Asian Journal of Chemistry Vol. 18, No. 1 (2006), 491–496

Synthesis and Characterization of N-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl) thiocarbamic 2,4-dihydroxy benzoyl hydrazine monohydrate

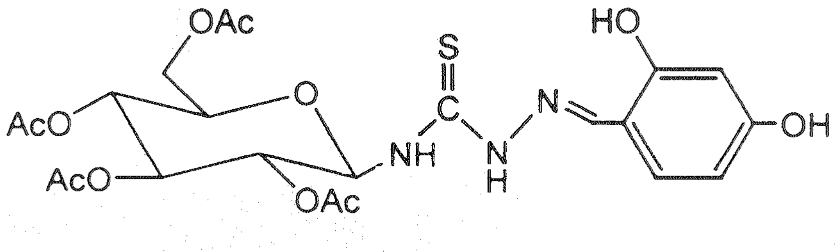
XUE-MEI LI, SU-JUAN YE, XU-LI TANG, CAI-FENG DING
and SHU-SHENG ZHANG*
College of Chemistry and Molecular Engineering
Qingdao University of Science and Technology, Qingdao, 266 042, P.R. China
E-mail: zhangshush@public.qd.sd.cn

A new complex of N-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl) thiocarbamic 2,4-dihydroxy benzoyl hydrazine monohydrate, $C_{22}H_{27}N_3O_{11}S{\cdot}H_2O$, has been synthesized and its structure is determined by X-ray crystallography and TG/DTG. The compound crystallizes in the orthorhombic system, space group $P4_32_12$, with cell dimensions of a = 12.0199 (7), b = 12.0199 (7), c = 38.877 (3) Å, V = 5616.9 (6) $Å^3$ and Z = 8. The hexopyranosyl ring adopts a ^4C conformation. All the substituents are in equatorial positions. The molecules are linked into a three-dimensional framework by intermolecular interactions. The atoms O3, O7, O9 and C14 show positional disorders.

Key Words: **Synthesis, Crystal structure, Thermal analysis.**

INTRODUCTION

Isothiocyanates 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]. 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. We have reported some structures of carbohydrate compounds[6, 7]. In the ongoing research, the title compound N-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl) thiocarbamic 2,4-dihydroxy benzoyl hydrazine monohydrate, (I), is synthesized. An X-ray crystal analysis of (I) was undertaken to establish its molecular structure.



Structure (I)

EXPERIMENTAL

The title compound was prepared according to the literature[8]. The solid product was collected by filtration and single crystal suitable for X-ray crystallographic analysis was obtained by slow evaporation of the filtrate at room temperature.

Crystal structure determinations and refinements

A 0.42 × 0.15 × 0.14 mm crystal of the title compound was mounted on a SMART 1000 CCD diffractometer. Reflection data were measured at 293(2) K using MoKα radiation ($\lambda = 0.071073$ nm) with a graphite monochromator. The technique used was ω-scan with θ limits $2.31 < \theta < 26.02°$. Empirical absorption correction was carried out by using the SADABS[9] program. 3263 reflections were measured, of which 2212 were unique $[I > 2\sigma(I)]$. The structure was solved by direct methods and refined by least squares on F^2 using the SHELXTL[10] software package. All non-H atoms were anisotropically refined except those having disorders. The hydrogen atoms were fixed geometrically and treated as riding, with C—H distances from 0.93–0.98 Å. The final conventional $R = 0.0647$ and $wR = 0.1991$ for $I > 2\sigma(I)$ with weighting scheme, $w = 1/[\sigma^2(Fo^2) + (0.1301P)^2 + 0.2976P]$, where $P = (Fo^2 + 2Fc^2)/3$. The molecular graphics were plotted using SHELXTL[10]. Atomic scattering factors and anomalous dispersion corrections were taken from International Tables for X-Ray Crystallography[11].

RESULTS AND DISCUSSION

The compound crystallizes in the orthorhombic system, space group $P4_32_12$, with cell dimensions of a = 12.0199 (7), b = 12.0199 (7), c = 38.877 (3) Å, V = 5616.9 (6) Å, and Z = 8. A view of the title compound, showing the displacement ellipsoids and the atomic numbering, is given in Fig. 1. Crystal data and structure refinement for the title compound are shown in Table-1. Table-2 contains

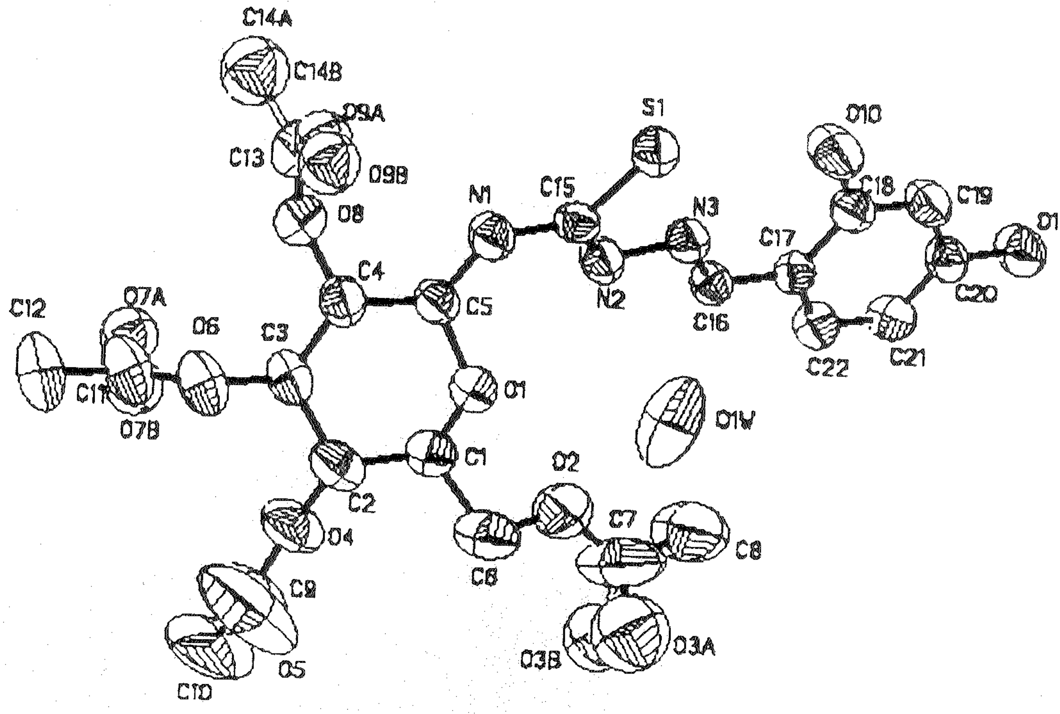


Fig. 1. The molecular structure of the title compound with the atomic numbering scheme

atomic positions and equivalent temperature factors for non-hydrogen atoms. Selected bond lengths and angles are presented in Table-3. The hydrogen-bonding interaction distances are listed in Table-4.

TABLE-1
CRYSTAL DATA AND STRUCTURE REFINEMENT PARAMETERS FOR THE TITLE COMPOUND

Formula	$C_{22}H_{27}N_3O_{11}S \cdot H_2O$
Formula weight	559.54
Colour/shape	Yellow/needle
Crystal system	Orthorhombic
Space group	$P4_32_12$
a (Å)	12.0199(7)
b (Å)	12.0199(7)
c (Å)	38.877(3)
V (Å^3)	5616.9(6)
Z	8
$D_{(calcd.)}$ (mg m^{-3})	1.323
μ (mm^{-1})	0.178
Crystal size (mm)	0.42 × 0.15 × 0.14
Temp. (K)	293(2)
θ ranges (°)	2.31–26.02
h/k (L)	−14, 14/−10, 14/−47, 46
Reflections collected	3335
Independent reflections	3263
Absorption correction	Empirical
Final R indices [$I > 2\sigma(I)$]	0.0647

The bond lengths and angles in **I** are in good agreement with those of O-ethyl and O-methyl N-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl)-thiocarbamate[6]. The hexopyranosyl ring adopts a $^4C_1$ conformation. The dihedral angles between the O-acetyl groups and the mean plane through the hexopyranosyl ring are in the range of 39.0 (4)–86.1 (3)°. While the anomeric dihydroxybenzoyl substituent makes a dihedral angle of 32.7 (2)° with the same ring. All the ring substituents are each plane and occupy equatorial positions, which is assumed to be the most stable conformation. In the structure of **I**, the relative orientation of the acetoxymethyl group is determined by the O1—C1—C6—O2 and C2—C1—C6—O2 torsion angles, being −69.0 (7) and 172.8 (5)°, respectively. These values are comparable to those in N-(β-D-glucopyranosyl)-S-phenylsulfenamide[12], where the corresponding O5—C5—C6—O6 and C4—C5—C6—O6 torsion angles are 72.4 (3) and −168.2 (3)°, respectively.

In the crystal of **I**, there is one water solvate molecule, which was incorporated during recrystallization. Within the unit, the water solvate molecule is involved in O11—H11A···O1W, intermolecular interaction. The water molecule is connected to the pyranosyl molecule *via* O1W—H1W1···O2 and O1W—H2W1···O1 intramolecular interactions. All the three O-acetyl groups attached at C2, C3 and C4 are involved in intramolecular interactions. The molecular packing is stabilized by other two intermolecular interactions, N1—H1A····S1 and C5—H5A····O11, which lead to the formation of a three-dimensional framework. The O3, O7, O9 and C14 atoms show positional disorders. Refinement of the site occupancies resulted in a major component with occupancies of 0.62% for O3 and 0.55% for O7, O9 and C14, respectively.

TABLE-2

ATOMIC COORDINATES AND EQUIVALENT ISOTROPIC DISPLACEMENT PARAMETERS (Å)^2

Atom	x	y	z	U_{eq}	Atom	x	y	z	U_{eq}
O1W	0.0190(5)	0.5111 (6)	0.27580 (1)	0.1230 (2)	C4	0.2911 (5)	0.3511 (5)	0.19760 (1)	0.0580 (1)
S1	0.2517 (1)	0.6962 (1)	0.27382 (3)	0.0574 (4)	C5	0.2583 (5)	0.3852 (4)	0.23404 (12)	0.0525 (12)
O1	0.1422 (3)	0.3612 (3)	0.23792 (9)	0.0584 (9)	C6	0.0055 (6)	0.2260 (7)	0.25200 (2)	0.0980 (2)
O2	0.0092 (5)	0.2545 (5)	0.28740 (1)	0.1150 (2)	C7	0.0750 (1)	0.2460 (1)	0.30730 (3)	0.1460 (5)
O3	–0.164 (1)	0.2180 (1)	0.29430 (2)	0.2920 (9)	C8	0.0620 (1)	0.2790 (1)	0.34210 (2)	0.1630 (6)
O4	0.1274 (4)	0.0873 (4)	0.19930 (1)	0.0930 (2)	C9	0.0610 (1)	0.0450 (1)	0.17530 (4)	0.1390 (4)
O5	0.0140 (1)	0.1058 (9)	0.15510 (3)	0.2070 (5)	C10	0.0510 (1)	0.0761 (8)	0.17760 (3)	0.1860 (6)
O6	0.2767 (4)	0.2123 (3)	0.15433 (9)	0.0710 (1)	C11	0.3520 (7)	0.1390 (6)	0.14330 (15)	0.0790 (19)
O7A	0.4190 (4)	0.0910 (3)	0.16120 (5)	0.1090 (9)	C12	0.3614 (7)	0.1363 (6)	0.10518 (15)	0.0960 (2)
O7B	0.3660 (7)	0.0630 (3)	0.16600 (1)	0.1090 (1)	C13	0.4464 (9)	0.4551 (8)	0.17930 (2)	0.1030 (3)
O8	0.4075 (4)	0.3620 (4)	0.19360 (1)	0.0810 (1)	C14	0.5681 (11)	0.4560 (12)	0.17770 (3)	0.2080 (8)
O9	0.3868 (8)	0.5284 (5)	0.16870 (2)	0.1300 (3)	C15	0.2558 (4)	0.5480 (4)	0.27026 (11)	0.0480 (11)
O10	0.2345 (5)	0.7146 (3)	0.37040 (1)	0.0890 (2)	C16	0.1928 (4)	0.4874 (4)	0.35228 (11)	0.0495 (12)
O11	0.1017 (4)	0.6626 (4)	0.48255 (9)	0.0850 (1)	C17	0.1705 (4)	0.5338 (4)	0.38613 (11)	0.0474 (12)
N1	0.2724 (4)	0.5016 (4)	0.23880 (1)	0.0580 (1)	C18	0.1918 (5)	0.6451 (4)	0.39421 (13)	0.0544 (13)
N2	0.2394 (4)	0.4868 (4)	0.29670 (1)	0.0580 (1)	C19	0.1705 (5)	0.6850 (5)	0.42655 (13)	0.0629 (15)
N3	0.2226 (4)	0.5474 (4)	0.32710 (1)	0.0540 (1)	C20	0.1244 (5)	0.6167 (5)	0.45131 (12)	0.0570 (13)
C1	0.1226 (5)	0.2449 (5)	0.23790 (1)	0.0660 (2)	C21	0.1049 (5)	0.5058 (5)	0.44441 (12)	0.0613 (15)
C2	0.1426 (5)	0.2058 (5)	0.20070 (2)	0.0680 (2)	C22	0.1287 (5)	0.4650 (5)	0.41152 (12)	0.0586 (14)
C3	0.2609 (5)	0.2314 (4)	0.19070 (1)	0.0610 (1)					

Thermal analysis

Thermal analysis curves of the title compound are shown in Fig. 2. Thermogravimetric (TG) analysis and differential thermogravimetric (DTG) analysis show that the thermal decomposition of the title compound includes two transitions. There are two peaks corresponding to exothermal processes—that is, a weak peak at 80.9°C corresponding to removal of water molecule and a strong peak at 222.8°C due to loss of the O-acetyl-glucopyranose moieties.

TABLE-3
SELECTED BOND DISTANCES (Å) AND BOND ANGLES (°) OF THE TITLE COMPOUND

Bond	Dist.	Bond	Distance	Bond	Distance
S1—C15	1.784 (6)	O7A—C11	1.250 (12)	N3—C16	1.261 (6)
O1—C1	1.416 (7)	O7B—C11	1.252 (14)	C1—C6	1.522 (10)
O1—C5	1.441 (7)	O8—C13	1.351 (10)	C1—C2	1.548 (8)
O2—C7	1.267 (12)	O8—C4	1.423 (8)	C2—C3	1.501 (9)
O2—C6	1.438 (9)	O9A—C13	0.919 (19)	C3—C4	1.510 (8)
O3A—C7	1.370 (19)	O9B—C13	1.480 (2)	C4—C5	1.524 (7)
O3B—C7	1.240 (2)	O10—C18	1.347 (7)	C7—C8	1.407 (13)
O4—C9	1.328 (12)	O11—C20	1.361 (6)	C9—C10	1.472 (16)
O4—C2	1.442 (8)	N1—C15	1.361 (6)	C11—C12	1.483 (9)
O5—C9	1.201 (15)	N1—C5	1.418 (7)	C13—C14B	1.320 (2)
O6—C11	1.329 (8)	N2—C15	1.281 (6)	C13—C14A	1.750 (3)
O6—C3	1.439 (6)	N2—N3	1.403 (6)		
Angle	(°)	Angle	(°)	Angle	(°)
C1—O1—C5	111.1 (4)	O1—C1—C6	107.5 (6)	C2—C3—C4	112.0 (5)
C7—O2—C6	123.2 (7)	O1—C1—C2	105.7 (5)	C8—C4—C3	107.4 (5)
C9—O4—C2	118.6 (8)	C6—C1—C2	115.4 (6)	O8—C4—C5	109.0 (5)
C11—O6—C3	120.8 (5)	O4—C2—C3	108.4 (5)	C3—C4—C5	111.2 (5)
C13—O8—C4	116.9 (7)	O4—C2—C1	108.2 (6)	N1—C5—O1	107.4 (5)
C15—N1—C5	120.4 (4)	C3—C2—C1	109.4 (5)	N1—C5—C4	110.6 (4)
C15—N2—N3	113.7 (4)	O6—C3—C2	110.1 (5)	O1—C5—C4	106.9 (4)
C16—N3—N2	113.5 (4)	O6—C3—C4	107.5 (5)		

TABLE-4
HYDROGEN-BONDING GEOMETRY (Å, °)

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1A···O9	0.86	2.36	3.071 (8)	140
N1—H1A···S1^{i}	0.86	2.48	3.029 (5)	122
O11—H11A···O1W^{ii}	0.82	1.83	2.645 (7)	175
C2—H2B···O5	0.98	2.22	2.640 (13)	105
C3—H3B···O7A	0.98	2.37	2.790 (4)	105
C4—H4A···O9	0.98	2.29	2.670 (9)	102
C5—H5A···O11^{iii}	0.98	2.55	3.417 (7)	148
O1W—H1W1···O2	0.86	2.29	3.136 (9)	170
O1W—H2W1···O1	0.85	2.58	3.029 (7)	115

Symmetry codes: (i) 1 − y, 1 − x, ½ − z; (ii) y − ½, ½ − x, 1/4 +z; (iii) 1/2−x, y − 1/2, 3/4 −z.

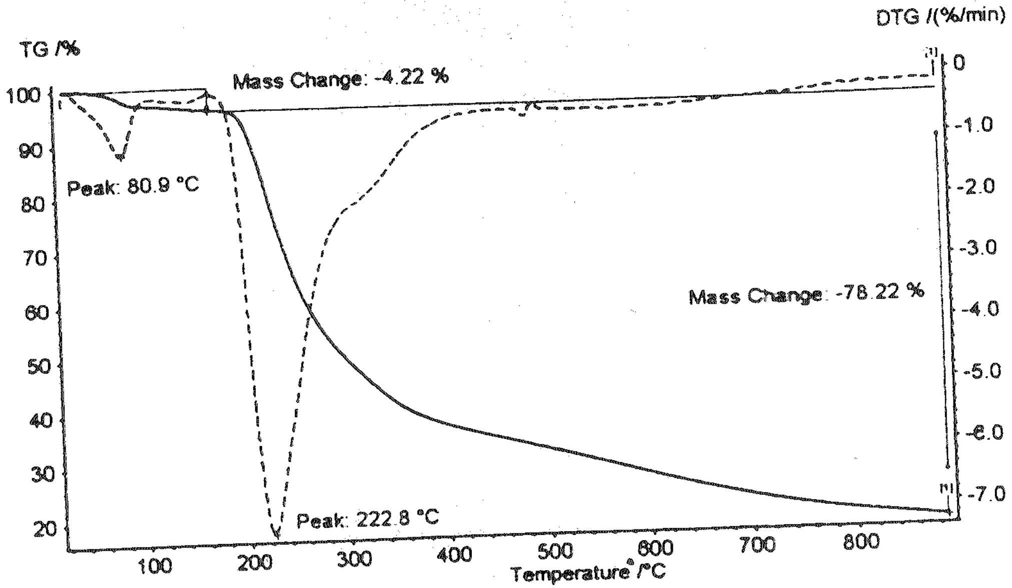


Fig. 2. Thermal analysis curves of the title compound

ACKNOWLEDGEMENTS

The project was supported by the Program for New Century Excellent Talents in University (No. NCET-04-0649) and the National Natural Science Foundation of China (No. 20275020 and 20475030).

REFERENCES

1. A.K. Mukerjee and R. Ashare, *Chem. Rev.*, **91**, 1 (1991).
2. C. Uriel and F. Santoyo-Gonzalez, *Synthesis*, 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. 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).
7. B. Yang, S.-S. Zhang, Y.-F. Wang, X.-M. Li and K. Jiao, *Acta Cryst.*, **E60**, 568 (2004).
8. J.-X. Yu, F.-M. Liu, W.-J. Lu, Y.-P. Li, L.-L. Tian and Y.-T. Liu, *Chem. J. Chinese Univer.*, **20**, 1233 (1999).
9. Sadabs: Program for Empirical Absorption Correction of Area Detector Data, University of Gottingen, Germany (1996).
10. G.M. Sheldrick, SHELXTI, v5 Reference Manual, Siemens Analytical X-ray Systems, Inc., Madison, Wisconsin, USA (1996).
11. A.J.C. Wilson, International Table for X-ray Crystallography, Volume C, Kluwer Academic Publishers, Dordrecht, Tables 6.1.1.4 (pp. 500–502) and 4.2.6.8 (pp. 219–222) respectively (1992).
12. C.K. Lee, A. Linden and A. Vasella, *Acta Cryst.*, **C51**, 1906 (1995).

(*Received*: 21 March 2005; *Accepted*: 3 October 2005) AJC-4429