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Zeolite-catalyzed Helferich-type glycosylation of long-chain alcohols. Synthesis of acetylated alkyl 1,2-*trans* glycopyranosides and alkyl 1,2-*cis* C2-hydroxy-glycopyranosides

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Abstract—Zeolite-catalyzed glycosylation of long-chain alcohols, using the inexpensive and readily available peracetylated β-D-gluco- and galactopyranoses as glycosyl donors under solvent free conditions, has been explored for the first time. Among the various forms (H-, Na-, Fe- and Zn) of β zeolite examined as catalysts in the reaction of 1,2,3,4,6-penta-*O*-acetyl-β-D-galactopyranose with cetyl alcohol, Fe-β zeolite gave the maximum yield of 63% of cetyl 2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranoside and cetyl 3,4,6-tri-*O*-acetyl-α-D-galactopyranoside. Fe-β Zeolite-catalyzed glycosylation was found to be general affording the title compounds in each case in a moderate yield, but with a good stereoselectivity. The yield of synthetically valuable acetylated long-chain alkyl 1,2-*cis* C2-hydroxy-glycopyranosides obtained in the present single-step procedure is considerably higher than that of the previously reported multi-step method employing the Stork silicon tether approach.

Keywords: Carbohydrates; Helferich glycosylation; Fatty alcohols; Alkyl C2-hydroxy-glycoside; β Zeolite; Non-ionic surfactant

1. Introduction

Alkyl glycosides have attracted tremendous interest in recent years in view of their diverse applications as food emulsifiers, cleaning agents, personal care products and textile lubricants.[1] Alkyl glycosides are also very useful as antimicrobial agents,[2] non-ionic detergents in the isolation of membrane proteins[3] and also as drug carriers.[4] Synthetic long-chain alkyl maltosides, in particular, are also known to enhance the absorption of nasal insulin.[5] Alkyl glycosides are termed as *green* surfactants as they are prepared from naturally occurring renewable sources (sugars and fatty alcohols) and are easily biodegradable. These molecules are also highly stable under alkaline conditions as compared to the corresponding sugar fatty acid esters.[6]

The first synthesis of a long-chain alkyl glucoside was achieved in 1911 by Fischer and Helferich,[7] who also observed for the first time the thermotropic liquid crystalline property of hexadecyl β-D-glucopyranoside. Many chemical[8] methods have subsequently been developed for the synthesis of alkyl glycosides. Among the different glycosyl donors used for the chemical synthesis of alkyl glycosides, the sugar peracetates are very inexpensive and readily available. The different Lewis acids employed for the synthesis of alkyl glycosides involving sugar peracetates as donors include $SnCl_4$, $ZnCl_2$–$POCl_3$, BF_3–Et_2O and $FeCl_3$.[9] In addition, several procedures for the synthesis of alkyl glycosides have been patented.[10] Enzymatic[11] synthesis of alkyl glycosides using glycosidases as catalysts has also gained interest due to their high specificity. However, owing to the limited availability and high cost of the suitable enzymes, the enzymatic approach has not been upgraded to industrial levels.[1a]

Thus, there is still a need to develop newer, environmentally friendly as well as economical routes to long-chain alkyl glycosides based on green chemistry. Heterogeneous catalysts such as zeolites have been extensively

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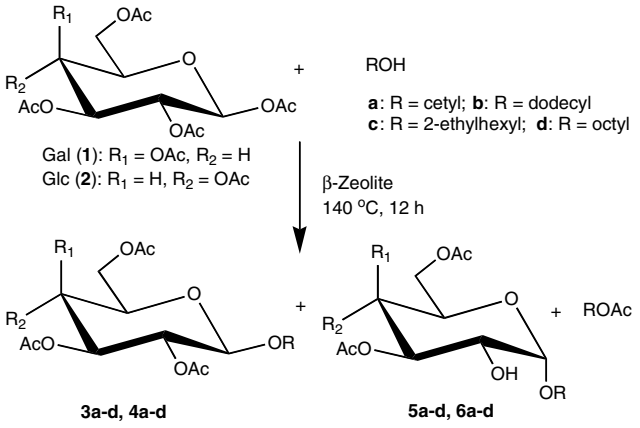
used for liquid-phase organic transformations.[12] As part of our program on the development of solid acid catalyzed carbohydrate transformations,[13] we have earlier demonstrated H-β zeolite as an efficient catalyst for the peracetylation of sugars.[14] The synthesis of various aryl glycopyranosides by H-β zeolite-catalyzed Helferich glycosylation was also reported recently from our laboratory.[15] We disclose herein the synthesis of several long-chain alkyl glycopyranosides under solvent free conditions using four different forms of β zeolite as catalysts and 1,2,3,4,6-penta-*O*-acetyl-β-D-glycopyranoses as the donors.

2. Results and discussion

The application of zeolites as heterogeneous catalysts for organic synthesis is an area of intense research. Among the various zeolites (H-EMT, H-Y, H-ZSM-5, H-ZSM-12, H-ZSM-22 and H-β zeolite) examined earlier in our laboratory as catalysts for peracetylation of sugars,[14] H-β zeolite proved to be a highly efficient catalyst probably due to its greater acid strength and larger pore openings and channel intersections. Hence, the same material was chosen for the present study. H-β Zeolite-catalyzed synthesis of long-chain alkyl glycopyranosides was initially examined using 1,2,3,4,6-penta-*O*-acetyl-β-D-galactopyranose (**1**) as the donor and cetyl alcohol (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 (EtOAc–hexane, 1:2.5) based on the extent of disappearance of peracetylated sugar donor, the reaction mixture was cooled to room temperature and worked up. Flash column chromatography of the crude product over silica gel (230–400 mesh) afforded predominantly cetyl 2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranoside (**3a**, $R_f = 0.6$; 42%) as well as cetyl 3,4,6-tri-*O*-acetyl-α-D-galactopyranoside (**5a**, $R_f = 0.2$; 19%) as the products both of which were



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

Table 1. β Zeolite-catalyzed reaction of penta-*O*-acetyl-β-D-galactopyranose with cetyl alcohol using Na-, H-, Fe- and Zn-β zeolite as catalyst

Catalyst	Yield of **3a** (%)	Yield of **5a** (%)	Total yield (%)
H-β Zeolite	42	19	61
Na-β Zeolite	35	23	58
Fe-β Zeolite	37	26	63
Zn-β Zeolite	33	17	50

characterized based on their physical and spectral data (Table 1). ^{1}H NMR spectral data of the less polar fraction ($R_f = 0.6$) (**3a**) matched well with those reported for cetyl 2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranoside.[9b]

The ^{1}H NMR spectrum of the more polar fraction ($R_f = 0.2$) (**5a**) exhibited a doublet at 4.98 ppm ($J = 3.8$ Hz) assignable to H-1 of an α-D-galactopyranoside. The singlets resonating at 2.15 and 2.07 ppm integrating for a total of nine protons revealed the presence of three acetyl groups. The anomeric proton signal in the two-dimensional ^{1}H NMR gradient COSY spectrum was observed to correlate with a doublet of doublets appearing at 3.95 ppm ($J = 3.8$ and 10.4 Hz). Hence, the latter signal was assigned to H-2. Comparison of the reported chemical shift (4.86 ppm) of H-2 of cetyl 2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranoside[9b] with the above data pointed out the upfield shift of H-2 of **5a** by 0.91 ppm due to the absence of an acetyl group at C-2. The ^{13}C NMR spectrum of compound **5a** displayed three acetoxy carbonyl carbon signals at 170.8, 170.4 and 170.2 ppm, while the anomeric carbon appeared at 98.6 ppm. The high resolution ESI-MS showed the molecular ion $[M+Na]^+$ peak at m/z 533.3356 consistent with the compound being a tri-O-acetylated cetyl galactoside. Thus the more polar fraction was characterized as cetyl 3,4,6-tri-*O*-acetyl-α-D-galactopyranoside (**5a**).

To examine the effect of varying Bronsted and Lewis acidity on the reaction yield and product selectivity, the above reaction was performed using Na, Fe and Zn forms of β zeolite under the same reaction conditions. These three reactions also afforded **3a** and **5a** as the predominant products (Table 1). However, in case of Fe-β zeolite, the combined yield of the two products was found to be the highest. Therefore, all the subsequent reactions were carried out by taking Fe-β zeolite as the catalyst. The reaction of **1** with three other long-chain alcohols also afforded the fully acetylated alkyl β-D-galactopyranosides and alkyl 3,4,6-tri-*O*-acetyl-α-D-galactopyranosides as the major products. The reaction 1,2,3,4,6-penta-*O*-acetyl-β-D-glucopyranose (**2**) with the four different long-chain alcohols under the same reaction conditions also led to the same product selectivity (Table 2), thus demonstrating the generality of Fe-β zeolite-catalyzed glycosylation of fatty alcohols.

Table 2. Fe-β Zeolite-catalyzed synthesis of alkyl glycoside using sugar peracetates as the donors and long-chain fatty alcohols as the acceptors

Sr. no.	Acceptor	Donor	Products	Yield (%)	Products	Yield (%)	Total yield (%)
1	Cetyl alcohol	**1**	**3a**	37	**5a**	26	63
2	Dodecyl alcohol	**1**	**3b**	38	**5b**	28	66
3	2-Ethylhexanol	**1**	**3c**	40	**5c**	23	63
4	Octanol	**1**	**3d**	43	**5d**	27	70
5	Cetyl alcohol	**2**	**4a**	33	**6a**	24	57
6	Dodecyl alcohol	**2**	**4b**	36	**6b**	25	61
7	2-Ethylhexanol	**2**	**4c**	37	**6c**	19	56
8	Octanol	**2**	**4d**	41	**6d**	24	65

All the known peracetylated alkyl β-D-glycopyranosides (**3b–d** and **4a–d**) and octyl 3,4,6-tri-*O*-acetyl-α-D-glucopyranoside (**6d**) were characterized based on comparison of their physical and spectral data with those reported in literature.[9,16] All the seven and hitherto unknown alkyl 3,4,6-tri-*O*-acetyl-α-D-glycopyranosides, **5a–d** and **6a–c**, have been fully characterized. A careful ^{1}H NMR analysis of two minor fractions, obtained from column chromatography of product mixture of each of the reactions revealed the formation of the fully acetylated alkyl α-D-glycopyranoside and alkyl 3,4,6-tri-acetyl-β-D-glycopyranoside, each in less than 5% yield. The total yield ranging from 57–70% (Table 2) of the major products obtained in the present procedure is quite good. Although the yield (33–43%) of the fully acetylated alkyl β-D-glycopyranosides is moderate, the efficiency of the present β zeolite-catalyzed method is comparable to the enzymatic synthesis of alkyl glycopyranosides both in terms of yield as well as stereoselectivity.[11] Incidentally, the yield and stereoselectivity of the acetylated alkyl 1,2-*trans* glycopyranosides and alkyl 1,2-*cis* C2-hydroxy-glycopyranosides observed here compare well with those of the corresponding aryl glycopyranosides reported earlier under similar H-β zeolite-catalyzed conditions.[15]

Acetylated alkyl C2-hydroxy-glycosides are potentially very useful intermediates for the synthesis of many biologically and industrially important targets such as dimeric anti-Shiga like toxin,[17a] Clarhamnoside (a glycospingolipid containing Galα(1,2)Gal sequence occurring in the marine sponge, *Agelas clathrodes*),[17b] Gemini surfactants[17c] and kojidextrins.[17d] In view of the significance of C2-hydroxy-glycosides, several methods have been developed for their synthesis.[18] However, each of these methods involve multiple steps. Although the formation of long-chain alkyl C2-hydroxy-glycopyranosides in trace amount was detected earlier based on TLC analysis in $SnCl_4$ catalyzed Helferich-type glycosylation,[9b] this is the first report on zeolite-catalyzed single-step synthesis of alkyl C2-hydroxy-glycosides from sugar peracetates and the yield obtained is also the highest. The stereoselective formation of 1,2-*cis* linkages, in general, is considerably more challenging. An extension of the Stork silicon tether approach by Bols,[16] represents the only report on the preparation of alkyl (octyl) 1,2-*cis* C2-hydroxy-glycopyranosides. This five-step synthesis starting from β-D-glucose pentaacetate (**2**) afforded octyl 3,4,6-tri-*O*-acetyl-α-D-glucopyranoside (**6d**) in an overall yield of only ~11%.

In conclusion, zeolite-catalyzed glycosylation of fatty alcohols using peracetylated sugars as donors was demonstrated for the first time. Fe-β zeolite-catalyzed glycosylation was found to be general for the preparation of various long-chain alkyl glycopyranosides in a moderate yield. The single-step synthesis reported here represents the most efficient methodology developed so far for acetylated alkyl 1,2-*cis* C2-hydroxy-glycopyranosides. The present solid acid catalyzed procedure would prove to be very useful for the preparation of these selectively functionalized compounds, which are valuable intermediates for the synthesis of (a) many naturally occurring oligosaccharides, also, naturally occurring glycoconjugates containing 1,2-linkages, and also (b) several alkyl 2-*O*-sulfo/2-halo-/2-azido/2-deoxy glycosides for various applications in glycobiology research.

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 EtOAc 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[19] at 100 °C. β Zeolite (Na form) was obtained from Süd-Chemie India Ltd, New Delhi and activated by heating to 540 °C prior to converting into various other forms as described below.

3.2. Preparation of H-β zeolite

Na-β Zeolite (10 g) was suspended in ammonium chloride solution (0.2 M, 150 mL) and stirred for 6 h at room temperature. The solid was filtered and washed several times with deionized water. The exchange operation was repeated four times. The ammonium-exchanged zeolite was then calcined at 450 °C for 12 h under the flow of air to furnish H-β zeolite.

3.3. Preparation of Zn-β zeolite

Na-β Zeolite (5 g) was stirred in an aqueous solution of zinc acetate (0.1 M, 150 mL) at 100 °C for 24 h. The solid was filtered and washed several times with deionized water. The exchanged zeolite was then calcined at 200 °C for 12 h under the flow of air to furnish Zn-β zeolite.

3.4. Preparation of Fe-β zeolite

Na-β Zeolite (5 g) was stirred in an aqueous solution of ferric nitrate (0.1 M, 150 mL) at 100 °C for 24 h. The solid was filtered and processed as mentioned above to furnish Fe-β zeolite.

3.5. General procedure for synthesis of alkyl 2,3,4,6-tetra-*O*-acetyl-β-D-glycopyranosides (3a–d, 4a–d) and alkyl 3,4,6-tri-*O*-acetyl-α-D-glycopyranosides (5a–d, 6a–d)

A mixture of penta-*O*-acetyl-β-D-glycopyranose (1 mmol) and long-chain fatty alcohol (5 mmol) was heated under stirring to form a homogeneous melt. To this melt, freshly activated β zeolite (0.2 g) was added and the mixture was heated at 140 °C. The progress of the reaction was monitored by TLC (EtOAc–hexane, 2:3). After 14 h, the reaction mixture was cooled to room temperature. To this mixture, chloroform (40 mL) was added and then heated at reflux for 1 h to extract the product from zeolite pores. The catalyst was then filtered and the extraction with chloroform was repeated twice. The combined filtrate was concentrated under reduced pressure to give a residue that was subjected to flash column chromatography over silica gel. Initial elution with a mixture of EtOAc and hexane (9:91) gave the fully acetylated alkyl glycopyranosides (**3a**–**d** and **4a**–**d**), while further elution with (11:89) mixture of the same solvents afforded the tri-O-acetylated C2-hydroxy-glycopyranosides (**5a**–**d**, **6a**–**d**).

3.6. Cetyl 3,4,6-tri-*O*-acetyl-α-D-galactopyranoside (5a)

Syrup; $[\alpha]_D$ +48.4 (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 5.42 (m, 1H, H-4), 5.13 (dd, 1H, $J = 3.2$, 10.4 Hz, H-3), 4.98 (d, 1H, $J = 3.8$ Hz, H-1), 4.19 (m, 1H, H-5), 4.15–4.09 (m, 2H, H-6a, H-6b), 3.95 (dd, 1H, $J = 3.8$, 10.4 Hz, H-2), 3.75 (m, 1H, *H*1′a), 3.51 (m, 1H, *H*1′b), 2.15, 2.07, 2.06 (3s, 9H, $3 \times COCH_3$), 1.65 (m, 2H, $-CH_2$), 1.35–1.10 (m, 26H, $13 \times -CH_2-$), 0.89 ppm (m, 3H, $-CH_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.8, 170.4, 170.2 ($3 \times -COCH_3$), 98.6 (C-1), 70.9, 68.9, 68.3, 67.1, 66.7, 61.9 (C-6), 31.9, 29.7, 29.7, 29.6, 29.6, 29.4, 29.4, 29.4, 26.2, 22.7, 20.8, 20.7, 20.6 ($3 \times -COCH_3$), 14.1 ($-CH_3$); ESI-MS: calcd for $C_{28}H_{50}O_9Na$ $[M+Na]^+$: 553.3353. Found: 553.3356.

3.7. Dodecyl 3,4,6-tri-*O*-acetyl-α-D-galactopyranoside (5b)

Syrup; $[\alpha]_D$ +52.5 (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 5.41 (m, 1H, H-4), 5.13 (dd, 1H, $J = 3.2$, 10.4 Hz, H-3), 4.98 (d, 1H, $J = 4.0$ Hz, H-1), 4.18 (m, 1H, H-5), 4.12–4.07 (m, 2H, H-6a, H-6b), 3.95 (dd, 1H, $J = 4.0$, 10.4 Hz, H-2), 3.75 (m, 1H, *H*1′a), 3.52 (m, 1H, *H*1′b), 2.15 (s, 3H, $COCH_3$), 2.07 (s, 6H, $2 \times COCH_3$), 1.63 (m, 2H, $-CH_2$), 1.43–1.16 (m, 18H, $9 \times -CH_2-$), 0.88 ppm (t, 3H, $-CH_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.8, 170.4, 170.2 ($3 \times -COCH_3$), 98.5 (C-1), 70.9, 68.9, 68.3, 67.1, 66.7, 61.9 (C-6), 31.9, 29.7, 29.7, 29.6, 29.5, 29.4, 29.4, 29.3, 26.2, 22.7, 20.9, 20.7, 20.7 ($3 \times -COCH_3$), 14.1 ($-CH_3$); ESI-MS: calcd for $C_{24}H_{42}O_9Na$ $[M+Na]^+$: 497.2727. Found: 497.2735.

3.8. 2′-Ethylhexyl 3,4,6-tri-*O*-acetyl-α-D-galactopyranoside (5c)

Syrup; ^1H NMR (400 MHz, $CDCl_3$): δ 5.42 (m, 1H, H-4), 5.10 (dd, 1H, $J = 3.3$, 10.3 Hz, H-3), 4.97 (d, 1H, $J = 3.6$ Hz, H-1), 4.17 (m, 1H, H-5), 4.15–4.08 (m, 2H, H-6a, H-6b), 3.97 (dd, 1H, $J = 3.6$, 10.3 Hz, H-2), 3.71 (m, 1H, *H*1′a), 3.39 (m, 1H, *H*1′b), 2.15, 2.08, 2.07 (3s, 9H, $3 \times COCH_3$), 1.64–1.15 (m, 9H), 0.99–0.78 ppm (m, 6H, $2 \times CH_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.8, 170.4, 170.2, 98.7 (C-1), 98.6 (C-1), 71.3, 70.9, 68.3, 67.2, 66.7, 62.0 (C-6), 39.5, 39.4, 31.9, 30.5, 30.4, 29.7, 29.3, 29.0, 23.9, 23.8, 23.0, 22.7, 20.8, 20.6, 20.6, 14.1, 14.0 ($-CH_3$), 11.1, 10.9 ($-CH_3$); ESI-MS: calcd for $C_{20}H_{34}O_9Na$ $[M+Na]^+$: 441.2101. Found: 441.2109.

3.9. Octyl 3,4,6-tri-*O*-acetyl-α-D-galactopyranoside (5d)

Syrup; $[\alpha]_D$ +18.8 (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 5.40 (m, 1H, H-4), 5.11 (dd, 1H, $J = 3.3$, 10.4 Hz, H-3), 4.97 (d, 1H, $J = 4.0$ Hz, H-1), 4.17 (m, 1H, H-5), 4.14–4.05 (m, 2H, H-6a, H-6b), 3.94 (m, 1H, H-2), 3.74 (m, 1H, *H*1′a), 3.50 (m, 1H, *H*1′b), 2.15 (s, 3H, $COCH_3$), 2.05 (s, 6H, $2 \times COCH_3$), 1.62 (m, 2H, $-CH_2$), 1.40–1.17 (m, 10H, $5 \times -CH_2-$), 0.87 ppm (m, 3H, $-CH_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.8,

170.4, 170.2 (3 × –*C*OCH$_3$), 98.5 (C-1), 70.8, 68.9, 68.3, 67.0, 66.7, 61.9 (C-6), 31.9, 29.7, 29.4, 29.2, 26.1, 22.6, 20.8, 20.7, 20.6 (3 × CO*C*H$_3$), 14.0 (–CH$_3$); ESI-MS: calcd for $C_{20}H_{34}O_9Na$ $[M+Na]^+$: 441.2101. Found: 441.2093.

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

Syrup; $[\alpha]_D$ +18.8 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.25 (t, 1H, 9.6 Hz, H-3), 5.03 (t, 1H, $J = 9.6$ Hz, H-4), 4.93 (d, 1H, $J = 3.8$ Hz, H-1), 4.29 (dd, 1H, $J = 4.6$, 12.3 Hz, H-6a), 4.09 (dd, 1H, $J = 2.1$, 12.3 Hz, H-6b), 3.98 (m, 1H, H-5), 3.76 (m, 1H, *H*1′a), 3.70 (dd, 1H, $J = 3.8$, 9.6 Hz, H-2), 3.52 (m, 1H, *H*1′b), 2.11 (s, 6H, 2 × COC*H*$_3$), 2.06 (s, 3H, COC*H*$_3$); 1.66 (m, 2H, –CH$_2$), 1.40–1.15 (m, 26H, 13 × –CH$_2$–), 0.88 ppm (m, 3H, –CH$_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.9, 170.7, 169.6, 98.2 (C-1), 73.6, 70.9, 69.0, 68.0, 67.6, 62.0 (C-6), 31.9, 29.7, 29.7, 29.6, 29.5, 29.4, 29.3, 26.1, 22.7, 20.9, 20.7, 20.6 (3 × –CO*C*H$_3$), 14.1 (–CH$_3$); ESI-MS: calcd for $C_{28}H_{50}O_9Na$ $[M+Na]^+$: 553.3353. Found: 553.3356.

3.11. Dodecyl 3,4,6-tri-*O*-acetyl-α-D-glucopyranoside (6b)

Syrup; $[\alpha]_D$ +25.2 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.24 (t, 1H, $J = 9.6$ Hz, H-3), 5.02 (t, 1H, $J = 9.6$ Hz, H-4), 4.93 (d, 1H, $J = 3.8$ Hz, H-1), 4.28 (dd, 1H, $J = 4.7$, 12.3 Hz, H-6a), 4.10 (dd, 1H, $J = 2.1$, 12.3 Hz, H-6b), 3.98 (m, 1H, H-5), 3.75 (m, 1H, *H*1′a), 3.70 (dd, 1H, $J = 3.8$, 9.6 Hz, H-2), 3.51 (m, 1H, *H*1′b), 2.11, 2.10, 2.05 (3s, 9H, 3 × COC*H*$_3$); 1.59 (m, 2H, –CH$_2$), 1.39–1.14 (m, 18H, 9 × –CH$_2$–), 0.89 ppm (m, 3H, –CH$_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.7, 170.3, 170.2 (3 × –*C*OCH$_3$), 98.5 (C-1), 70.9, 68.9, 68.3, 67.1, 66.7, 61.9 (C-6), 31.9, 29.7, 29.6, 29.5, 29.4, 29.3, 26.2, 22.7, 20.8, 20.7, 20.6 (3 × –CO*C*H$_3$), 14.1 (–CH$_3$); ESI-MS: calcd for $C_{24}H_{42}O_9Na$: 497.2727 $[M+Na]^+$. Found: 497.2726.

3.12. 2′-Ethylhexyl 3,4,6-tri-*O*-acetyl-α-D-glucopyranoside (6c)

Syrup; ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.22 (t, 1H, $J = 9.7$ Hz, H-3), 5.02 (t, 1H, $J = 9.7$ Hz, H-4), 4.91 (d, 1H, $J = 3.9$ Hz, H-1), 4.27 (dd, 1H, $J = 4.9$, 12.3 Hz, H-6a), 4.10 (dd, 1H, $J = 2.1$, 12.3 Hz, H-6b), 3.96 (m, 1H, H-5), 3.74–3.62 (m, 2H, *H*1′a, H-2), 3.39 (m, 1H, *H*1′b), 2.11, 2.10, 2.06 (3s, 9H, –COC*H*$_3$), 1.70–1.10 (m, 9H), 0.94–0.78 ppm (m, 6H, 2 × CH$_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.1, 170.6, 169.6 (3 × –*C*OCH$_3$), 98.4 (C-1), 98.3 (C-1), 73.6, 71.4, 71.0, 68.1, 67.8, 62.1 (C-6), 39.5, 39.4, 30.4, 30.4, 29.0, 23.9, 23.7, 23.0, 20.9, 20.7, 20.6 (3 × –CO*C*H$_3$), 14.0 (–CH$_3$), 11.1, 10.9 (–CH$_3$); ESI-MS: calcd for $C_{20}H_{34}O_9Na$ $[M+Na]^+$: 441.2101. Found: 441.2102.

3.13. Octyl 3,4,6-tri-*O*-acetyl-α-D-glucopyranoside (6d)

Syrup; $[\alpha]_D$ +113 (*c* 0.2 CH_2Cl_2); lit.[16] $[\alpha]_D$ +116 (*c* 0.2, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.24 (t, 1H, $J = 9.7$ Hz, H-3), 5.02 (t, 1H, $J = 9.7$ Hz, H-4), 4.93 (d, 1H, $J = 3.9$ Hz, H-1), 4.28 (dd, 1H, $J = 4.6$, 12.2 Hz, H-6a), 4.11 (dd, 1H, $J = 2.1$, 12.2 Hz, H-6b), 3.97 (m, 1H, H-5), 3.76 (m, 1H, *H*1′a), 3.70 (dd, 1H, $J = 3.9$, 9.7 Hz, H-2), 3.52 (m, 1H, *H*1′b), 2.11, 2.10, 2.05 (3s, 9H, 3 × COC*H*$_3$), 1.55 (m, 2H, –CH$_2$), 1.42–1.15 (m, 10H, 5 × –CH$_2$–), 0.89 ppm (m, 3H, –CH$_3$).

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.carres.2006.12.014.

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