Synthesis and Crystal Structure of *O*-Methyl-*N*-(2,3,4-tri-*O*-acetyl-*β*-D-xylopranosyl)-thiocarbamate

BO YANG, SHU-SHENG ZHANG*, JI-ZHI LI, XUE-MEI LI AND KUI JIAO
College of Chemistry and Molecular Engineering,
Qingdao University of Science and Technology
266042 Qingdao, Shandong, P. R. China

(Received 29th May, 2004, revised 8th February, 2005)

Summary: In the title compound, $C_{13}H_{19}NO_8S$, **I**, the hexopranosyl ring adopts a chair conformation. All the substituents are in equatorial positions. There are three intramolecular interactions, each forming a five-membered ring. The molecules are linked by C5 H5B...O2, C9-H9B...O8B and C7-H7A...S1 interactions into three dimensional framework. The atom O8 shows a positional disorder.

Introduction

Isothiocynantes are versatile reagents in organic chemistry [1]. By exploiting the strong electrophilic character of the NCS group, a wide variety of other functional groups can be accessed which, in turn, may be subjected to other transformations, such as cycloadditions and nucleophilic addition [2]. Many nomadic sugars play an important role in biology [3]. They could control various gene expressions to adjust the upgrowth, development, detendent reaction and the biology of organs. Many biologically important products have a sugar unit joined through an atom (O, S, N or C) or a group of atoms [4]. Glycosyl isothiocyanates have been used for the preparation of a variety of carbohydrate derivatives of synthetic, biological and pharmaceutical interest [5], such as the synthesis of glycosyl thiourea derivatives, glycosylamino heterocycles, N-glycopeptides or nucleoside analogs. In addition, they have been recently transformed into glycosyl isoyanides and glycosyl thioformamides [6]. Keeping these facts in view, the new title compound O-Methyl-N-(2,3,4-tri-O-acetyl-*β*-*D*-xylopyranosyl)-thiocarbamate has been synthesized, and its crystal structure has been determined by X-ray diffraction method.

Results and Discussion

In the title compound, the bond lengths and angles (Fig. 1) are within normal ranges [7], and are comparable with those in the related compounds, O-ethyl and O-methyl N-(2,3,4,6- tetra-O-acetyl- β-D-glucopranosyl)-thiocarbamate [8]. The hexopra-nosyl ring adopts a chair conformation, with atoms C1 and

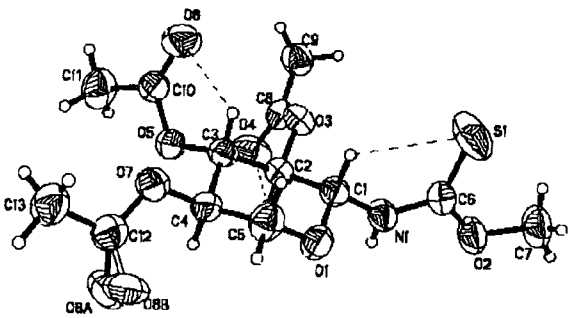

Fig. 1. The structure of the compound I showing 50 probability displacement ellipsoids and the atom numbering scheme

C4 deviating by −0.685(2) and 0.704(4) Å, respectively, from the mean plane through the other four atoms. The substituents attached to the hexopyranosyl ring are each planar, except for the acetoxyl moiety connected with atom C4. All the substituents are in equatorial positions with respect to the ring, which is different from the previously reported structure [9]. The thiocarbamate group is almost perpendicular to the mean plane of the hexopyranosyl ring, with the dihedral angle of 89.0(2). While the dihedral angles between the O-acetyl groups and this plane are 69.9(3), 60.5(6) and 73.9(3), respectively.

In the structure of **I**, the S1 atom is in a synperiplanar conformation with respect to atom C1 [the C1-N1-C6-S1 torsion angle is −12.7(8)], while

*To whom all correspondence should be addressed.

the O2 is antiperiplanar with the C1-N1-C6-O2 torsion angle of 170.3(5). The mean plane of the thiocarbamate fragment is approximately orthogonal to the O3/O4/C8/C9 mean plane, with the dihedral angle of 87.2(3). Meanwhile, the plane of the thiocarbamate group makes dihedral angles of 52.9(3) and 39.7(6) with respect to the other two substituents, O5/O6/C10/C11 and O7/C12/C13, respectively.

In the title compound, the acetyl group attached to atom O7 shows a positional disorder, the major and minor components (O8A and O8B) are displaced in the opposite directions from the O7/C12/13 plane, with the occupancy being 63% and 37%.

In the crystal structure of **I**, there are three intramolecular interactions, viz. C1H1B...S1, C2 H2A...O4 and C3 H3A...O6 (Fig. 1), forming three closed five-membered rings. In the crystal structure, the molecules are linked by C5 H5B...O2, C9-H9B...O8B and C7-H7A...S1 interactions into three dimensional framework (Fig. 2 and Table 1).

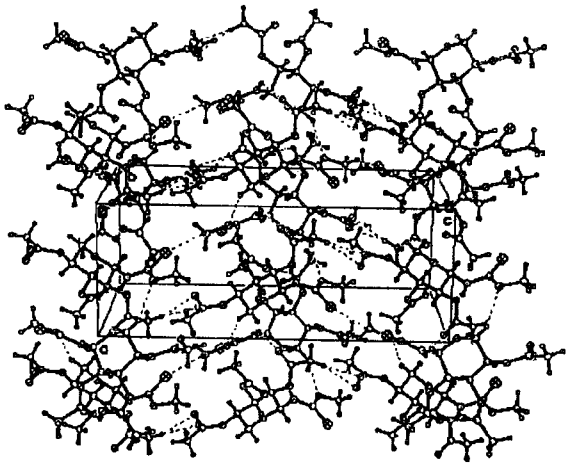

Fig. 2. Packing diagram of the title compound

Table 1. Hydrogen-bonding geometry (Å, °)

D-H...A	D-H	H...A	D...A	DH...A
C1-H1B...S1	0.98	2.67	3.146(4)	110
C2-H2A...O4	0.98	2.63	2.716(7)	100
C3-H3A...O6	0.98	2.35	2.719(7)	101
C1-H9B...O8B^{i}	0.96	2.45	3.39(5)	166
C5-H5B...O2^{ii}	0.97	2.48	3.382(7)	154
C7-H7A...S1^{iii}	0.96	2.82	3.478(7)	126

Symmetry code: (i) 3/2-x, 1-y, 1/2+z; (ii) –1/2+x, 1/2-y, -z; (iii) 1-x, -1/2+y,1/2-z

Experimental

General

D-xylose is biochemical reagent. Toluene was redistilled under reflux. The other chemicals were obtained form a commercial source and used without further purification. IR spectrum was taken by Nicolet 510 P FT-IR spectrometer (KBr). Elemental analysis was performed by Perkin-Elmer 240. The melting point was determined on an X-4 micro-scropic melting apparatus.

Preparation of 2,3,4-tri-O-acetyl-β-D-xylopyranosyl isothiocyanate

To the solution of acetic anhydride, 4.0 g xylose (46 mmol) was added at 0~5, the solution was stirred for 2 h below 10. After 12 mL bromine and 10 mL water were added dropwise, the reaction was maintained for 0.5 h, then toluene (150 mL) and 13.0 g lead thiocyanate (40 mmol) were added with stirring under reflux for 4h. After the solvent was removed under reduced pressure, the deposits were obtained in petroleum ether. The colorless crystals were obtained by recrystallization from ethyl acetate/ petroleum ether (1/3), yield 78.

Preparation of the title compound

A solution of 0.4 g (2,3,4-tri-O-acetyl)-β-D-xylopyranosyl isothiocyanate (6 mmol) in methanol (20 mL) was added dropwise to boiling methanol (30 mL). The boiling solution was stirred for 2 h under reflux. After filtration, the clear colourless filtrate was left at room temperature until the single crystals for X-ray analysis were obtained. m.p.: 165~166. Anal. Calcd. (%) for $C_{13}H_{10}NO_8S$: C, 44.69; H, 5.48; N, 4.01. Found (%): C, 44.83; H, 5.51; N, 4.13. IR: υ (cm^{-1}): 3311 (N-H); 1265 (C=S); 906 (β-sugar); 1745 (C=O); 1035-1080, 1201-1246 (double shoulder peaks of xylopyranosyl ring); 2949 ($-CH_3$); 1080, 1220, υ=140 (C-O-C)

Crystallographic Data and Structure Determination [10]

A summary of the key crystallographic information is given in Table 2. A suitable crystal of the title compound was mounted on a Nonius CAD4 diffractometer. Reflection data were measured at 20°C using Mo-Kα radiation (λ = 0.71073 Å) with a graphite monochromator [11]. The technique used was ω-scan with θ limits $3.84 < \theta < 24.96°$. Empirical absorption correction were carried out by

using the SADABS [12] program. Selected bond lengths and angles are presented in Table 3.

Table-2: Summary of crystallographic results for compound (I)

Formula	$C_{13}H_{10}NO_8S$
Formula weight	349.35
Color/shape	Colorless/block
Crystal system	Orthorhombic
Space group	P2(1)2(1)1(1)
a / Å	7.7923 (16)
b/ Å	10.845 (2)
c/ Å	19.820 (4)
V/ Å^3	1674.9 (6)
Z value	4
$D_{calcd.}$/g.cm^{-3}	1.385
μ/ mm^{-1}	0.232
Crystal size/mm	0.34×0.24×0.22
Temp. /K	293(2)
θ ranges/°	3.84-24.96
h/k/l	-9,0/-12,0/-23,0
Reflections collected	1432
Independent reflections	1708
Absorption correction	Empirical
Final *R* indices[$I>2\sigma(I)$]	R_1= 0.0567 wR_2=0.1553

Table 3. Selected geometric parameters (Å, °)

S1-C6	1.628(5)	C1-C2	1.522(7)
N1-C6	1.343(6)	C2-C3	1.529(7)
N1-C1	1.425(6)	C3-C4	1.512(7)
O1-C1	1.423(6)	C4-C5	1.517(7)
O1-C5	1.435(6)		
C1-N1-C6-O2	170.3(5)	C4-O7-C12-O8B	17 (6)
C1-N1-C6-S1	-12.7(8)	C4-O7-C12-O8A	-22 (5)

The structure of the title compound was solved by direct methods and refined by least squares on F^2 by using the *SHELXTL* [13] software package. All non-H atoms were anisotropically refined. All H atoms were fixed geometrically and treated as riding, with C-H distances = 0.96-0.98 Å and U_{iso}(H) = 1.2U_{eq}(C) [For the methyl H atoms U_{iso}(H) = 1.5U_{eq}(C)]. The final conventional R(F) = 0.0567 and $wR(F^2)$ = 0.1553 for I > 2σ(I) with weighting scheme, $\omega = 1 / [\sigma^2(F_o^2) + (0.0675P)^2 + 1.4202P]$, where $P = (Fo^2+2Fc^2)/3$. The molecular graphics were plotted using SHELXTL. Atomic scattering factors and anomalous dispersion corrections were taken from International Tables for X-ray Crystallography [14]. Software used to prepare material for publication: SHELXTL, PARST [15] and PLATON [16].

Acknowledgements

We thank the National Natural Science Foundation of China (Nos. 20275020, 20475030) and the Outstanding Adult-young Scientific Research Encouraging Foundation of Shandong Province (No. 03BS081) for financial support.

References

1. A. K. Mukerjel and R. Ashare, *Chem Rev*, **91**, 1 (1991).
2. C. Uriel and F. Santoyo-González, *Synthesis*, **12**, 2049 (1999).
3. A. Varki, *Glycobiology*, **3**, 97 (1993).
4. M. Avalos, R. Babiano, P. Cintas, L. Jimenez, J. C. Palacios and J. Fuentes, *J Chem Soc Perkin Trans*, **1**, 495 (1990).
5. H. Parrot-Lopez, H. Galons, A. W. Coleman, J. Mahnteau and M. Miocque, *Tetrahedron Lett*, **33**, 209 (1992).
6. G. Yasuo, S. Isao and S. Masao, *Synthetic Communications*, **29**, 1493 (1999).
7. F. H. Allen, O. Kennard, D. G.. Watson, L. Brammer, A. G. Orpen and R. Taylor, *J Chem Soc Perkin Trans*, **2**, S1 (1987).
8. S. S. Zhang, Z. W. Wang, M. Li, K. Jiao, I. A. Razak, S. S. S. Raj and H.-K. Fun, *Acta Cryst*, **C57**, 566 (2001).
9. J. N. Low, C. Garcia, M. Melruizo, J. Colo, M. Nogueras, A. Sånchez, M. D. López and M. E. Light, *Acta Cryst*, C57, 222 (2001).
10. CCDC 225509 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).
11. Siemens. SMART and SAINT. Area Detector Control and Integration Software. Siemens Analytical X-ray Systems, Inc., Madison, Wisconsin, USA. (1996).
12. SADABS. Program for Empirical Absorption correction of Area Detector Data, University of Gottingen, Germany. (1996).
13. G. M. Sheldrick, *SHELXTL*, v5 Reference Manual, Siemens Analytical X-ray Sysytems, Inc., Madison, Wisconsin, USA. (1996).
14. A. J. C. Wilson, *International Table for X-ray Crystallography*, volume C, Kluwer Academic Publishers, Dordrecht: Tables 6.1.1.4 (pp. 500) and 4.2.6.8 (pp. 219) respectively (1992).
15. M. J. Nardelli, *App. Cryst*, **28**, 659 (1995).
16. A. L. Spek, *Acta Cryst*, **A46**, C-34 (1990).