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Synthesis and Crystal Structure of 2,3,4-Tri-O-acetyl-β-D-xylopyranosyl Isothiocyanate

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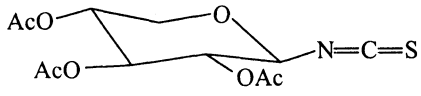
The crystal structure of 2,3,4-tri-O-acetyl-β-D-xylopyranosyl isothiocynate, $C_{12}H_{15}NO_7S$, has been synthesized and its structure is determined by X-ray crystallography and TG/DTG method. The crystal belongs to triclinic system, space group PI with unit cell constants a = 7.824(3), b = 9.252(3), c = 10.827(4) Å, α = 91.565(6), β = 101.021(7), γ = 90.696(6)°, V = 768.8(5) Å^3, Z = 1, D_c = 1.371 g/cm^3, μ = 0.241 mm^{-1}, R and wR are 0.0474 and 0.1171 respectively for 3548 unique reflections with 3018 observed reflections [I > 2σ(I)]. All the ring substituents are in plane and occupy equatorial positions.

Key Words: Synthesis, Crystal structure, Xylopyranosyl isothiocyanate.

INTRODUCTION

The studies on the carbohydrate-containing compounds were extremely increased during the last three decades as they have been found to have many interesting and useful biological activities instead of being assumed possessing only structural support and energy storing functions[1, 2]. Isothiocyanates are versatile reagents in organic chemistry, since they easily undergo many important reactions, such as cycloadditions and nucleophilic additions[3, 4]. Glycosyl isothiocyanates have been used for the preparation of a vareity of carbohydrate derivatives of synthetic, biological and pharmaceutical interst. They have served as glycosidase inhibitors and for the synthesis of glycosyl thiourea derivatives, glycosylamino hetercocycles, nucleoside analogues or N-glycopeptides[5, 6]. In this paper, an X-ray crystal analysis of $C_{12}H_{15}NO_7S$ was undertaken to establish its molecular structure. The formular structure of the title compound is as shown below.



Structure of 2,3,4-tri-O-acetyl-β-D-xylopyranosyl isothiocynate

EXPERIMENTAL

D-Xylose is a biochemical reagent. Toluene was redistilled under reflux. The other chemicals were obtained from a commercial source and used without further purification. To a solution of acetic anhydride, 20 g xylose (133 mmol) was added at 0–5°C; the solution was stirred for 2 h below 10°C. After this, 12 mL bromine and 10 mL water were added dropwise, the reaction was maintained for 0.5 h, then toluene (50 mL) and 43.6 g lead thiocynate (133 mmol) were added with stirring under reflux for 4 h. Then the solvent was removed under reduced pressure; the deposits were obtained in petroleum ether. Crystals suitable for X-ray crystallographic analysis were obtained from ethyl acetate/petroleum ether (1 : 10, v/v).

Crystal data and structure determination

A colourless single crystal with approximate dimension of $0.50 \times 0.13 \times 0.07$ nm was mounted on a glass fibre in a random orientation. The data were collected by Bruker Smart 1000 CCD diffractometer with graphite monochromated MoK_α radiation ($\lambda = 0.71073$ Å) using ω scan mode in the range of $1.92 \leq \theta \geq 25.96°$ at temperature 293(2) K. A total of 4341 reflections were collected with 3548 unique ones ($R_{int} = 0.0037$), of which 3018 reflections with $I > 2\sigma(I)$ were considered to be observed and used in the succeeding refinements. Intensity data were corrected for Lp factors and empirical absorption. Empirical absorption correction was carried out by using the SADABS[7] program. The structure was solved by direct methods and expanded by using Fourier differential techniques with SHELXL-97[8]. All non-hydrogen atoms were located with successive difference Fourier syntheses. The structure was refined by full-matrix last-squares method of F^2 with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were added according to the theoretical models. Full matrix least-squares refinement gave the final $R = 0.0474$ and $wR = 0.1171$, $w = 1/[\sigma^2(F_0^2) + (0.0563P)^2 + 0.1627P]$, where $P = (F_0^2 + 2F_c^2)/3$. Atomic scattering factors and anomalous dispersion corrections were taken from international tables for X-ray crystallography[9].

RESULTS AND DISCUSSION

Fig. 1 shows a perspective view of the monomeric unit with the atomic numbering scheme of the title compound. Fig. 2 shows a perspective view of the crystal packing in the unit cell for the compound. A summary of the key crystallographic information is given in Table-1. The final atomic parameters and equivalent isotropic thermal parameters for the non-hydrogen atoms are given in Table-2. Selected bond lengths and bond angles are illustrated in Tables 3 and 4, respectively. The hydrogen bonding geometries are shown in Table-5.

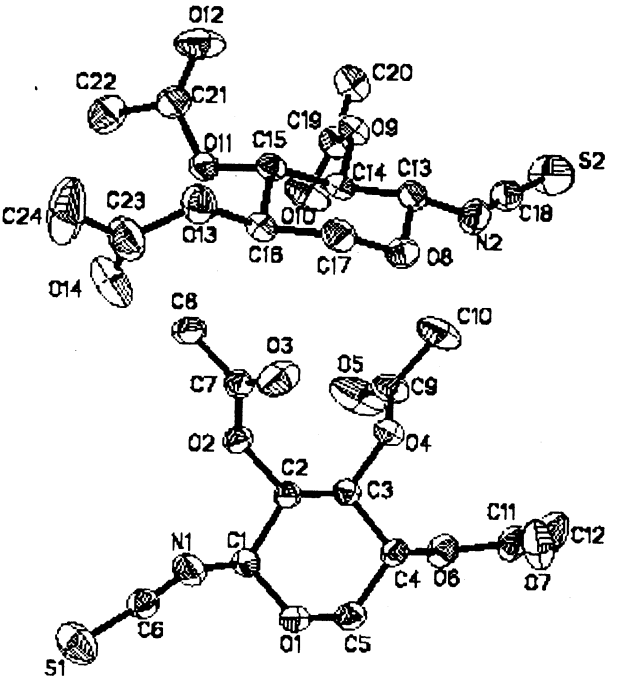


Fig. 1. The molecular structure of the title compound with the atomic numbering scheme

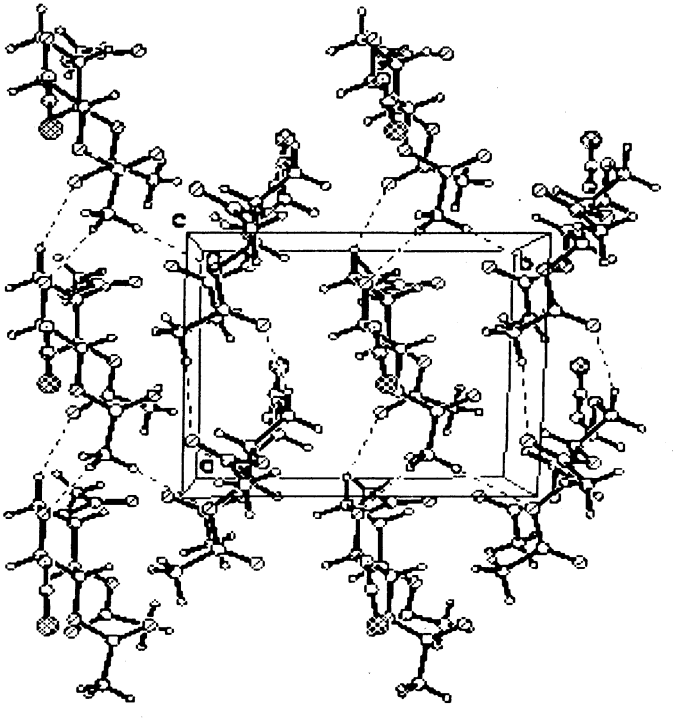


Fig. 2. A view of the crystal packing for the title compound

TABLE-1
ATOMIC COORDINATES AND THERMAL PARAMETERS ($Å^2$)

Atomic	x	y	z	U_{eq}
S1	0.4969 (2)	0.74486 (19)	0.20152 (14)	0.0975 (5)
S2	–0.5727 (2)	1.4196 (2)	–0.57657 (14)	0.1084 (7)
O1	0.3440 (3)	0.7442 (3)	–0.2130 (2)	0.0542 (7)
O2	–0.0736 (4)	0.8478 (3)	–0.1377 (2)	0.0510 (7)
O3	–0.0737 (3)	1.0883 (4)	–0.1099 (4)	0.0857 (11)
O4	–0.1034 (3)	0.9427 (3)	–0.3918 (2)	0.0509 (7)
O5	–0.3300 (5)	0.7937 (5)	–0.4456 (6)	0.1360 (2)
O6	0.1020 (4)	0.7828 (4)	–0.5343 (3)	0.0668 (9)
O7	0.1966 (7)	0.9927 (6)	–0.5964 (4)	0.1173 (17)
O8	–0.1474 (4)	1.4790 (3)	–0.1673 (3)	0.0560 (7)
O9	–0.6049 (3)	1.3730 (3)	–0.2240 (2)	0.0488 (7)
O10	–0.6276 (5)	1.1316 (4)	–0.2492 (4)	0.0859 (11)
O11	–0.4813 (3)	1.2770 (3)	0.0309 (2)	0.0492 (7)
O12	–0.7103 (5)	1.4095 (4)	0.0530 (4)	0.0967 (13)
O13	–0.1822 (4)	1.4496 (4)	0.1608 (3)	0.0643 (8)
O14	–0.1272 (9)	1.2273 (7)	0.2274 (5)	0.1400 (2)
N1	0.2699 (6)	0.7733 (5)	–0.0199 (3)	0.0724 (12)
N2	–0.3366 (5)	1.4527 (5)	–0.3539 (3)	0.0648 (10)
C1	0.2020 (6)	0.7423 (4)	–0.1492 (4)	0.0504 (10)
C2	0.0713 (5)	0.8570 (4)	–0.2014 (3)	0.0443 (9)
C3	0.0087 (5)	0.8275 (4)	–0.3408 (3)	0.0454 (9)
C4	0.1624 (5)	0.8239 (4)	–0.4040 (3)	0.0483 (9)
C5	0.2904 (6)	0.7120 (5)	–0.3448 (4)	0.0562 (11)
C6	0.3707 (6)	0.7558 (5)	0.0722 (4)	0.0564 (11)
C7	–0.1375 (6)	0.9716 (5)	–0.0987 (4)	0.0519 (10)
C8	–0.2943 (6)	0.9458 (5)	–0.0451 (5)	0.0671 (13)
C9	–0.2696 (6)	0.9128 (6)	–0.4442 (5)	0.0711 (13)
C10	–0.3605 (8)	1.0426 (7)	–0.4979 (6)	0.0980 (2)
C11	0.1193 (7)	0.8829 (9)	–0.6220 (5)	0.0850 (18)
C12	0.0289 (9)	0.8297 (11)	–0.7504 (5)	0.1280 (3)
C13	–0.3246 (5)	1.4808 (4)	–0.2224 (3)	0.0488 (10)
C14	–0.4248 (5)	1.3652 (4)	–0.1653 (3)	0.0441 (9)
C15	–0.4020 (5)	1.3932 (4)	–0.0247 (3)	0.0433 (9)
C16	–0.2089 (5)	1.4009 (4)	0.0310 (4)	0.0480 (9)

Atomic	x	y	z	U_{eq}
C17	–0.1205 (6)	1.5117 (5)	–0.0358 (4)	0.0550 (10)
C18	–0.4451 (7)	1.4392 (5)	–0.4468 (4)	0.0636 (12)
C19	–0.6931 (7)	1.2473 (5)	–0.2629 (4)	0.0545 (10)
C20	–0.8764 (7)	1.2740 (6)	–0.3211 (5)	0.0725 (14)
C21	–0.6328 (6)	1.2987 (5)	0.0680 (4)	0.0589 (11)
C22	–0.6898 (7)	1.1671 (6)	0.1263 (5)	0.0800 (15)
C23	–0.1349 (8)	1.3548 (9)	0.2493 (6)	0.0934 (19)
C24	–0.1020 (11)	1.4265 (11)	0.3761 (5)	0.0144 (4)

TABLE-2
SELECTED BOND LENGTHS (Å)

Bond	Dist.	Bond	Dist.
S1—C6	1.558 (5)	O13—C23	1.320 (7)
S2—C18	1.565 (6)	O13—C16	1.440 (5)
O1—C1	1.417 (5)	O14—C23	1.201 (9)
O1—C5	1.430 (5)	N1—C6	1.163 (6)
O2—C7	1.345 (5)	N1—C1	1.420 (6)
O2—C2	1.438 (5)	N2—C18	1.188 (6)
O3—C7	1.203 (5)	N2—C13	1.425 (5)
O4—C9	1.338 (5)	C1—C2	1.526 (5)
O4—C3	1.442 (4)	C2—C3	1.511 (5)
O5—C9	1.143 (6)	C3—C4	1.493 (5)
O6—C11	1.367 (7)	C4—C5	1.517 (6)
O6—C4	1.438 (5)	C7—C8	1.473 (6)
O7—C11	1.175 (8)	C9—C10	1.479 (7)
O8—C13	1.401 (5)	C11—C12	1.501 (8)
O8—C17	1.423 (5)	C13—C14	1.531 (5)
O9—C19	1.359 (5)	C14—C15	1.513 (6)
O9—C14	1.435 (5)	C15—C16	1.516 (5)
O10—C19	1.93 (5)	C16—C17	1.505 (6)
O11—C21	1.338 (5)	C19—C20	1.479 (6)
O11—C15	1.438 (5)	C21—C22	1.488 (7)
O12—C21	1.196 (6)	C23—C24	1.484 (10)

TABLE-3
SELECTED BOND ANGLES (°)

Angle	(°)	Angle	(°)
C1—O1—C5	112.1 (3)	O4—C3—C2	109.0 (3)
C7—O2—C2	118.1 (3)	C4—C3—C2	109.0 (3)
C9—O4—C3	119.6 (3)	O6—C4—C3	108.2 (3)
C11—O6—C4	117.4 (4)	O6—C4—C5	108.5 (3)
C13—O8—C17	111.3 (3)	C3—C4—C5	110.2 (3)
C19—O9—C14	118.2 (3)	O1—C5—C4	109.9 (3)
C21—O11—C15	119.3 (3)	N1—C6—S1	174.3 (4)
C23—O13—C16	118.7 (5)	O3—C7—O2	122.8 (4)
C6—N1—C1	151.6 (4)	O3—C7—C8	125.3 (4)
C18—N2—C13	139.1 (5)	O2—C7—C8	111.9 (4)
O1—C1—N1	107.3 (4)	O5—C9—O4	121.6 (5)
O1—C1—C2	109.9 (3)	O5—C9—C10	126.6 (5)
N1—C1—C2	109.9 (3)	O4—C9—C10	111.7 (5)
O2—C2—C3	109.6 (3)	O7—C11—O6	122.9 (5)
O2—C2—C1	108.1 (3)	O7—C11—C12	127.0 (6)
C3—C2—C1	109.2 (3)	O6—C11—C12	110.2 (6)
O4—C3—C4	108.9 (3)		

TABLE-4
THE HYDROGEN BOND LENGTHS (Å) AND
BOND ANLGE (°) FOR THE TITLE COMPOUND

Donor-H---Acceptor	D—H	H---A	D---A	D—H---A
C2—H2B---O3	0.98	2.28	2.687 (5)	104
C3—H3A---O5	0.98	2.27	2.687 (6)	105
C4—H4A---O7	0.98	2.25	2.689 (6)	106
C5—H5B---O5^{i}	0.97	2.51	3.437 (7)	160
C10—H10A---O7^{ii}	0.96	2.50	3.447 (8)	168
C14—H14A---O10	0.98	2.29	2.697 (5)	104
C15—H15A---O12	0.98	2.32	2.707 (6)	103
C16—H16A---O14	0.98	2.31	2.684 (7)	102
C17—H17B---O12^{i}	0.97	2.43	3.326 (6)	154
C20—H20A---O4^{ii}	0.96	2.56	3.515 (6)	173
C20—H20C---O8^{ii}	0.96	2.56	3.484 (6)	161

Symmetry codes: (i) 1 + x , y, z; (ii) x – 1, y, z.

The structure of (I) consists of two crystallographically independent molecules A and B in the asymmetric unit of the non-centrosymmetric space group P1. The bond lengths and angles of A and B agree with each other and are comparable with those in the related structure of 2,3,4,6-tetra-O-acetyl-β-D-glycopyranosyl isothiocyanate[10]. In both A and B, the hexopyranosyl ring adopts a chair conformation. All the ring substituents are in plane and occupy equatorial positions. In both molecules, the S atom is in a synperiplanar conformation with respect to the linked ring C-atom, with the C1-N1-C6-S1 and C13-N2-C18-S2 torsion angles of 175 (4) and 178 (4)°, respectively.

In both molecules A and B, all the ketonic O-atoms are involved in C—H---O intramolecular interactions, each forming a five-membered ring. In the crystal packing, the molecules are linked into chains along the a-axis, the C20-H20A---O4 (1 + x, y, z) hydrogen bond interconnecting two adjacent molecular chains into ribbons. The ribbons are stacked one above the other along the b-direction.

Thermal analysis

Thermal analysis curves of the title compound are shown in Fig. 3. Thermogravimetric (TG) analysis and differential thermogravimetric (DTG) analysis show that the thermal decomposition occurs in the range of 170–240°C, with the largest rate at 226.2°C.

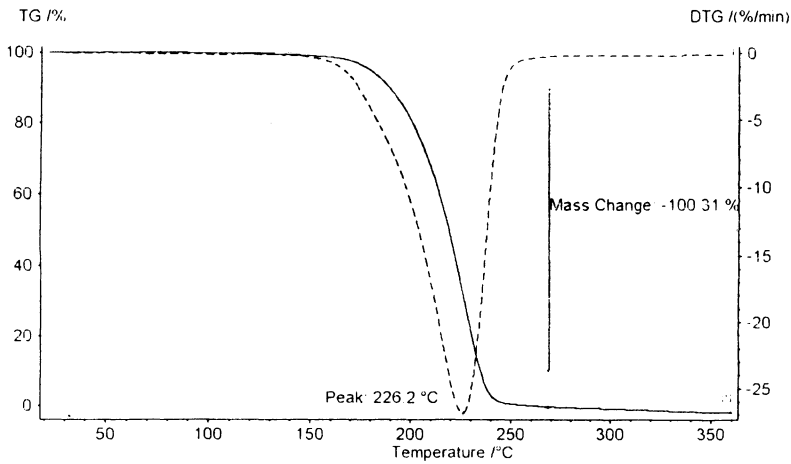


Fig. 3. Thermal analysis curves of the title compound

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CELL MEMBRANE

Wetting in the rain, not insane! The membrane,
The coat and the covering of every unit of life!
Restless and dynamic almost like a liquid,
It controls transport as it creates a partition!

Bathed in the aqua to have the polar heads soaked,
With the tails in love with the tails, touched and moved!
Governed by hydrophilic and hydrophobic interactions,
The ampiphiles organize themselves to create and sustain!

The cell membrane always contains many proteins,
That act as the carriers and the ubiquitous channels!
It also contains cholesterol and UFA's that aid in the fluidity,
And the carbohydrates that help to build the community.

Rigid and flexible, cholesterol is an ampiphile by design,
Glycoproteins and glycolipids stay in vigilance day and night!

Ions and dipoles must lock on the carriers to cross the barrier,
But the non-polar ones that dissolve in the fat, can easily diffuse!
The mediated transports display saturation and specificity,
And the 'active ones' require the expenditure of energy!
Membrane! The coat and the covering of every unit of life!
Let us witness that the membrane plays many key roles in life!

—Dr. Fazlul Huq