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Stereoselective single-step synthesis and X-ray crystallographic investigation of acetylated aryl 1,2-*trans* glycopyranosides and aryl 1,2-*cis* C2-hydroxy-glycopyranosides

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Abstract—Reported is an attractive and environmentally friendly method for the synthesis of the title compounds in moderate yield using inexpensive 1,2,3,4,6-penta-*O*-acetyl-β-D-gluco- and galactopyranoses as sugar donors, five different phenols as acceptors and H-β zeolite as the catalyst. The yield (23–28%) of aryl 3,4,6-tri-*O*-acetyl-α-D-glycopyranosides obtained in this single-step procedure is considerably higher than that obtained using previously reported methods. Treatment of an orthoacetate, 3,4,6-tri-*O*-acetyl-[1,2-*O*-(1-*p*-fluorophenoxyethylidene)]-α-D-glucopyranose, with *p*-fluorophenol under the same solvent-free reaction conditions also led to the formation of the title compounds in similar yield and composition. X-ray crystallographic analysis of phenyl 3,4,6-tri-*O*-acetyl-α-D-glucopyranoside and *p*-fluorophenyl 3,4,6-tri-*O*-acetyl-α-D-glucopyranoside showed that the molecular packing is stabilized by C–H···O, C–H···π and C–H···F interactions, in addition to regular hydrogen bonding patterns.

Keywords: Carbohydrates; Helferich glycosidation; Aryl C-2-hydroxy-glycoside; H-β Zeolite; X-ray crystallography; C–H···O; C–H···F and C–H···π interactions

1. Introduction

Aryl O-glycosides occur widely in nature and their complex structures and diverse biological activities make them attractive targets for synthesis. Applications of aryl O-glycosides include their use as chromogenic substrates for glycosidases[1] and as inhibitors of carbohydrate–lectin interactions.[2] Preparation of fully acetylated aryl glycosides using sugar peracetates as donors and Lewis/Brønsted acids as catalysts was first reported by Helferich and Schmitz-Hillebrecht in 1933.[3] Although several effective donors, such as glycosyl trichloroacetimidates and thioglycosides have subsequently been introduced, sugar peracetates are still commonly used for the chemical synthesis[4] of O-glycosides in view of their ready availability, low cost and ease of preparation. The various catalysts[4,5] employed for Helferich glycosidation include $ZnCl_2$, *p*-TsOH, $POCl_3$, H_2SO_4, BF_3–Et_2O, $SnCl_4$, $FeCl_3$ and $AlCl_3$. Depending on the nature of catalyst and reaction conditions, either α- or β-glycopyranosides have been obtained as the major product in varying yield. Although a few speculations have been made previously, the mechanism of the Helferich glycosidation still remains to be elucidated.

Acetylated aryl glycopyranosides carrying a free C2–OH group have been isolated from several medicinal plants belonging to the genera *Bidens*[6a,c–e] and *Senecio*,[6b] the fern *Phegopteris connectilis*[6f] and also from the marine organism, *Euplexaura anastomosans*.[7] One such natural product viz., moritoside, inhibits cell division of fertilized starfish eggs,[7a] while others have been shown to exhibit diverse bioactivities including moderate cytotoxicity[7b,c] and inhibition of viral replication.[6c] Many reports have appeared in the recent literature on the stereoselective formation of protected aryl 1,2-*trans*

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C2-hydroxyglycopyranosides[8] and all these are based on multi-step procedures. The stereoselective formation of 1,2-*cis* linkages is, in general, considerably more challenging.[9] Extension of the Stork silicon tether approach by Bols[10] represents the *only report* on the preparation of aryl 1,2-*cis* C2-hydroxy-glycopyranosides. This five-step synthesis starting from β-D-glucose pentaacetate (**1**) afforded phenyl 3,4,6-tri-*O*-acetyl-α-D-glucopyranoside (**6a**) in less than 12% overall yield.

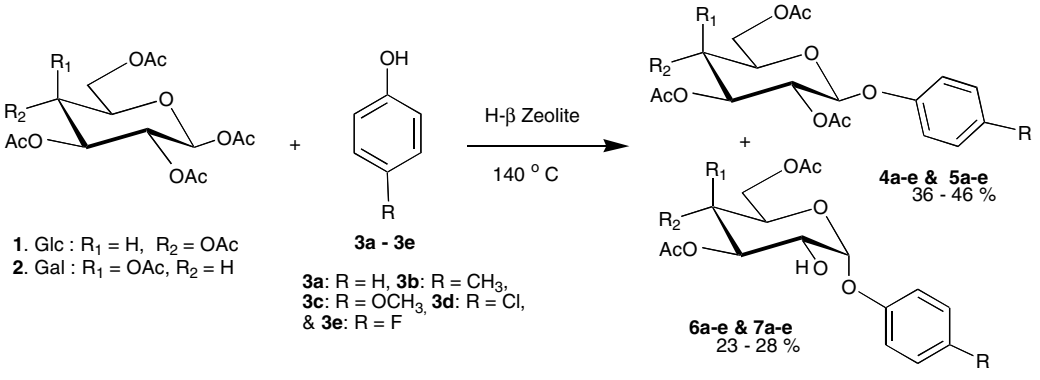
As part of our major research program aimed at developing environmentally friendly synthetic methodologies for carbohydrate transformations, we have found that H-β zeolite is an efficient catalyst for the peracetylation of sugars.[11] Exploration of the Helferich reaction of several phenols with 1,2,3,4,6-penta-*O*-acetyl-β-D-gluco- and galactopyranoses has now led to the stereoselective synthesis of aryl 2,3,4,6-tetra-*O*-acetyl-β-D-glycopyranosides, **4a**–**e** and **5a**–**e** and aryl 3,4,6-tri-*O*-acetyl-α-D-glycopyranosides **6a**–**e** and **7a**–**e** (Scheme 1) in moderate yields. We also demonstrate, for the first time, that the H-β zeolite-catalyzed transformation of an orthoacetate, 3,4,6-tri-*O*-acetyl-[1,2-*O*-(1-*p*-fluorophenoxyethylidene)]-α-D-glucopyranose, to **4e** and **6e** in similar yield. Single crystal X-ray analysis of **6a** and **6e** reveals similarities in molecular recognition patterns involving C–H···O as well as C–H···π interactions in the crystal packing of both compounds as well as differences of which the most notable is a C–H···F interaction in the latter compound.

2. Results and discussion

2.1. Synthesis and mechanistic study

Zeolites have been shown to be efficient catalysts for several liquid-phase organic transformations.[12] The inherent shape selectivity and the potential to fine tune the Brønsted/Lewis acidity of zeolites makes them ideal catalysts for Helferich glycosidation yet they are hitherto unexplored in this regard. Among the various zeolites examined as catalysts for peracetylation of sugars,[11] H-β zeolite proved to be highly efficient due probably to its greater acid strength and larger pore openings and channel intersections. Hence, the same catalyst was chosen for the present study. The feasibility of H-β zeolite catalyzed Helferich glycosidation was initially examined using β-D-glucose pentaacetate as the donor (**1**) and phenol (**3a**, 5 equiv) as the acceptor at 140 °C under *solvent free* conditions (Scheme 1). After 12 h, when the conversion reached a maximum as shown by TLC analysis, the reaction mixture was cooled to room temperature and worked-up. Column chromatography of the crude product over silica gel afforded predominantly phenyl 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranoside (**4a**; 46%) as well as phenyl 3,4,6-tri-*O*-acetyl-α-D-glucopyranoside (**6a**, 23%) both of which were characterized based on comparison of their physical and spectral data with those reported in the literature.[13,10] Careful ^{1}H NMR analysis of two minor fractions obtained from column chromatography did reveal the formation of the corresponding α-anomer of **4a** and β-anomer of **6a** each in less than 5% yield. The stereoselectivity of the H-β zeolite catalyzed reaction was found to be general with respect to different substituted phenols (**3a**–**e**) and also with β-D-galactose pentaacetate (**2**) (Table 1).

All the other known peracetylated aryl β-D-glycopyranosides (**4b**–**e**) were characterized based on comparison of their physical and spectral data with those reported in the literature.[13] The hitherto unknown aryl 3,4,6-tri-*O*-acetyl-α-D-glycopyranosides **6b**–**e** and **7a**–**e** have been fully characterized using two-dimensional ^{1}H NMR spectroscopy and ESI-MS analysis. All compounds **6a**–**e** and **7a**–**e** exhibited only three methyl signals of the acetyl groups in their ^{1}H NMR spectra. The anomeric proton signal in the NMR spectra of **6a**–**e** and **7a**–**e** appears at around 5.50 ppm as a doublet with a coupling constant value of about 3.7 Hz revealing the presence of 1,2-*cis* glycosidic linkage. The H-2 signal is observed in the region 3.80–4.20 ppm, up-field shifted from the region of 5.10–5.30 ppm noted for the corre-



Scheme 1. H-β Zeolite catalyzed synthesis of acetylated aryl 1,2-*trans*-glycopyranosides and aryl 1,2-*cis* C2-hydroxy-glycopyranosides.

Table 1. H-β Zeolite catalyzed reaction of sugar peracetates with phenols

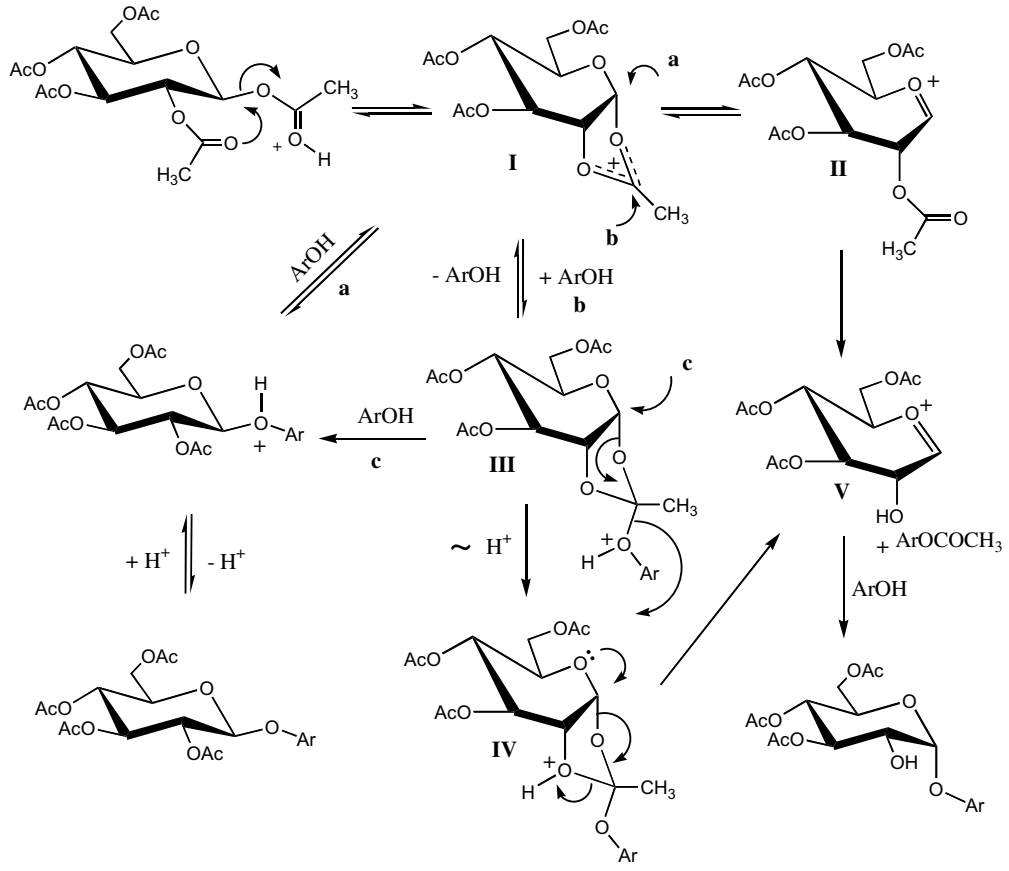
Entry no.	Phenols	R	Sugar	Product **4/5**	% Yield[a]	Product **6/7**	% Yield[a]	Total **4**+**6/5**+**7** % Yield[a]
1	**3a**	H	**1**	**4a**	46	**6a**	23	69
2	**3b**	CH_3	**1**	**4b**	40	**6b**	25	65
3	**3c**	OCH_3	**1**	**4c**	40	**6c**	23	63
4	**3d**	Cl	**1**	**4d**	40	**6d**	25	65
5	**3e**	F	**1**	**4e**	38	**6e**	26	64
6	**3a**	H	**2**	**5a**	43	**7a**	26	69
7	**3b**	CH_3	**2**	**5b**	43	**7b**	28	71
8	**3c**	OCH_3	**2**	**5c**	42	**7c**	27	69
9	**3d**	Cl	**2**	**5d**	36	**7d**	24	60
10	**3e**	F	**2**	**5e**	37	**7e**	28	65

[a] Based on isolated pure product.

sponding fully protected aryl glycosides, confirming the free nature of the C2 hydroxyl group in **6a**–**e** and **7a**–**e**. The ^{13}C–^{19}F coupling constants observed for the *p*-fluorophenyl glycosides **6e** and **7e** are in reasonable agreement with those reported for *p*-fluorophenyl ethers.[14] Furthermore, the identity of **6a** and **6e** as phenyl 3,4,6-tri-*O*-acetyl-α-D-glucopyranoside and *p*-fluorophenyl 3,4,6-tri-*O*-acetyl-α-D-glucopyranoside, respectively, has been unambiguously established by single crystal X-ray diffractometry (see below). The total yield (60–71%) of the aryl 2,3,4,6-tetra-*O*-acetyl-β-D-glycopyranoside and aryl 3,4,6-tri-*O*-acetyl-α-D-glycopyranoside obtained in each of the reactions is quite good considering that the reaction conversion is about 85–90%. As phenols in general are poor nucleophiles as compared to alcohols, earlier methods of Lewis acid catalyzed Helferich glycosidation often employed activated forms of phenols such as higher-toxicity tributyltin derivatives,[15] to achieve higher yields. The excellent activation of the sugar peracetate by the solid acid H-β zeolite obviates the need for such modification of phenols.

In spite of the fact that the Helferich method has been widely employed for aryl glycoside synthesis for the past 70 years, the reaction mechanism remains to be established. The role of neighbouring group participation by the carbonyl oxygen of 2-*O*-acyl group on the stereoselectivity of various chemical glycosidation methods has been extensively studied.[16] Brønsted acid-catalyzed Helferich glycosidations have invariably been performed using 1,2-*trans* peracetylated sugars. An early key step in the mechanism of the H-β zeolite-catalyzed Helferich glucosidation is expected to be the C2 acetate assisted cleavage of the glycosidic bond of the activated (protonated) peracetate leading to the formation of the 1,3-dioxolenium ion (I, Scheme 2). Nucleophilic attack by the phenol at the anomeric carbon of I results in the stereoselective formation of aryl 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranoside. Alternatively, conversion of I to the protonated form of the orthoacetate, III, followed by a nucleophilic attack at the anomeric carbon could also lead to the same product, particularly in view of the fact that phenol is used in excess. Formation of a minor amount of the corresponding α-glucopyranoside could be rationalized through the intermediacy of the glycosyl oxocarbenium ion, II. A control reaction involving pure *p*-fluorophenyl 2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranoside as a substrate and 4 equiv of *p*-fluorophenol under same the conditions employed in Scheme 1 led to only 5% anomerization revealing the predominance of the 1,3-dioxolenium ion I over II as otherwise the thermodynamically more stable α-anomer would have been obtained as the major product. The use of $ZnCl_2$ has been known to bring about 34% anomerization of phenyl 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranoside under Helferich reaction conditions.[13a]

The formation of acetylated alkyl 2-hydroxy-glycopyranosides during Helferich-type glycosidations has been reported earlier.[17] Acyl transfer accompanied by the formation of glycopyranosides with a free C2 OH group has been studied in detail.[18] Whitfield and co-workers[18f] have recently shown from theoretical calculations that orthoesters are not intermediates in acyl transfer but can be converted to an intermediate or intermediates that lead to either acyl transfer or glycoside formation. To gain some insight into the formation of C2–OH derivatives **6a**–**e** and **7a**–**e**, we have examined the reaction of an orthoacetate, 3,4,6-tri-*O*-acetyl-[1,2-*O*-(1-*p*-fluorophenoxyethylidene)]-α-D-glucopyranose,[19] with *p*-fluorophenol (4 equiv) in the presence of H-β zeolite under the same conditions employed in Scheme 1. This reaction afforded **4e** and **6e** in 31% and 26% yields, respectively. The α-anomer of **4e** (7%) and β-anomer of **6e** (<2%) were also formed. The yields of these two minor products obtained from the reaction of **1** with **3e** are 4% and <2%, respectively, while the major products **4e** and **6e** are obtained in 38% and 26% yields, respectively (see Table 1, entry 5), pointing out reasonably good agreement between these two reactions in terms of product yield, composition and stereoselectivity. Based on the results described above and considering that the activation provided by H-β zeolite does not appear to be strong enough for the facile departure of the anomeric acetate to lead to the direct formation of the intermediate II, it is likely that the aryl



Scheme 2. Plausible reaction mechanism.

2-hydroxy-glucopyranosides result from the intermediate V, which in turn is formed via IV from the protonated orthoacetate, III, by proton transfer.

2.2. X-ray crystallographic study

A systematic crystallographic study of the structural and conformational aspects of glycosides provided the key understanding of the differences in the electronic properties of α- and β-pyranosides and the preferred gauche conformation of the glycosidic bond.[20] Crystal structure data of a relatively large number of alkyl glycosides are available but, in contrast, those of aryl glycosides are rather limited. A single-crystal X-ray investigation of **6a** and **6e** was undertaken not only to unambiguously establish their structures but also to unravel their conformation and the features of non-covalent weak interactions such as the regular hydrogen bond and the C–H···X (where X = O/F/π) interactions that could govern their molecular assembly. This knowledge would be valuable in correlating the structure with the biological activity[7] of the naturally occurring acetylated aryl C2-hydroxy-glycopyranosides. The occurrence of C–H···O interactions in carbohydrate crystal structures have been well documented in the literature.[21] The interactions between the hydrophobic C–H groups of carbohydrate residues and the π-electron systems of aromatic amino-acid residues have been suggested to play an important role in the ligand-recognition function of carbohydrate-binding proteins.[22]

The details of the crystal data, intensity data collection and structure refinement for **6a** and **6e** are provided in Table 2. The ORTEP depictions for **6a** and **6e** with atom numbering are shown in Figure 1. Selected bond lengths and bond angles involving non-hydrogen atoms are provided in Table 3. The C–C bond lengths, which vary between 1.488(9) and 1.530(8) Å, are comparable to those observed in most sugar derivatives. Between the endocyclic C–O bond lengths, namely C1–O5 and C5–O5, the former is found to be shorter than the latter. This trend is generally observed for several glycopyranosides and the shortening of the C1–O5 bond has been attributed to a stabilizing effect arising from the delocalization of the glycosidic oxygen lone pair of electrons into the anti-bonding C1–O1 orbital.[23] Both experimental and theoretical studies on aldopyranoses have shown earlier that the C1–O1 bond as well as O5–C1–O1 angle in $^4C_1$(D)-α configuration are greater than those in the $^4C_1$(D)-β configuration.[24] Comparative analysis of these parameters for compounds **6a**, **6e**, *p*-nitrophenyl 2,3,4,6-

Table 2. Data collection and refinement parameters for compounds **6a** and **6e**

Parameter	Compound **6a**	Compound **6e**
Empirical formula	$C_{18}H_{22}O_8$	$C_{18}H_{21}FdO_9$
Formula weight	366.36	400.35
Temperature	293(2) K	293(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system space group	$P2_12_12_1$, orthorhombic	$P2_12_12_1$, orthorhombic
Unit cell dimensions	$a = 8.5875(15)$ Å, $b = 9.7868(16)$ Å, $c = 22.431(4)$ Å	$a = 8.653(5)$ Å, $b = 9.787(4)$ Å, $c = 22.437(3)$ Å
Volume	1885.2(5) A^3	1900.0(13) A^3
Z	4	4
Calculated density	1.291 Mg/m^3	1.400 Mg/m^3
Absorption coefficient	0.102 mm^{-1}	0.112 mm^{-1}
$F(000)$	776	840
Crystal size	$0.3 \times 0.2 \times 0.2$ mm	$0.3 \times 0.2 \times 0.2$ mm
Theta range for data collection	2–25°	2–25°
Index ranges	$0 <= h <= 10$, $0 <= k <= 11$, $0 <= l <= 26$	$0 <= h <= 10$, $0 <= k <= 11$, $0 <= l <= 26$
Reflections collected/unique	1916/1916 [R(int) = 0.0000]	1937/1937 [R(int) = 0.0000]
Completeness to 2 theta	99.4%	99.9%
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data restraint parameters	1916/1/249	1937/0/258
Goodness-of-fit on F^2	1.018	1.032
Final R indices [2<sigma>(I)]	$R_1 = 0.0530$, $wR_2 = 0.1242$	$R_1 = 0.0588$, $wR_2 = 0.1251$
R indices (all data)	$R_1 = 0.1085$, $wR_2 = 0.1490$	$R_1 = 0.1192$, $wR_2 = 0.1554$

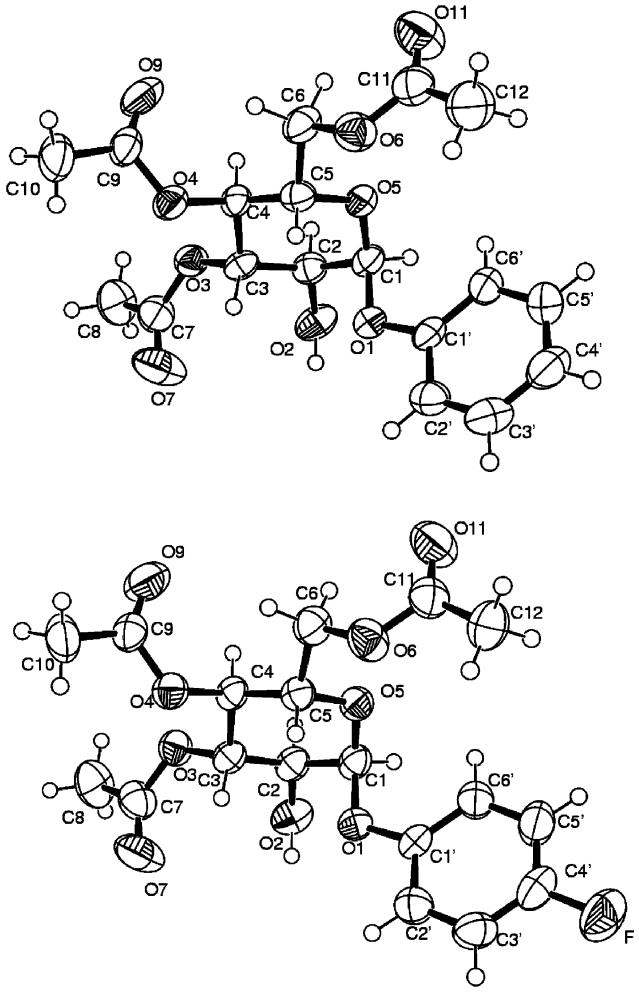


Figure 1. ORTEP with atom numbering of compounds **6a** and **6e**.

tetra-*O*-acetyl-β-D-glucopyranoside (**8**)[25a] and the free *p*-nitrophenyl α-D-glucopyranoside (**9**)[25b] (Table 3) supports these earlier findings.

The torsion angles, C4–C5–C6–O6 and O5–C5–C6–O6, observed for **6a** and **6e** are both close to −60° and 180°, respectively (Table 3), pointing out that the hydroxymethyl group in these compounds adopts a *gt* conformation. The O5–C1–O1–C1′ torsion angle values of compounds **6a** and **6e** are −73.9(5)° and −77.4(6)°, respectively, falling within the range ±60–85° observed for other aryl pyranosides.[25] Similarly, the C6′–C1′–O1–C1 torsion angle of compounds **6a** and **6e** are −0.3(6)° and −0.7(9)°, which are close to −7.3° reported for **8**.[25b] Thus, the phenyl ring in both **6a** and **6e** is coplanar with the anomeric carbon atom C1 and this orientation facilitates maximum delocalization of electrons from the lone-pair orbitals of O1 with the π orbitals of the phenyl ring. All three acetate groups in each of the compounds **6a** and **6e** adopt the *Z* conformation.

The molecular assembly of **6a** and **6e** in the solid state is driven by an infinite chain of hydrogen bonds involving C2–OH as the donor and O9 as the acceptor and extending along the crystallographic *a*-axis (Table 4). The packing in compound **6e** is also stabilized by a unique and strong finite chain of C5–H···F hydrogen bonds [d(D···A) = 3.526 Å, <DHA = 168°] (Fig. 2). Other features of molecular packing common to both the compounds include several C–H···O interactions (Table 4). Besides accepting the hydrogen from C2–OH, O9 is also hydrogen bonded to C2–H thus serving as a bifurcated acceptor (Fig. 3). The oxygen atom (O2) of C2–OH is, in turn, tri-coordinated as it is bonded to C4-H as well as C6-H. Furthermore,

Table 3. Selected bond lengths, bond angles and torsion angles of compounds **6a** and **6e**

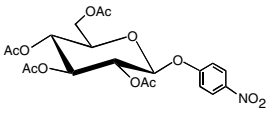
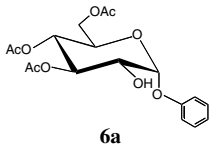
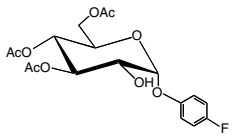
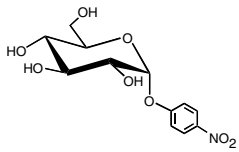
Parameter	 **8**[25a]	 **6a**	 **6e**	 **9**[25b]
Bond lengths				
C1–O1	1.408(3)	1.426(5)	1.416(7)	1.424(7)
C1–O5	1.417(3)	1.393(5)	1.387(8)	1.408(7)
C5–O5	1.432(3)	1.422(5)	1.437(7)	1.452(7)
C1′–O1	1.383(3)	1.393(5)	1.384(7)	1.374(6)
C4′–F			1.384(8)	—
Bond angle				
O5–C1–O1	107.9(2)	111.8(3)	112.8(5)	111.0(3)
Torsion angles				
O5–C5–C6–C6	63.5(2)	−73.9(5)	−77.4(6)	—
C4–C5–C6–C6	−177.9(2)	165.9(3)	165.0(5)	—
O5–C1–O1–C1′	−73.6(2)	−66.8(4)	−67.0(7)	71.8
C6′–C1′–O1–C1	18.4(6)	−0.3(6)	−0.7(9)	−7.3

Table 4. Hydrogen bonds in compound **6a** and **6e**

Hydrogen bonds	H···A in Å	D···A in Å	<DHA in °
Phenyl 3,4,6-tri-O-acetyl-α-D-glucopyranoside (**6a**)			
C8–H···O11	2.700	3.406	131
C4–H···O2	2.645	3.454	140
C6–H···O2	2.713	3.488	128
C12–H···O7	2.673	3.529	149
C2–H···O9	2.561	3.361	139
O2–H···O9	2.163	2.904	140
C6–H···π(C2′)	2.724	3.644	151
C2′–H···π(C4′)	2.893	3.506	125
p-Fluorophenyl 3,4,6-tri-O-acetyl-α-D-glucopyranoside (**6e**)			
C5–H···F	2.559	3.526	168
C4–H···O2	2.686	3.490	139
C6–H···O2	2.671	3.466	139
C12–H···O7	2.600	3.529	150
C2–H···O9	2.566	3.356	138
O2–H···O9	2.232	2.957	140
C6–H···π (C2′)	2.858	3.717	148

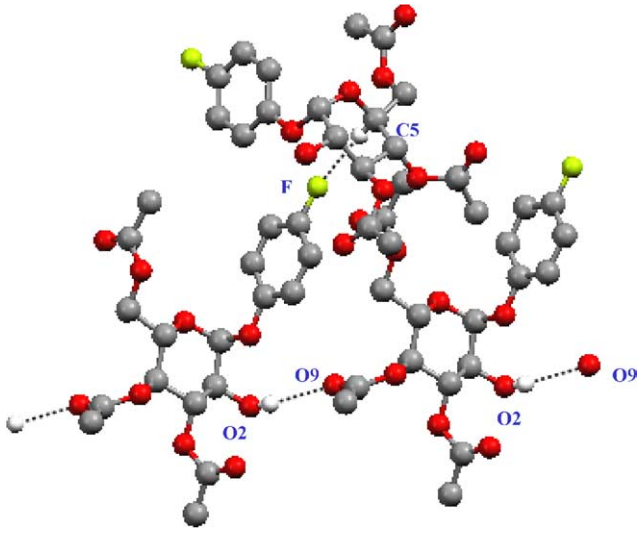


Figure 2. Molecular packing of *p*-fluorophenyl 3,4,6-tri-*O*-acetyl-α-D-glucopyranoside (**6e**) showing an infinite chain (C2–OH···O9) and a finite chain (C5–H···F) of hydrogen bonds. Most of the hydrogen atoms are omitted for clarity.

C–H···π interactions lend additional stability to the packing in both these compounds (Table 4 and Fig. 3).

In conclusion, we have developed an attractive and environmentally friendly method for the synthesis of acetylated aryl 1,2-*trans* glycopyranosides and aryl 1,2-*cis* C2-hydroxy-glycopyranosides from readily available and inexpensive hexopyranose pentaacetates. The present single-step procedure affording aryl 3,4,6-tri-*O*-acetyl-α-D-glycopyranosides in a moderate yield of 23–28% is preferable to the reported multi-step methodology that gives an overall yield of less than 12%. Except the phenyl derivative, all the nine aryl 3,4,6-tri-*O*-acetyl-α-D-gluco- and galactopyranosides synthesized are hitherto unknown. Besides the biological importance mentioned earlier, C2-hydroxy-glycosides are also valuable intermediates for the synthesis of 2-deoxy, 2-azido and 2-halo glycosides. Furthermore, acetylated glycosides with free C2–OH group serve as key intermediates for the synthesis of oligosaccharides and glycoconjugates containing 1,2-linkages that occur in bacteria, plants as well as higher animals.[26] Given the significance of C2-hydroxy-glycosides, the present methodology should prove to be useful for diverse applications in glycobiology research. X-ray crystallographic analysis of two aryl 3,4,6-tri-*O*-acetyl-α-D-glucopyranosides has shown that the molecular packing is stabilized by C–H···O, C–H···π and C–H···F interactions in addition to regular hydrogen bonding. These findings will be

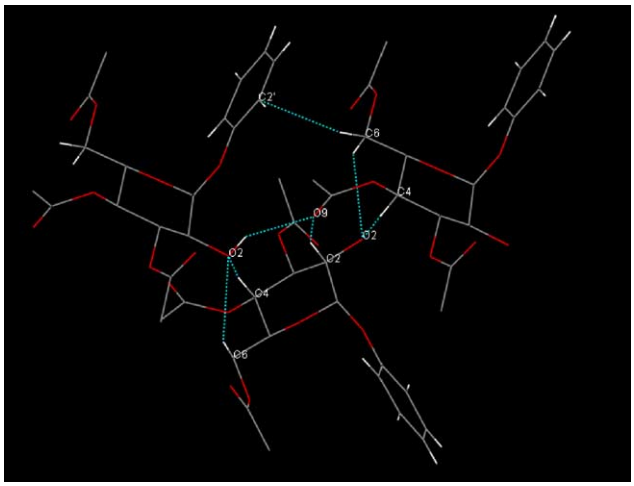


Figure 3. The molecular packing of phenyl 3,4,6-tri-*O*-acetyl-α-D-glucopyranoside (**6a**) displaying several C–H···O and C–H···π interactions. Most of the hydrogen atoms are omitted for clarity.

useful in studies directed towards obtaining a better understanding of carbohydrate–protein interactions.

3. Experimental

3.1. General information

Thin layer chromatograms were performed on 25 mm E. Merck silica gel plates (60F-254). Detection was done by spraying the plates with 10% sulfuric acid in ethanol and heating on a hot plate. Column chromatography was performed using silica gel (230–400 mesh) under flash conditions using a mixture of ethyl acetate and hexane. Optical rotations were measured at 30 °C on a JASCO-DIP 200 digital polarimeter using a cell of 10 mm length. NMR spectra were recorded on a Bruker AV400 spectrometer. ESI-MS spectra were measured on a Micromass Q-Tof mass spectrometer. All free sugars used were purchased from Sigma–Aldrich USA or from Pfanstiehl Laboratories Inc. USA. Sugar peracetates were prepared by using NaOAc and Ac_2O at 100 °C. Beta-zeolite (Na form) was obtained from Süd-Chemie India Ltd., New Delhi and activated by heating to 540 °C prior to converting into the H^+-form. Ethyl acetate, hexane, chloroform and Ac_2O were of laboratory grade and all were distilled once before use.

3.2. General procedure for the synthesis of aryl 2,3,4,6-tetra-*O*-acetyl-β-D-glycopyranosides (4a–e and 5a–e) and aryl 3,4,6-tri-*O*-acetyl-α-D-glycopyranosides (6a–e and 7a–e)

A mixture of sugar peracetate (**1** or **2**, 1.0 mmol) and phenol (**3**, 5 mmol) taken into a 100 mL round-bottom flask and was heated to ~100 °C in a silicone oil bath. Freshly activated H-β-zeolite (200 mg) was added to the melt obtained. The resulting mixture was magnetically stirred and the temperature raised to 140 °C. The progress of the reaction was monitored by TLC (EtOAc/hexane, 1:2). Following the completion of reaction (10–16 h), the reaction mixture was cooled to room temperature, diluted with chloroform (50 mL) and heated at reflux for 1.5 h to extract the product from the zeolite pores. The catalyst was then filtered. This extraction procedure was repeated twice. The combined filtrate was concentrated to give a residue that was subjected to flash column chromatography over silica gel using a mixture of EtOAc and hexane as the eluent to furnish the title compounds.

3.3. Phenyl 3,4,6-tri-*O*-acetyl-α-D-glucopyranoside (6a)

$[\alpha]_D$ +173 (*c* 0.5, CH_2Cl_2) [lit.10 $[\alpha]_D$ +170 (*c* 0.5, CH_2Cl_2)]; ^1H NMR (400 MHz, $CDCl_3$): δ 7.30–6.94 (m, 5H, Ph), 5.54 (d, 1H, $J = 3.6$ Hz, H-1), 5.39 (t, 1H, $J = 9.8$ Hz, H-3), 5.05 (t, 1H, $J = 9.8$ Hz, H-4), 4.20 (dd, 1H, $J = 4.8$, 12.4 Hz, H-6a), 4.04 (m, 1H, H-5), 3.98 (dd, 1H, $J = 2.0$, 12.4 Hz, H-6b), 3.80 (dd, 1H, $J = 3.6$, 9.9 Hz, H-2), 2.14–1.90 (3s, 9H, $COCH_3$).

3.4. *p*-Cresyl 3,4,6-tri-*O*-acetyl-α-D-glucopyranoside (6b)

$[\alpha]_D$ +52.3 (*c* 1, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$): δ 7.13 (d, 2H, $J = 8.5$ Hz, H-2′, H-6′), 7.02 (d, 2H, $J = 8.5$ Hz, H-3′, H-5′), 5.56 (d, 1H, $J = 3.7$ Hz, H-1), 5.46 (t, 1H, $J = 9.8$ Hz, H-3), 5.13 (t, 1H, $J = 9.8$ Hz, H-4), 4.28 (dd, 1H, $J = 4.6$, 12.3 Hz, H-6a), 4.16–4.09 (m, 1H, H-5), 4.05 (dd, 1H, $J = 2.1$, 12.3 Hz, H-6b), 3.86 (dd, 1H, $J = 3.8$, 9.9 Hz, H-2), 2.32 (s, 3H, $PhCH_3$-*p*), 2.14 (s, 3H, $COCH_3$), 2.06 (s, 6H, $COCH_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.3, 170.6, 169.6 ($3 \times COCH_3$), 153.9 (C-1′), 132.7 (C-4′), 130.1 (C-2′, C-6′), 116.6 (C-3′, C-5′), 97.2 (C-1), 73.4, 70.9, 68.3, 67.8, 61.7 (C-6), 29.6 ($PhCH_3$), 20.7, 20.6, 20.5 ($COCH_3$); ESI-MS: Calcd for $C_{19}H_{24}O_9Na$ ($[M+Na]^+$): 419.1318, found: 419.1297.

3.5. *p*-Methoxyphenyl 3,4,6-tri-*O*-acetyl-α-D-glucopyranoside (6c)

$[\alpha]_D$ +25.8 (*c* 1, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$): δ 7.07 (d, 2H, $J = 9.1$ Hz, H-2′, H-6′), 6.86 (d, 2H, $J = 9.1$ Hz, H-3′, H-5′), 5.50 (d, 1H, $J = 3.7$ Hz, H-1), 5.42 (t, 1H, $J = 9.8$ Hz, H-3), 5.12 (t, 1H, $J = 9.8$ Hz, H-4), 4.28 (dd, 1H, $J = 4.8$, 12.2 Hz, H-6a), 4.18–4.12 (m, 1H, H-5), 4.08 (dd, 1H, $J = 2.1$, 12.2 Hz, H-6b), 3.86 (dd, 1H, $J = 3.8$, 9.9 Hz, H-2), 3.80 (s, 3H, $PhOCH_3$-*p*), 2.14, 2.07, 2.06 (3s, 3H each, $COCH_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.3, 170.6, 169.6 ($3 \times COCH_3$), 155.6, 150.0, 118.0, 114.7, 97.8 (C-1), 73.3, 70.9, 68.2, 67.8, 61.8 (C-6), 55.7 (OCH_3), 20.9,

20.7, 20.6 ($3 \times CO\underline{C}H_3$); ESI-MS: Calcd for $C_{19}H_{24}O_{10}Na$ ($[M+Na]^+$): 435.1267, found: 435.1280.

3.6. *p*-Chlorophenyl 3,4,6-tri-*O*-acetyl-α-D-glucopyranoside (6d)

$[\alpha]_D$ +60.2 (*c* 1, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$): δ 7.30 (d, 2H, $J = 8.9$ Hz, H-3′, H-5′), 7.09 (d, 2H, $J = 8.9$ Hz, H-2′, H-6′), 5.57 (d, 1H, $J = 3.7$ Hz, H-1), 5.45 (t, 1H, $J = 9.8$ Hz, H-3), 5.13 (t, 1H, $J = 9.8$ Hz, H-4), 4.27 (dd, 1H, $J = 4.6$, 12.1 Hz, H-6a), 4.10 - 4.02 (m, 2H, H-5, H-6b), 3.89 (dd, 1H, $J = 3.7$, 9.9 Hz, H-2), 2.14, 2.07, 2.06 (3s, 3H each, $COCH_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.3, 170.5, 169.5 ($3 \times \underline{C}OCH_3$), 154.6 (C-1′), 129.7 (C-4′), 128.4 (C-2′, C-6′), 118.0 (C-3′, C-5′), 97.2 (C-1), 73.2, 70.8, 68.5, 67.6, 61.6 (C-6), 20.8, 20.6, 20.5 ($CO\underline{C}H_3$); ESI-MS: Calcd for $C_{18}H_{21}O_9NaCl$ ($[M+Na]^+$): 439.0772, found: 439.0772.

3.7. *p*-Fluorophenyl 3,4,6-tri-*O*-acetyl-α-D-glucopyranoside (6e)

Mp 136 °C; $[\alpha]_D$ +30.2 (*c* 1, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$): δ 7.14–6.99 (m, 4H, C_6H_4F-*p*), 5.52 (d, 1H, $J = 3.7$ Hz, H-1), 5.44 (t, 1H, $J = 9.8$ Hz, H-3), 5.12 (t, 1H, $J = 9.8$ Hz, H-4), 4.25 (dd, 1H, $J = 4.0$, 12.1 Hz, H-6a), 4.13–4.06 (m, 2H, H-5, H-6b), 3.87 (dd, 1H, $J = 3.8$, 9.9 Hz, H-2), 2.13, 2.07, 2.06 (3s, 3H each, $COCH_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.3, 170.5, 169.6 ($3 \times \underline{C}OCH_3$), 158.7 ($J_{C4',F} = 240.1$ Hz, C-4′), 152.2 (C-1′), 118.1 ($J_{C',F} = 8.2$ Hz, C-2′, C-6′), 116.2 ($J_{C',F} = 23.1$ Hz, C-3′, C-5′), 97.2 (C-1), 73.2, 70.8, 68.4, 67.7, 61.8 (C-6), 20.8, 20.6, 20.5 ($CO\underline{C}H_3$); ESI-MS: Calcd for $C_{18}H_{21}O_9FNa$ ($[M+Na]^+$): 423.1067, found: 423.1058.

3.8. Phenyl 3,4,6-tri-*O*-acetyl-α-D-galactopyranoside (7a)

Mp 168 °C; $[\alpha]_D$ +117.1 (*c* 1, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$): δ 7.38–7.08 (m, 5H, Ph), 5.68 (d, 1H, $J = 3.8$ Hz, H-1), 5.50 (d, 1H, H-4), 5.39 (dd, 1H, $J = 3.5$, 10.8 Hz, H-3), 4.35 (t, 1H, $J = 6.9$ Hz, H-5), 4.20–4.06 (m, 3H, H-2, H-6a, H-6b), 2.19, 2.07, 1.98 (3s, 3H each, $COCH_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.8, 170.4, 170.1 ($3 \times \underline{C}OCH_3$), 156.1 (C-1′), 129.7, 128.1, 116.8, 97.6 (C-1), 70.6, 68.2, 67.6, 67.1, 61.6 (C-6), 20.8, 20.6, 20.5 ($CO\underline{C}H_3$); ESI-MS: Calcd for $C_{18}H_{22}O_9Na$ ($[M+Na]^+$): 405.1162, found: 405.1161.

3.9. *p*-Cresyl 3,4,6-tri-*O*-acetyl-α-D-galactopyranoside (7b)

$[\alpha]_D$ +152.8 (*c* 1, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$): δ 7.13 (d, 2H, $J = 8.4$ Hz, H-2′, H-6′), 7.01 (d, 2H, $J = 8.4$ Hz, H-3′, H-5′), 5.60 (d, 1H, $J = 3.8$ Hz, H-1), 5.49 (d, 1H, H-4), 5.37 (dd, 1H, $J = 3.3$, 10.4 Hz, H-3), 4.34 (t, 1H, $J = 6.6$ Hz, H-5), 4.16–4.07 (m, 3H, H-2, H-6a, H-6b), 2.32 (s, 3H, PhCH_3-*p*), 2.18, 2.11, 2.08 (3s, 3H each, $COCH_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.8, 170.3, 170.1 ($3 \times \underline{C}OCH_3$), 154.1 (C-1′), 133.0 (C-4′), 130.1 (C-2′, C-6′), 116.9 (C-3′, C-5′), 98.0 (C-1), 70.6, 68.1, 67.5, 67.2, 61.6 (C-6), 29.6 (Ph$\underline{C}H_3$-*p*), 20.8, 20.6, 20.5 ($CO\underline{C}H_3$); ESI-MS: Calcd for $C_{19}H_{24}O_9Na$ ($[M+Na]^+$): 419.1318, found: 419.1339.

3.10. *p*-Methoxyphenyl 3,4,6-tri-*O*-acetyl-α-D-galactopyranoside (7c)

$[\alpha]_D$ +117.1 (*c* 1, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$): δ 7.05 (d, 2H, $J = 9.1$ Hz, H-2′, H-6′), 6.86 (d, 2H, $J = 9.1$ Hz, H-3′, H-5′), 5.54 (d, 1H, $J = 3.6$ Hz, H-1), 5.50 (d, 1H, H-4), 5.36 (dd, 1H, $J = 3.2$, 10.4 Hz, H-3), 4.40 (t, 1H, $J = 6.6$ Hz, H-5), 4.14–4.10 (m, 3H, H-2, H-6a, H-6b), 3.80 (s, 3H, PhOCH_3-*p*), 2.18, 2.11, 2.20 (3s, 3H each, $COCH_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.9, 170.4, 170.2 ($3 \times \underline{C}OCH_3$), 155.6 (C-1′), 150.2 (C-4′), 118.4 (C-2′, C-6′), 114.7 (C-3′, C-5′), 98.6 (C-1), 70.6, 68.2, 67.5, 67.2, 61.8 (C-6), 55.6 (PhO$\underline{C}H_3$-*p*), 20.8, 20.7, 20.6 ($CO\underline{C}H_3$); ESI-MS: Calcd for $C_{19}H_{24}O_{10}Na$ ($[M+Na]^+$): 435.1267, found: 435.1262.

3.11. *p*-Chlorophenyl 3,4,6-tri-*O*-acetyl-α-D-galactopyranoside (7d)

$[\alpha]_D$ +147.3 (*c* 1, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$): δ 7.30 (d, 2H, $J = 8.8$ Hz, H-3′, H-5′), 7.07 (d, 2H, $J = 8.8$ Hz, H-2′, H-6′), 5.62 (d, 1H, $J = 3.7$ Hz, H-1), 5.49 (d, 1H, H-4), 5.36 (dd, 1H, $J = 3.2$, 10.4 Hz, H-3), 4.30 (t, 1H, $J = 6.4$ Hz, H-5), 4.19–4.05 (m, 3H, H-2, H-6a, H-6b), 2.18, 2.11, 1.98 ppm (3s, 3H each, $COCH_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.8, 170.3, 170.1 ($3 \times \underline{C}OCH_3$), 154.7 (C-1′), 129.6 (C-4′), 128.3, 118.2, 97.9 (C-1), 70.4, 68.0, 67.8, 67.1, 61.6 (C-6), 20.8–20.6, ($3 \times CO\underline{C}H_3$); ESI-MS: Calcd for $C_{18}H_{21}O_9NaCl$ ($[M+Na]^+$): 439.0772, found: 439.0781.

3.12. *p*-Fluorophenyl 3,4,6-tri-*O*-acetyl-α-D-galactopyranoside (7e)

Mp 127 °C; $[\alpha]_D$ +177.9 (*c* 1, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$): δ 7.09–6.99 (m, 4H, C_6H_4F-*p*), 5.56 (d, 1H, $J = 3.9$ Hz, H-1), 5.47 (d, 1H, H-4), 5.35 (dd, 1H, $J = 3.4$, 10.8 Hz, H-3), 4.32 (t, 1H, $J = 6.8$ Hz, H-5), 4.15–4.08 (m, 3H, H-2, H-6a, H-6b), 2.20, 2.07, 2.00 (3s, 3H each, $COCH_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.8, 170.3, 170.1 ($3 \times \underline{C}OCH_3$), 158.7 ($J_{C4',F} = 240.1$ Hz, C-4′), 152.3 (C-1′), 118.4 ($J_{C',F} = 8.1$ Hz, C-2′, C-6′), 116.1 ($J_{C',F} = 23.1$ Hz, C3′, C-5′), 98.4 (C-1), 70.5, 68.1, 67.7, 67.2, 61.7 (C-6), 20.8, 20.6, 20.5 ($3 \times CO\underline{C}H_3$); ESI-MS: Calcd for $C_{18}H_{21}O_9FNa$ ($[M+Na]^+$): 423.1067, found: 423.1071.

3.13. Preparation of single crystals and X-ray crystallographic analysis of phenyl 3,4,6-tri-*O*-acetyl-α-D-glucopyranoside (6a) and *p*-fluorophenyl 3,4,6-tri-*O*-acetyl-α-D-glucopyranoside (6e)

Compound **6a** and **6e** were crystallized from a mixture of EtOAc and hexane at room temperature. X-ray diffraction data were collected at room temperature in the ω–2θ scan mode on an Enraf-Nonius CAD4 diffractometer and the relevant details of data collection and refinement are given in Table 2. The structure was solved by direct methods using SHELXS-97 and the refinement was done by full matrix using SHELXL-97.[27a] ORTEP of the compound was drawn using Wingx[27b] and the packing diagrams using Mercury 1.2.1., provided by CCDC, Cambridge.

Supplementary data

Complete structural data (CCDC # 230387 and 230388) have been deposited at the Cambridge Crystallographic Data Centre which can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44) 1123-336-033; or email: deposit@ccdc.cam.ac.uk).

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