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Note

Molecular and crystal structure of ethyl 2,3,4-tri-*O*-acetyl-β-D-xylopyranosyl-(1→3)-2,4-di-*O*-acetyl-1-thio-β-D-xylopyranoside

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Abstract

The molecular and crystal structure of ethyl 2,3,4-tri-*O*-acetyl-β-D-xylopyranosyl-(1→3)-2,4-di-*O*-acetyl-1-thio-β-D-xylopyranoside was determined by single crystal X-ray diffraction. The crystal belongs to the triclinic system, space group $P1$, $a = 10.928(3)$, $b = 12.082(2)$, $c = 5.498(2)$Å, $\alpha = 95.39(2)$, $\beta = 100.07(2)$, $\gamma = 93.84(2)°$, $D_{cal} = 1.257\ g\,cm^3$, $Z = 1$ and $V = 708.9(3)$Å^3. The structure was solved by the direct method and refined by the full-matrix least-squares procedure to $R = 0.0624$ for 1891 reflections with $F_o > 4.0\ \sigma(F_o)$. All the hydrogen atoms were fixed geometrically. The glycosidic linkage conformation angles ϕ(O-5–C-1–O-1–C-3′) and ψ(C-1–O-1–C-3′–C-2′) are −96.7° and −171.7°, respectively. These are dissimilar to those of other β(1→3) linked acetylated oligosaccharides. The intramolecular O-5...O-4′ distance is 2.95Å, which may be attributed to the glycosidic linkage conformation.

Keywords: Conformation of β-(1→3) linkage; Xylopyranose disaccharide; Crystal structure; X-ray diffraction

Systematic study of crystal structures of small molecules contribute vastly to the conformational study of the related macromolecule. The numbers of single-crystal analyses of oligosaccharides are quite limited due to difficulties in preparation, purification and crystallization of these compounds. Not many single-crystal analyses of xylopyranoses are available in the literature, and almost no single-crystal analyses of a β-(1→3)-linked xylopyranose is found to be seen in the Cambridge Structural Database [1]. An acetylated derivative of a β-(1→3)-linked xylopyranose has been reported in this paper.

1. Experimental

X-ray measurement.—Crystal data and X-ray diffraction analyses data are given in Table 1. Single crystals of the title compound were grown by slow evaporation of an ethanol–hexane mixture.

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The X-ray intensities were measured on a Rigaku AFC5R diffractometer with graphite monochromated Cu–Kα radiation ($\lambda = 1.5418$)Å. Since no significant intensity deterioration was observed during data collection, no decay correction was applied. The data were corrected for Lorentz and polarization effects. No absorption correction was applied ($\mu = 15.4\,cm^{-1}$). A total of 2100 independent reflections were measured up to 2θ value of 120° of which 1891 reflections with $[F_o > 4\sigma(F_o)]$ were used for the following analysis.

Structure determination.—The initial positions of 34 of the 36 non-hydrogen atoms in the disaccharide unit were obtained by the direct method with the SHELXS-86 [2] program for space group *P*1, and the remaining atoms were determined by Fourier techniques. These atomic positions, together with anisotropic temperature factors, were refined by the full-matrix least-squares procedure after several refinement cycles with isotropic temperature factors. Further refinement of the atomic parameters were carried out using the package SHELXL93 [3]. All the hydrogen atoms were fixed geometrically, riding over the parent atom, and were not refined. The final *R* factor was 0.0624. The final atomic parameters with the final anisotropic temperature factors have been deposited.[1]

The atomic scattering factors were taken from the *International Tables for X-ray Crystallography* [4]. Computations were performed on an Iris Indigo workstation with the help of teXsan [5] and SHELXL93 program.

The molecular structure of ethyl 2,3,4-tri-*O*-acetyl-β-D-xylopyranosyl-(1→3)-2,4-di-*O*-acetyl-1-thio-β-D-xylopyranoside is shown in Fig. 1. All bond lengths and angles and torsion angles are in proximity of the ideal values. The bond lengths and bond angles and the torsion angles have been deposited.[1] Both the pyranose rings show the $^4C_1$ conformation.

The orientation at β-(1→3)-linkage is described by a set of two torsion angles around the glycosidic bonds C-1–O-1 and O-1–C-3′, and they are denoted by ϕ and ψ. The values obtained in this study are ϕ (O-5–C-1–O-1–C-3′) = −96.7° and ψ(C-1–O-1–C-3′–C-2′) = −171.7°. The value of ϕ and ψ are similar to those of other β(1→3)-linked

Table 1
Crystal data and X-ray diffraction analyses data for ethyl 2,3,4-tri-*O*-acetyl-β-D-xylopyranosyl-(1→3)-2,4-di-*O*-acetyl-1-thio-β-D-xylopyranoside

Crystal data
$C_{22}H_{32}O_{13}S$, mol wt 536.55, *P*1, $Z = 1$
Cell dimensions: $a = 10.928(3)$, $b = 12.082(2)$, $c = 5.498(2)$Å, $\alpha = 95.39(2)$, $\beta = 100.07(2)$, $\gamma = 93.84(2)°$
$V = 708.9(3)$ Å^3, based on 25 reflections with $78.89 < 2\theta < 79.90°$ using monochromated Cu-Kα radiation, $\lambda = 1.5418$ Å,
$\mu = 15.4\,cm^{-1}$ $D_{cal} = 1.26\,g\,cm^{-3}$

Structure determination and refinement data
Crystal dimensions 0.50×0.25×0.10 mm
Scan mode = $\omega - 2\theta$
Scan speed = 16°/min
Scan width $(\Delta\omega) = (2.15 + 0.3\tan\theta)°$
No. of reflections measured, 2229
No. of unique reflections, 2100
Range of h, k, l: $0 < h < 12$, $-13 < k < 13$, $-6 < l < 6$
$\theta_{max} = 60°$, observation: parameter ratio = 5.77
Residual electron difference density + 0.25 eÅ^{-3}
Final agreement factors:
$R = 0.0624$, 1891 reflections, $F_o > 4.0\sigma(F_o)$
S (goodness of fit) = 1.078
Function minimized: $R = [w(|F_o|^2 - |F_c|^2)]$, using least-square weights
$w = 1/[\sigma^2(F_o^2) + (a \times P^2) + (b \times P)]$ where $P = [f \times \max(0, F_o^2) + (1 - f) \times F_c^2]a = 0.0195$, $b = 0.9206$, $f = 0.33333$
Intensity data were processed using the program teXsan.[a]
A few cycles of refinement were carried out using SHELX93.[b]

[a] Ref. [5].
[b] Ref. [3].

[1]Tables of atomic coordinates, bond lengths, and bond angles have been deposited with the Cambridge Crystallographic Data Centre. These tables may be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, UK, CB2 1EZ.

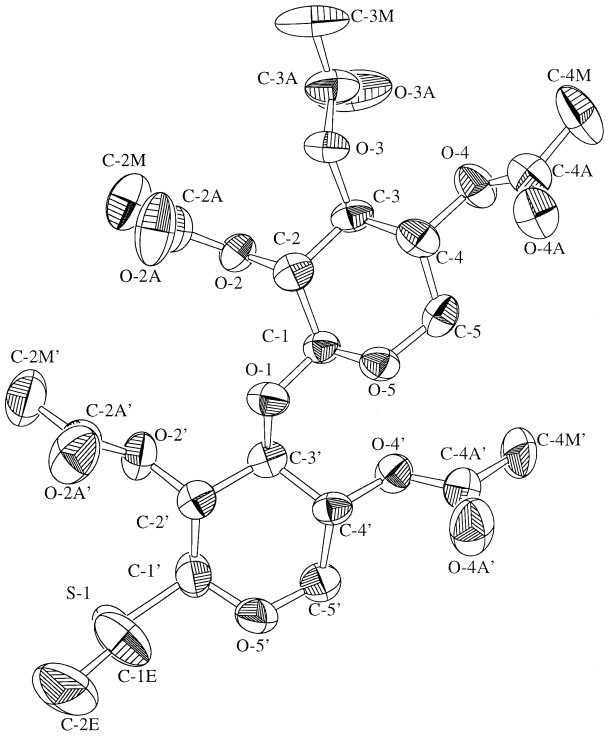

Fig. 1. Molecular structure of the ethyl 2,3,4,-tri-*O*-acetyl-β-D-xylopyranosyl-(1→3)-2,4-di-*O*-acetyl-1-thio-β-D-xylopyranoside. 50% probability thermal ellipsoids are shown for nonhydrogen atoms.

deacetylated oligosaccharides [6,7], while dissimilar to those of β-(1→3)-linked acetylated oligosaccharides [8–12]. This may be attributed to the absence of a C-6 atom in this case of xylopyranoses, and, therefore, no steric hinderances for the pyranose rings to be nearly on the same plane even when the side groups are acetylated. The bridge angle τ(C-1–O-1–C-3′) = 117.6°. In many related compounds the values of ϕ are restrained in a small region, which may be attributed to the exo-anomeric effect [13]. On the other hand, those of ψ are less restrained and are found to concentrate around either of the two values namely −110° and −160°. In the later case an intramolecular hydrogen bond O-4′···O-5 is normally present, while there was no hydrogen-bond formation in the present case because of the introduction of acetate substituents. In spite of the absence of an intramolecular hydrogen bond the O-4′···O-5 intramolecular distance is found to be 2.95Å.

The packing of the molecules in the unit cell is shown in Fig. 2. The molecules are held by van der Waals forces only. Short intermolecular nonbonded contacts are found, namely, O-4A–C-5 = 3.30(1)Å, O-5′–C-3M = 3.36(2) Å, C-3–O-4A = 3.35(1)Å.

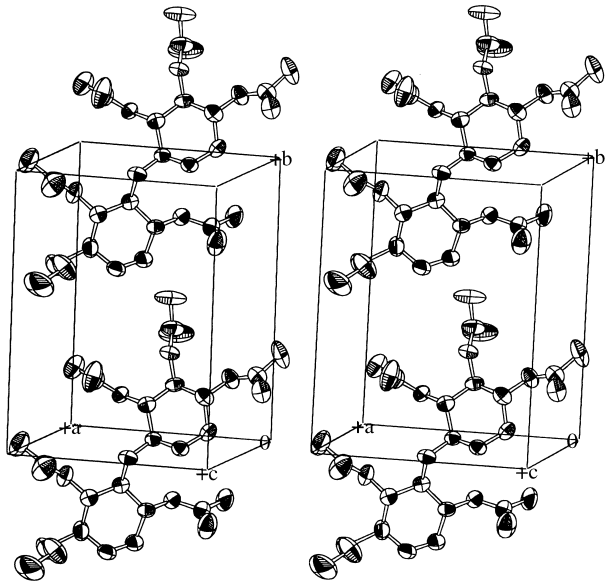

Fig. 2. Stereo view of the molecular packing.

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