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3-Formylphenyl-2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranoside

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Key indicators

Single-crystal X-ray study
T = 183 K
Mean σ(C–C) = 0.004 Å
R factor = 0.043
wR factor = 0.104
Data-to-parameter ratio = 9.7

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

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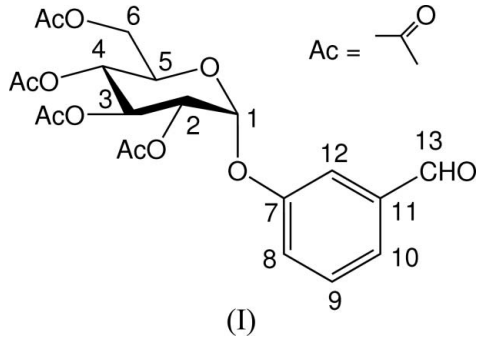
The title compound, $C_{21}H_{24}O_{11}$, crystallizes exclusively as the α-anomer. The 3-formylphenyl substituent at C1 is in the axial position, whereas all other groups are in equatorial positions. As a consequence, the *re*-face of the aldehyde group is somewhat shielded by the C6 acetyl group.

Comment

Formylphenyl-functionalized sugars are known as components in glycoconjugated porphyrins or chlorins, which are applied as tumor-localizing photosensitizers in photodynamic therapy (Hirohara *et al.*, 2005; Sol *et al.*, 1999; Driaf *et al.*, 1996; Kohata *et al.*, 1994) or as catalysts for cyclohexane oxidation (Zhang *et al.*, 2000). As part of our efforts to utilize sugar-derived Schiff base ligands in the coordination chemistry of transition metals as precursors for chiral catalysts (Becher *et al.*, 2006; Burkhardt *et al.*, 2006; Roth *et al.*, 2006), the title compound, (I), has been synthesized.



(I)

We describe here the structure of the α-anomer of 3-formylphenyl-2,3,4,6-tetra-*O*-acetyl-D-glucopyranoside and compare it with the related structure of the β-anomer (Burkhardt *et al.*, 2007).

The glucose backbone is substituted with a 3-formylphenyl group at the anomeric carbon atom, C1. The hydroxy groups at C2, C3, C4 and C6 are protected with acetyl groups. Due to its hydrophobic substituents, the compound is soluble in less polar solvents such as $CHCl_3$.

The crystal structure shows that the sugar ring adopts the stable $^4C_1$ chair conformation. The 3-formylphenyl substituent at C1 is in an axial position, corresponding to the exclusive presence of the α-anomer of the saccharide. This is confirmed by the ^{1}H NMR data; H1 leads to a doublet with $^3J_{1,2}$ = 3.7 Hz associated with the *cis* configuration of protons H1 and H2, which is smaller than that observed for the *trans* configured β-anomer ($^3J_{1,2}$ = 7.9 Hz). The formyl group (C13, O7) does not deviate significantly from coplanarity with the benzene ring.

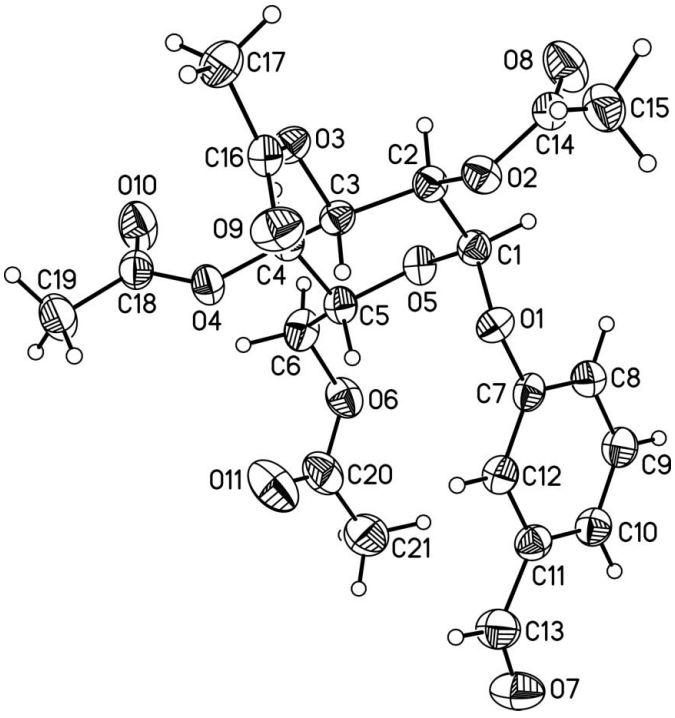


Figure 1
A view of the molecular structure of the title compound. Displacement ellipsoids are drawn at the 50% probability level.

The aldehyde group of the 3-formylphenyl substituent is directed towards the acetyl group at C6. The mean plane of the 3-formylphenyl substituent (defined by C7–C13, O7) and the mean sugar plane (defined by C1, C3, C4 and O5) subtend an angle of 74.74 (10)°. As a consequence, this leads to a shielding effect of the *Re*-face of the aldehyde group in the α-anomer by the C6 acetyl group, whereas for the β-anomer, with a corresponding dihedral angle of 148.14 (9)° (Burkhardt *et al.*, 2007), neither the *Re*- nor the *Si*-face of the aldehyde group is shielded. Assuming that the solid-state structure of 3-formylphenyl-2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranoside is retained in solution, a substrate attack from the *Si*-face should be preferred.

Experimental

The melting point is reported uncorrected and was determined *via* a VEB Analytik Dresden HMK 72/41555. Infrared spectra and Raman spectra were collected on a Bruker IFS55/Equinox spectrometer with an FRA 106/S module. ^{1}H and ^{13}C NMR experiments were carried out on a Bruker Avance 400 MHz spectrometer. Mass spectra were measured on a MAT95XL Finnigan instrument. Elemental analyses were determined on LECO CHN/932 and VARIO EL III elemental analyzers. All substances were purchased from commercial suppliers and used without further purification. 3-Formylphenyl-2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranoside was synthesized following a literature procedure (Williams, 1940). β-D-Glucose pentaacetate (30.00 g, 0.077 mol) and 3-hydroxybenzaldehyde (30.00 g, 0.246 mol) were melted together. After addition of $ZnCl_2$ (3.00 g, 0.022 mol) the brown liquefied material was stirred for 30 min at 393–403 K. The cooled mixture was extracted with toluene. The organic layer was washed three times with an NaOH solution (5%) until clear and finally with water until neutral. After drying over Na_2SO_4 and complete removal of the solvent, a yellow syrup remained which was triturated with hexane and then taken up in methanol. Overnight the product precipitated at room temperature as colorless prisms [yield: 6.34 g, 18.2%; m.p. = 396–397 K (methanol)]. IR (KBr): 2958 (ν_{as} CH_2); 1742 (O–C═O); 1704 (ν CH═O); 1586; 1489 (ν C═C); 1432 (δ_{as} CH_3, δ CH_2); 1375 (δ_s CH_3); 1276, 1223, 1172, 1150, 1119, 1102, 1066, 1035 (ν C–O); 969; 929; 906; 808; 799; 710; 682; 649; 613 cm^{-1}. Raman: 3081, 3045, 3024, 2995 (ν C–H arom.); 2957 (ν_{as} CH_3); 2939 (ν_{as} CH_2); 2874, 2770 (ν_s CH_3, CH_2); 1746, 1735 (ν O–C ═O); 1704 (ν CH═O); 1604; 1585; 1432 (δ_{as} CH_3, δ CH_2); 1400, 1383 (δ_s CH_3); 1345; 1287, 1259, 1240, 1171, 1139, 1119, 1072 (ν C–O); 1002; 900; 892; 862; 799; 743; 678; 668; 649; 550; 537; 522; 486 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6, 298 K): 1.89, 2.00, 2.30 (3*s*, 12 H, CH_3); 3.96 (*dd*, 1H, $^2J_{6e6a}$ = 12.2 Hz, $^3J_{6e5}$ = 2.1 Hz, H6e); 4.06–4.09 (*m*, 1H, H5); 4.15 (*dd*, 1H, $^2J_{6a6e}$ = 12.2 Hz, $^3J_{6a5}$ = 5.8 Hz, H6a); 5.09 (*dd*, 1H, $^3J_{43}$ = $^3J_{45}$ = 9.8 Hz, H4); 5.10 (*dd*, 1H, $^3J_{23}$ = 10.4 Hz, $^3J_{21}$ = 3.7 Hz, H2); 5.53 (*dd*, 1H, $^3J_{34}$ = $^3J_{32}$ = 9.8 Hz, H3); 5.94 (*d*, 1H, $^3J_{12}$ = 3.7 Hz, H1); 7.46–7.66 (*m*, 4H, H8–10, H12); 9.99 (*s*, 1H, H13) p.p.m. ^{13}C NMR (100 MHz, DMSO-d_6, 298 K): 20.3, 20.4 (CH_3); 61.5 (C6); 67.9, 68.0 (C2, C4); 69.3, 69.4 (C3, C5); 94.0 (C1); 116.8 (C12); 123.4, 123.5, 130.6 (C8, C9, C10); 137.7 (C11); 156.0 (C7); 169.3, 169.6, 169.7, 169.9 (C═O Acetyl); 192.7 (C13) p.p.m. ESI-MS: *m/z* (%) = 475 [M + Na]$^+$ (100), 507 [M + MeOH + Na]$^+$ (34). Analysis calculated for $C_{21}H_{24}O_{11}$: C 55.75, H 5.35%; found C 55.80, H 5.12%.

Crystal data

$C_{21}H_{24}O_{11}$	Z = 4
M_r = 452.40	D_x = 1.394 Mg m^{-3}
Orthorhombic, $P2_12_12_1$	Mo $K\alpha$ radiation
a = 5.5451 (2) Å	μ = 0.11 mm^{-1}
b = 14.5307 (5) Å	T = 183 (2) K
c = 26.7501 (7) Å	Prism, colorless
V = 2155.37 (12) Å^3	0.3 × 0.3 × 0.2 mm

Data collection

Nonius KappaCCD diffractometer	2832 independent reflections
φ and ω scans	2187 reflections with $I > 2\sigma(I)$
Absorption correction: none	R_{int} = 0.049
12655 measured reflections	θ_{max} = 27.5°

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0495P)^2 + 0.4767P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)]$ = 0.043	$(\Delta/\sigma)_{max}$ = 0.007
$wR(F^2)$ = 0.104	$\Delta\rho_{max}$ = 0.19 e Å^{-3}
S = 1.05	$\Delta\rho_{min}$ = −0.22 e Å^{-3}
2832 reflections	
293 parameters	
H-atom parameters constrained	

H atoms were positioned geometrically, C—H = 0.95 (Csp^2), 0.98 (methyl), 0.99 (methylene) and 1.00 Å (methine), and treated as riding atoms with fixed displacement parameters, U_{iso}(H) = xU_{eq}(C), where x = 1.5 for methyl groups and 1.2 for all others. In the absence of significant anomalous scattering effects the Flack (1983) parameter was indeterminate (Flack & Bernardinelli, 2000); hence the Friedel equivalents were merged prior to the final refinement. The absolute configuration was assigned by reference to the chiral starting material and the evidence provided by NMR spectroscopy.

Data collection: *COLLECT* (Nonius 1998); cell refinement: *DENZO* (Otwinowski & Minor, 1997); data reduction: *DENZO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997);

molecular graphics: *SHELXL97* and *XP* (Siemens, 1990); software used to prepare material for publication: *XP*.

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