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Bis(methyl 2,4,6-tri-*O*-acetyl-β-D-allofuranosid-3-yl)sulfane

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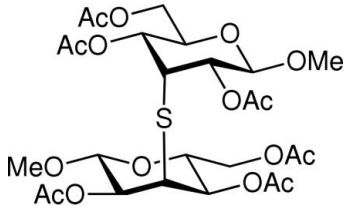
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.005 Å; R factor = 0.039; wR factor = 0.110; data-to-parameter ratio = 11.3.

The title compound, $C_{26}H_{38}O_{16}S$, crystallizes with two unique half molecules in the asymmetric unit, where the central S atom in each of the unique molecules is positioned on a twofold rotation axis. The only major conformational difference between the two molecules concerns one of the acetyl groups. Except for that acetyl group, the atoms of the two different molecules, in an overlay of one molecule on the other, differ on average by only 0.06 (6) Å from each other.

Related literature

For general background, see: Cumpstey (2006). For synthesis of the trifluoromethanesulfonate precursor to the title compound, see: Grandjean & Lukacs (1996). For geometrical calculations, see: Cremer & Pople (1975); Norrestam (1991).



Experimental

Crystal data

$C_{26}H_{38}O_{16}S$
M_r = 638.62
Monoclinic, $C2$
a = 22.6458 (13) Å
b = 7.2018 (3) Å
c = 21.3260 (12) Å
β = 109.258 (7)°
V = 3283.4 (3) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.17 mm^{-1}
T = 293 (2) K
0.30 × 0.05 × 0.05 mm

Data collection

Oxford Diffraction Xcalibur-II with Sapphire-III CCD diffractometer
Absorption correction: multi-scan (*CrysAlis RED*; Oxford Diffraction, 2007)
T_{min} = 0.95, T_{max} = 1.00 (expected range = 0.942–0.992)
10820 measured reflections
4492 independent reflections
3486 reflections with $I > 2\sigma(I)$
R_{int} = 0.021

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.039
$wR(F^2)$ = 0.110
S = 1.05
4492 reflections
398 parameters
1 restraint
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.24 e Å^{-3}
$\Delta\rho_{min}$ = −0.27 e Å^{-3}
Absolute structure: Flack (1983), 1101 Friedel pairs
Flack parameter: −0.03 (9)

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2007); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2007); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Bergerhoff, 1996); software used to prepare material for publication: *PLATON* (Spek, 2003).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SJ2366).

References

Bergerhoff, G. (1996). *DIAMOND*. Gerhard-Domagk-Strasse 1, 53121 Bonn, Germany.
Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.
Cumpstey, I. (2006). *Synlett*, pp. 1711–1714.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Grandjean, C. & Lukacs, G. (1996). *J. Carbohydr. Chem.* **15**, 831–856.
Norrestam, R. (1991). *ROTERA*. Stockholm University, Sweden.
Oxford Diffraction (2007). *CrysAlis CCD* and *CrysAlis RED*. Versions 1.171.31.8. Oxford Diffraction Ltd, Abingdon, Oxfordshire, England.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.

supplementary materials

Acta Cryst. (2007). E**63**, o4197 [**doi:10.1107/S1600536807047150**]

Bis(methyl 2,4,6-tri-*O*-acetyl-*β*-D-allofuranosid-3-yl)sulfane

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Comment

The title compound (I) was synthesized as part of a program towards the synthesis of thioether-linked disaccharides as new glycomimetics (Cumpstey, 2006). The title compound crystallizes with two unique half molecules in the asymmetric unit. Both molecules are shown in Fig. 1. Both of the sulfur atoms are positioned on a two fold axis whereby the second half of each molecule is generated through the two fold rotation. A packing view of the structure is shown in Fig 2. The conformations of the sugar rings in the two molecules are very similar as can be seen from corresponding geometrical parameters for the two rings. The Cremer Pople parameters (Cremer & Pople, 1975) for the ring O15→ C11→ C12→ C13→ C14→ C15 are: Q=0.587 (3) Å, θ=0.0 (3)° and φ=159 (9)° while for the ring O25→ C21→ C22→ C23→ C24→ C25 they are: Q=0.597 (3) Å, θ=1.3 (3)° and φ=244 (7)°. Both rings are on C-form. The major conformational difference between the molecules is shown in an overlay of the two unique half molecules (Fig. 3), the acetyl group starting at O16 in one of the molecules deviates significantly from the corresponding acetyl group, beginning with O26 in the other molecule. The rest of the atoms, except for these two acetyl groups, have an average deviation of 0.06 (6)Å between the atoms of one residue and the overlaid residue.

Experimental

The title compound (I) was prepared from the trifluoromethanesulfonate derivative (III) (Grandjean & Lukacs, 1996) as follows: sodium sulfide nonahydrate (475 mg, 2.0 mmol) was dried by heating under vacuum and then allowed to cool to RT. Molecular sieves 4Å (*ca* 500 mg) and acetonitrile (6 ml) were added, followed by trifluoromethanesulfonate (III) (500 mg, 1.0 mmol). The mixture was stirred at 50°C for 3 h, after which time it was diluted with dichloromethane (50 ml) and filtered through Celite. The filtrate was washed with HCl (1*M*, 50 ml) then $NaHCO_3$ (sat. 50 ml), then dried (Na_2SO_4), filtered and concentrated. The residue was purified by flash column chromatography (3:1 pentane:ethyl acetate) to give the thioether (II) (331 mg, 90%). Thioether (II) (214 mg) was dissolved in THF (3 ml) and cooled to −78 C, while ammonia (*ca* 20 ml) was condensed in. Sodium (*ca* 140 mg) was added to give a deep blue solution, followed by MeOH (0.04 ml). After 2 min, NH_4Cl was added until the blue colour disappeared and the solvents were allowed to evaporate. The crude material was then acetylated with acetic anhydride (3 + 1.6 ml) and pyridine (3 + 1.6 ml) overnight. Methanol (8 ml) and ethyl acetate (40 ml) were then added and the mixture was washed with HCl (1*M*, 30 ml) then $NaHCO_3$ (sat. 30 ml), then dried (Na_2SO_4), filtered and concentrated. The residue was purified by flash column chromatography (2:1 toluene:ethyl acetate) to give the title compound (I) (131 mg, 71%). Crystals were grown from methanol solution by slow evaporation of the solvent.

Refinement

Several of the *O*-acyl groups showed substantial disorder most clearly shown by the elongated ellipsoids especially of O14B, O16B and O24B. This disorder most probably occurs due to the absence of strong intermolecular hydrogen bonding interactions. Attempts to model the disorder did not improve the fit, thus it is represented only by the elongated ellipsoids. All hydrogen atoms were geometrically positioned and refined with riding motion, d(C—H)=0.96, 0.97,0.98 Å for CH_3,

CH_2 and CH respectivly. The U_{iso}(H) = 1.5U_{eq}(C) for CH_3 and 1.2U_{eq}(C) for CH_2 and CH. The transformation for the overlay (Fig. 3) was calculated with the program ROTERA (Norrestam, 1991).

Figures

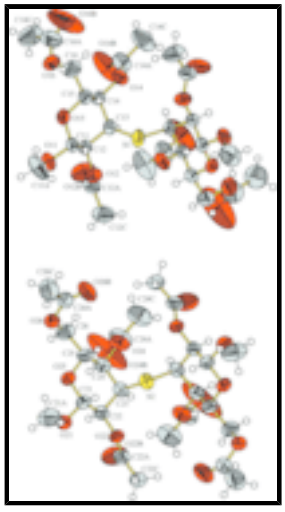


Fig. 1. Fig. 1. The two unique molecules of (I). Both sulfur atoms lie on twofold rotation axes so that the labelled atoms are related to the unlabelled atoms by the symmetry operations [−*x*,*y*,-*z* + 1] for the upper molecule and [−*x* + 1,*y*,-*z*] for the lower molecule. Displacement ellipsoids are drawn at the 50% level. Hydrogen atoms shown as small circles of arbitrary radii.

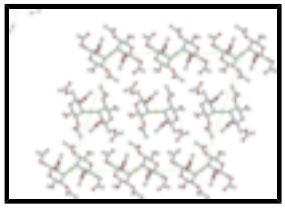


Fig. 2. Packing view of (I) along the *b* axis.

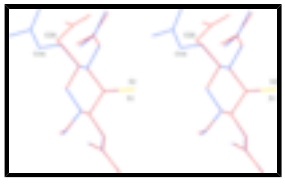


Fig. 3. Stereoview of an overlay of the two unique half molecules of the title compound. The yellow atom is the central sulfur atom of each complete molecule while the red or blue atoms designate each unique residue. The two residues differ from each other only after the C16/C26 and the atoms in the acetyl group attached to C16/C26.

Fig. 4. The formation of the title compound.

Bis(methyl 2,4,6-tri-*O*-acetyl-β-*D*-allofuranosid-3-yl)sulfane

Crystal data

$C_{26}H_{38}O_{16}S$	F_{000} = 1352
M_r = 638.62	D_x = 1.292 Mg m^{-3}
Monoclinic, *C*2	Mo *K*α radiation λ = 0.71073 Å
Hall symbol: C 2y	Cell parameters from 5794 reflections
a = 22.6458 (13) Å	θ = 3.8–32.1º
b = 7.2018 (3) Å	μ = 0.17 mm^{-1}
c = 21.3260 (12) Å	*T* = 293 (2) K
β = 109.258 (7)º	Prism, colourless

V = 3283.4 (3) Å^3	0.30 × 0.05 × 0.05 mm
Z = 4	

Data collection

Oxford Diffraction Xcalibur-II with Sapphire-III CCD diffractometer	4492 independent reflections
Radiation source: Enhance (Mo) X-ray Source	3486 reflections with $I > 2\sigma(I)$
Monochromator: graphite	R_{int} = 0.021
Detector resolution: 16.5467 pixels mm^{-1}	θ_{max} = 25.7º
T = 293(2) K	θ_{min} = 3.9º
ω scans at different θ	h = −27→25
Absorption correction: multi-scan (CrysAlis RED; Oxford Diffraction, 2007)	k = −5→8
T_{min} = 0.95, T_{max} = 1.00	l = −25→26
10820 measured reflections	

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)]$ = 0.039	$w = 1/[\sigma^2(F_o^2) + (0.0718P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2)$ = 0.110	$(\Delta/\sigma)_{max} < 0.001$
S = 1.05	$\Delta\rho_{max}$ = 0.24 e Å^{-3}
4492 reflections	$\Delta\rho_{min}$ = −0.27 e Å^{-3}
398 parameters	Extinction correction: SHELXL97 (Sheldrick, 1997), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
1 restraint	Extinction coefficient: 0.0036 (7)
Primary atom site location: structure-invariant direct methods	Absolute structure: Flack (1983), 1101 Friedel pairs
Secondary atom site location: difference Fourier map	Flack parameter: −0.03 (9)

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}
S1	0.0000	0.92953 (13)	0.5000	0.0534 (3)
C13	0.06297 (12)	0.7707 (4)	0.49958 (13)	0.0444 (6)
H13	0.0447	0.6545	0.4777	0.053*
C14	0.10871 (13)	0.7272 (4)	0.56881 (13)	0.0473 (7)
H14	0.1396	0.6380	0.5639	0.057*
C15	0.14320 (13)	0.8986 (5)	0.60214 (13)	0.0520 (7)
H15	0.1131	0.9893	0.6078	0.062*
O15	0.17528 (8)	0.9763 (3)	0.56093 (9)	0.0549 (5)
C11	0.13600 (12)	1.0308 (4)	0.49624 (13)	0.0479 (7)
H11	0.1064	1.1268	0.4992	0.057*
C12	0.10163 (12)	0.8597 (4)	0.46103 (13)	0.0465 (7)
H12	0.1324	0.7692	0.4567	0.056*
O14	0.07742 (10)	0.6447 (3)	0.61058 (10)	0.0607 (6)
C14A	0.08051 (18)	0.4616 (6)	0.6179 (2)	0.0791 (10)
O14B	0.1048 (3)	0.3678 (5)	0.5886 (3)	0.173 (2)
C14C	0.0512 (3)	0.3921 (8)	0.6656 (3)	0.127 (2)
H14A	0.0396	0.2643	0.6561	0.191*
H14B	0.0146	0.4643	0.6620	0.191*
H14C	0.0804	0.4024	0.7099	0.191*
C16	0.19207 (16)	0.8600 (6)	0.66876 (16)	0.0745 (10)
H16A	0.2140	0.9738	0.6869	0.089*
H16B	0.1722	0.8132	0.6995	0.089*
O16	0.23542 (11)	0.7255 (5)	0.66035 (11)	0.0822 (8)
C16A	0.2510 (2)	0.5855 (8)	0.6984 (2)	0.1022 (15)
O16B	0.2344 (4)	0.5756 (11)	0.7444 (3)	0.272 (5)
C16C	0.2925 (2)	0.4510 (10)	0.6811 (3)	0.1246 (19)
H16C	0.3351	0.4924	0.6992	0.187*
H16D	0.2810	0.4416	0.6337	0.187*
H16E	0.2885	0.3316	0.6993	0.187*
O11	0.17385 (10)	1.0956 (4)	0.46204 (11)	0.0665 (6)
C11A	0.1962 (3)	1.2802 (7)	0.4788 (3)	0.1078 (17)
H11A	0.1622	1.3661	0.4625	0.162*
H11B	0.2276	1.3073	0.4589	0.162*
H11C	0.2140	1.2914	0.5262	0.162*
O12	0.06299 (9)	0.9156 (3)	0.39597 (9)	0.0605 (6)
C12A	0.05499 (17)	0.7933 (6)	0.34735 (16)	0.0647 (9)
O12B	0.07856 (16)	0.6436 (5)	0.35551 (13)	0.1047 (10)
C12C	0.0102 (2)	0.8648 (7)	0.28403 (17)	0.0952 (14)
H12A	0.0015	0.7691	0.2509	0.143*
H12B	0.0281	0.9701	0.2694	0.143*
H12C	−0.0280	0.9012	0.2910	0.143*
S2	0.5000	0.97527 (14)	0.0000	0.0504 (3)
C23	0.46337 (14)	0.8177 (4)	0.04313 (13)	0.0484 (7)
H23	0.4889	0.7050	0.0555	0.058*
C24	0.39672 (15)	0.7633 (4)	0.00179 (14)	0.0545 (8)

H24	0.3807	0.6756	0.0274	0.065*
C25	0.35471 (13)	0.9327 (5)	−0.01386 (14)	0.0555 (7)
H25	0.3706	1.0234	−0.0386	0.067*
O25	0.35581 (8)	1.0108 (3)	0.04826 (9)	0.0588 (6)
C21	0.41579 (12)	1.0751 (5)	0.08979 (13)	0.0510 (7)
H21	0.4316	1.1737	0.0679	0.061*
C22	0.45988 (13)	0.9110 (5)	0.10616 (13)	0.0495 (7)
H22	0.4447	0.8204	0.1315	0.059*
O21	0.40895 (10)	1.1376 (4)	0.14776 (10)	0.0702 (7)
C21A	0.3779 (2)	1.3135 (9)	0.1412 (2)	0.124 (2)
H21A	0.4072	1.4111	0.1424	0.186*
H21B	0.3616	1.3296	0.1771	0.186*
H21C	0.3442	1.3177	0.0997	0.186*
O22	0.52012 (8)	0.9780 (3)	0.14720 (8)	0.0509 (5)
C22A	0.55538 (16)	0.8637 (6)	0.19447 (15)	0.0627 (9)
O22B	0.53879 (16)	0.7114 (5)	0.20135 (15)	0.1117 (11)
C22C	0.61622 (14)	0.9470 (7)	0.23186 (15)	0.0776 (11)
H22A	0.6287	0.9063	0.2772	0.116*
H22B	0.6126	1.0798	0.2302	0.116*
H22C	0.6470	0.9090	0.2125	0.116*
O24	0.39636 (12)	0.6743 (3)	−0.05891 (11)	0.0684 (6)
C24A	0.3899 (2)	0.4933 (6)	−0.06424 (18)	0.0844 (11)
O24B	0.3825 (4)	0.4096 (5)	−0.0215 (2)	0.248 (4)
C24C	0.3930 (3)	0.4115 (7)	−0.1262 (2)	0.1039 (14)
H24A	0.3988	0.2797	−0.1208	0.156*
H24B	0.4274	0.4647	−0.1368	0.156*
H24C	0.3547	0.4366	−0.1616	0.156*
C26	0.28733 (15)	0.8875 (6)	−0.05192 (17)	0.0718 (10)
H26A	0.2854	0.8141	−0.0907	0.086*
H26B	0.2701	0.8136	−0.0241	0.086*
O26	0.25050 (9)	1.0513 (4)	−0.07258 (10)	0.0655 (6)
C26A	0.24722 (15)	1.1191 (6)	−0.13217 (16)	0.0696 (10)
O26B	0.27403 (14)	1.0533 (6)	−0.16579 (13)	0.1082 (11)
C26C	0.2064 (2)	1.2840 (9)	−0.1493 (2)	0.1140 (19)
H26C	0.2038	1.3269	−0.1928	0.171*
H26D	0.2236	1.3805	−0.1174	0.171*
H26E	0.1654	1.2520	−0.1489	0.171*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0376 (5)	0.0389 (6)	0.0859 (7)	0.000	0.0233 (5)	0.000
C13	0.0406 (14)	0.0391 (15)	0.0542 (15)	0.0011 (12)	0.0165 (13)	−0.0042 (13)
C14	0.0430 (15)	0.0508 (17)	0.0515 (15)	0.0151 (13)	0.0202 (13)	0.0019 (14)
C15	0.0488 (15)	0.061 (2)	0.0486 (15)	0.0013 (15)	0.0193 (13)	−0.0055 (14)
O15	0.0415 (9)	0.0675 (14)	0.0551 (11)	−0.0040 (10)	0.0153 (8)	−0.0043 (11)
C11	0.0423 (14)	0.0547 (18)	0.0510 (15)	−0.0002 (13)	0.0211 (13)	−0.0010 (14)
C12	0.0439 (15)	0.0516 (17)	0.0445 (14)	0.0054 (13)	0.0154 (12)	−0.0029 (13)

O14	0.0732 (13)	0.0534 (14)	0.0690 (12)	0.0163 (11)	0.0415 (11)	0.0114 (11)
C14A	0.097 (3)	0.051 (2)	0.107 (3)	0.014 (2)	0.059 (2)	0.012 (2)
O14B	0.297 (6)	0.0479 (18)	0.278 (5)	0.008 (3)	0.233 (5)	−0.002 (3)
C14C	0.173 (5)	0.080 (3)	0.176 (5)	0.033 (3)	0.120 (4)	0.059 (4)
C16	0.070 (2)	0.094 (3)	0.0546 (19)	0.008 (2)	0.0140 (17)	−0.009 (2)
O16	0.0631 (14)	0.117 (2)	0.0610 (13)	0.0220 (15)	0.0127 (12)	0.0186 (16)
C16A	0.123 (4)	0.104 (4)	0.086 (3)	0.003 (3)	0.043 (3)	0.030 (3)
O16B	0.424 (10)	0.215 (7)	0.290 (7)	0.180 (7)	0.271 (8)	0.177 (6)
C16C	0.123 (4)	0.121 (5)	0.118 (3)	0.048 (4)	0.023 (3)	0.018 (4)
O11	0.0615 (13)	0.0736 (16)	0.0782 (13)	−0.0127 (12)	0.0416 (11)	−0.0053 (13)
C11A	0.131 (4)	0.090 (3)	0.133 (4)	−0.048 (3)	0.085 (3)	−0.014 (3)
O12	0.0692 (12)	0.0607 (14)	0.0450 (11)	0.0031 (11)	0.0101 (9)	−0.0033 (11)
C12A	0.074 (2)	0.073 (3)	0.0491 (18)	−0.009 (2)	0.0232 (17)	−0.0021 (18)
O12B	0.138 (3)	0.097 (3)	0.0672 (15)	0.026 (2)	0.0173 (16)	−0.0258 (17)
C12C	0.115 (3)	0.100 (3)	0.057 (2)	−0.021 (3)	0.011 (2)	0.004 (2)
S2	0.0613 (6)	0.0382 (5)	0.0579 (6)	0.000	0.0282 (5)	0.000
C23	0.0598 (18)	0.0373 (16)	0.0488 (15)	−0.0016 (13)	0.0190 (14)	0.0019 (13)
C24	0.071 (2)	0.0448 (17)	0.0457 (15)	−0.0159 (16)	0.0166 (15)	0.0003 (14)
C25	0.0516 (15)	0.061 (2)	0.0480 (15)	−0.0126 (15)	0.0085 (13)	−0.0003 (15)
O25	0.0420 (10)	0.0770 (16)	0.0533 (11)	−0.0082 (10)	0.0100 (9)	−0.0079 (11)
C21	0.0415 (15)	0.0599 (18)	0.0476 (15)	0.0003 (14)	0.0093 (12)	−0.0031 (14)
C22	0.0518 (15)	0.0502 (17)	0.0466 (14)	−0.0089 (14)	0.0164 (12)	0.0023 (14)
O21	0.0554 (12)	0.097 (2)	0.0535 (11)	0.0139 (13)	0.0119 (10)	−0.0157 (12)
C21A	0.102 (3)	0.154 (5)	0.091 (3)	0.076 (4)	−0.001 (3)	−0.036 (3)
O22	0.0438 (9)	0.0566 (12)	0.0459 (9)	0.0004 (10)	0.0060 (8)	0.0055 (10)
C22A	0.066 (2)	0.076 (3)	0.0431 (16)	0.0171 (19)	0.0140 (16)	0.0132 (17)
O22B	0.119 (2)	0.087 (2)	0.100 (2)	−0.007 (2)	−0.0042 (18)	0.044 (2)
C22C	0.0615 (19)	0.111 (3)	0.0533 (17)	0.012 (2)	0.0090 (15)	0.004 (2)
O24	0.1048 (17)	0.0452 (13)	0.0560 (11)	−0.0225 (12)	0.0276 (12)	−0.0062 (10)
C24A	0.143 (3)	0.047 (2)	0.066 (2)	−0.011 (2)	0.037 (2)	0.0012 (19)
O24B	0.606 (13)	0.048 (2)	0.171 (4)	−0.011 (4)	0.237 (6)	−0.003 (3)
C24C	0.156 (4)	0.069 (3)	0.088 (3)	−0.025 (3)	0.042 (3)	−0.024 (2)
C26	0.062 (2)	0.074 (3)	0.068 (2)	−0.0157 (19)	0.0062 (17)	0.0081 (19)
O26	0.0550 (12)	0.0881 (17)	0.0511 (11)	−0.0059 (12)	0.0145 (9)	0.0006 (12)
C26A	0.062 (2)	0.091 (3)	0.0586 (19)	0.0005 (19)	0.0241 (17)	0.0071 (19)
O26B	0.126 (2)	0.138 (3)	0.0759 (16)	0.043 (2)	0.0538 (17)	0.0097 (18)
C26C	0.118 (4)	0.132 (5)	0.106 (3)	0.047 (4)	0.055 (3)	0.041 (3)

Geometric parameters (Å, °)

S1—C13^{i}	1.831 (3)	S2—C23	1.824 (3)
S1—C13	1.831 (3)	S2—C23^{ii}	1.824 (3)
C13—C12	1.526 (4)	C23—C24	1.527 (4)
C13—C14	1.530 (4)	C23—C22	1.528 (4)
C13—H13	0.9800	C23—H23	0.9800
C14—O14	1.437 (3)	C24—O24	1.442 (4)
C14—C15	1.508 (5)	C24—C25	1.515 (5)
C14—H14	0.9800	C24—H24	0.9800
C15—O15	1.426 (3)	C25—O25	1.432 (4)

C15—C16	1.511 (4)	C25—C26	1.509 (4)
C15—H15	0.9800	C25—H25	0.9800
O15—C11	1.428 (3)	O25—C21	1.432 (3)
C11—O11	1.377 (3)	C21—O21	1.372 (3)
C11—C12	1.517 (4)	C21—C22	1.511 (4)
C11—H11	0.9800	C21—H21	0.9800
C12—O12	1.432 (3)	C22—O22	1.439 (3)
C12—H12	0.9800	C22—H22	0.9800
O14—C14A	1.327 (5)	O21—C21A	1.432 (6)
C14A—O14B	1.173 (5)	C21A—H21A	0.9600
C14A—C14C	1.474 (5)	C21A—H21B	0.9600
C14C—H14A	0.9600	C21A—H21C	0.9600
C14C—H14B	0.9600	O22—C22A	1.342 (4)
C14C—H14C	0.9600	C22A—O22B	1.184 (5)
C16—O16	1.432 (5)	C22A—C22C	1.473 (5)
C16—H16A	0.9700	C22C—H22A	0.9600
C16—H16B	0.9700	C22C—H22B	0.9600
O16—C16A	1.269 (6)	C22C—H22C	0.9600
C16A—O16B	1.163 (5)	O24—C24A	1.313 (5)
C16A—C16C	1.478 (8)	C24A—O24B	1.151 (5)
C16C—H16C	0.9600	C24A—C24C	1.470 (6)
C16C—H16D	0.9600	C24C—H24A	0.9600
C16C—H16E	0.9600	C24C—H24B	0.9600
O11—C11A	1.425 (6)	C24C—H24C	0.9600
C11A—H11A	0.9600	C26—O26	1.428 (5)
C11A—H11B	0.9600	C26—H26A	0.9700
C11A—H11C	0.9600	C26—H26B	0.9700
O12—C12A	1.327 (4)	O26—C26A	1.340 (4)
C12A—O12B	1.190 (5)	C26A—O26B	1.181 (4)
C12A—C12C	1.488 (5)	C26A—C26C	1.474 (7)
C12C—H12A	0.9600	C26C—H26C	0.9600
C12C—H12B	0.9600	C26C—H26D	0.9600
C12C—H12C	0.9600	C26C—H26E	0.9600
$C13^{i}$—S1—C13	102.64 (18)	C23—S2—$C23^{ii}$	103.03 (19)
C12—C13—C14	106.2 (2)	C24—C23—C22	107.0 (2)
C12—C13—S1	109.04 (19)	C24—C23—S2	113.33 (19)
C14—C13—S1	113.80 (18)	C22—C23—S2	109.5 (2)
C12—C13—H13	109.2	C24—C23—H23	109.0
C14—C13—H13	109.2	C22—C23—H23	109.0
S1—C13—H13	109.2	S2—C23—H23	109.0
O14—C14—C15	109.3 (2)	O24—C24—C25	110.0 (2)
O14—C14—C13	111.6 (2)	O24—C24—C23	110.1 (2)
C15—C14—C13	111.6 (2)	C25—C24—C23	110.5 (2)
O14—C14—H14	108.1	O24—C24—H24	108.7
C15—C14—H14	108.1	C25—C24—H24	108.7
C13—C14—H14	108.1	C23—C24—H24	108.7
O15—C15—C14	108.7 (2)	O25—C25—C26	106.8 (2)
O15—C15—C16	106.7 (2)	O25—C25—C24	107.1 (2)

C14—C15—C16	113.4 (3)	C26—C25—C24	113.2 (3)
O15—C15—H15	109.3	O25—C25—H25	109.9
C14—C15—H15	109.3	C26—C25—H25	109.9
C16—C15—H15	109.3	C24—C25—H25	109.9
C15—O15—C11	114.94 (19)	C25—O25—C21	115.02 (19)
O11—C11—O15	107.9 (2)	O21—C21—O25	107.3 (2)
O11—C11—C12	108.7 (2)	O21—C21—C22	108.1 (2)
O15—C11—C12	108.0 (2)	O25—C21—C22	108.0 (3)
O11—C11—H11	110.7	O21—C21—H21	111.1
O15—C11—H11	110.7	O25—C21—H21	111.1
C12—C11—H11	110.7	C22—C21—H21	111.1
O12—C12—C11	107.5 (2)	O22—C22—C21	107.4 (2)
O12—C12—C13	111.4 (2)	O22—C22—C23	111.6 (2)
C11—C12—C13	111.5 (2)	C21—C22—C23	111.3 (2)
O12—C12—H12	108.8	O22—C22—H22	108.8
C11—C12—H12	108.8	C21—C22—H22	108.8
C13—C12—H12	108.8	C23—C22—H22	108.8
C14A—O14—C14	117.8 (2)	C21—O21—C21A	113.5 (3)
O14B—C14A—O14	121.7 (3)	O21—C21A—H21A	109.5
O14B—C14A—C14C	124.7 (4)	O21—C21A—H21B	109.5
O14—C14A—C14C	113.6 (3)	H21A—C21A—H21B	109.5
C14A—C14C—H14A	109.5	O21—C21A—H21C	109.5
C14A—C14C—H14B	109.5	H21A—C21A—H21C	109.5
H14A—C14C—H14B	109.5	H21B—C21A—H21C	109.5
C14A—C14C—H14C	109.5	C22A—O22—C22	117.4 (3)
H14A—C14C—H14C	109.5	O22B—C22A—O22	121.8 (3)
H14B—C14C—H14C	109.5	O22B—C22A—C22C	126.1 (3)
O16—C16—C15	109.1 (3)	O22—C22A—C22C	112.0 (3)
O16—C16—H16A	109.9	C22A—C22C—H22A	109.5
C15—C16—H16A	109.9	C22A—C22C—H22B	109.5
O16—C16—H16B	109.9	H22A—C22C—H22B	109.5
C15—C16—H16B	109.9	C22A—C22C—H22C	109.5
H16A—C16—H16B	108.3	H22A—C22C—H22C	109.5
C16A—O16—C16	121.0 (3)	H22B—C22C—H22C	109.5
O16B—C16A—O16	119.3 (6)	C24A—O24—C24	119.1 (3)
O16B—C16A—C16C	125.4 (5)	O24B—C24A—O24	119.5 (4)
O16—C16A—C16C	115.3 (4)	O24B—C24A—C24C	124.4 (4)
C16A—C16C—H16C	109.5	O24—C24A—C24C	116.1 (3)
C16A—C16C—H16D	109.5	C24A—C24C—H24A	109.5
H16C—C16C—H16D	109.5	C24A—C24C—H24B	109.5
C16A—C16C—H16E	109.5	H24A—C24C—H24B	109.5
H16C—C16C—H16E	109.5	C24A—C24C—H24C	109.5
H16D—C16C—H16E	109.5	H24A—C24C—H24C	109.5
C11—O11—C11A	114.5 (3)	H24B—C24C—H24C	109.5
O11—C11A—H11A	109.5	O26—C26—C25	111.8 (3)
O11—C11A—H11B	109.5	O26—C26—H26A	109.2
H11A—C11A—H11B	109.5	C25—C26—H26A	109.2
O11—C11A—H11C	109.5	O26—C26—H26B	109.2
H11A—C11A—H11C	109.5	C25—C26—H26B	109.2

H11B—C11A—H11C	109.5	H26A—C26—H26B	107.9
C12A—O12—C12	116.9 (3)	C26A—O26—C26	116.0 (3)
O12B—C12A—O12	123.2 (3)	O26B—C26A—O26	123.4 (4)
O12B—C12A—C12C	125.8 (4)	O26B—C26A—C26C	125.3 (4)
O12—C12A—C12C	110.9 (4)	O26—C26A—C26C	111.3 (3)
C12A—C12C—H12A	109.5	C26A—C26C—H26C	109.5
C12A—C12C—H12B	109.5	C26A—C26C—H26D	109.5
H12A—C12C—H12B	109.5	H26C—C26C—H26D	109.5
C12A—C12C—H12C	109.5	C26A—C26C—H26E	109.5
H12A—C12C—H12C	109.5	H26C—C26C—H26E	109.5
H12B—C12C—H12C	109.5	H26D—C26C—H26E	109.5
C13^{i}—S1—C13—C12	147.8 (2)	C23^{ii}—S2—C23—C22	151.4 (2)
C13^{i}—S1—C13—C14	−93.8 (2)	C23^{ii}—S2—C23—C24	−89.2 (2)
C12—C13—C14—O14	179.1 (2)	C22—C23—C24—O24	179.8 (2)
S1—C13—C14—O14	59.1 (3)	S2—C23—C24—O24	59.0 (3)
C12—C13—C14—C15	56.5 (3)	C22—C23—C24—C25	58.1 (3)
S1—C13—C14—C15	−63.5 (3)	S2—C23—C24—C25	−62.8 (3)
O14—C14—C15—O15	178.6 (2)	O24—C24—C25—O25	178.4 (2)
C13—C14—C15—O15	−57.6 (3)	C23—C24—C25—O25	−59.8 (3)
O14—C14—C15—C16	60.0 (3)	O24—C24—C25—C26	60.9 (3)
C13—C14—C15—C16	−176.1 (2)	C23—C24—C25—C26	−177.2 (2)
C14—C15—O15—C11	60.2 (3)	C26—C25—O25—C21	−175.8 (3)
C16—C15—O15—C11	−177.1 (3)	C24—C25—O25—C21	62.6 (3)
C15—O15—C11—O11	−177.7 (3)	C25—O25—C21—O21	−177.5 (3)
C15—O15—C11—C12	−60.4 (3)	C25—O25—C21—C22	−61.2 (3)
O11—C11—C12—O12	−62.6 (3)	O21—C21—C22—O22	−64.9 (3)
O15—C11—C12—O12	−179.32 (19)	O25—C21—C22—O22	179.29 (18)
O11—C11—C12—C13	175.1 (2)	O21—C21—C22—C23	172.7 (2)
O15—C11—C12—C13	58.4 (3)	O25—C21—C22—C23	56.8 (3)
C14—C13—C12—O12	−177.0 (2)	C24—C23—C22—O22	−176.6 (2)
S1—C13—C12—O12	−54.0 (3)	S2—C23—C22—O22	−53.4 (3)
C14—C13—C12—C11	−56.9 (3)	C24—C23—C22—C21	−56.6 (3)
S1—C13—C12—C11	66.1 (3)	S2—C23—C22—C21	66.6 (3)
C15—C14—O14—C14A	−136.4 (3)	O25—C21—O21—C21A	−74.9 (4)
C13—C14—O14—C14A	99.7 (3)	C22—C21—O21—C21A	168.8 (3)
C14—O14—C14A—O14B	−4.3 (7)	C21—C22—O22—C22A	145.7 (2)
C14—O14—C14A—C14C	175.5 (4)	C23—C22—O22—C22A	−92.1 (3)
O15—C15—C16—O16	−62.7 (4)	C22—O22—C22A—O22B	2.1 (5)
C14—C15—C16—O16	57.0 (4)	C22—O22—C22A—C22C	178.7 (2)
C15—C16—O16—C16A	−132.0 (4)	C25—C24—O24—C24A	−134.0 (4)
C16—O16—C16A—O16B	−7.2 (9)	C23—C24—O24—C24A	104.0 (4)
C16—O16—C16A—C16C	175.8 (4)	C24—O24—C24A—O24B	2.7 (8)
O15—C11—O11—C11A	−78.7 (4)	C24—O24—C24A—C24C	−177.2 (3)
C12—C11—O11—C11A	164.4 (3)	O25—C25—C26—O26	69.2 (3)
C11—C12—O12—C12A	146.0 (3)	C24—C25—C26—O26	−173.2 (3)
C13—C12—O12—C12A	−91.5 (3)	C25—C26—O26—C26A	89.9 (3)
C12—O12—C12A—O12B	−0.7 (5)	C26—O26—C26A—O26B	−2.0 (5)
C12—O12—C12A—C12C	175.7 (3)	C26—O26—C26A—C26C	178.1 (4)

Symmetry codes: (i) −*x*, *y*, −*z*+1; (ii) −*x*+1, *y*, −*z*.

Fig. 1

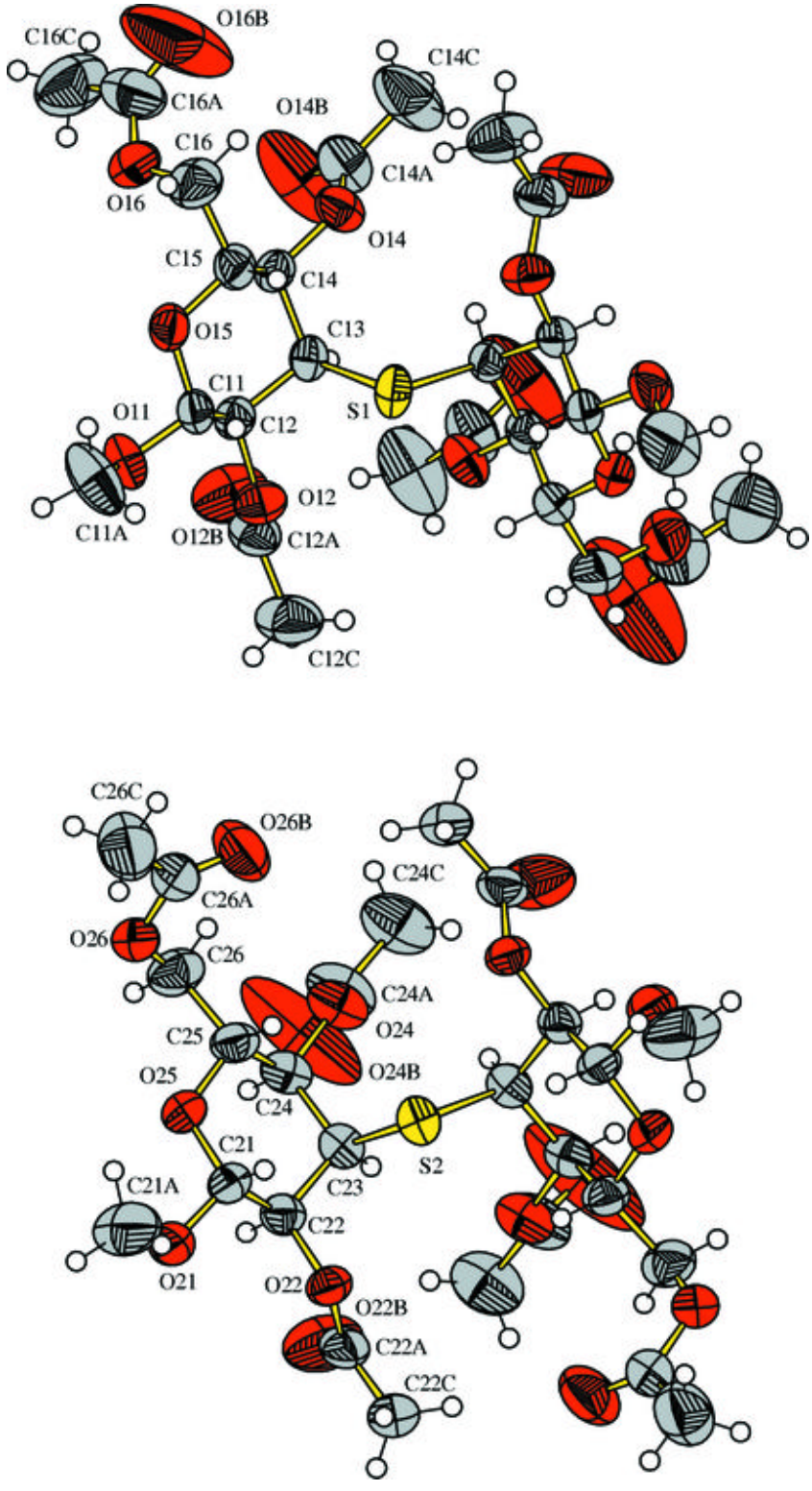


Fig. 2

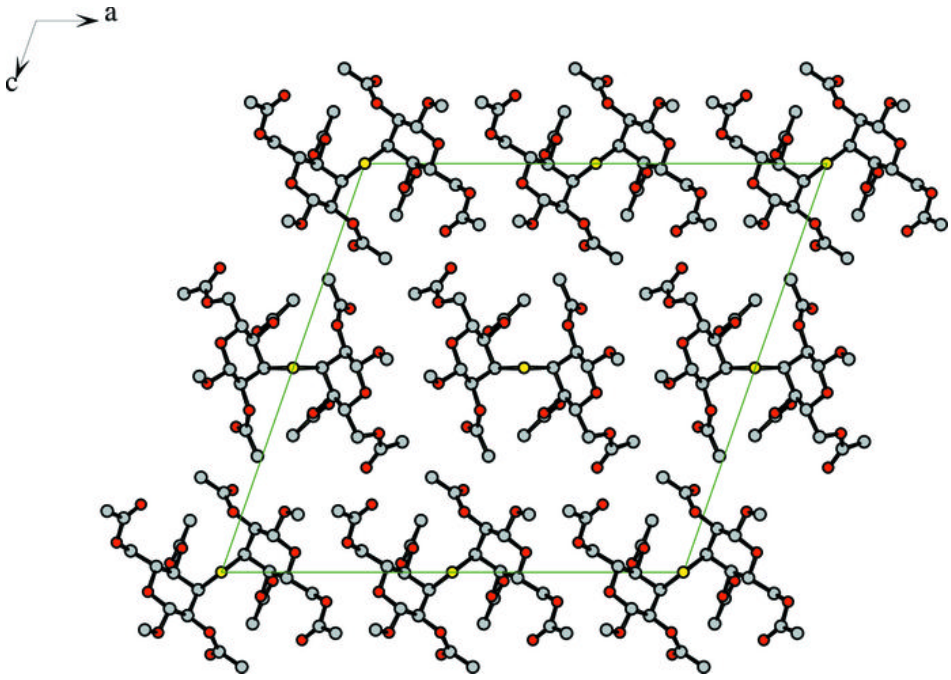


Fig. 3

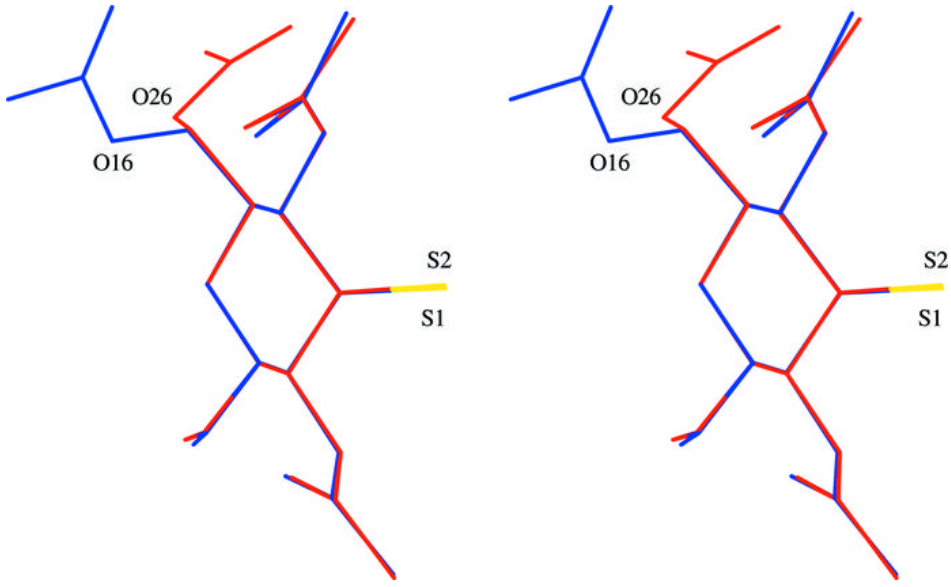
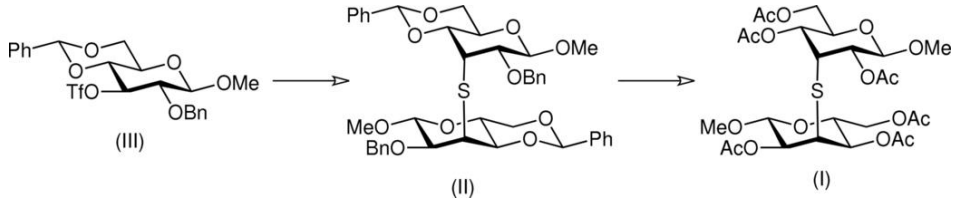


Fig. 4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