this reaction, thiophenol (0.8 ml, 7.74 mmol) was added to the mixture at 0°C. The reaction mixture was allowed to stir for additional 4 h at room temperature. Finally, the reaction mixture was diluted with CH_2Cl_2, and washed with aqueous $NaHCO_3$ and brine. The organic layer was dried over $MgSO_4$, and solvent was removed *in vacuo* to afford a crude thioglycoside product. The crude product was recrystalized from CH_2Cl_2 at room temperature, affording single crystals of (I).

Refinement

All the H atoms were included in the riding-model approximation, with C—H = 0.93–0.98 Å, and with U_{iso}(H) = 1.2 or 1.5U_{eq}(C).

Figures

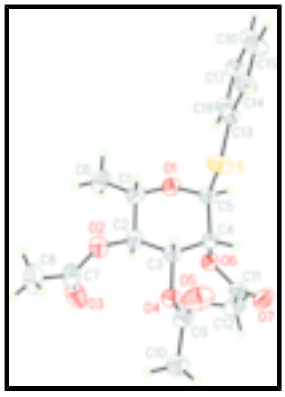


Fig. 1. The molecular structure of the title compound, showing the atom numbering scheme. Displacement ellipsoids for non-H atoms are represented at the 30% probability level.

Phenyl 2,3,4-tri-*O*-acetyl-1-thio-α-*L*-rhamnopyranoside

Crystal data

$C_{18}H_{22}O_7S$	F_{000} = 404
M_r = 382.42	D_x = 1.275 Mg m^{-3}
Monoclinic, $P2_1$	Mo $K\alpha$ radiation λ = 0.71073 Å
Hall symbol: P 2yb	Cell parameters from 29 reflections
a = 9.3919 (11) Å	θ = 6.0–12.4º
b = 11.6665 (13) Å	μ = 0.20 mm^{-1}
c = 9.5762 (9) Å	T = 295 (2) K
β = 108.336 (8)º	Plate, colourless
V = 996.00 (19) Å^3	0.8 × 0.8 × 0.2 mm
Z = 2	

Data collection

Bruker P4 diffractometer	R_{int} = 0.016
Radiation source: fine-focus sealed tube	θ_{max} = 25.0º
Monochromator: graphite	θ_{min} = 2.2º
T = 295(2) K	h = −11→1
ω scans	k = −13→1
Absorption correction: empirical (using intensity measurements) (North *et al.*, 1968)	l = −11→11
T_{min} = 0.906, T_{max} = 1.000	3 standard reflections
2399 measured reflections	every 97 reflections
2014 independent reflections	intensity decay: none
1726 reflections with $I > 2\sigma(I)$	

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.035$	$w = 1/[\sigma^2(F_o^2) + (0.0528P)^2 + 0.0914P]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.095$	$(\Delta/\sigma)_{max} < 0.001$
$S = 1.06$	$\Delta\rho_{max} = 0.15$ e Å^{-3}
2014 reflections	$\Delta\rho_{min} = -0.15$ e Å^{-3}
236 parameters	Extinction correction: SHELXL97 (Sheldrick, 1997), $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
1 restraint	Extinction coefficient: 0.071 (5)
Primary atom site location: structure-invariant direct methods	Absolute structure: Flack (1983), with how many Friedel pairs?
Secondary atom site location: difference Fourier map	Flack parameter: 0.15 (11)

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 (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
S	0.71622 (9)	0.58066 (11)	0.27509 (10)	0.0893 (4)
O1	0.9073 (2)	0.5858 (2)	0.1105 (2)	0.0684 (6)
O2	1.1033 (3)	0.3275 (2)	0.2803 (3)	0.0776 (6)
O3	1.3394 (4)	0.3395 (3)	0.2778 (5)	0.1269 (12)
O4	1.2028 (2)	0.4910 (2)	0.5112 (2)	0.0700 (6)
O5	1.0905 (4)	0.4401 (4)	0.6729 (3)	0.1258 (13)
O6	1.1337 (2)	0.6904 (2)	0.3493 (2)	0.0647 (6)
O7	1.1768 (3)	0.7723 (3)	0.5708 (3)	0.1008 (9)
C1	0.9412 (4)	0.4654 (4)	0.1286 (3)	0.0732 (9)
H1A	0.8576	0.4255	0.1481	0.088*
C2	1.0808 (4)	0.4495 (3)	0.2584 (3)	0.0651 (8)
H2A	1.1672	0.4845	0.2384	0.078*
C3	1.0615 (3)	0.4993 (3)	0.3959 (3)	0.0615 (8)
H3A	0.9853	0.4555	0.4234	0.074*
C4	1.0142 (3)	0.6235 (3)	0.3728 (3)	0.0607 (8)

H4A	0.9894	0.6525	0.4584	0.073*
C5	0.8789 (3)	0.6376 (3)	0.2326 (3)	0.0661 (8)
H5A	0.8627	0.7197	0.2123	0.079*
C6	0.9561 (5)	0.4222 (5)	−0.0152 (4)	0.1013 (14)
H6A	0.8632	0.4338	−0.0926	0.152*
H6B	0.9799	0.3420	−0.0068	0.152*
H6C	1.0347	0.4635	−0.0375	0.152*
C7	1.2363 (5)	0.2831 (4)	0.2874 (4)	0.0862 (11)
C8	1.2399 (7)	0.1577 (4)	0.3079 (6)	0.1234 (18)
H8A	1.3371	0.1291	0.3126	0.185*
H8B	1.1650	0.1228	0.2267	0.185*
H8C	1.2199	0.1397	0.3978	0.185*
C9	1.2027 (4)	0.4579 (4)	0.6445 (4)	0.0773 (9)
C10	1.3577 (5)	0.4463 (5)	0.7456 (4)	0.1005 (13)
H10A	1.3550	0.4221	0.8406	0.151*
H10B	1.4080	0.5189	0.7546	0.151*
H10C	1.4107	0.3904	0.7073	0.151*
C11	1.2070 (4)	0.7624 (3)	0.4583 (3)	0.0685 (8)
C12	1.3237 (5)	0.8277 (5)	0.4201 (5)	0.1000 (13)
H12A	1.3734	0.8781	0.4997	0.150*
H12B	1.2784	0.8719	0.3328	0.150*
H12C	1.3955	0.7756	0.4028	0.150*
C13	0.5623 (3)	0.6339 (3)	0.1330 (3)	0.0634 (8)
C14	0.4234 (3)	0.6131 (4)	0.1486 (4)	0.0804 (10)
H14A	0.4167	0.5725	0.2299	0.096*
C15	0.2955 (4)	0.6515 (4)	0.0456 (5)	0.0940 (13)
H15A	0.2029	0.6381	0.0588	0.113*
C16	0.3018 (4)	0.7092 (4)	−0.0761 (4)	0.0826 (10)
H16A	0.2141	0.7330	−0.1470	0.099*
C17	0.4385 (4)	0.7316 (3)	−0.0930 (4)	0.0762 (9)
H17A	0.4438	0.7725	−0.1746	0.091*
C18	0.5683 (3)	0.6936 (4)	0.0104 (3)	0.0752 (9)
H18A	0.6607	0.7084	−0.0025	0.090*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S	0.0608 (4)	0.1375 (10)	0.0750 (5)	0.0014 (6)	0.0291 (4)	0.0332 (6)
O1	0.0708 (11)	0.0835 (16)	0.0546 (11)	−0.0044 (12)	0.0251 (9)	0.0021 (11)
O2	0.0880 (15)	0.0677 (16)	0.0893 (15)	−0.0044 (13)	0.0454 (13)	−0.0008 (13)
O3	0.109 (2)	0.112 (3)	0.187 (3)	0.026 (2)	0.086 (2)	0.017 (3)
O4	0.0659 (12)	0.0861 (17)	0.0605 (12)	0.0013 (12)	0.0233 (10)	0.0060 (12)
O5	0.119 (2)	0.196 (4)	0.0671 (14)	−0.034 (3)	0.0365 (15)	0.014 (2)
O6	0.0648 (12)	0.0733 (14)	0.0601 (11)	−0.0079 (11)	0.0253 (10)	−0.0048 (11)
O7	0.1001 (18)	0.133 (3)	0.0669 (13)	−0.0129 (18)	0.0227 (13)	−0.0250 (16)
C1	0.079 (2)	0.078 (2)	0.0663 (18)	−0.0140 (18)	0.0280 (16)	−0.0045 (18)
C2	0.0703 (18)	0.066 (2)	0.0684 (17)	−0.0064 (16)	0.0353 (15)	−0.0024 (16)
C3	0.0561 (16)	0.075 (2)	0.0580 (15)	−0.0048 (16)	0.0242 (13)	0.0023 (15)

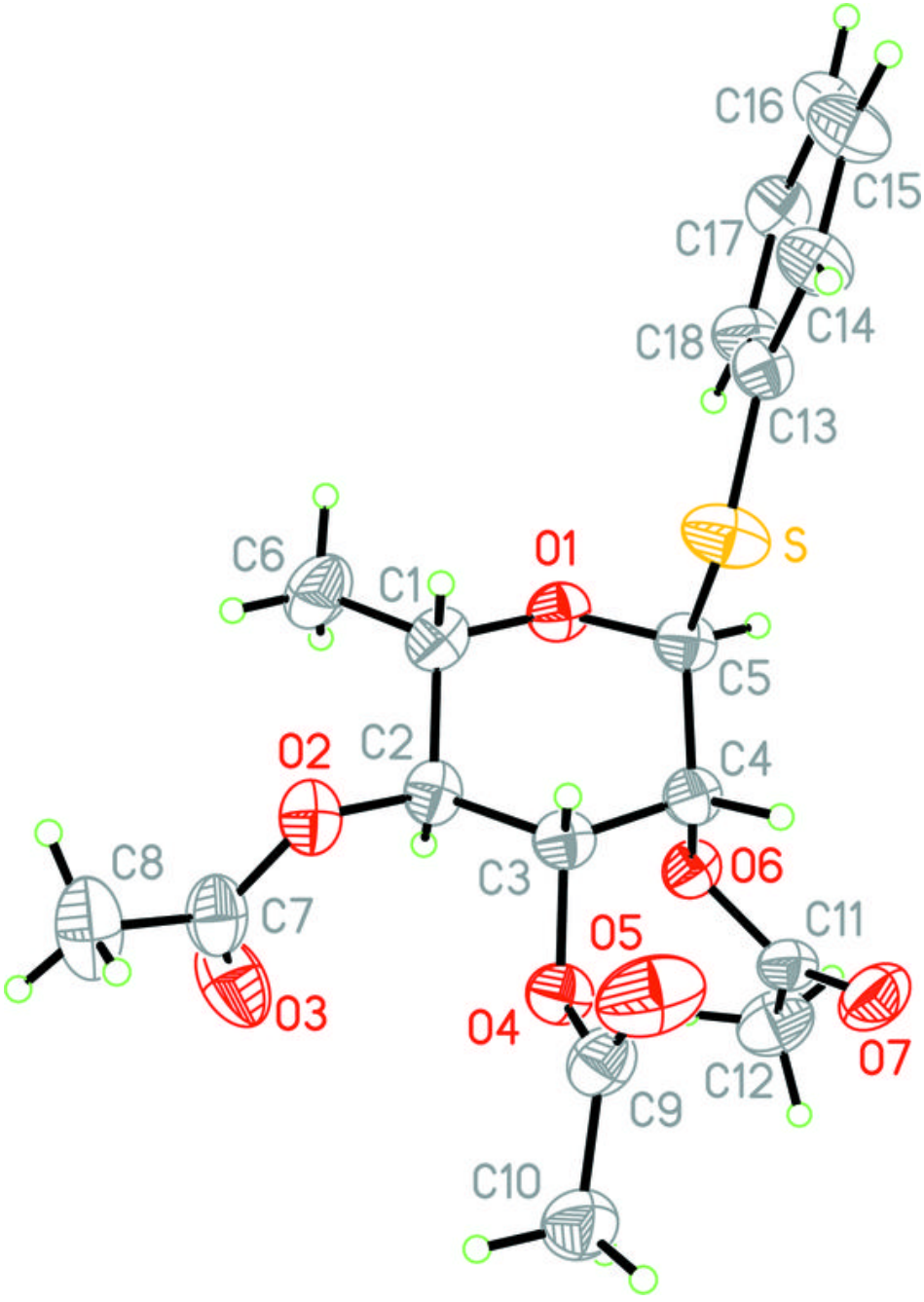
C4	0.0561 (15)	0.077 (2)	0.0561 (15)	−0.0040 (15)	0.0273 (13)	−0.0025 (14)
C5	0.0604 (15)	0.083 (2)	0.0590 (16)	0.0003 (17)	0.0252 (13)	0.0051 (16)
C6	0.131 (4)	0.107 (3)	0.0647 (19)	−0.003 (3)	0.028 (2)	−0.013 (2)
C7	0.114 (3)	0.077 (3)	0.084 (2)	0.009 (2)	0.055 (2)	−0.001 (2)
C8	0.185 (5)	0.084 (3)	0.126 (4)	0.026 (3)	0.084 (4)	0.008 (3)
C9	0.094 (2)	0.078 (2)	0.0596 (18)	−0.005 (2)	0.0231 (18)	0.0009 (17)
C10	0.116 (3)	0.094 (3)	0.076 (2)	0.013 (3)	0.009 (2)	0.004 (2)
C11	0.0626 (17)	0.072 (2)	0.0609 (17)	0.0046 (16)	0.0051 (14)	0.0010 (17)
C12	0.098 (3)	0.097 (3)	0.098 (3)	−0.032 (3)	0.020 (2)	−0.001 (3)
C13	0.0618 (15)	0.0681 (19)	0.0667 (17)	−0.0021 (16)	0.0294 (14)	0.0037 (16)
C14	0.0677 (18)	0.091 (3)	0.090 (2)	0.0028 (19)	0.0366 (17)	0.024 (2)
C15	0.0639 (19)	0.118 (4)	0.107 (3)	0.006 (2)	0.0362 (19)	0.027 (3)
C16	0.069 (2)	0.087 (3)	0.092 (2)	0.014 (2)	0.0260 (17)	0.011 (2)
C17	0.080 (2)	0.082 (2)	0.0682 (18)	0.0037 (19)	0.0257 (16)	0.0099 (18)
C18	0.0639 (17)	0.098 (3)	0.0676 (18)	−0.0056 (19)	0.0264 (15)	0.0052 (19)

Geometric parameters (Å, °)

S—C13	1.758 (3)	C6—H6C	0.9600
S—C5	1.826 (3)	C7—C8	1.475 (7)
O1—C5	1.414 (4)	C8—H8A	0.9600
O1—C1	1.439 (5)	C8—H8B	0.9600
O2—C7	1.333 (5)	C8—H8C	0.9600
O2—C2	1.445 (4)	C9—C10	1.479 (5)
O3—C7	1.198 (5)	C10—H10A	0.9600
O4—C9	1.334 (4)	C10—H10B	0.9600
O4—C3	1.439 (4)	C10—H10C	0.9600
O5—C9	1.186 (5)	C11—C12	1.473 (5)
O6—C11	1.348 (4)	C12—H12A	0.9600
O6—C4	1.442 (4)	C12—H12B	0.9600
O7—C11	1.202 (4)	C12—H12C	0.9600
C1—C2	1.508 (5)	C13—C18	1.381 (5)
C1—C6	1.513 (5)	C13—C14	1.381 (4)
C1—H1A	0.9800	C14—C15	1.368 (5)
C2—C3	1.502 (4)	C14—H14A	0.9300
C2—H2A	0.9800	C15—C16	1.363 (6)
C3—C4	1.511 (5)	C15—H15A	0.9300
C3—H3A	0.9800	C16—C17	1.369 (5)
C4—C5	1.540 (4)	C16—H16A	0.9300
C4—H4A	0.9800	C17—C18	1.380 (5)
C5—H5A	0.9800	C17—H17A	0.9300
C6—H6A	0.9600	C18—H18A	0.9300
C6—H6B	0.9600		
C13—S—C5	103.93 (15)	O2—C7—C8	111.9 (4)
C5—O1—C1	114.2 (2)	C7—C8—H8A	109.5
C7—O2—C2	118.8 (3)	C7—C8—H8B	109.5
C9—O4—C3	118.4 (3)	H8A—C8—H8B	109.5
C11—O6—C4	116.7 (2)	C7—C8—H8C	109.5
O1—C1—C2	108.7 (3)	H8A—C8—H8C	109.5

O1—C1—C6	107.2 (3)	H8B—C8—H8C	109.5
C2—C1—C6	113.8 (3)	O5—C9—O4	122.5 (3)
O1—C1—H1A	109.0	O5—C9—C10	126.6 (4)
C2—C1—H1A	109.0	O4—C9—C10	110.8 (3)
C6—C1—H1A	109.0	C9—C10—H10A	109.5
O2—C2—C3	107.8 (3)	C9—C10—H10B	109.5
O2—C2—C1	106.9 (3)	H10A—C10—H10B	109.5
C3—C2—C1	111.2 (3)	C9—C10—H10C	109.5
O2—C2—H2A	110.3	H10A—C10—H10C	109.5
C3—C2—H2A	110.3	H10B—C10—H10C	109.5
C1—C2—H2A	110.3	O7—C11—O6	123.1 (3)
O4—C3—C2	108.1 (2)	O7—C11—C12	125.2 (4)
O4—C3—C4	109.6 (3)	O6—C11—C12	111.6 (3)
C2—C3—C4	110.7 (3)	C11—C12—H12A	109.5
O4—C3—H3A	109.5	C11—C12—H12B	109.5
C2—C3—H3A	109.5	H12A—C12—H12B	109.5
C4—C3—H3A	109.5	C11—C12—H12C	109.5
O6—C4—C3	109.5 (2)	H12A—C12—H12C	109.5
O6—C4—C5	106.0 (2)	H12B—C12—H12C	109.5
C3—C4—C5	110.7 (3)	C18—C13—C14	118.2 (3)
O6—C4—H4A	110.2	C18—C13—S	126.4 (2)
C3—C4—H4A	110.2	C14—C13—S	115.4 (2)
C5—C4—H4A	110.2	C15—C14—C13	120.6 (3)
O1—C5—C4	110.9 (2)	C15—C14—H14A	119.7
O1—C5—S	114.7 (2)	C13—C14—H14A	119.7
C4—C5—S	106.6 (2)	C16—C15—C14	120.9 (3)
O1—C5—H5A	108.1	C16—C15—H15A	119.5
C4—C5—H5A	108.1	C14—C15—H15A	119.5
S—C5—H5A	108.1	C15—C16—C17	119.4 (3)
C1—C6—H6A	109.5	C15—C16—H16A	120.3
C1—C6—H6B	109.5	C17—C16—H16A	120.3
H6A—C6—H6B	109.5	C16—C17—C18	120.2 (3)
C1—C6—H6C	109.5	C16—C17—H17A	119.9
H6A—C6—H6C	109.5	C18—C17—H17A	119.9
H6B—C6—H6C	109.5	C17—C18—C13	120.6 (3)
O3—C7—O2	123.4 (4)	C17—C18—H18A	119.7
O3—C7—C8	124.7 (5)	C13—C18—H18A	119.7

Fig. 1


C16
C15
C17
C14
C18
C13
S
O1
C6
C1
C5
O2
C2
C4
C8
C3
O6
C7
C11
O5
O3
O4
O7
C12
C9
C10