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The crystal structures of 1,2,3,4,6-penta-*O*-trimethylacetyl- and 1,2,3,4,6-penta-*O*-dimethylacetyl-β-D-glucopyranose

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Abstract—The crystal structures of 1,2,3,4,6-penta-*O*-trimethylacetyl-β-D-glucopyranose (**1**) and 1,2,3,4,6-penta-*O*-dimethylacetyl-β-D-glucopyranose (**2**) have been determined by X-ray diffraction analysis and compared with that reported for 1,2,3,4,6-penta-*O*-acetyl-β-D-glucopyranose (**3**). Whereas **1** has a well ordered structure, the acyl groups in **2** at positions 1 and 2 of the pyranose ring show disorder with respect to the positions of the α-methyl groups. As with **3**, the C=O bonds of the acyl groups at positions 1–4 show a preference for near alignment with respective ring C–H bonds, but there are, nevertheless, significant differences in the torsional angles defining this arrangement. Intermolecular weak hydrogen bonding in the three compounds is not significantly different and involves carbonyl oxygen atoms as the acceptors.

Keywords: X-ray crystallography; Crystal structure; Penta-*O*-acyl-β-D-glucopyranose

1. Introduction

The use of supercritical carbon dioxide ($scCO_2$) as an environmentally acceptable, cheap and safe alternative to organic-based solvents is of considerable commercial interest in the quest for the so-called 'green chemistry' but, because of its weak polarity, solubility levels of polar solutes are often very low.[1] An approach to overcome this limitation is to use $scCO_2$ compatible surfactants and while fluorine containing compounds are good CO_2-philes, their high cost, difficult syntheses and environmental concerns over their use has led to a search for 'non-fluorous' hydrocarbon alternatives. Of special interest, therefore, was a report[2] of the high solubility of α- and β-D-glucopyranose pentaacetates in $scCO_2$, which is believed to result from favourable Lewis acid–base interactions between the carbon of carbon dioxide and ester carbonyl oxygen,[3] with an additional contribution from weak hydrogen bonding between the α-H of an acyl group and an oxygen atom of carbon dioxide.[4,5] In order to gain further insight into the importance of structural factors influencing such interactions, we have recently studied the solubility in $scCO_2$ of a series of peracylated β-D-glucopyranoses[†] and discovered a remarkable difference in behaviour of 1,2,3,4,6-penta-*O*-trimethylacetyl-β-D-glucopyranose (**1**) and 1,2,3,4,6-penta-*O*-dimethylacetyl-β-D-glucopyranose (**2**), with the former exhibiting a similar solubility to 1,2,3,4,6-penta-*O*-acetyl-β-D-glucopyranose (**3**). Since solubility depends amongst other factors on intra- and inter-molecular forces in a solute, we were prompted to investigate the crystal structures of **1** and **2** and compare these with the published data for **3**.[6] Interestingly, despite the crystallinity of **1**, **2** and **3**, 1,2,3,4,6-penta-*O*-propionyl-β-D-glucopyranose, containing just one α-Me substituent in the acyl groups, has only been reported as a liquid.[7]

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Table 1. Crystal data and structure refinement for 1,2,3,4,6-penta-*O*-trimethylacetyl-β-D-glucopyranose (**1**) and 1,2,3,4,6-penta-*O*-dimethylacetyl-β-D-glucopyranose (**2**)

	Compound **1**	Compound **2**
Formula	$C_{31}H_{52}O_{11}$	$C_{26}H_{42}O_{11}$
Formula weight	600.75	530.62
Crystal system	Orthorhombic	Monoclinic
Space group	$P2_12_12_1$	$P2_1$
Unit cell dimensions		
a (Å)	6.1191(11)	10.9884(4)
b (Å)	20.375(3)	6.1637(2)
c (Å)	27.014(5)	22.0198(7)
β (°)		98.923(3)
V (Å^3)	3368.0(10)	1473.33(9)
Z (molecules/cell)	4	2
D_{calcd} (Mg/m^3)	1.185	1.196
$F(000)$	1304	572
Absorption coefficient (mm^{-1})	0.089	0.093
Crystal size (mm)	$0.9 \times 0.11 \times 0.11$	$0.72 \times 0.70 \times 0.26$
Data collection, θ range	3.5–25.0°	3.8–27.5°
Reflections collected	35,815	19,273
Unique reflections	5921 ($R_{int} = 0.197$)	6683 ($R_{int} = 0.039$)
Observed reflections ($I > 2\sigma(I)$)	3575	5074
Data/restraints/parameters	5921/0/379	5057/1/368
Goodness-of-fit on F^2	0.913	1.039
Final R indices ('observed' data)	$R_1 = 0.060$, $wR_2 = 0.114$	$R_1 = 0.059$, $wR_2 = 0.128$
Final R indices (all data)	$R_1 = 0.114$, $wR_2 = 0.130$	$R_1 = 0.080$, $wR_2 = 0.137$
Absolute structure parameter, x	0.9(13)	−0.4(11)
Largest diff. peak and hole	0.20 and −0.33 e Å^{-3}	0.35 and −0.16 e Å^{-3}
Location of largest diff. peak	Close to O2	Near C 62

2. Results and discussion

Compounds **1**[8] and **2**[9] were prepared by literature procedures and suitable crystals were obtained by slow evaporation of solutions in ethyl acetate–hexane. Crystal data, structure determination and refinement data for **1** and **2** are given in Table 1, selected bond lengths, bond angles and torsion angles are given as Supplementary data in Tables S1–S3, and the resulting ORTEP views of these two compounds with the numbering of the atoms are shown in Figures 1 and 2, respectively. Data on intermolecular hydrogen bonds in the crystals of **1**–**3** are collected in Table 2.

2.1. Compound 1

The penta-*O*-trimethylacetyl derivative **1** crystallised in the $P2_12_12_1$ space group. The pyranose ring exists in a near perfect $^4C_1$ conformation with Cremer–Pople puckering parameters[10] of $Q = 0.608(4)$ Å, $\theta = 4.1(4)°$ and $\phi = 80(4)°$, the last value indicating a slight distortion towards a conformation intermediate between E_1 and $^2H_1$ conformations.[‡] In both **1** and **3** there is near coplanarity of each C(ring)–O–C=O segment and, as observed with many pyranose acetates, the favoured alignment of the acyl groups in **1** places carbonyl oxygen to carbon double bonds in near alignment with, and in the same direction as, the corresponding ring C–H bonds, but with significant variations from similar bonds in **3**. The thermal ellipsoid plot shows that the α-Me carbons are ordered at all positions (although there is considerable vibrational movement in some), a feature at variance with the penta-*O*-dimethylacetyl derivative **2** (see below).

2.1.1. Bond lengths. A comparison of the bond lengths in **1** with corresponding lengths in **3**[6] showed a small average bond length difference of 0.014 Å for bonds in the pyranose ring and 0.013 Å for bonds directly exocyclic to the ring with a maximum variation of 0.041 Å for C5–C6, but the limited accuracy of bond lengths in **3** (e.s.d.'s 0.008 Å) has been noted.[6]

2.1.2. Bond angles. The bond angles within the ring of **1** are close (difference <1.5°) to those of **3**, except for C1–C2–C3 where the latter compound shows an increase of 7.1° in this angle over that in **1**. Exocyclic bond angles show a variation of <1.1° except for O3–C3–C2, which is increased by 3.4° over that in **3**.

2.1.3. Torsion angles. For an undistorted six-membered ring in a chair conformation and with equal bond

[‡] Based on the published[6] crystal structure data, pentaacetate **3** exists in a $^4C_1$ conformation with Cremer–Pople puckering parameters of $Q = 0.565(5)$ Å, $\theta = 9.2(5)°$ and $\phi = 325(3)°$, showing a slight distortion of the chair ring towards a $^0H_5$ conformation.

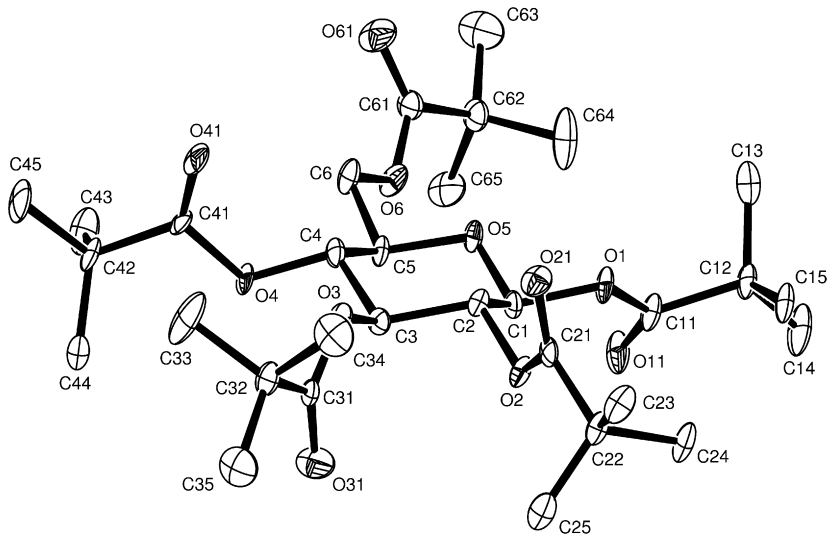

Figure 1. ORTEP diagram of **1** (thermal ellipsoids at 30% probability level) showing atom numbering scheme. Hydrogen atoms have been omitted for clarity.

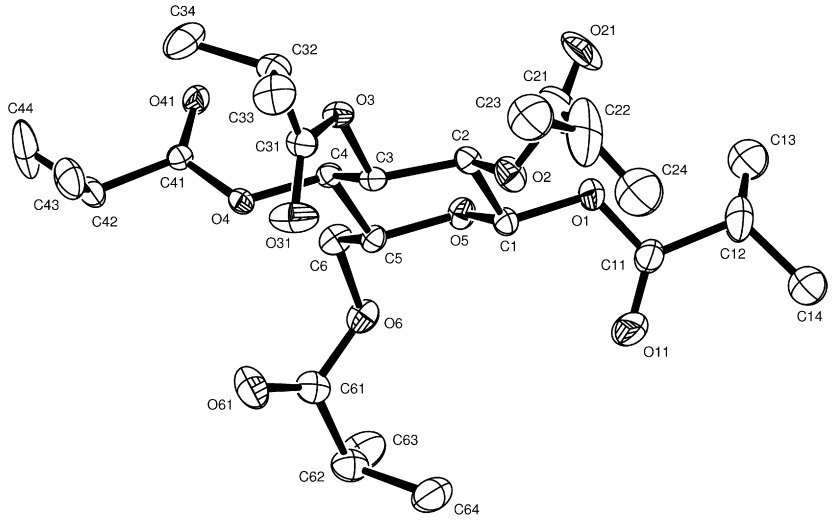

Figure 2. ORTEP diagram of **2** (thermal ellipsoids at 30% probability level) showing atom numbering scheme. Hydrogen atoms have been omitted for clarity. Only a major conformational arrangement is shown for each of the disordered groups in the dimethylacetyl side chains at C1 and C2.

lengths, the alignment of a C=O bond with the corresponding ring C–H bond at C1 would be revealed by torsion angles of 120° at C2–C1–O1–C11 and O5–C1–O1–C11, assuming planarity of the C1–O1–C11–O11 segment, with a similar situation obtaining at the other three secondary positions, C2–C4. In **1**, such planarity is nearly achieved with the largest deviation being −6.1° at C4, and in compound **3** the maximum deviation (+4.4°) from planarity is also at C4 for such torsional angles.[6] Despite the tendency for alignment of C=O with ring C–H bonds mentioned previously, in **1** there is a distinct movement away from perfect alignment at C1–C4. Thus, for ring position 1, the angles defined by C2–C1–O1–C11 and by O5–C1–O1–C11 are +159.8° and −82.7°, respectively, indicating an approximate displacement, averaged from these figures and assuming the aforementioned idealised geometry of the chair ring, of +38.6° away from alignment of the C1–H1 and O1–C11 bonds[§] (and therefore also with the C11–O11 bond, neglecting the small deviation of C1–O1–C11–O11 from planarity). Similar calculations using torsional angles at ring positions 2, 3 and 4, with similar assumptions, show mean deviations from coalignment of the ring C–H

[§]The positive sign indicates a clockwise torsional angle for the fragment C11–O1–C1–H1, following the sign convention of Klyne and Prelog,[11] with a corresponding correlation for similarly calculated angles at the other ring positions.

Table 2. Intermolecular 'weak' hydrogen bond data for compounds **1**–**3**

Compound		C–H···O	H···O (Å)	D···A (Å)	∠C–H···O (°)
1	a	C4–H4···O31	2.42	3.241(5)	141
	a	C2–H2···O31	2.53	3.349(5)	141
	b	C5–H5···O61	2.61	3.448(5)	144
	c	C65–H65B···O11	2.68	3.554(6)	152
2	d	C1–H1···O41	2.39	3.224(3)	142
	d	C3–H3···O41	2.44	3.263(3)	141
	d	C5–H5···O41	2.52	3.358(3)	143
	e	C6–H6B···O11	2.48	3.407(4)	159
	f	C14–H14A···O21	2.58	3.501(10)	160
	g	C34–H34A···O11	2.70	3.632(5)	164
3	a	C3–H3···O21	2.54	3.351(6)	142
	a	C1–H1···O21	2.64	3.433(6)	141
	b	C12–H12B···O11	2.69	3.550(8)	150
	h	C12–H12C···O61	2.68	3.492(11)	143
	i	C22–H22C···O11	2.59	3.499(8)	159
	j	C6–H6B···O41	2.60	3.542(8)	166

Symmetry codes: [a] $x+1, y, z$; [b] $x-1, y, z$; [c] $x+1/2, -y+3/2, -z+1$; [d] $x, y-1, z$; [e] $x, y+1, z$; [f] $-x+1, y-1/2, -z$; [g] $x+1, y+1, z$; [h] $x-1/2, -y+3/2, -z+2$; [i] $-x, y-1/2, -z+5/2$; [j] $x+1/2, -y+1/2, -z+2$.

bonds and the C=O bond of the attached acyloxy group of +14.9°, +7.3° and −3.2°, respectively, which compare with similarly calculated values of +29.3°, 0°, −17.3° and −18.1° for **3**[1] at positions 1, 2, 3 and 4 of the ring. Around the C5–C6 bond, the arrangement in both **1** and **3** is *gauche*/*trans* with the O5–C5–C6–O6 angle in **1** at +62.1° and the corresponding angle in **3** at +79.6°. Torsion angles in **1** along the C–Me to carbonyl–carbon bonds (e.g., C14–C12–C11–O11 = −12.6°) reveal approximate alignment of one of the C–Me bonds of the CMe_3 group with the carbon–oxygen double bond, with other corresponding values for the 2-, 3-, 4- and 6-trimethylacetyl groups being +5.7°, +2.1°, −13° and −8.3°.

2.1.4. Hydrogen bonding. The peracylated β-D-glucopyranoses do not possess donors such as N–H or O–H, which are usually associated with hydrogen bonding, but short C–H···O distances within crystal structures are recognised as denoting 'weak hydrogen bonding'[12] and have often been noted from the analysis of crystalline carbohydrate compounds.[13] Applying the criteria[13] H···O <2.7 Å and D–H···A >90°, with analysis using the PARST97 program,[14] four intermolecular weak hydrogen bonds were detected, and intramolecular hydrogen bonds were revealed between ring hydrogen atoms H1,2,3,4 and the carbonyl oxygen atom of the associated trimethylacetyl group, for example H1···O11.

2.2. Compound 2

The penta-*O*-dimethylacetyl derivative **2** crystallised in the $P2_1$ space group. The pyranose ring adopts a nearly ideal $^4C_1$ conformation with Cremer–Pople puckering parameters of $Q = 0.605(2)$ Å, $\theta = 3.5(2)°$ and $\phi = 313(3)°$, which indicates that the slight distortion is towards the $B_{2,5}$ conformation with flattening at the C2 apex. A notable distinction from the crystal structure of **1** is the considerable disorder shown within the Me_2CH–C(O)–O– groups at C1 and C2. In **2**, although the C1–O1–C11–O11 torsion angle is small (+4.7°) as expected, and is in the range shown by similar angles in **1** and **3**, the *gem*-dimethyl groups of the acyl group at this position are not uniquely located, several distinct positions being indicated, showing that several conformational energy minima exist for rotation about the Me_2CH–C(O) (C11–C12) bond. At C2, the situation is further complicated by the fact that two stereo-arrangements exist about the O2 to carbonyl–carbon bond (O2–C21) with two distinct sites for the carbonyl oxygen atom. Dihedral angles defined by C2 and the alternate carbonyl oxygen atoms, O21 and O21A (the former has a higher site occupancy), are −14.8° and 21.3°, respectively. Correspondingly, there are two sites for the α-carbon atom of the isopropyl group, C22 and C22A, and there are also several feasible positions, which have not been fully resolved, for the two methyl groups.

However, there is no such uncertainty with regard to the acyloxy functions at C3, C4 and C6 where the spatial positions of oxygen atoms and methyl groups at each centre are uniquely defined. Figure 2 depicts those arrangements in **2** for acyl groups at O1 and O2 with probabilities of about 40%.

2.2.1. Bond lengths. The maximum variation in ring bond lengths of **2** from those of corresponding bonds in pentaacetate **3** is 0.016 Å for C4–C5, and for lengths of bonds directly *exo* to the ring is 0.013 Å for C1–O1.

2.2.2. Bond angles. Within the ring, bond angles of **2** lie close to those in pentaacetate **3** with a maximum differ-

ence of 3.9° and there is little difference (<2.8°) in bond angles for bonds to substituents attached directly to the pyranose ring.

2.2.3. Torsion angles. As with **1** and **3**, the favoured arrangement of the acyl functions at O1–O4 places the carbonyl oxygen to carbon double bond in near alignment with the corresponding ring C–H bond. With the same assumptions as noted in the estimation of related torsion angles in **1**, deviations from such alignment at ring positions 1, 2, 3 and 4 are approximately +27.2°, −5.7°, 0.1° and +18.4°, respectively. Similar to compounds **1** and **3**, there is a *gauche*/*trans* arrangement at C5–C6 with O5–C5–C6–O6 angle of +77.4°. However, there is a notable difference in the angle C5–C6–O6–C61 for **2** (+85.5°) and **1** (−147.6°), the latter being comparable to that reported[1] for **3** (−162.7°).

There is considerable variation in the stereo-arrangement of methyl groups about the Me_2CH–C(O) bonds at ring positions C1 and C2, as already indicated. With reference to the particular structure shown in Figure 2, both the *gem*-methyl groups in an acyl function occupy approximately *synclinal* positions with respect to O2 and O6, but at position C3 the carbonyl oxygen O31 is unequally disposed between the *gem*-methyl groups (O31–C31–C32–C33 = + 27.6° and O31–C31–C32–C34 = −93.7°). At both positions 1 and 4, one of the *gem*-methyl groups is nearly eclipsed with the carbonyl oxygen O11 or O41, respectively (O11–C11–C12–C14 = −13°, O11–C11–C12–C13 = 126.2° and O41–C41–C42–C44 = + 5.4°, O41–C41–C42–C43 = −117.6°).

This variation in torsion angles about the individual Me_2CH–C(O) bonds in the structure shown in Figure 2 is further exemplified in the acyl groups at ring positions 1 and 2 in the structure as refined, where considerable disorder is observed, as indicated previously.

2.2.4. Hydrogen bonding. Applying the criteria[13] H···O <2.7 Å and D–H···A >90°, with analysis using the PARST97 program,[14] six intermolecular hydrogen bonds were detected (not including those involving disordered methyl groups of low site occupancy), and intramolecular hydrogen bonds were revealed between ring hydrogen atoms H1,2,3,4 and the carbonyl oxygen atom of the associated dimethylacetyl group.

2.3. Intermolecular hydrogen bonding in compounds 1–3

In crystalline structures, hydrogen atoms in C–H bonds have a tendency to form intermolecular contacts with oxygen and such C–H···O hydrogen bonds can influence crystal packing,[12] this being especially true for carbohydrates with their large potential for such interactions. Analysis of neutron diffraction data on carbohydrate crystals[13] has shown that there is no 'cut-off' based on van der Waals contacts, but suggests that within the large number of such hydrogen atoms studied as potential donors, ~65% came within a limit of 2.7 Å for the H···O bond length. In an attempt to find an explanation, based on intermolecular forces in the solid state, for the remarkable enhanced solubility of esters **1** and **3** in liquid carbon dioxide compared to that of **2**, we analysed the crystal structural data for these compounds, using the 2.7 Å parameter for the intermolecular hydrogen bond. We surmised that the low solubility of **2** might be associated with a more extensive intermolecular hydrogen bonding pattern in its crystalline state than that occurring in **1** and **3**, leading to a disadvantageous free energy change on dissolution, because of the necessary breaking of a greater number of intermolecular hydrogen bonds. However, in **1**, **2** and **3** the numbers of such bonds so detected were very similar, being 4, 6 and 6, respectively, each bond involving a carbonyl oxygen atom as the receptor. If the cut-off distance was raised to 3.0 Å, the number of bonds detected was still similar, at 13, 15 and 13, respectively. The small differences in these numbers between all three compounds suggest that destruction of intermolecular hydrogen bonding during breakdown of the supermolecular organisation of the solids on dissolution in liquid carbon dioxide cannot be a basis on which to explain the distinct difference in solubility of **2** compared to **1** and **3** in supercritical carbon dioxide.

3. Experimental

Compound **1**, prepared by the published procedure,[8] had mp 158–159 °C, lit.[8] mp 156–158 °C; $[\alpha]_D^{20}$ +12.9 (*c* 0.26, $CHCl_3$), lit.[8] $[\alpha]_D^{20}$ +10.9 ($CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 5.68 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1), 5.36 (dd, 1H, $J_{2,3} = J_{3,4}$ 9.6 Hz, H-3), 5.20 (dd, 1H, H-2), 5.15 (dd, 1H, $J_{4,5}$ 9.6 Hz, H-4). 4.16–4.00 (m, 2H, H-6a, H-6b), 3.90–3.70 (m, 1H, H-5), 1.30–1.00 (m, 45H, 5 × COC*Me*$_3$). HRESIMS: calcd for $C_{31}H_{56}NO_{11}$ $[M+NH_4]^+$: *m*/*z* 618.3848; found: 618.3848.

Compound **2**, prepared by the published procedure,[9] had mp 104–106 °C, lit.[9] mp 106 °C; $[\alpha]_D^{20}$ +8.0 (*c* 0.69, $CHCl_3$), lit.[9] $[\alpha]_D^{20}$ +40 ($CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 5.72 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1), 5.31 (dd, 1H, $J_{2,3} = J_{3,4}$ 9.6 Hz, H-3), 5.18 (dd, 1H, H-2), 5.16 (dd, 1H, $J_{4,5}$ 9.6 Hz, H-4). 4.22 (dd, 1H, $J_{5,6a}$ 5.0, $J_{6a,6b}$ 12.8 Hz, H-6a), 4.10 (dd, 1H, $J_{5,6b}$ 2.0 Hz, H-6b), 3.85 (ddd, 1H, H-5), 2.37–2.60 (m, 5H, 5 × COC*H*Me$_2$), 1.20–1.00 (m, 30H, 5 × COCH*Me*$_2$). HRESIMS: calcd for $C_{26}H_{46}NO_{11}$ $[M+NH_4]^+$: *m*/*z* 548.3065; found: 548.3062.

3.1. Crystal structure analysis

Transparent colourless crystals of **1** and **2** were obtained by slow evaporation over several weeks from ethyl acetate–hexane (1:2 v/v) solutions and for each analysis a

suitable crystal of **1** (needle) or **2** (block) was mounted on a glass fibre, in oil, fixed in a cold [140(1) K] nitrogen stream on an Oxford Diffraction Xcalibur-3 CCD diffractometer equipped with Mo Kα radiation ($\lambda = 0.71073$ Å) and graphite monochromator. Intensity data were measured by thin-slice ω- and φ-scans. Crystal data and further experimental details are given in Table 1. Data were processed using the CrysAlis-CCD and -RED programs.[15] The structures were determined by direct methods routines in the SHELXS program[16] and refined by full-matrix least squares methods on F^2s in SHELXL.[16]

For **1**, the non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were included in idealised positions and their U_{iso} values were set to ride on the U_{eq} values of the parent carbon atoms. The absolute configuration could not be determined from the data measured; the Flack parameter x for the configuration shown (correct for the structure prepared from D-glucose) is 0.9(13), but for the inverted (incorrect) structure is 0.1(13). In the final difference map the highest peak (ca. 0.2 e Å^{-3}) was close to O2.

For **2**, there is disorder in the dimethylacetyl groups at O1 and O2; there are several sites for the pairs of terminal methyl groups in both side groups and these have not been fully resolved. The non-hydrogen atoms in sites of more than 55% occupancy were refined with anisotropic thermal parameters; atoms in the minor sites were refined isotropically. Hydrogen atoms were included in idealised positions and their U_{iso} values were set to ride on the U_{eq} values of the parent carbon atoms. In the difference map final the highest peak (ca. 0.35 e Å^{-3}) was near C62.

For both determinations, scattering factors for neutral atoms were taken from Ref. 17. Computer programs used in this analysis were run through WinGX[18] on a Dell Precision 370 PC.

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Supplementary data

Complete crystallographic data for the structural analysis of **1** and **2** have been deposited with the Cambridge Crystallographic Data Centre, CCDC numbers 641613 and 641612, respectively. Copies of this information may be obtained free of charge from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033, e-mail: deposit@ccdc.cam.ac.uk or via: www.ccdc.cam.ac.uk). Supplementary data (tables containing selected bond lengths, bond angles and torsion angles for compounds **1**–**3**) associated with this article can be found, in the online version, at doi:10.1016/j.carres.2007.06.023.

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