Crystal structure of ethyl 2,3,4,6-tetra-*O*-acetyl-1-thio-α-D-mannopyranoside, $C_{16}H_{24}O_9S$

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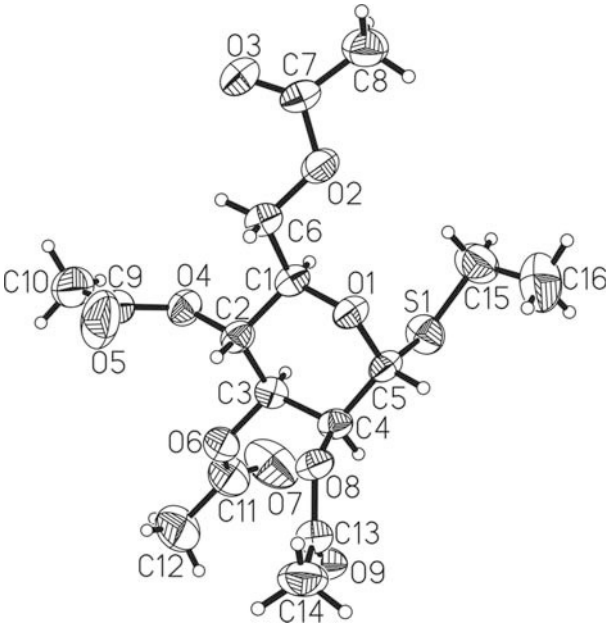

Abstract

$C_{16}H_{24}O_9S$, orthorhombic, $P2_12_12_1$ (no. 19), a = 9.188(2) Å, b = 9.251(2) Å, c = 23.697(3) Å, V = 2014.2 Å^3, Z = 4, $R_{gt}(F)$ = 0.070, $wR_{ref}(F^2)$ = 0.158, T = 293 K.

Source of material

The title compound was obtained as the major product by the reaction of 1,2,3,4,6-penta-*O*-acetyl-α-D-mannopyranose with ethyl mercaptan in the presence of $BF_3 \cdot Et_2O$ in CH_2Cl_2 as solvent [1]. Isolation of the desired product by fractionated crystallization of the crude product from petrol ether, ethyl acetate and acetone afforded the title compound as colourless block-shaped crystals. NMR spectroscopic data showed values according to the literature [2].

Experimental details

H atoms were located on difference Fourier map, but refined with fixed individual displacement parameters, using a riding model with d(C—H) ranging from 0.96 to 0.98 Å. In addition, methyl groups were allowed to rotate but not to tip.

Discussion

The absolute configuration of the crystal structure of the title compound could be determined by anomalous dispersion characterized by the Flack parameter of x = –0.02(15). The result is in accordance to the absolute configuration expected by the synthetic pathway. The sulphur contacts were clearly identified as S1—C5 and S1—C15 with distances of 1.838(4) Å and 1.801(5) Å, respectively. The crystal structure is stabilized by a number of weak intermolecular hydrogen bonds: d(H5···O3) = 2.56 Å, ∠(C5–H5···O3) = 134°; d(H10B···O9) = 2.52 Å, ∠(C10–H10B···O9) = 125°; d(H14A···O2) = 2.65 Å, ∠(C14–H14A···O1) = 148°; d(H15A···O9) = 2.64 Å; ∠(C15–H15A···O9) = 172°.

Table 1. Data collection and handling.

Crystal:	colorless block, size 0.25 × 0.30 × 0.55 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	2.03 cm^{-1}
Diffractometer, scan mode:	Nicolet P3, Wyckoff
$2\theta_{max}$:	56°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	5433, 4863
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 3642
$N(param)_{refined}$:	236
Programs:	SHELXS-97 [3], SHELXL-97 [4], SHELXTL-Plus [5]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(1)	4*a*	0.3066	0.5934	1.0427	0.049
H(2)	4*a*	0.2155	0.3860	1.1251	0.051
H(3)	4*a*	0.1220	0.6777	1.1134	0.050
H(4)	4*a*	–0.1019	0.5974	1.0811	0.049
H(5)	4*a*	–0.0325	0.4704	0.9965	0.051
H(6A)	4*a*	0.4953	0.4264	1.0670	0.061
H(6B)	4*a*	0.3937	0.2993	1.0470	0.061
H(8A)	4*a*	0.5356	0.4625	0.8926	0.102
H(8B)	4*a*	0.6824	0.3766	0.8964	0.102
H(8C)	4*a*	0.6808	0.5440	0.9066	0.102
H(10A)	4*a*	0.4894	0.6538	1.2188	0.141
H(10B)	4*a*	0.5957	0.5230	1.2273	0.141
H(10C)	4*a*	0.4602	0.5411	1.2669	0.141
H(12A)	4*a*	–0.0430	0.5503	1.2693	0.142
H(12B)	4*a*	–0.1793	0.6491	1.2594	0.142
H(12C)	4*a*	–0.0353	0.7156	1.2836	0.142
H(14A)	4*a*	–0.1754	0.1625	1.1087	0.104
H(14B)	4*a*	–0.3381	0.2132	1.1065	0.104
H(14C)	4*a*	–0.2581	0.1998	1.1647	0.104
H(15A)	4*a*	0.1743	0.7711	0.9119	0.088
H(15B)	4*a*	0.2270	0.6182	0.9315	0.088
H(16A)	4*a*	0.0990	0.5986	0.8490	0.149
H(16B)	4*a*	–0.0373	0.6703	0.8773	0.149
H(16C)	4*a*	0.0151	0.5172	0.8970	0.149

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Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S(1)	4*a*	0.0570(1)	0.7066(1)	0.99404(5)	0.0666(7)	0.0494(5)	0.0608(6)	0.0089(5)	0.0033(6)	0.0075(5)
O(1)	4*a*	0.1712(2)	0.4400(3)	1.0175(1)	0.032(1)	0.045(1)	0.049(1)	0.001(1)	–0.002(1)	–0.008(1)
C(1)	4*a*	0.2850(3)	0.4929(4)	1.0528(2)	0.033(2)	0.039(2)	0.050(2)	–0.001(1)	–0.002(1)	–0.003(2)
O(2)	4*a*	0.4599(3)	0.4258(3)	0.9840(1)	0.036(1)	0.080(2)	0.051(2)	0.006(1)	–0.004(1)	–0.014(1)
C(2)	4*a*	0.2343(4)	0.4863(4)	1.1140(2)	0.035(2)	0.043(2)	0.049(2)	–0.006(2)	–0.004(1)	–0.001(2)
O(3)	4*a*	0.6947(3)	0.4192(4)	1.0074(1)	0.039(1)	0.107(2)	0.071(2)	0.002(2)	–0.007(1)	0.012(2)
C(3)	4*a*	0.0979(4)	0.5762(4)	1.1206(1)	0.042(2)	0.041(2)	0.042(2)	–0.002(2)	0.003(2)	–0.001(2)
O(4)	4*a*	0.3431(3)	0.5498(3)	1.1502(1)	0.045(1)	0.056(2)	0.052(2)	–0.006(1)	–0.009(1)	–0.003(1)
C(4)	4*a*	–0.0200(4)	0.5296(4)	1.0797(2)	0.035(2)	0.040(2)	0.048(2)	0.003(1)	0.004(1)	0.001(2)
C(5)	4*a*	0.0399(4)	0.5201(4)	1.0199(2)	0.029(2)	0.048(2)	0.049(2)	0.004(2)	–0.004(1)	–0.002(2)
O(5)	4*a*	0.3914(5)	0.3367(5)	1.1899(2)	0.095(3)	0.098(3)	0.120(3)	–0.015(2)	–0.041(2)	0.055(3)
O(6)	4*a*	0.0488(3)	0.5621(3)	1.1779(1)	0.052(1)	0.063(2)	0.046(1)	0.003(1)	0.005(1)	–0.002(1)
C(6)	4*a*	0.4170(4)	0.4005(5)	1.0415(2)	0.037(2)	0.063(2)	0.053(2)	0.004(2)	0.002(2)	0.001(2)
C(7)	4*a*	0.6023(4)	0.4311(4)	0.9728(2)	0.033(2)	0.042(2)	0.062(2)	0.004(2)	0.003(2)	–0.007(2)
O(7)	4*a*	–0.0472(5)	0.7837(4)	1.1741(2)	0.144(4)	0.071(2)	0.090(3)	0.028(3)	0.043(3)	–0.007(2)
O(8)	4*a*	–0.0683(3)	0.3860(3)	1.0944(1)	0.031(1)	0.045(1)	0.058(2)	0.000(1)	0.002(1)	0.002(1)
C(8)	4*a*	0.6275(5)	0.4557(6)	0.9117(2)	0.058(3)	0.078(3)	0.067(3)	0.005(2)	0.010(2)	–0.009(3)
O(9)	4*a*	–0.2644(3)	0.4807(4)	1.1375(1)	0.053(2)	0.070(2)	0.079(2)	0.002(2)	0.024(2)	–0.005(2)
C(9)	4*a*	0.4060(4)	0.4646(7)	1.1891(2)	0.043(2)	0.109(4)	0.043(2)	–0.006(2)	–0.003(2)	0.017(2)
C(10)	4*a*	0.4960(5)	0.5537(8)	1.2291(2)	0.061(3)	0.169(6)	0.052(3)	–0.006(3)	–0.008(2)	–0.019(4)
C(11)	4*a*	–0.0239(6)	0.6759(6)	1.1997(2)	0.079(3)	0.071(3)	0.055(3)	0.004(3)	0.009(2)	–0.015(2)
C(12)	4*a*	–0.0749(7)	0.6450(7)	1.2582(2)	0.102(4)	0.131(5)	0.051(3)	0.019(4)	0.016(3)	–0.015(3)
C(13)	4*a*	–0.1980(4)	0.3779(5)	1.1209(2)	0.041(2)	0.060(2)	0.049(2)	–0.003(2)	0.002(2)	0.003(2)
C(14)	4*a*	–0.2467(5)	0.2247(5)	1.1256(2)	0.052(2)	0.071(3)	0.085(3)	–0.012(2)	0.014(2)	0.017(3)
C(15)	4*a*	0.1416(6)	0.6785(6)	0.9264(2)	0.077(3)	0.078(3)	0.066(3)	0.001(3)	0.014(2)	0.016(3)
C(16)	4*a*	0.0462(8)	0.6101(7)	0.8836(2)	0.124(5)	0.101(4)	0.072(3)	0.015(4)	–0.021(4)	–0.010(3)

References

1. Büsselmann, L.: Enzymatische Modifikationen von Kohlenhydraten. Universität Düsseldorf, 2008.
2. Valerio, S.; Iadonisi, A.; Adinolfi, M.; Ravida, A.: Novel approaches for the synthesis and activation of thio- and selenoglycoside donors. J. Org. Chem. **72** (2007) 6097-6106.
3. Sheldrick, G. M.: SHELXS-97. Program for the Solution of Crystal Structures. University of Göttingen, Germany 1997.
4. Sheldrick, G. M.: SHELXL-97. Program for the Refinement of Crystal Structures. University of Göttingen, Germany 1997.
5. Sheldrick, G. M.: SHELXTL-Plus. Structure Determination Software Suite. Release 4.1. Siemens Analytical Systems Inc., Madison, Wisconsin, USA 1991.