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1,2,3-Tri-*O*-acetyl-5-deoxy-5-methylthio-β-D-ribofuranose

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Key indicators

Single-crystal X-ray study
T = 296 K
Mean σ(C–C) = 0.004 Å
R factor = 0.035
wR factor = 0.087
Data-to-parameter ratio = 15.5

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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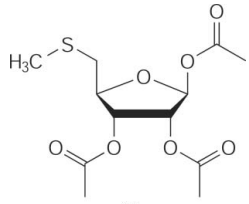
In the structure of the title compound, $C_{12}H_{18}O_7S$, no alteration of the relative configuration compared with D-(−)-ribose is observed.

Comment

5-Methylthioribose (MTR) was synthesized from D-(−)-ribose following the procedure described by Ishikura *et al.* (1962). We report here the crystal structure of 1,2,3-tri-*O*-acetyl-5-deoxy-5-methylthio-β-D-ribofuranose, (I), obtained by acetylation of MTR. Acetylation of free hydroxyl groups is a common protecting procedure in carbohydrate chemistry (Greene & Wuts, 1999). Acetylated carbohydrates are extremely useful intermediates in the synthesis of natural products or analogues. Following a procedure devised by Euzen *et al.* (2005), the title compound was further converted into the ammonium salt of 5-deoxy-5-methylthio-β-D-ribofuranose 1-phosphate (MTR-1P). MTR-1P is known to be an intermediate in the methionine salvage pathway (Bumann *et al.*, 2004) and will therefore be utilized for enzymatic studies.



(I)

The crystal structure of (I) was determined in order to confirm its molecular structure. As expected, no alteration of the relative configuration compared with D-(−)-ribose is observed. The anomeric centre has the β configuration. The ring system shows a C_2'-*exo* conformation, with a pseudorotation phase angle of −24° (Saenger, 1984) and a C3—C4—O—C1 torsion angle of −3.5 (2)°. There are clear indications for an anomeric effect at C1: the 1′-*O*-acetyl group is oriented axially [O12—C1—O—C4 −88.8 (2)°], and C1—O is shorter by 0.019 Å and C1—O12 is longer by 0.023 Å than the standard bond lengths in furanoses of 1.421 (12) and 1.410 (14) Å, respectively (Allen *et al.*, 1992).

Experimental

5-Methylthioribose (570 mg, 3.1 mmol) was dissolved in dry pyridine (6.5 ml) under nitrogen and cooled to 273 K. Acetic anhydride (3 equivalents, 2.7 ml, 28.5 mmol) was added to the solution *via* a syringe over 5 min. The reaction mixture was stirred at room temperature for 18 h, and then the reaction was treated with ice–water (40 ml) and stirred for 15 min. The mixture was then extracted with dichloromethane. The organic layer was washed with 1 *M* HCl

(2 × 50 ml) and water (2 × 50 ml), dried over $MgSO_4$ and concentrated *in vacuo*. Purification of the crude product by flash column chromatography on silica gel with cyclohexane–*tert*-butyl methyl ether (1:1) as solvent gave the title compound (300 mg, 31%). Crystals of (I) were obtained by evaporation of a cyclohexane/*tert*-butyl methyl ether (2:3) solution at room temperature. Analysis: R_F 0.32 (cyclohexane/*tert*-butyl methyl ether, 1:1, silica-gel plate 60 F_{254}); ^{1}H NMR (400 MHz, $CDCl_3$, δ, p.p.m.): 2.11, 2.08, 2.06 (3*s*, 9H, CH_3CO), 2.14 (*s*, 3H, CH_3S), 2.75 (*d*, 2H, J = 5.8 Hz, H5), 4.36 (*q*, 1H, J = 6.0 Hz, H4), 5.33 (*m*, 1H, H2), 5.36 (*m*, 1H, H3), 6.12 (*bs*, 1H, H1); ^{13}C NMR (75 MHz, $CDCl_3$, δ, p.p.m.): 16.6 (CH_3S), 20.6, 20.6, 21.2 (CH_3CO), 37.5 (C5), 73.0 (C3), 74.5 (C2), 81.3 (C4), 98.3 (C1), 169.2, 169.5, 169.8 (C═O); high-resolution MS (ESI+), *m*/*z*, calculated for $C_{12}H_{18}O_7NaS$: $[M+Na]^+$ 329.0670; found: 329.0661; IR (solid, ν, cm^{-1}): 3014, 2928, 1751, 1431, 1363, 1314, 1260, 1213, 1124, 1085, 1060, 1033, 1004.

Crystal data

$C_{12}H_{18}O_7S$
M_r = 306.32
Monoclinic, $P2_1$
a = 8.6831 (4) Å
b = 9.8249 (5) Å
c = 9.6824 (5) Å
β = 110.766 (2)°
V = 772.35 (7) Å^3
Z = 2
D_x = 1.317 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 1624 reflections
θ = 2.3–22.2°
μ = 0.24 mm^{-1}
T = 296 (2) K
Prism, colourless
0.43 × 0.30 × 0.16 mm

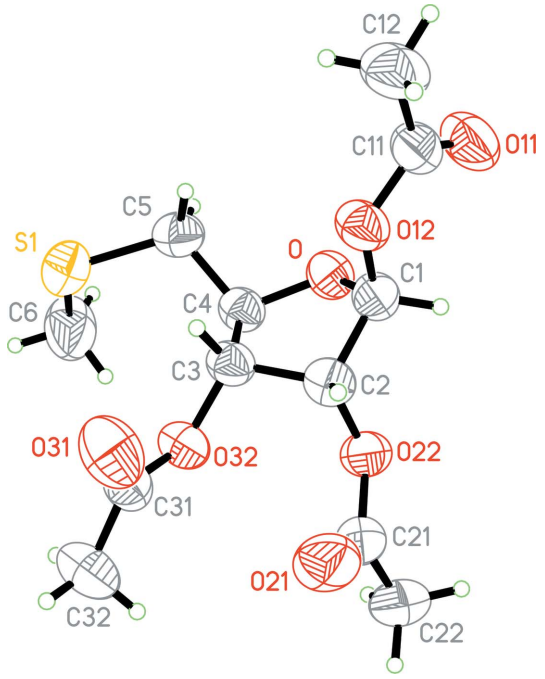


Figure 1
The molecular structure of (I), showing the atomic numbering scheme and 50% probability displacement ellipsoids.

Data collection

Siemens SMART 1K CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.853, T_{max} = 0.963
4361 measured reflections
2912 independent reflections
2272 reflections with $I > 2\sigma(I)$
R_{int} = 0.015
θ_{max} = 27.9°
$h = -11 \rightarrow 11$
$k = -12 \rightarrow 11$
$l = -12 \rightarrow 11$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.035
$wR(F^2)$ = 0.087
S = 1.04
2912 reflections
188 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0424P)^2 + 0.0345P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.008
$\Delta\rho_{max}$ = 0.11 e Å^{-3}
$\Delta\rho_{min}$ = −0.14 e Å^{-3}
Absolute structure: Flack (1983), with 1136 Friedel pairs
Flack parameter: 0.04 (8)

Table 1
Selected geometric parameters (Å, °).

C1—O	1.402 (3)	C2—C3	1.524 (3)
C1—O12	1.433 (3)	C3—C4	1.525 (3)
C1—C2	1.514 (3)	C4—O	1.450 (3)
O—C4—C3	105.86 (17)	C1—C2—C3	101.47 (18)
O—C1—O12	110.60 (18)	C2—C3—C4	103.60 (18)
O12—C1—C2	105.43 (19)	C1—O—C4	110.02 (16)
O12—C1—O—C4	−88.8 (2)	C1—C2—C3—C4	32.5 (2)
C4—O—C1—C2	25.0 (2)	C2—C3—C4—O	−19.0 (2)
O—C1—C2—C3	−35.7 (2)	C3—C4—O—C1	−3.5 (2)

H atoms were placed in calculated positions (C—H = 0.97–0.98 Å) and were included in the refinement in a riding-model approximation, with U_{iso}(H) = 1.2U_{eq}(C), or 1.5U_{eq}(C) for methyl H.

Data collection: *SMART* (Bruker, 2003); cell refinement: *SAINT* (Bruker, 2003); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2003); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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