Notes

Structures of *N*-(2,3,4,6-Tetra-*O*-acetyl-β-*D*-glycosyl)thiocarbamic Benzoyl Hydrazine

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The crystal structure of *N*-(2,3,4,6-tetra-*O*-acetyl-β-*D*-glycosyl)-thiocarbamic benzoyl hydrazine ($C_{22}H_{27}N_3O_9S$) was determined by X-ray diffraction method. The hexopyranosyl ring adopts a chair conformation. All the ring substituents are in the equatorial positions. The acetoxyl-methyl group is in synclinal conformation. The S atom is in synperiplanar conformation while the benzoyl hydrazine moiety is *anti*-periplanar. The thiocarbamic moiety is almost coplanar with the benzoyl hydrazine group. There are two intramolecular hydrogen bonds and one intermolecular hydrogen bond for each molecule in the crystal structure. The molecules form a network structure through intermolecular hydrogen bonds.

Keywords crystal structure, hydrogen bonds, conformation

Introduction

Many nomadic sugars play an important role in biology.[1] They could control various gene expressions to adjust the upgrowth, development, detendent reaction and the biology of organs.[2] Glycosyl isothiocyanates have been widely used as valuable intermediates in the synthesis of glycosyl thiourea derivatives.[3] The isothiocyanates and glycosyl isothiocyanates have been the focus of synthetic attention during recent years and have potential pharmacological properties.[4] They have also attracted considerable interest because of the *anti*-HIV activity shown by 1-deoxynojirimycin, castanospermine and some of their derivatives.[5] These inhibitors act competitively against the glycosidases governing the processing of the glycoproteins of the viral coat and thereby alter viral infectivity.[6] It was found that *N*-(2, 3, 4, 6-tetra-*O*-acetyl-β-*D*-glycosyl)-*S*-phenylsulfenamide had weak irreversible inhibition, which might be triggered by protonation of the amino group. In an attempt to find new enzyme-activated irreversible inhibitors for glucosidases, *N*-β-*D*-glucopyranosyl-*S*-phenylsulfennamide was synthesized.[7] In this paper, the X-ray structure of *N*-(2,3, 4, 6-tetra-*O*-acetyl-β-*D*-glycosyl)-thiocarbamic benzoyl hydrazine was reported.

Experimental

Materials

Methylbenzene was redistilled under reflux. The other chemicals were obtained from a commercial source and used without further purification.

Preparation of N-amino-N′-(2,3,4,6-tetra-O-acetyl-β-D-glycosyl) thiourea

Ethanol (100 mL) and hydrazine hydrate (50% aqueous solution, 1.2 mL) were mixed below 5 ℃ in ice-bath. 2,3,4,6-Tetra-*O*-acetyl-β-*D*-glycosyl isothiocyanate (3.9 g, 10 mmol) in ethanol (30 mL) was added dropwise with stirring. The solution was filtrated after stirring for 10 min. The colorless crystals (3.8 g) were obtained by recrystallization from ethyl acetate/

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Received July 19, 2001; revised September 17, 2001; accepted October 29, 2001.
Project supported by the Natural Science Foundation of Shandong Province (No. Q99B16) and the National Natural Science Foundation of China (No. 20075013).

petroleum ether (1/3). Yield 90%.

Preparation of the title compound

Tetramethylene oxide (30 mL), *N*-amino-*N'*-(2,3,4,6-tetra-*O*-acetyl-β-*D*-glycosyl)thiourea (1.62 g, 4 mmol) and benzaldehyde (0.45 mL, 4 mmol) were mixed with stirring under reflux in oil-bath for 3 h. After the solution evaporated by distillation at reduced pressure, white deposits were obtained in petroleum ether. The colorless crystals (1.6 g) were obtained by recrystallization from ethyl acetate/petroleum ether (1/3). Yield 81%.

The title compound was recrystallized in ethyl acetate/petroleum ether (1/2). After filtration, the clear colorless filtrate stood at room temperature. Single crystals suitable for X-ray analysis were obtained from the mixed solvent.

X-*ray structure determination*

A summary of the crystallographic information is given in Table 1, selected bond distances and angles are listed in Table 2, and the atomic coordinates are listed in Table 3. The selected crystal of *N*-(2,3,4,6-tetra-*O*-acetyl-β-*D*-glycosyl)-thiocarbamic benzoyl hydrazine was mounted on a SMART CCD diffractometer. Diffraction data were measured at 20 ℃ using graphite monochromated Mo Kα (λ = 0.071073 nm) radiation with a detector distance of 4 cm and swing angle of −35°. The collected data were reduced by using the program SAINT[8] and empirical absorption correction was made by using the SADABS[9] program. The structure was solved by direct method and refined by full-matrix least-squares method on F_{obs}^2 by using the SHELXTL[10] software package. All non-H atoms were anisotropically refined. The hydrogen atoms were located by difference synthesis and refined isotropically. Atomic scattering factors and anomalous dispersion corrections were taken from International Table for X-Ray Crystallography.[11]

Results and discussion

Description of the structure

The title compound crystallized in orthorhombic

Table 1 Summary of crystallographic data for the complex

Empirical formula	$C_{22}H_{27}N_3O_9S$
Formula weight	509.53
Temperature	293(2) K
Wavelength	0.071073 nm
Crystal system, space group	orthorhombic $P2_12_12_1$
Unit cell dimensions	
a (nm)	0.99972(9)
b (nm)	1.2622(7)
c (nm)	2.0841(3)
V (nm^3)	2.6236(1)
Z	4
Calculated density (g/cm^3)	1.290
Absorption coefficient (mm^{-1})	0.176
F(000)	1072
Crystal size	0.40 mm × 0.12 mm × 0.10 mm
Theta range for data collection (°)	1.89—24.99
Limiting indices	$-11 \leqslant h \leqslant 11$, $-15 \leqslant k \leqslant 11$, $-24 \leqslant l \leqslant 24$
Reflections collected/unique	14879/4599 [R_{int} = 0.1088]
Completeness to theta = 24.99	100%
Absorption correction	Empirical
Max. and min. transmission	0.9826 and 0.9330
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	4599/0/316
Goodness-of-fit on F^2	0.937
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0681, wR_2 = 0.1654
R indices (all data)	R_1 = 0.1192, wR_2 = 0.1916
Largest diff. peak and hole (e·nm^{-3})	807 and −323

Table 2 Selected bond distances [nm] and angles [°] for the complex.

Bond	Distance (nm)	Bond	Distance (nm)	Bond	Distance (nm)
O(1)—C(5)	0.1442(6)	O(1)—C(1)	0.1445(6)	O(2)—C(13)	0.1188(9)
O(2)—C(12)	0.1453(7)	O(4)—C(4)	0.1456(5)	O(6)—C(8)	0.1350(7)
O(6)—C(3)	0.1441(6)	O(8)—C(6)	0.1361(6)	O(8)—C(2)	0.1449(5)
C(1)—N(15)	0.1423(6)	C(1)—C(2)	0.1534(7)	C(2)—C(3)	0.1540(6)
C(3)—C(4)	0.1515(7)	C(4)—C(5)	0.1517(7)	C(5)—C(12)	0.1521(7)
N(15)—C(16)	0.1337(6)	C(16)—N(17)	0.1342(6)	N(17)—N(18)	0.1379(5)
N(18)—C(19)	0.1273(6)				

Bond	Angle(°)	Bond	Angle(°)
C(5)-O(1)-C(1)	114.1(4)	C(13)-O(2)-C(12)	116.8(8)
C(10)-O(4)-C(4)	117.2(4)	C(8)-O(6)-C(3)	117.9(4)
C(6)-O(8)-C(2)	116.4(4)	N(15)-C(1)-O(1)	105.4(4)
N(15)-C(1)-C(2)	110.2(4)	O(1)-C(1)-C(2)	109.0(4)
O(8)-C(2)-C(1)	109.4(4)	O(8)-C(2)-C(3)	106.3(4)
C(1)-C(2)-C(3)	110.5(4)	O(6)-C(3)-C(4)	108.7(4)
O(6)-C(3)-C(2)	107.7(4)	C(4)-C(3)-C(2)	107.5(4)
O(4)-C(4)-C(3)	108.5(4)	O(4)-C(4)-C(5)	107.3(4)
C(3)-C(4)-C(5)	110.0(4)	O(1)-C(5)-C(4)	107.7(4)
O(1)-C(5)-C(12)	103.6(4)	C(4)-C(5)-C(12)	114.2(5)
O(9)-C(6)-O(8)	123.2(5)	O(7)-C(8)-O(6)	123.0(6)
O(5)-C(10)-C(11)	126.6(5)	O(4)-C(10)-C(11)	109.8(5)
O(2)-C(12)-C(5)	111.9(5)	O(2)-C(13)-O(3)	127.0(1)
C(16)-N(15)-C(1)	125.0(4)	N(15)-C(16)-N(17)	114.5(4)
N(15)-C(16)-S(1)	125.3(4)	N(17)-C(16)-S(1)	120.1(4)
C(16)-N(17)-N(18)	119.7(4)	C(19)-N(18)-N(17)	117.6(4)
N(18)-C(19)-C(20)	119.8(5)		

Table 3 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($A^2 \times 10^3$) for the complex.

Atom	x	y	z	U_{eq}[a]	Atom	x	y	z	U_{eq}[a]
S(1)	486(1)	4131(1)	9476(1)	51(1)	O(1)	-2196(4)	2079(3)	9172(2)	49(1)
O(2)	-3668(6)	1328(5)	7649(3)	107(2)	O(3)	-2757(6)	2745(6)	7310(3)	131(2)
O(4)	-2531(3)	-488(3)	8378(2)	54(1)	O(5)	-4556(4)	-1011(4)	8724(2)	74(1)
O(6)	-1276(3)	-1045(3)	9571(2)	51(1)	O(7)	698(6)	-1570(4)	9174(3)	106(2)
O(8)	296(3)	598(3)	10123(2)	48(1)	O(9)	-565(4)	1002(4)	11084(2)	71(1)
C(1)	-995(5)	1931(4)	9548(2)	45(1)	C(2)	-987(5)	803(4)	9821(2)	40(1)
C(3)	-1133(5)	-17(4)	9279(2)	42(1)	C(4)	-2409(5)	242(4)	8917(2)	44(1)
C(5)	-2326(5)	1352(4)	8642(2)	46(1)	C(6)	337(6)	676(4)	10774(3)	52(1)
C(7)	1683(6)	296(6)	11007(3)	79(2)	C(8)	-284(8)	-1757(5)	9481(3)	71(2)
C(9)	-610(11)	-2777(5)	9800(3)	117(3)	C(10)	-3685(5)	-1024(5)	8323(3)	53(1)
C(11)	-3730(7)	-1574(6)	7696(3)	96(3)	C(12)	-3596(7)	1718(5)	8304(3)	69(2)
C(13)	-3226(9)	1887(7)	7242(6)	109(3)	C(14)	-3352(9)	1455(8)	6534(3)	116(3)
N(15)	-1082(5)	2685(3)	10054(2)	49(1)	C(16)	-592(5)	3671(4)	10032(2)	42(1)
N(17)	-1033(4)	4311(3)	10501(2)	47(1)	N(18)	-1903(4)	3924(3)	10958(2)	44(1)
C(19)	-2317(5)	4564(5)	11386(2)	51(1)	C(20)	-3200(5)	4188(5)	11891(2)	55(2)
C(21)	-3602(7)	4891(7)	12369(3)	96(3)	C(22)	-4385(9)	4593(11)	12875(4)	113(3)
C(23)	-4770(8)	3554(13)	12912(4)	124(4)	C(24)	-4413(7)	2794(8)	12431(4)	100(3)
C(25)	-3636(6)	3142(5)	11934(3)	67(2)					

[a] U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

system, space group $P2_12_12_1$. A perspective view of a molecule with the atomic numbering scheme of the title compound is shown in Fig. 1 and a perspective view of the crystal packing in the unit cell is shown in Fig. 2.

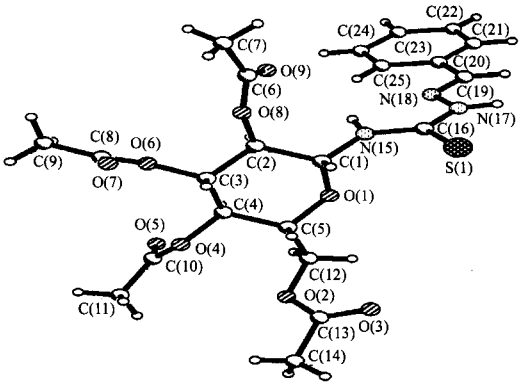

Fig. 1 Molecular structure of the title compound with the atomic numbering scheme.

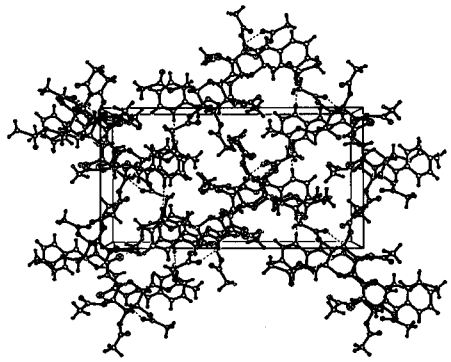

Fig. 2 A view of the crystal packing down the *b* axis.

The bond lengths and angles are normal and agree well with those of *D*-glucopyranose,[12] *N*-*D*-glucopyranosyl-hydroxylamine[13] and *N*-*D*-glucopyranosyl-*S*-phenylsulfenamide.[14] The hexopyranosyl ring adopts a normal $^4C_1$ chair conformation with total puckering amplitude, Q_T of 0.601(5).[15] The dihedral angle between the acetyl group and the mean plane of the hexopyranosyl ring is in the range of 65.9(3)° to 89.5(3)°. The acetoxymethyl substituent makes a dihedral angle of 51.6(3)° with the hexopyranosyl ring. The thiocarbamic moiety and benzoyl hydrazine group are almost coplanar with the maximum deviation of 0.071(1)°. The plane, meanwhile, makes a dihedral angle of 74.4(2)° with the hexopyranosyl ring. All the ring substituents are in the equatorial positions to the ring. The acetyl group is in the synclinal conformation to C(4)—C(5) and O(1)—C(5) bonds similar to *N*-β-*D*-glucopyranosyl-*S*-phenylsulfenamide.[15] The S atom is in synperiplanar conformation with respect to the C(1) atom while the benzoyl hydrazine moiety is *anti*-periplanar.

The N(15)—H···O(9) and N(15)—H···N(18) separations are 0.3063(6) and 0.2582(6) nm, respectively, which suggests two intramolecular hydrogen bonds. There is N(17)—H···O(5) intermolecular hydrogen bond in the crystal structure, with the donor and acceptor distances of 0.3064(6) nm. The molecules form a network structure through intermolecular hydrogen bonds.

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(E0107193 LI, L. T.; FAN, Y. Y.)