

O-Ethyl and O-methyl N-(2,3,4,6-tetra-O-acetyl- $\beta$ -D-glucopyranosyl)-thiocarbamateShusheng Zhang,<sup>a</sup> Zhongwei Wang,<sup>a</sup> Ming Li,<sup>a</sup> Kui Jiao,<sup>a</sup> Ibrahim Abdul Razak,<sup>b</sup> S. Shanmuga Sundara Raj<sup>b</sup> and Hoong-Kun Fun<sup>b\*</sup><sup>a</sup>Department of Applied Chemistry, Qingdao Institute of Chemical Technology, Qingdao 266042, People's Republic of China, and <sup>b</sup>X-ray Crystallography Unit, School of Physics, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia  
Correspondence e-mail: hkfun@usm.my

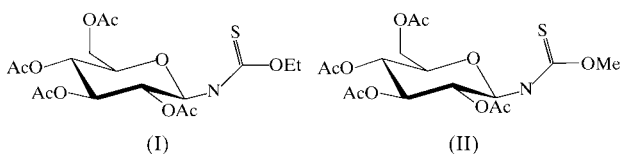
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In both the title structures, *O*-ethyl *N*-(2,3,4,6-tetra-*O*-acetyl- $\beta$ -D-glucopyranosyl)thiocarbamate, C<sub>17</sub>H<sub>25</sub>NO<sub>10</sub>S, and *O*-methyl *N*-(2,3,4,6-tetra-*O*-acetyl- $\beta$ -D-glucopyranosyl)thiocarbamate, C<sub>16</sub>H<sub>23</sub>NO<sub>10</sub>S, the hexopyranosyl ring adopts the <sup>4</sup>C<sub>1</sub> conformation. All the ring substituents are in equatorial positions. The acetoxy group is in a *gauche-gauche* conformation. The S atom is in a synperiplanar conformation, while the C–N–C–O linkage is antiperiplanar. N–H...O intermolecular hydrogen bonds link the molecules into infinite chains and these are connected by C–H...O interactions.

## Comment

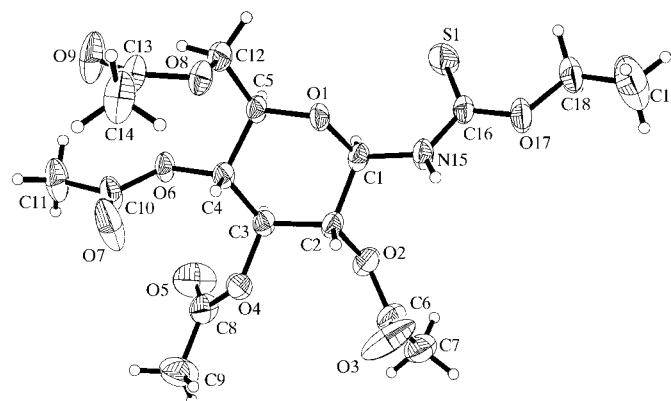
Glycosyl isothiocyanates have been widely used as valuable intermediates in the synthesis of glycosylthiourea derivatives (Yasuo *et al.*, 1999). Isothiocyanates and glycosyl isothiocyanates have been the focus of synthetic attention in recent years and have potential pharmacological properties (Mukerjee & Ashare, 1991). 1-Deoxynojirimycin, castanospermine and some of their derivatives have also shown anti-HIV activity (Tyms *et al.*, 1990). Many biologically important products have a sugar unit joined through an atom (O, S, N or C) or a group of atoms (Avalos *et al.*, 1990). Here, we report the X-ray structures of *O*-ethyl *N*-(2,3,4,6-tetra-*O*-acetyl- $\beta$ -D-glucopyranosyl)thiocarbamate, (I), and *O*-methyl *N*-(2,3,4,6-tetra-*O*-acetyl- $\beta$ -D-glucopyranosyl)thiocarbamate, (II).



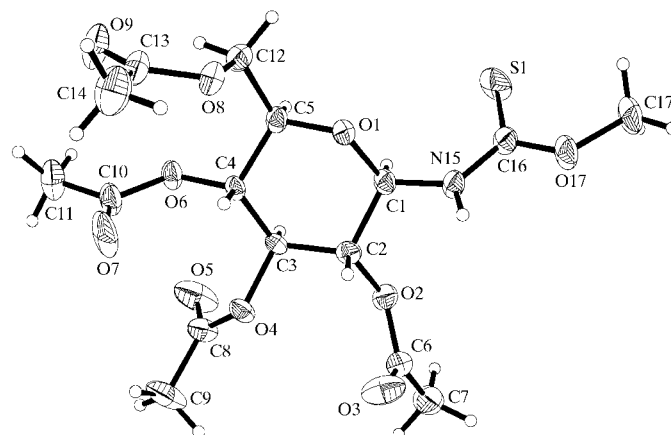
The bond lengths and angles in (I) and (II) are normal and agree with those of D-glucopyranose (Ferrier, 1963), *N*-( $\beta$ -D-glucopyranosyl)hydroxylamine (Mostad, 1978) and *N*-( $\beta$ -D-

glucopyranosyl)-*S*-phenylsulfenamide (Lee *et al.*, 1995). The hexopyranosyl ring in both structures adopts a <sup>4</sup>C<sub>1</sub> conformation, with puckering parameters (Cremer & Pople, 1975)  $Q = 0.605$  (3),  $q_2 = 0.076$  (3) and  $q_3 = 0.601$  (3) Å, and  $\theta = 7.0$  (3) and  $\varphi_2 = 6$  (2)°, for (I), and  $Q = 0.590$  (5),  $q_2 = 0.054$  (4) and  $q_3 = 0.587$  (5) Å, and  $\theta = 5.3$  (4) and  $\varphi_2 = 2$  (5)°, for (II). The dihedral angles between the *O*-acetyl groups and the mean plane through the hexopyranosyl ring are in the range 74.9 (2)–89.6 (1)° in (I) and 72.6 (2)–88.9 (2)° in (II). The anomeric substituent, meanwhile, makes dihedral angles of 64.7 (1) and 65.2 (2)° in (I) and (II), respectively, with the same ring. All ring substituents are in equatorial positions with respect to the ring in both structures.

In both structures, the acetoxy group is in a *gauche-gauche* conformation, with O1–C5–C12–O8 and C4–C5–C12–O8 torsion angles of –70.0 (3) and 50.0 (4)°, respectively, for (I), and –71.4 (5) and 49.0 (5)°, respectively, for (II). These values may be compared with those in *N*-( $\beta$ -D-glucopyranosyl)-*S*-phenylsulfenamide (Lee *et al.*, 1995), where the corresponding O5–C5–C6–O6 and C4–C5–C6–O6



**Figure 1**  
The molecular structure of (I) with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.



**Figure 2**  
The molecular structure of (II) with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

torsion angles are 72.4 (3) and  $-168.2$  (3) $^\circ$ , respectively. The S atom is in a synperiplanar conformation with respect to atom C1, while the C1–N15–C16–O17 linkage is antiperiplanar in both structures.

In the crystals of (I) and (II), N–H $\cdots$ O intermolecular hydrogen bonds (Table 3) form infinite chains along the *a* axis. These chains are interconnected by C–H $\cdots$ O interactions (Table 3) to form an elongated spring-like structure along the *b* axis.

## Experimental

For the preparation of (I), a solution of 2,3,4,6-tetra-*O*-acetyl- $\beta$ -D-glycosyl isothiocyanate (0.3 g) in ethanol (20 ml) was added dropwise to boiling ethanol (20 ml). The boiling solution was stirred for 2 h under reflux. After filtration, the clear colourless filtrate was left at room temperature until single crystals suitable for X-ray analysis were obtained. Compound (II) was prepared in a similar manner replacing ethanol with methanol.

### Compound (I)

#### Crystal data

C<sub>17</sub>H<sub>25</sub>NO<sub>10</sub>S  
*M<sub>r</sub>* = 435.44  
 Monoclinic, *P*2<sub>1</sub>  
*a* = 7.7492 (2) Å  
*b* = 10.4470 (3) Å  
*c* = 14.3852 (3) Å  
 $\beta$  = 100.810 (1) $^\circ$   
*V* = 1143.90 (5) Å<sup>3</sup>  
*Z* = 2

#### Data collection

Siemens SMART CCD area-detector diffractometer  
 $\omega$  scans  
 Absorption correction: empirical (*SADABS*; Sheldrick, 1996)  
*T<sub>min</sub>* = 0.921, *T<sub>max</sub>* = 0.945  
 7784 measured reflections

#### Refinement

Refinement on *F*<sup>2</sup>  
 $R[F^2 > 2\sigma(F^2)] = 0.062$   
 $wR(F^2) = 0.168$   
*S* = 0.88  
 5034 reflections  
 267 parameters  
 H atoms treated by a mixture of independent and constrained refinement

**Table 1**

Selected geometric parameters (Å,  $^\circ$ ) for (I).

O1–C5	1.436 (4)	C2–C3	1.538 (5)
O1–C1	1.449 (4)	C3–C4	1.530 (5)
C1–C2	1.538 (5)	C4–C5	1.558 (4)
C6–O2–C2–C1	127.3 (3)	C10–O6–C4–C5	–134.1 (3)
C6–O2–C2–C3	–114.3 (4)	O1–C5–C12–O8	–70.0 (3)
C8–O4–C3–C4	98.4 (4)	C4–C5–C12–O8	50.0 (4)
C8–O4–C3–C2	–140.3 (3)	C1–N15–C16–O17	177.2 (3)
C10–O6–C4–C3	106.4 (3)	C1–N15–C16–S1	–2.2 (5)

### Compound (II)

#### Crystal data

C<sub>16</sub>H<sub>23</sub>NO<sub>10</sub>S  
*M<sub>r</sub>* = 421.41  
 Monoclinic, *P*2<sub>1</sub>  
*a* = 7.3543 (2) Å  
*b* = 10.2555 (1) Å  
*c* = 14.0142 (4) Å  
 $\beta$  = 100.684 (2) $^\circ$   
*V* = 1038.66 (4) Å<sup>3</sup>  
*Z* = 2

*D<sub>x</sub>* = 1.347 Mg m<sup>–3</sup>  
 Mo *K* $\alpha$  radiation  
 Cell parameters from 3438 reflections  
 $\theta$  = 1.44–28.31 $^\circ$   
 $\mu$  = 0.207 mm<sup>–1</sup>  
*T* = 293 (2) K  
 Needle, colourless  
 0.26  $\times$  0.12  $\times$  0.08 mm

#### Data collection

Siemens SMART CCD area-detector diffractometer  
 $\omega$  scans  
 Absorption correction: empirical (*SADABS*; Sheldrick, 1996)  
*T<sub>min</sub>* = 0.953, *T<sub>max</sub>* = 0.985  
 7436 measured reflections

2723 independent reflections (plus 1428 Friedel-related reflections)  
 2094 reflections with  $I > 2\sigma(I)$   
*R<sub>int</sub>* = 0.078  
 $\theta_{\max}$  = 28.29 $^\circ$   
 $h$  = –9  $\rightarrow$  9  
 $k$  = –10  $\rightarrow$  13  
 $l$  = –13  $\rightarrow$  18

#### Refinement

Refinement on *F*<sup>2</sup>  
 $R[F^2 > 2\sigma(F^2)] = 0.072$   
 $wR(F^2) = 0.184$   
*S* = 0.86  
 4151 reflections  
 258 parameters  
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0843P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} < 0.001$   
 $\Delta\rho_{\max} = 0.28 \text{ e } \text{Å}^{-3}$   
 $\Delta\rho_{\min} = -0.34 \text{ e } \text{Å}^{-3}$   
 Extinction correction: *SHELXTL* (Sheldrick, 1997)  
 Extinction coefficient: 0.035 (5)  
 Absolute structure: Flack (1983)  
 Flack parameter = –0.17 (17)

**Table 2**

Selected geometric parameters (Å,  $^\circ$ ) for (II).

O1–C5	1.422 (5)	C2–C3	1.515 (6)
O1–C1	1.436 (5)	C3–C4	1.510 (6)
C1–C2	1.517 (6)	C4–C5	1.522 (6)
C6–O2–C2–C3	–106.9 (5)	C10–O6–C4–C5	–134.2 (4)
C6–O2–C2–C1	134.0 (4)	O1–C5–C12–O8	–71.4 (5)
C8–O4–C3–C4	96.8 (5)	C4–C5–C12–O8	49.0 (5)
C8–O4–C3–C2	–142.7 (5)	C1–N15–C16–O17	174.7 (4)
C10–O6–C4–C3	105.3 (5)	C1–N15–C16–S1	–4.3 (7)

**Table 3**

Hydrogen-bonding geometry for (I) and (II) (Å,  $^\circ$ ).

<i>D</i> –H $\cdots$ <i>A</i>	Compound	<i>D</i> –H	H $\cdots$ <i>A</i>	<i>D</i> $\cdots$ <i>A</i>	<i>D</i> –H $\cdots$ <i>A</i>
N15–H15A $\cdots$ O5 <sup>i</sup>	(I)	0.90 (3)	2.15 (3)	3.046 (5)	178 (3)
N15–H15A $\cdots$ O5 <sup>ii</sup>	(II)	0.81 (6)	2.08 (6)	2.884 (7)	175 (6)
C5–H5A $\cdots$ O9 <sup>iii</sup>	(I)	0.98	2.56	3.431 (5)	149
C5–H5A $\cdots$ O9 <sup>iv</sup>	(II)	0.98	2.55	3.386 (7)	143

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

After checking their presence in the difference map, all H atoms were fixed geometrically and allowed to ride on their parent atoms (C–H = 0.96–0.98 Å). However, the H atom on N15 in both structures, which is involved in intermolecular hydrogen bonding, was located from a difference Fourier map and was refined isotropically. The C7, C11 and C14 methyl groups of (I) were refined using rotating-group refinement.

For both compounds, data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*, *PARST* (Nardelli, 1995) and *PLATON* (Spek, 1990).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BJ1013). Services for accessing these data are described at the back of the journal.

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