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

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Key indicators

Single-crystal X-ray study
T = 183 K
Mean σ(C–C) = 0.003 Å
R factor = 0.038
wR factor = 0.089
Data-to-parameter ratio = 9.1

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

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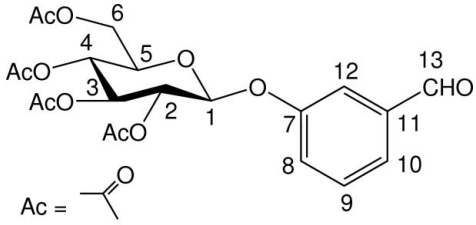
In the title compound, $C_{21}H_{24}O_{11}$, all substituents of the protected sugar are in equatorial positions, with the exclusive presence of the β-anomer. The glucose ring adopts the stable chair conformation.

Comment

The background to this study has been set out in the preceding paper (Burkhardt *et al.*, 2007), where the structure of the α-anomer is presented. The crystal structure of the related 2-formylphenyl-2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranoside has already been published (Cousins *et al.*, 1997).



(I)

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

The crystal structure reveals a $^4C_1$ chair conformation for the sugar ring, with the 3-formylphenyl substituent at C1 in the equatorial position, corresponding to the exclusive presence of the β-anomer of the saccharide. This is confirmed by the observation of a doublet resonance for H1 in the ^{1}H NMR with $^3J_{1,2}$ = 7.9 Hz, indicative of the *trans* configuration of the axially positioned protons H1 and H2. The aldehyde group of the 3-formylphenyl substituent is directed towards the acetyl group at C6, with a dihedral angle between the mean plane of the 3-formylphenyl substituent (defined by by C7–C13, O7) and the mean sugar plane (defined by C2, C3, C5, O5) of 148.14 (9)°. Therefore, neither the *Re*- nor the *Si*-face of the aldehyde group are shielded by any acetyl substituents at C2 or C6. As a consequence, no stereoinduction can be expected for catalysts utilizing this sugar derivative as a ligand.

Although the orientation of the aldehyde group of the α-anomer is similar to that in the β-anomer, the angle subtended by the mean plane of the 3-formylphenyl substituent and the mean sugar plane of 74.74 (10)° is significantly smaller. In contrast to the β-anomer, the *Re*-face of the aldehyde group of the α-anomer is slightly shielded by the C6 acetyl group. Assuming that the solid-state structure of the 3-formylphenyl-

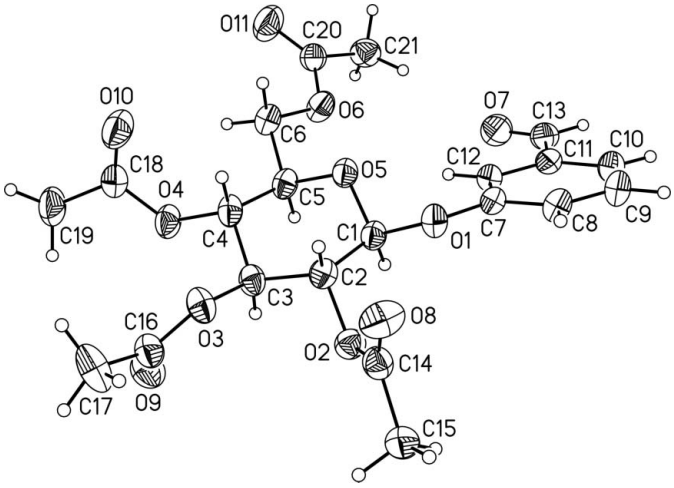


Figure 1
A view of the molecular structure of the title compound. Displacement ellipsoids are drawn at the 50% probability level.

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 given uncorrected. The instruments used for the melting point determination, spectroscopic measurements and the elemental analyses are detailed in the preceding paper. All substances were purchased from commercial suppliers and used without further purification. 3-Formylphenyl-2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranoside was synthesized following the procedure reported by Pavlov *et al.* (2001). (yield: 3.49 g, 31.7%). A solution of 10.00 g α-D-acetobromglucose (0.024 mol) in 122 ml $CHCl_3$ was added to a suspension of 5.97 g (0.049 mol) 3-hydroxybenzaldehyde, 3.41 g (0.061 mol) KOH and 5.61 g (0.025 mol) benzyltriethylammonium chloride in 49 ml water. The two-phase system was refluxed for 5 h. The brown organic layer was separated and washed four times alternately with 100 ml of a 1 *M* KOH solution and water. After drying over Na_2SO_4 and complete removal of the solvent, a dark orange syrup remained. Recrystallization twice from hot ethanol afforded the product in the form of colorless blocks [m.p. = 397–399 K (ethanol)]. IR (KBr): 3065 (ν C–H arom.); 2975 (ν_{as} CH_3); 2941 (ν_{as} CH_2); 2864 (ν_s CH_3, CH_2); 1761, 1733 (O–C═O); 1699 (ν CH═O); 1593; 1484 (ν C═C); 1455 (δ_{as} CH_3, δ CH_2); 1382 (δ_s CH_3); 1321; 1235, 1218, 1168, 1137, 1087, 1057, 1035 (ν C–O); 897; 802; 769; 689; 609 cm^{-1}. Raman: 3075, 3065, 3028, 2996 (ν C–H arom.); 2975 (ν_{as} CH_3); 2941 (ν_{as} CH_2); 2883, 2865; 2753 (ν_s CH_3, CH_2); 1751, 1733 (ν O–C═O); 1698 (ν CH═O); 1593; 1433 (δ_{as} CH_3, δ CH_2); 1380 (δ_s CH_3); 1320; 1262, 1243, 1169, 1159, 1125, 1085 (ν C–O); 998; 925; 899; 873; 768; 647; 616; 536; 487; 443 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6, 298 K): 1.96, 2.00, 2.01, 2.02 (4*s*, 12H, CH_3); 4.08 (*dd*, 1H, $^2J_{6e6a}$ = 12.2 Hz, $^3J_{6e5}$ = 2.4 Hz, H6e); 4.17 (*dd*, 1H, $^2J_{6a6e}$ = 12.2 Hz, $^3J_{6a5}$ = 6.1 Hz, H6a); 4.26–4.30 (*m*, 1H, H5); 5.00 (*dd*, 1H, $^3J_{43}$ = $^3J_{45}$ = 9.8 Hz, H4); 5.09 (*dd*, 1H, $^3J_{23}$ = 9.8 Hz, $^3J_{21}$ = 7.9 Hz, H2); 5.41 (*dd*, 1H, $^3J_{34}$ = $^3J_{32}$ = 9.6 Hz, H3); 5.67 (*d*, 1H, $^3J_{12}$ = 7.9 Hz, H1); 7.31–7.65 (*m*, 4H, H8–10, H12); 9.98 (*s*, 1H, H13) p.p.m. ^{13}C NMR (100 MHz, DMSO-d_6, 298 K): 20.3 (CH_3); 61.7 (C6); 68.1 (C4); 70.6 (C2); 71.0 (C5); 71.9 (C3); 97.0 (C1); 115.7 (C12); 122.8, 124.9, 130.6 (C8, C9, C10); 137.7 (C11); 156.8 (C7); 169.1, 169.3, 169.5, 170.0 (C═O Acetyl); 192.6 (C13) p.p.m. ESI–MS: *m/z* (%) = 475 $[M + Na]^+$ (100), 507 $[M + MeOH + Na]^+$ (45). Analysis calculated for $C_{21}H_{24}O_{11}$ C 55.75, H 5.35%; found C 55.97, H 5.19%.

Crystal data

$C_{21}H_{24}O_{11}$	Z = 2
M_r = 452.40	D_x = 1.382 Mg m^{-3}
Monoclinic, $P2_1$	Mo $K\alpha$ radiation
a = 11.126 (2) Å	μ = 0.11 mm^{-1}
b = 8.0199 (16) Å	T = 183 (2) K
c = 12.414 (3) Å	Block, colorless
β = 101.15 (3)°	0.3 × 0.3 × 0.2 mm
V = 1086.8 (4) $Å^3$	

Data collection

Nonius KappaCCD diffractometer	2662 independent reflections
φ and ω scans	2100 reflections with $I > 2\sigma(I)$
Absorption correction: none	R_{int} = 0.037
7838 measured reflections	θ_{max} = 27.5°

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0473P)^2 + 0.0368P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)]$ = 0.038	
$wR(F^2)$ = 0.089	
S = 1.05	$(\Delta/\sigma)_{max} < 0.001$
2662 reflections	$\Delta\rho_{max}$ = 0.15 e $Å^{-3}$
293 parameters	$\Delta\rho_{min}$ = −0.19 e $Å^{-3}$
H-atom parameters constrained	

H atoms were positioned geometrically and treated as riding atoms with fixed displacement parameters; C—H = 0.95 (Csp^2), 0.98 (methyl), 0.99 (methylene) and 1.00 Å (methine). 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: *XP* (Siemens, 1990); software used to prepare material for publication: *SHELXL97* and *XP*.

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