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Methyl 3,4-*O*-dibenzoyl-2-*O*-benzyl-1-thio-β-L-fucopyranoside

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Key indicators

Single-crystal X-ray study
T = 295 K
Mean σ(C–C) = 0.009 Å
R factor = 0.047
wR factor = 0.142
Data-to-parameter ratio = 11.2

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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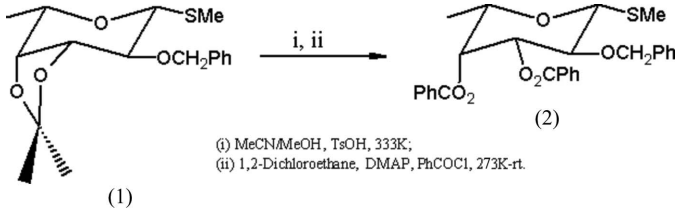
The title compound, $C_{28}H_{28}O_6S$, is a protected fucose donor, synthesized as part of our investigations into the preparation of complex oligosaccharides. The benzoyl groups are equatorial and axial, while the thioether and ether groups are equatorial. The carboxylate O atoms form a number of intra- and intermolecular C—H···O interactions.

Comment

As part of our ongoing investigations into the development of solid-phase syntheses of oligosaccharides, a range of appropriately derivatized donor sugars has been synthesized. It is well established that for stereospecific glycosidic linkage formation, both selective protection of the various hydroxyl groups and a suitably reactive anomeric leaving group are required (Jain & Matta, 1990). When employing fucose donor sugars, it is important to moderate the reactivity of the incumbent fucosyl saccharide, due to the high acid sensitivity of fucosyl glycosidic linkages. It was thought that the title compound, (2), would display reasonable acid stability and also provide excellent anomeric selectivity.



(1) (2)

Determination of the crystal structure of (2) showed it to crystallize in the space group $P2_12_12_1$ with one discrete molecule in the asymmetric unit (Fig. 1). The benzoyl phenyl rings on C3 and C4 are equatorial and axial, respectively. The thioether and ether groups on C1 and C2 are both equatorial. The carboxylate O atoms (O3/O4/O5/O6) form a number of intra- and intermolecular C—H···O interactions (Table 2).

Experimental

Tosic acid, TsOH (100 mg), was added to a solution of methyl 2-*O*-benzyl-3,4-*O*-isopropylidene-1-thio-β-L-fucopyranoside, (1) (11.74 g, 0.05 mol) in MeCN/MeOH (1:1, 350 ml). The reaction mixture was then stirred at 333 K overnight, after which time it was cooled to room temperature and neutralized by the addition of triethylamine (2 ml). The solvent was removed *in vacuo*, and the resulting residue was passed through a plug of silica (eluent: ethylacetate/petroleum ethers, 1:1), to give methyl 2-*O*-benzyl-1-thio-β-L-fucopyranoside as a

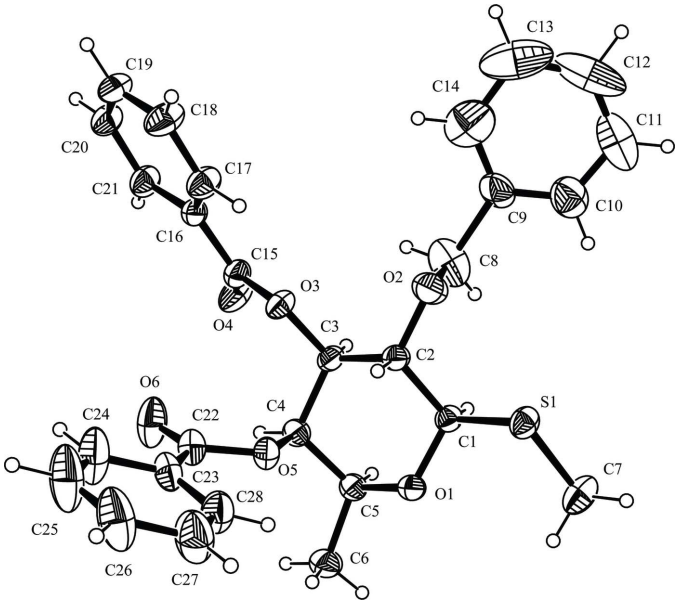


Figure 1
View of compound (2) with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

clear oil (yield 9.90 g, 96%). This compound (6.40 g, 22.53 mmol) was dissolved in 1,2-dichloroethane (100 ml) followed by the addition of dimethylaminopyridine (DMAP, 6.89 g, 56.34 mmol). The solution was cooled to 273 K and benzoyl chloride (6.55 g, 56.34 mmol) was added dropwise. The reaction mixture was returned to room temperature and stirred for 2 h. At this time, DMAP (1.31 g, 11.27 mmol) was added to drive the reaction to completion. After a further hour, the reaction mixture was diluted with chloroform (100 ml) and washed with 10% citric acid solution (2 × 200 ml), saturated sodium hydrogen carbonate solution (2 × 200 ml) and saturated brime solution (2 × 200 ml). The layers were separated and the organic layer dried over Na_2SO_4. The solution was filtered, concentrated and purified by column chromatography (ethyl acetate/petroleum ether, 1:5) to provide the title compound, (2), as colourless crystals (yield 9.95 g, 90%). R_F = 0.7 (ethyl acetate/petroleum ether, 1:1); ^{1}H NMR ($CDCl_3$): δ 7.98–7.96 (*m*, 2H, Ar), 7.76–7.74 (*m*, 2H, Ar), 7.56–7.52 (*m*, 1H, Ar), 7.45–7.39 (*m*, 3H, Ar), 7.26–7.20 (*m*, 2H, Ar), 7.14–7.07 (*m*, 5H, Ar), 5.59 (*dd*, 1H, H-4, $J_{4,5}$ = 0.74 Hz), 5.35 (*dd*, 1H, H-3, $J_{3,4}$ = 3.42 Hz), 4.77, 4.58 (2 × *d*, 2H, $PhCH_2-$), 4.50 (*d*, 1H, H-1, $J_{1,2}$ = 9.23 Hz), 3.95–3.90 (*m*, 1H, H-5), 3.87 (*dd*, 1H, H-2, $J_{2,3}$ = 9.63 Hz), 2.27 (*s*, 3H, $-SCH_3$), 1.23 (*d*, 3H, $-CH_3$, $J_{5,6}$ = 6.16 Hz); ^{13}C NMR ($CDCl_3$): δ 166.11, 165.78 (C═O), 137.67, 133.61, 133.38 (aromatic C1), 130.10, 129.89, 129.82, 129.79, 128.57, 128.51, 128.08 (aromatic C), 85.79 (C1), 75.91 (C2), 75.69 ($PhCH_2$), 75.35 C3), 73.52 (C5), 72.01 (C4), 16.86 (C6), 13.25 ($-SCH_3$); TOF HRMS calculated $C_{28}H_{28}O_6S$ 492.1607 found *m*/*z* (ion, relative intensity): 493.1662 ([*M*+H]$^+$, 33%).

Crystal data

$C_{28}H_{28}O_6S$
M_r = 492.57
Orthorhombic, $P2_12_12_1$
a = 11.725 (2) Å
b = 20.396 (3) Å
c = 11.040 (2) Å
V = 2640.1 (8) Å^3
Z = 4
D_x = 1.239 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
θ = 7.7–10.6°
μ = 0.16 mm^{-1}
T = 295 K
Block, colourless
0.35 × 0.20 × 0.15 mm

Data collection

Rigaku AFC-7R diffractometer
ω scans
Absorption correction: none
3971 measured reflections
3548 independent reflections
2276 reflections with $I > 2\sigma(I)$
R_{int} = 0.011
θ_{max} = 27.5°
$h = 0 \rightarrow 15$
$k = -10 \rightarrow 26$
$l = -14 \rightarrow 14$
3 standard reflections
every 150 reflections
intensity decay: 0.2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.047
$wR(F^2)$ = 0.142
S = 1.03
3548 reflections
317 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F_o^2) + (0.0607P)^2 + 1.0014P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.57 e Å^{-3}
$\Delta\rho_{min}$ = −0.25 e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.0076 (14)
Absolute structure: Flack (1983), 139 Friedel pairs
Flack parameter: −0.19 (15)

Table 1
Selected geometric parameters (Å, °).

S1—C1	1.802 (4)	O3—C3	1.442 (5)
S1—C7	1.784 (5)	O3—C15	1.345 (5)
O1—C1	1.432 (5)	O4—C15	1.211 (5)
O1—C5	1.442 (5)	O5—C4	1.441 (5)
O2—C2	1.403 (5)	O5—C22	1.355 (5)
O2—C8	1.295 (8)	O6—C22	1.218 (6)
C1—S1—C7	101.6 (2)	C3—O3—C15	117.8 (3)
C1—O1—C5	112.1 (3)	C4—O5—C22	119.6 (3)
C2—O2—C8	112.3 (4)		

Table 2
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C1—H1···O4^{i}	0.96	2.55	3.417 (5)	151
C2—H2···O5	0.94	2.54	2.920 (4)	104
C4—H4···O6	0.95	2.36	2.726 (6)	102
C7—H7*A*···O4^{i}	0.95	2.58	3.452 (6)	152
C17—H17···O3	0.95	2.40	2.738 (5)	100
C28—H28···O5	0.95	2.39	2.721 (6)	100

Symmetry code: (i) $+x-\frac{1}{2}, -y+\frac{1}{2}, -z+1$.

H atoms were positioned geometrically (C—H = 0.90–0.97 Å) and fixed in the refinement, with U_{iso}(H) = 1.2U_{eq}(C). The absolute configuration for (2) was assigned assuming unmodified configurations for the chiral centres of (1). The absolute configuration determined with low precision from anomalous scattering effects is in accord with the known configuration of the starting material (Jain & Matta, 1990). The peripheral C atoms in phenyl ring C9—C14 exhibit high anisotropic displacement parameters.

Data collection: *MSC/AFC7 Diffractometer Control Software for Windows* (Molecular Structure Corporation, 1999); cell refinement: *MSC/AFC7 Diffractometer ControlSoftware for Windows*; data reduction: *TEXSAN for Windows* (Molecular Structure Corporation, 2001); program(s) used to solve structure: *TEXSAN for Windows*; program(s) used to refine structure: *TEXSAN for Windows* and *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP3* (Farrugia, 1997); software used to prepare material for publication: *TEXSAN for Windows* and *PLATON* (Spek, 2003).

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