Carbohydrate Research, 144 (1985) 197–203
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

THE CRYSTAL STRUCTURE OF ISOBUTYL 2,3,4-TRI-*O*-ACETYL-1-THIO-β-D-XYLOPYRANOSIDE

GEORGE A. JEFFREY, JOHN R. RUBLE, AND BAHMAN SEPEHRNIA
Department of Crystallography, University of Pittsburgh, Pittsburgh, Pennsylvania 15260 (U.S.A.)
(Received November 19th, 1984; accepted for publication, May 28th, 1985)

ABSTRACT

Isobutyl 2,3,4-tri-*O*-acetyl-1-thio-β-D-xylopyranoside is monoclinic, $P2_1$, with $a = 10.134(4)$, $b = 7.748(3)$, $c = 11.726(4)$ Å, $\beta = 96.63(3)°$, V = 914.55 Å^3, $Z = 2$, $D_m = 1.262$, $D_x = 1.264$ g·cm^{-3}, μ(MoKα) = 226 M^{-1}. The X-ray intensities of 1724 reflections were measured with Nb-filtered MoKα radiation ($\lambda = 0.7107$ Å) at room temperature. The structure was solved by direct methods, and refined by full-matrix least squares, with anisotropic thermal parameters for the carbon and oxygen atoms and isotropic thermal parameters for the hydrogen atoms, to a final agreement factor of R = 0.08. The molecule has the $^4C_1$(D) conformation, with puckering parameters Q = 0.582 Å, $\theta = 5.6°$, $\varphi = 334.7°$. The acetyl groups have the planar, (*S*)-*cis* configuration most commonly observed. They are oriented, as in many other per-*O*-acetylated aldopyranosides, with the acetyl planes within ±30° of the C–H bond at the ring-carbon atom to which they are attached. Although this is primarily a van der Waals structure, there is some evidence for CH---O hydrogen-bonding.

EXPERIMENTAL

A sample of isobutyl 2,3,4-tri-*O*-acetyl-1-thio-β-D-xylopyranoside, $C_{15}H_{24}O_7S$, was provided by Dr. M. Claeyssens, Rijks Universitat, Ghent, Belgium. Crystals were obtained as monoclinic prisms by slow evaporation of a solution in dimethyl sulfoxide. The density was measured by flotation techniques in potassium iodide solution. A crystal (0.45 × 0.40 × 0.30 mm^3) was mounted with the *b* axis 4° off the Φ axis of a CAD-4 diffractometer. The unit-cell parameters were determined by least-squares fit of sin θ values, for 36 reflections with $17° \leq \theta \leq 21°$. The intensity data were collected at room temperature for $0 \leq h \leq 11$, $0 \leq k \leq 9$, and $-13 \leq l \leq +13$ to a $(\sin\theta/\lambda)_{max}$ of 0.593 Å^{-1}. Three standard reflections (500, 040, 006) showed a maximum deviation of 2.7 σ. The structure was solved by means of[1] MULTAN-78, using the 242 E values greater than 1.4. The positions of the 23 non-hydrogen atoms corresponded to maxima within the first 36 peaks of the E-map. Difference-Fourier maps showed only 7 methylene-hydrogen atomic positions. Therefore, the nine methylene-hydrogen atomic positions were

0008-6215/85/$ 03.30

calculated from the non-hydrogen coordinates. These hydrogen atoms, together with isotropic temperature-factors equivalent to the atoms to which they are bonded, were included in the refinement, but not refined. The positions of the fifteen methyl hydrogen atoms could not be determined, and were not included in the structure-factor calculation. The atomic scattering factors for C, O, and S were those of Cromer and Waber[2] and for hydrogen, those of Stewart *et al.*[3]. The refinement was by full-matrix least-squares[4], minimizing $\Sigma w\Delta^2$, where $\Delta = (|F_o| - k|F|)$, $w = 1/\sigma^2(F_o)$, and $\sigma^2(F_o) = [\sigma^2_{counter} + 0.02\,F_o^2]$ for 1311 observed reflections. The strong $10\bar{1}$ ($F_o = 57.5$, $F_c = 65.2$) and 101 ($F_o = 56.2$, $F_c = 69.4$) reflections, affected by extinction, were excluded from the refinement, which converged with $R = \Sigma(|\Delta|)/\Sigma|F_o| = 0.08$, $wR = [\Sigma w\Delta^2/wF_o^2]^{1/2} = 0.05$, and $S = [\Sigma w\Delta^2/(m - n)]^{1/2} = 1.797$. There were no shifts in any of the 207 parameters greater than 0.01 σ. The atomic notation and thermal ellipsoids[5] are shown in Fig. 1. Final atomic parameters and equivalent, isotropic temperature-factors are given in Table I* and bond lengths in Table II. Lists of valence angles and principal torsion-angles have been deposited*.

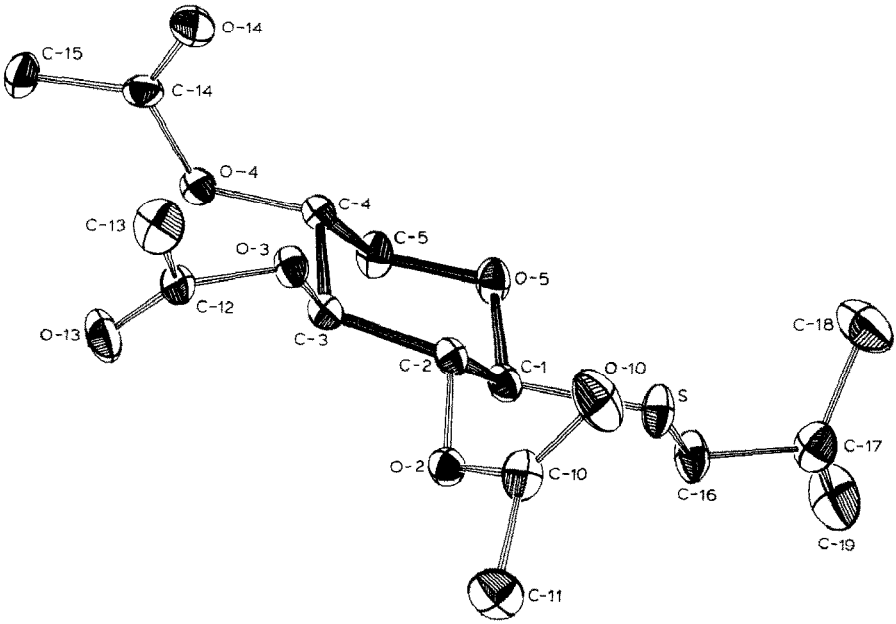


Fig. 1. The atomic notation and thermal ellipsoids (at 15% probability)[5] of isobutyl 2,3,4-tri-*O*-acetyl-1-thio-β-D-xylopyranoside.

*Lists of structure factors, anisotropic thermal parameters, valence angles, and principal torsion-angles have been deposited with, and can be obtained from, Elsevier Science Publishers B.V , BBA Data Deposition, P. O. Box 1527, Amsterdam, The Netherlands. Reference should be made to No BBA/DD/319/*Carbohydr. Res.*, 144 (1985) 197–203

TABLE I

ATOMIC PARAMETERS AND EQUIVALENT ISOTROPIC TEMPERATURE-FACTORS[a] FOR ISOBUTYL 2,3,4-TRI-*O*-ACETYL-1-THIO-β-D-XYLOPYRANOSIDE

Atom	*x*	*y*	*z*	B_{eq}
S	8240(2)	2750	1608(1)	55(1)
C-1	7770(6)	1756(9)	2900(5)	45(2)
C-2	6925(5)	181(9)	2558(5)	39(1)
C-3	6669(5)	−899(8)	3577(5)	39(1)
C-4	7965(6)	−1239(8)	4342(5)	42(2)
C-5	8674(6)	427(10)	4611(5)	52(2)
C-10	5351(7)	386(10)	861(6)	55(2)
C-11	3910(7)	838(13)	455(6)	72(2)
C-12	5106(6)	−3250(9)	3610(6)	47(2)
C-13	4668(7)	−4893(10)	2983(6)	67(2)
C-14	7752(5)	−3736(9)	5552(6)	47(2)
C-15	7490(7)	−4274(10)	6729(5)	60(2)
C-16	9022(7)	4688(10)	2181(6)	63(2)
C-17	9902(7)	5473(11)	1383(6)	68(2)
C-18	11033(8)	4336(14)	1105(9)	102(3)
C-19	10448(9)	7257(13)	1916(9)	105(3)
O-2	5635(4)	716(6)	2010(3)	45(1)
O-3	6073(3)	−2501(6)	3108(3)	42(1)
O-4	7690(4)	−1994(6)	5422(3)	45(1)
O-5	8966(4)	1204(6)	3573(3)	54(1)
O-10	6142(5)	−143(9)	297(4)	84(2)
O-13	4690(4)	−2695(7)	4447(4)	68(1)
O-14	8016(5)	−4678(7)	4782(4)	60(1)
H-1	727	260	335	
H-2	738	−54	200	
H-3	602	−28	403	
H-4	855	−204	394	
H-51	953	20	512	
H-52	809	122	501	
H-161	957	441	293	
H-162	830	555	232	
H-17	934	574	64	

[a]Fractional coordinates × 10^4 for non-hydrogen atoms; × 10^3 for hydrogen atoms. B_{eq} × 10 (in Å^2) for non-hydrogen atoms is defined by $B_{eq} = 4/3\Sigma\beta_{ij}a_i^2$. Estimated standard deviations, given in parentheses, refer to the least significant digit.

Thermal-motion analysis. — A rigid-body, thermal-motion analysis was carried out[6] by using the six ring-atoms and the four atoms adjacent to the ring. The overall fit was good, with ⟨r.m.s. U_{ij}(obs) − U_{ij}(calc)⟩ = 0.036 Å^2 and $\sigma(U_{ij})$ = 0.044 Å^2. The rigid-body motion of 10 atoms based on the inertial axes was as follows.

	r.m.s.	I_1 *(degrees)*	I_2 *(degrees)*	I_3 *(degrees)*
T	0.24 Å	64.68	123.26	44.07
	0.22	88.53	35.00	55.05
	0.20	154.76	103.60	69.16
ω	4.97°	78.45	56.49	144.04
	3.33	88.31	149.47	120.47
	1.03	169.02	85.0	99.74

The values of the bond lengths corrected for thermal motion were longer by 0.002 to 0.009 Å.

DISCUSSION

The molecule has the expected $^4C_1$(D) conformation, with[7] $Q = 0.582$ Å, $\theta = 5.6°$, $\varphi = 334.7°$. The ring C–C bond-lengths, corrected for thermal motion, range from 1.499 to 1.534 Å. The C-1–O-5, O-5–C-5 bond-lengths differ by 0.019 Å, but this difference is not significant in terms of the standard deviations. The oxygen

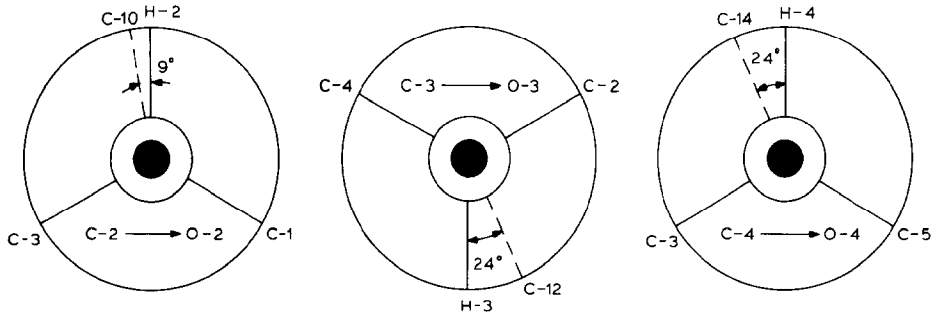
TABLE II

BOND LENGTHS[a] IN ISOBUTYL 2,3,4-TRI-*O*-ACETYL-1-THIO-β-D-XYLOPYRANOSIDE

Ring	*Length (Å)*	*Isobutyl thio group*	*Length (Å)*
C-1–C-2	1.518(6) [1.524]	C-1–S	1.812(6) [1.815]
C-2–C-3	1.506(8) [1.509]	S–C-16	1.792(7) [1 799]
C-3–C-4	1 526(8) [1.534]	C-16–C-17	1 494(11) [1.499]
C-4–C-5	1.494(9) [1.499]	C-17–C-18	1.511(13) [1 518]
C-5–O-5	1.419(8) [1.421]	C-17–C-19	1.590(13) [1.596]
C-1–O-5	1 433(7) [1.440]		
Acetoxyl groups			
C-2–O-2	1.449(7) [1 457]		
O-2–C-10	1.369(8) [1.373]		
C-10–O-10	1.171(9) [1.176]		
C-10–C-11	1.523(11) [1.532]		
C-3–O-3	1 459(7) [1 465]		
O-3–C-12	1 333(7) [1.338]		
C-12–O-13	1.192(8) [1.196]		
C-12–C-13	1.511(10) [1.517]		
C-4–O-4	1.451(7) [1.454]		
O-4–C-14	1.359(8) [1.363]		
C-14–O-14	1.214(8) [1.218]		
C-14–C-15	1 495(10) [1.498]		

[a]Distances in Å; values in brackets are corrected for thermal motion. Estimated standard deviations, given in parentheses, refer to the least significant digit

ring-valence angle of 110.6° is normal. The thioglycosidic torsion-angle has a normal *exo-anomeric* value of −69.9°. The two C–S bond-lengths of 1.815 and 1.799 Å are not significantly different. The O-5–C-1–S valence-angle is less than tetrahedral (107.5°), in agreement with the mean value of 107.4° for the methyl β-D-pyranosides[8]. The isobutyl group is so oriented that C-17–C-19 is almost *trans* to S–C-16, with S–C-16–C-17–C-19 = 175.2°. The acetyl groups have the (*S*)-*cis* conformation with the C–O and C=O bonds eclipsed. This is the conformation most commonly observed in simple esters[9] and predicted by theory for methyl formate[10]. The acetyl groups are planar, with the non-hydrogen atoms deviating



less than 0.009 Å from their mean plane. Their orientation is similar to that observed in many other acetylated pyranose molecules, with the C=O group *syn-diaxial* to the C–H bond at the ring-carbon atom to which the group is attached[11–14]. The acetoxyl group on C-2 is so oriented that the C=O bond almost eclipses the pyranoside exocyclic C–H bond, with C-10–O-2–C-2–H-2 = −8.7°, but the other

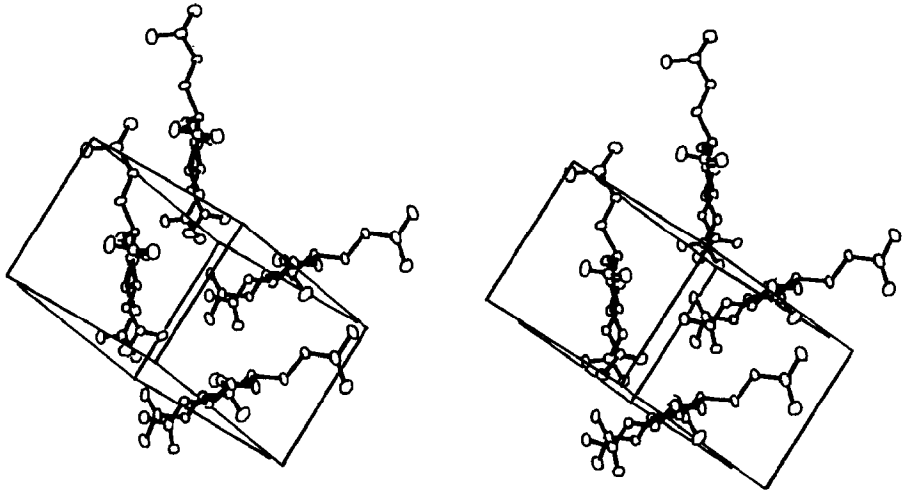


Fig. 2. Molecular packing in the crystal structure of isobutyl 2,3,4-tri-*O*-acetyl-1-thio-β-D-xylopyranoside.

TABLE III

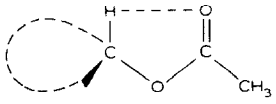
GEOMETRY OF C-H---O=C CONTACTS[a]

	H---O	*C–H---O*	*H---O–C*
Intramolecular	*Å*	*degrees*	*degrees*
C-2–H-2---O-10=C	2.26	104	84
C-3–H-3---O-13=C	2.39	99	82
C-4–H-4---O-14=C	2.36	99	83
Intermolecular			
C-5–H-51---O-14=C	2.48	144	107
C-1–H-1---O-14=C	2.75	134	148
C-3–H-3---O-13=C	2 83	154	88
C-16–H-161---O-14=C	2.91	108	152
C-16–H-162---O-3–C	2.96	167	105
C-5–H-52---O-13=C	3 08	150	91

[a]The hydrogen atoms were placed in calculated positions at 1.0 Å from the carbon atoms, and at 110° angles. Distances in Å, angles in degrees.

two acetoxyl groups are midway between the eclipsed and staggered orientation with respect to the exocyclic C–H bonds, with C-12–O-3–C-3–H-3 = −23.8° and C-14–O-4–C-4–H-4 = −24.4°, as shown in the "Newman" projections down the C-2–O-2, C-3–O-3, and C-4–O-4 bonds. The molecular packing, illustrated in Fig. 2, is of a general, van der Waals type.

It was pointed out twenty years ago[15] that there is significant evidence that the eclipsed orientation of the acetoxyl group with respect to the axial C–H group, shown in **1**, is the favored orientation. A recent analysis[16] of the occurrence of C-H---O=C hydrogen bonds supports the view that there is a significant, attractive interaction when the H---O separation is necessarily less than 2.5 Å, as shown in Table III.



1

In this structure, there are also four intermolecular separations, from methylene-hydrogen atoms to the carbonyl-oxygen atoms O-13 and O-14, that might qualify as hydrogen bonds, as shown in Table III. Only the shortest of these, C-5–H-51---O-14, meets the criterion[15] that H---O < W_H + W_O, where W_H and W_O are the van der Waals radii of 1.20 and 1.50 Å, respectively. This criterion may be over-restrictive, however, for this molecular type of crystal structure, because the closest intermolecular H---H separations observed are H-51---H-161 = 3.44 Å,

H-4---H-162 = 3.58 Å, H-4---H-51 = 4.02 Å. With a van der Waals radius for hydrogen of 1.7 Å from these separations, all the interactions in Table III would be classified as C-H---O hydrogen-bonds.

ACKNOWLEDGMENT

This research was supported by the National Institutes of Health, Grant No. GM-24526.

REFERENCES

1 P. MAIN, S. E. HULL, L. LESSINGER, G. GERMAIN, J. P. DECLERCQ, AND M. M. WOOLFSON, *MULTAN-78, A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data,* Univs. of York, England, and Louvain-la-Neuve, Belgium, 1978.
2 D. T. CROMER AND J. T. WABER, *Acta Crystallogr.*, 18 (1965) 104–108.
3 R. F. STEWART, E. R. DAVIDSON, AND W. T. SIMPSON, *J. Chem. Phys.*, 42 (1965) 3175–3184.
4 W. R. BUSING, K. O. MARTIN, AND H. A. LEVY, *ORFLS,* Technical Report ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tennessee, 1962.
5 C. K. JOHNSON, *ORTEP II,* Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, Tennessee, 1976.
6 V. SCHOMAKER AND K. N. TRUEBLOOD, *Acta Crystallogr., Sect. B,* 24 (1968) 63–76.
7 D. CREMER AND J. A. POPLE, *J. Am. Chem. Soc.*, 97 (1975) 1354–1358.
8 G. A. JEFFREY, J. A. POPLE, J. S. BINKLEY, AND S. VISHVESHWARA, *J. Am. Chem. Soc.*, 100 (1978) 373–379.
9 F. LEUNG AND R. H. MARCHESSAULT, *Can. J. Chem.*, 52 (1974) 2516–2521
10 G. I. L. JONES AND N. L. OWEN, *J. Mol. Struct.*, 18 (1973) 1–32.
11 I. G. JOHN AND L. RADOM, *J. Mol. Struct.*, 36 (1977) 133–147.
12 W. CHOONG, J. F. MCCONNELL, N. C. STEPHENSON, AND J. D. STEVENS, *Aust. J. Chem.*, 33 (1980) 979–985.
13 J. D. OLIVER AND L. C. STRICKLAND, *Acta Crystallogr., Sect. C,* 40 (1984) 820–824.
14 T. TAGA, S. SUMIYA, K. OSAKI, T. UTAMURA, AND K. KOIZUMI, *Acta Crystallogr., Sect. B,* 37 (1981) 963–966.
15 A. M. MATHIESON, *Tetrahedron Lett.*, (1965) 4137–4143.
16 R. TAYLOR AND O. KENNARD, *J. Am. Chem. Soc.*, 104 (1982) 5063–5070.