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Short Communication

Efficient glycosylation of unprotected sugars using sulfamic acid: A mild eco-friendly catalyst

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ABSTRACT

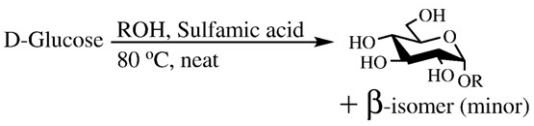
Sulfamic acid, a mild and environmentally benign catalyst has been successfully used in the Fischer glycosylation of unprotected sugars for the preparation alkyl glycosides. A diverse range of aliphatic alcohols have been used to prepare a series of alkyl glycosides in good to excellent yield.

1. Introduction

Carbohydrates in the form of glycosides and glycoconjugates play important roles in many biological processes [1]. As a consequence, the chemistry of glycosides and glycoconjugates has gained much attention for many years [2,3]. Alkyl glycosides are useful intermediates in the synthesis of complex oligosaccharides and natural products. Starting from the pioneering work of Koenigs and Knorr [4] for the glycoside formation, several glycosylation techniques have appeared in the literature [5,6], which often require judicious protecting group manipulations. Glycoside bond formation without involving tedious protection–deprotection techniques is always welcome in the synthetic carbohydrate chemistry. Fischer glycosylation offers a useful method for the preparation of simple alkyl or aryl glycosides from the unprotected, unactivated reducing sugars [7]. Conventionally, Fischer glycosylation involves the treatment of a reducing sugar with an alcohol at an elevated temperature in the presence of a protic or Lewis acid [8,9] to furnish an alkyl glycoside. The conventional Fischer glycosylation reaction has been improved using heterogeneous solid acid catalysts [10,11], microwave irradiation [12], ultrasonication [13], reduced pressure [14] and room temperature ionic liquids [15,16] etc. Despite of their usefulness, the reaction conditions suffer from a number of serious shortcomings such as use of large excess of alcohols (important concern for expensive alcohols), strong mineral acids or Lewis acids, preparation of catalysts in some cases, longer reaction time, decomposition of the product under reaction condition, requirement of special techniques (e.g. microwave, ultrasonication) etc. Therefore, there is a constant need to develop a mild, eco-friendly reaction condition for the Fischer glycosylation for the preparation of alkyl glycosides. In this context, it was envisioned that application of a mild catalyst/condition could be beneficial to access a diverse range of unprotected alkyl glycosides under Fischer glycosylation. In the recent past, we noted the application of sulfamic acid (SA) as a mild eco-friendly catalyst in several organic transformations [17–19]. Sulfamic acid has unique structural properties such as zwitterionic form ($H_3N^+SO_3^-$), moderate acidity (pKa = 1.0), non-volatile, non-corrosive, and inexpensive. We sought to explore the catalytic activity of SA in the Fischer glycosylation of unprotected and unactivated reducing sugars under neat reaction condition. We report herein our findings on SA catalyzed Fischer glycosylation of unprotected reducing sugars with a diverse range of alcohols to furnish alkyl glycosides (Scheme 1).

2. Results and discussion

In the initial set of reactions, D-glucose (**1**) was allowed to react with a varied quantity of benzyl alcohol (3–10 equiv.) in the presence of SA (0.2 equiv. to 0.5 equiv.) at 60 °C to 100 °C in a neat reaction condition. After a series of experimentation it was observed that



Scheme 1. Sulfamic acid (SA) catalyzed Fischer glycosylation of unprotected reducing sugars for the preparation of alkyl glycosides.

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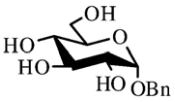
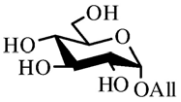
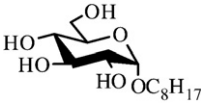
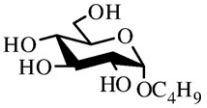
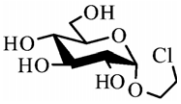
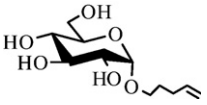
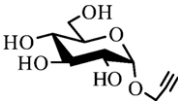
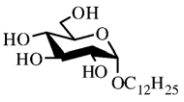
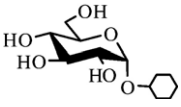
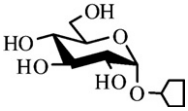
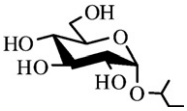
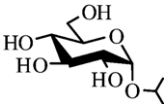
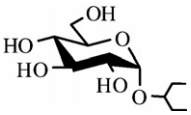
Table 1
Sulfamic acid (SA) catalyzed Fischer glycosylation of unprotected reducing sugars for the preparation of alkyl glycosides[a].

Sl. No.	Unprotected sugar	Alcohol	Product	Time (h)	Yield (%)	α/β	Ref
1	D-Glucose (**1**)	Benzyl alcohol	 **6**	5.0	81	6	[20]
2		Allyl alcohol	 **7**	4.0	82	5.5	[21]
3		1-Octanol	 **8**	5.0	80	11	[10]
4		1-Butanol	 **9**	4.0	85	4	[22]
5		2-Chloro ethanol	 **10**	5.0	82	9	[23]
6		4-Pentenol	 **11**	4.0	80	8	[24]
7		Propargyl alcohol	 **12**	4.0	78	9	[10]
8		1-Dodecanol	 **13**	5.0	72	8	[10]
9		Cyclohexanol	 **14**	4.0	76	6	[25]
10		Cyclopentanol	 **15**	4.0	72	4	[26]
11		2-Butanol	 **16**	4.0	75	4	[27]
12		2-Propanol	 **17**	3.5	80	3	[28]
13		3-Pentanol	 **18**	4.0	78	5	–

(continued on next page)

Table 1 (*continued*)

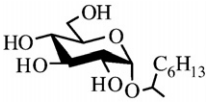
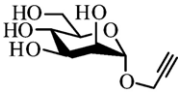
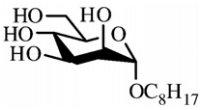
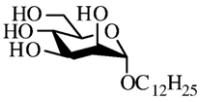
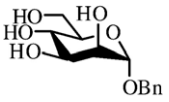
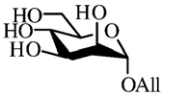
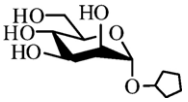
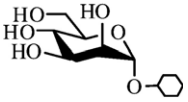
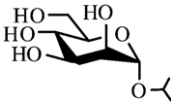
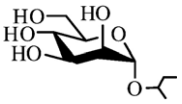
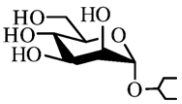
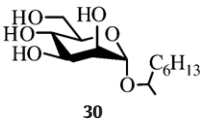
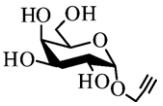
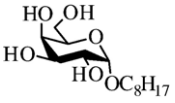
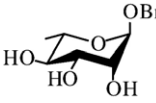
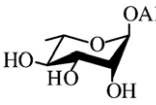
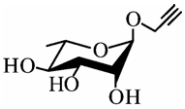
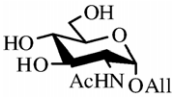
Sl. No.	Unprotected sugar	Alcohol	Product	Time (h)	Yield (%)	α/β	Ref
14		2-Octanol	 **19**	7.0	70	5	–
15		Tert-butanol	No Product	9.0	–	–	–
16		2-Methyl-2-butanol	No Product	9.0	–	–	–
17	D-Mannose (**2**)	Propargyl alcohol	 **20**	3.0	76	α	[10]
18		1-Octanol	 **21**	4.0	80	6	[29]
19		1-Dodecanol	 **22**	6.0	70	α	[29]
20		Benzyl alcohol	 **23**	3.0	73	7	[21]
21		Allyl alcohol	 **24**	3.0	78	α	[21]
22		Cyclopentanol	 **25**	4.0	75	5	–
23		Cyclohexanol	 **26**	4.0	72	8	[30]
24		2-Propanol	 **27**	3.0	82	9	[31]
25		2-Butanol	 **28**	3.0	76	8	[32]
26		3-pentanol	 **29**	4.0	75	6	–
27		2-Octanol	 **30**	7.0	72	5	–
28	D-Galactose (**3**)	Propargyl alcohol	 **31**	4.0	78	8	[10]

Table 1 (*continued*)

Sl. No.	Unprotected sugar	Alcohol	Product	Time (h)	Yield (%)	α/β	Ref
29		1-Octanol	 **32**	4.0	76	6	[33]
30	L-Rhamnose (**4**)	Benzyl alcohol	 **33**	2.5	82	α	[34]
31		Allyl alcohol	 **34**	2.5	85	α	[34]
32		Propargyl alcohol	 **35**	2.5	80	α	[10]
33	*N*-Acetyl-D-glucosamine (**5**)	Allyl alcohol	 **36**	3.0	74	4	[35]

[a] All reactions were carried out at 80 °C. All: Allyl; Bn: benzyl.

reaction of D-glucose (**1**) with benzyl alcohol (4.0 equiv.) in the presence of SA (0.2 equiv.) at 80 °C led to the formation of benzyl D-glucoside (**6**) in 81% yield in 5 h as anomeric mixture (α:β = 6:1). The reaction condition has been generalized by treating a set of aliphatic alcohols with D-glucose (**1**) under similar reaction condition to furnish a series of alkyl glucosides in excellent yield. Apart from the preparation of different glucosides, other unprotected monosaccharides (e.g. D-mannose, D-galactose, *N*-acetyl-D-glucosamine, L-rhamnose etc.) were also allowed to react with different alcohols under similar reaction condition to furnish corresponding glycosides in satisfactory yield. Reaction of a series of primary and secondary alcohols with free sugars gave satisfactory yield of alkyl glycosides. However, treatment of tertiary alcohols with free sugars under the similar reaction conditions resulted in the decomposition of the reagents and did not furnish any product may be due to the polymerization of tertiary alcohols in the presence of acid under the reaction conditions. The findings of the treatment of various 1°, 2° and 3° alcohols with different unprotected sugars in the presence of SA at 80 °C are presented in Table 1. For detailed characterization of the products, after completion of the reaction the crude products were acetylated by adding acetic anhydride to the reaction mixture in the presence of SA already present in the reaction mixture. In this case, SA can act simultaneously as an acidic catalyst for Fischer glycosylation and acetylation. It is worth mentioning that because of the mild acidity of SA, the products were not decomposed with time as in the case of some strong acidic catalysts. The NMR spectral analysis of the acetylated products revealed the formation of the products as a mixture of α- and β-anomers. The ratio of the anomeric mixture of the products was determined by comparing the integration values of the peaks in the ^{1}H NMR and ^{13}C NMR spectra. Although a mixture of the anomers were formed, α-product was the major isomer in all cases. A large scale formation of benzyl D-glucoside from D-glucose (100 mmol) was achieved in similar yield using similar stoichiometric reagents and reaction condition. Although furanosidic glycosides and acyclic acetals were formed in small quantities in some of the earlier reported reaction conditions [8], no such by products were formed under the present reaction condition. In a control experiment, a mixture of D-glucose and benzyl alcohol was allowed to stir at 80 °C without SA. No trace of the formation of product was observed even after 16 h confirming the catalytic activity of SA. A comparative study on the catalytic potential of SA with other reported catalysts has also been performed, which is presented in Table 2. In the comparative study, using triflic acid as a protic acid catalyst the reaction proceeded with almost similar yield of the product that obtained with sulfamic acid. However, use of sulfamic acid in this purpose is beneficial because of the fact that triflic acid is moisture sensitive and corrosive in nature. From the comparative study it is evident that SA can be considered as a useful alternative to the existing reaction protocols. All known compounds gave acceptable spectral data matched with the cited references.

3. Conclusion

In conclusion, sulfamic acid (SA) has been successfully applied as a catalyst in the Fischer glycosylation for the preparation of alkyl glycosides from unprotected and unactivated reducing sugars. The reaction condition is reasonably mild, high yielding, applicable for scale-up preparation and can be considered as an attractive alternative to the existing procedures.

4. Experimental

4.1. General methods

All reactions were monitored by thin layer chromatography over silica gel coated TLC plates. The spots on TLC were visualized by warming ceric sulphate (2% $Ce(SO_4)_2$ in 2 N H_2SO_4) sprayed plates in

Table 2
Comparisons of the catalytic potential of different catalysts in the Fischer glycosylation of D-glucose using benzyl alcohol at 80 °C.

Sl. No.	Catalyst	Catalyst load	Time (h)	Yield (%)
1	$BF_3.OEt_2$	1.0 equiv.	16	52
2	Amberlite IR 120	100 mg/mmol	24	60
3	$Sc(OTf)_3$	0.1 equiv.	24	55
4	$HClO_4$–SiO_2	50 mg/mmol	5	72
5	Sulfamic acid	0.2 equiv.	5	81
6	TfOH	0.2 equiv.	5	77

hot plate. Silica gel 230–400 mesh was used for column chromatography. ^{1}H and ^{13}C NMR spectra were recorded on Brucker Advance DPX 200 MHz using $CDCl_3$ as solvent and TMS as internal reference unless stated otherwise. Chemical shift value is expressed in δ ppm. ESI-MS were recorded on a Micromass Quttro II mass spectrometer. Commercially available grades of organic solvents of adequate purity are used in all reactions.

4.2. Typical procedure for the Fischer glycosylation

To a suspension of D-glucose (0.9 g, 5.0 mmol) in benzyl alcohol (2.0 mL, 20.0 mmol) was added sulfamic acid (100 mg, 1.0 mmol) at room temperature and the neat reaction mixture was allowed to stir at 80 °C for 5 h (Table 1). After completion of the reaction, the solvents was removed under pressure and the crude product was passed through a short pad of silica using CH_2Cl_2-CH_3OH (20:1) to furnish pure compound **6** (1.1 g, 81%). In order to prepare the analytical sample for NMR spectral analysis, excess benzyl alcohol was removed from the reaction mixture and acetic anhydride (3.0 mL) was added to it and the reaction mixture was allowed to stir at 60 °C for 2 h. The solvents were removed under reduced pressure and the crude product was passed through a short pad of silica using hexane-EtOAc (3:1) to furnish pure acetylated compound **6**. Following the similar reaction methodology a series of alkyl glycosides were prepared in excellent yield. All products were acetylated for their characterization by NMR spectral analysis. Selected spectral data of compounds are presented below.

4.2.1. 1-Butyl 2,3,4,6-tetra-O-acetyl-α-D-Glucopyranoside (9)

^{1}H NMR (200 Hz, $CDCl_3$): δ 5.38 (t, J = 10.0 Hz each, 1 H, H-3), 5.07–4.91 (m, 2 H, H-1, H-4), 4.75 (dd, J = 10.2, 3.6 Hz, 1 H, H-2), 4.24–4.15 (m, 1 H, H-5), 4.08–3.90 (m, 2 H, H-6_{ab}), 3.68–3.57 (m, 1 H, OCH_{2a}), 3.42–3.31 (m, 1 H, OCH_{2b}), 2.02, 1.99, 1.96, 1.94 (4 s, 12 H, 4 COCH_3), 1.60-1.52 (m, 2 H, CH_2), 1.46-1.30 (m, 2 H, CH_2), 0.84 (t, J = 7.2 Hz each, 3 H, CH_3); ^{13}C NMR (50 Hz, $CDCl_3$): δ 170.5, 170.0, 169.5, 169.3 (4 $COCH_3$), 95.7 (C-1), 71.1, 70.4, 68.8, 68.5, 67.3, 62.0, 29.8, 20.8 (2 C), 20.7 (2 C), 19.3, 13.9; ESI-MS: m/z = 427.1 $[M+Na]^+$.

4.2.2. 2-Chloroethyl 2,3,4,6-tetra-O-acetyl-α-D-Glucopyranoside (10)

^{1}H NMR (200 Hz, $CDCl_3$): δ 5.39 (dd, J = 10.2 Hz each, 1 H, H-3), 5.08 (d, J = 3.8 Hz, 1 H, H-1), 4.92 (t, J = 10.1 Hz each, 1 H, H-4), 4.78 (dd, J = 10.2, 3.8 Hz, 1 H, H-2), 4.24–3.99 (m, 3 H, H-5, H-$6_{a,b}$), 3.93–3.82 (m, 1 H, OCH_{2a}), 3.77-3.52 (m, 3 H, OCH_2), 2.02, 1.99, 1.96, 1.94 (4 s, 12 H, 4 COCH_3); ^{13}C NMR (50 Hz, $CDCl_3$): δ 171.5, 170.1, 169.9, 169.5 (4 $COCH_3$), 96.2 (C-1), 70.8, 70.1, 69.0, 68.5, 67.8, 61.9, 42.5, 20.7 (4C; 4 $COCH_3$); ESI-MS: m/z = 433.1 $[M+Na]^+$.

4.2.3. 4-Pentenyl 2,3,4,6-tetra-O-acetyl-α-D-Glucopyranoside (11)

^{1}H NMR (200 Hz, $CDCl_3$): δ 5.88–5.71 (m, 1 H, $CH=CH_2$), 5.47 (t, J = 9.6 Hz each, 1 H), 5.15–4.99 (m, 4 H, H-1, H-4, $CH=CH_2$), 4.84 (dd, J = 10.0, 3.6 Hz, 1 H, H-2), 4.31–4.23 (m, 1 H, H-5), 4.16–3.99 (m, 2 H, H-6_{ab}), 3.78–3.67 (m, 1 H, OCH_{2a}), 3.56–3.40 (m, 1 H, OCH_{2b}), 2.11, 2.06, 2.0, 1.99 (4 s, 12 H, 4 COCH_3), 2.0–1.90 (m, 2 H, CH_2), 1.77–1.67 (m, 2 H, CH_2); ^{13}C NMR (50 Hz, $CDCl_3$): δ 170.5, 170.0, 169.5, 169.3 (4 $COCH_3$), 137.7, 115.4, 95.8 (C-1), 71.0, 70.3, 68.7, 67.9, 67.3, 62.0, 30.2, 28.6, 20.7 (4C, 4 $COCH_3$); ESI-MS: m/z = 439.1 $[M+Na]^+$.

4.2.4. Cyclohexyl 2,3,4,6-tetra-O-acetyl-α-D-Glucopyranoside (14)

^{1}H NMR (200 Hz, $CDCl_3$): δ 5.38 (t, J = 10.0 Hz each, 1 H, H-3), 5.08 (d, J = 3.9 Hz, 1 H, H-1), 4.86 (t, J = 10.0 Hz each, 1 H, H-4), 4.67 (dd, J = 10.0, 3.8 Hz, 1 H, H-2), 4.16–3.91 (m, 3 H, H-5, H-6_{ab}), 3.57–3.43 (m, 1 H), 1.99, 1.93, 1.91, 1.90 (4 s, 12 H, 4 COCH_3), 1.82-1.61 (m, 4 H), 1.40-1.15 (m, 6 H); ^{13}C NMR (50 Hz, $CDCl_3$): δ 170.5, 170.0, 169.5, 169.0 (4 $COCH_3$), 94.0 (C-1), 76.8, 71.1, 70.3, 68.8, 67.2, 62.0, 33.2, 31.6, 25.6, 24.0, 23.7, 20.7 (4 C, 4 $COCH_3$); ESI-MS: m/z = 453.1 $[M+Na]^+$.

4.2.5. Cyclopentyl 2,3,4,6-tetra-O-acetyl-α-D-Glucopyranoside (15)

^{1}H NMR (200 Hz, $CDCl_3$): δ 5.40 (t, J = 9.8 Hz each, 1 H, H-3), 5.11 (d, J = 3.8 Hz, 1 H, H-1), 4.94 (t, J = 9.8 Hz each, 1 H, H-4), 4.74 (dd, J = 9.8, 3.8 Hz, 1 H, H-2), 4.26–3.99 (m, 3 H, H-5, H-6_{ab}), 3.67–3.60 (m, 1 H, –CH), 2.04, 1.98, 1.97, 1.95 (4 s, 12 H, 4 COCH_3), 1.70–1.45 (m, 8 H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 170.6, 170.1, 169.6, 169.4 (4 $COCH_3$), 94.3 (C-1), 81.5, 71.4, 70.9, 70.3, 67.2, 62.1, 33.1, 31.8, 23.3, 22.9, 20.7 (2 C), 20.6 (2 C) (4 $COCH_3$); ESI-MS: 439.1 $[M+Na]^+$.

4.2.6. 2-Butyl 2,3,4,6-tetra-O-acetyl-α-D-Glucopyranoside (16)

^{1}H NMR (200 Hz, $CDCl_3$): δ 5.47 (t, J = 10.2 Hz each, 1 H, H-3), 5.18 (d, J = 3.7 Hz, 1 H, H-1), 5.05 (t, J = 10.2 Hz each, 1 H, H-4), 4.82 (dd, J = 10.1, 3.7 Hz, 1 H, H-2), 4.24–4.22 (m, 1 H, H-6_a), 4.15–4.07 (m, 2 H, H-5, H-6_b), 3.69–3.60 (m, 1 H, CH), 2.08, 2.03, 2.00 (3 s, 12 H, 4 COCH_3), 1.24-1.21 (m, 2 H, CH_2), 1.09 (d, J = 6.0 Hz, 3 H, CH_3), 0.88 (t, J = 7.4 Hz each, 3 H, CH_3); ^{13}C NMR (50 MHz, $CDCl_3$): δ 170.7 (2 C), 170.2, 169.7 (4 $COCH_3$), 95.7 (C-1), 78.2, 72.9, 71.1, 70.2, 68.7, 62.2, 24.9, 20.8 (2 C), 20.6 (2 C) (4 $COCH_3$), 19.2, 10.3; ESI-MS: 427.1 $[M+Na]^+$.

4.2.7. 2-Propyl 2,3,4,6-tetra-O-acetyl-α-D-Glucopyranoside (17)

^{1}H NMR (200 Hz, $CDCl_3$): δ 5.46 (t, J = 9.8 Hz each, 1 H, H-3), 5.17 (d, J = 3.9 Hz, 1 H, H-1), 5.02 (t, J = 9.8 Hz each, 1 H, H-4), 4.79 (dd, J = 9.8, 3.8 Hz, 1 H, H-2), 4.25–4.21 (m, 1 H, H-5), 4.12–4.05 (m, 2 H, H-6_{ab}), 3.92–3.83 (m, 1 H, CH), 2.08, 2.04, 2.02, 2.00 (4 s, 12 H, 4 COCH_3), 1.23–1.20 (m, 3 H, CH_3), 1.13–1.10 (m, 3 H, CH_3); ^{13}C NMR (50 MHz, $CDCl_3$): δ 170.8, 170.3, 170.2, 169.7 (4 $COCH_3$), 94.2 (C-1), 71.5, 71.0, 70.2, 68.8, 67.1, 62.2, 23.1, 21.6, 20.7 (2 C), 20.6 (2 C) (4 $COCH_3$); ESI-MS: 413.1 $[M+Na]^+$.

4.2.8. 3-Pentyl 2,3,4,6-tetra-O-acetyl-α-D-Glucopyranoside (18)

^{1}H NMR (200 Hz, $CDCl_3$): δ 5.52 (t, J = 9.8 Hz each, 1 H, H-3), 5.14 (d, J = 3.8 Hz, 1 H, H-1), 4.96 (t, J = 9.8 Hz each, 1 H, H-4), 4.83 (dd, J = 9.8, 3.8 Hz, 1 H, H-2), 4.26–4.04 (m, 3 H, H-5, H-6_{ab}), 3.48–3.36 (m, 1 H, CH-), 2.09, 2.03, 2.01, 1.98 (4 s, 12 H, 4 COCH_3), 1.62–1.43 (m, 4 H, 2 CH_2CH_3), 0.94–0.82 (m, 6 H, 2 CH_2CH_3); ^{13}C NMR (50 MHz, $CDCl_3$): δ 170.6, 170.1, 169.7, 169.3 (4 $COCH_3$), 95.1 (C-1), 82.5, 71.7, 71.5, 70.3, 67.4, 62.2, 26.7, 25.3, 20.7 (4 C, 4 $COCH_3$), 9.9, 9.5; ESI-MS: 441.1 $[M+Na]^+$.

4.2.9. 2-Octyl 2,3,4,6-tetra-O-acetyl-α-D-Glucopyranoside (19)

^{1}H NMR (200 Hz, $CDCl_3$): δ 5.45 (t, J = 9.6 Hz each, 1 H, H-3), 5.10 (d, J = 3.4 Hz, 1 H, H-1), 4.96 (t, J = 9.6 Hz each, 1 H, H-4), 4.82 (dd, J = 9.6, 3.4 Hz, 1 H, H-2), 4.27–4.03 (m, 3 H, H-5, H-6_{ab}), 3.70–3.60 (m, 1 H, CH), 2.04, 2.02, 2.00, 1.98 (4 s, 12 H, 4 COCH_3), 1.54–1.15 (m, 10 H), 1.10 (d, J = 6.1 Hz, 3 H, CH_3), 0.84 (t, J = 6.6 Hz, 3 H, CH_3); ^{13}C NMR (50 MHz, $CDCl_3$): δ 170.8, 170.5, 169.8, 169.6 (4 $COCH_3$), 96.1 (C-1), 73.1, 71.8, 71.5, 70.5, 68.9, 62.4, 36.9, 32.0, 25.5, 22.8, 21.7, 20.7 (4 C, 4 $COCH_3$), 19.9, 14.2; ESI-MS: 483.2 $[M+Na]^+$.

4.2.10. Cyclopentyl 2,3,4,6-tetra-O-acetyl-α-D-Mannopyranoside (25)

^{1}H NMR (200 Hz, $CDCl_3$): δ 5.38 (dd, J = 10.0, 3.3 Hz, 1 H, H-3), 5.24 (t, J = 9.9 Hz each, 1 H, H-4), 5.14–5.12 (m, 1 H, H-2), 4.85 (br s, 1 H, H-1), 4.27–4.01 (m, 3 H, H-5, H-6_{ab}), 3.51–3.31 (m, 1 H, CH), 2.10, 2.04, 1.99, 1.94 (4 s, 12 H, 4 COCH_3), 1.57–0.76 (m, 8 H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 170.6, 169.9, 169.8, 169.4 (4 $COCH_3$), 96.5 (C-1), 81.7, 70.2, 68.7, 68.2, 66.3, 62.6, 26.6, 25.3, 20.9, 20.6 (2 C), 20.3 (4 COCH_3), 9.9, 9.0; ESI-MS: 439.1 $[M+Na]^+$.

4.2.11. Cyclohexyl 2,3,4,6-tetra-O-acetyl-α-D-Mannopyranoside (26)

^{1}H NMR (200 Hz, $CDCl_3$): δ 5.36 (dd, J = 10.0, 3.3 Hz, 1 H, H-3), 5.23 (t, J = 9.9 Hz each, 1 H, H-4), 5.16–5.15 (m, 1 H, H-2), 4.92 (br s, 1 H, H-1), 4.26–4.21 (m, 1 H, H-6_a), 4.12–4.03 (m, 2 H, H-5, H-6_b), 3.59–3.51 (m, 1 H, CH), 2.12, 2.06, 2.01, 1.96 (4 s, 12 H, 4 COCH_3), 1.84–0.66 (m, 4 H), 1.50–1.18 (m, 6 H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 170.6, 170.2, 169.9, 169.8 (4 $COCH_3$), 95.8 (C-1), 76.7, 70.3, 69.2, 68.4, 66.5,

62.6, 33.1, 31.4, 25.4, 24.0, 23.8, 20.9, 20.7 (3C) (4 COCH$_3$); ESI-MS: 453.1 $[M+Na]^+$.

4.2.12. 2-Propyl 2,3,4,6-tetra-O-acetyl-α-D-Mannopyranoside (27)

^{1}H NMR (200 Hz, $CDCl_3$): δ 5.29 (dd, $J=10.0$, 3.3 Hz, 1 H, H-3), 5.19 (t, $J=9.9$ Hz each, 1 H, H-4), 5.11–5.10 (m, 1 H, H-2), 4.85 (br s, 1 H, H-1), 4.23–4.18 (m, 1 H, H-6$_a$), 4.08–3.97 (m, 2 H, H-5, H-6$_b$), 3.87–3.82 (m, 1 H, CH), 2.08, 2.02, 1.97, 1.92 (4 s, 12 H, 4 COCH$_3$), 1.18 (d, $J=6.2$ Hz, 3 H), 1.09 (d, $J=6.2$ Hz, 3 H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 170.5, 170.0, 169.7, 169.6 (4 COCH$_3$), 95.8 (C-1), 70.8, 70.1, 69.0, 68.3, 66.3, 62.5, 22.9, 21.4, 20.8, 20.6 (3 C) (4 COCH$_3$); ESI-MS: 413.1 $[M+Na]^+$.

4.2.13. 2-Butyl 2,3,4,6-tetra-O-acetyl-α-D-Mannopyranoside (28)

^{1}H NMR (200 Hz, $CDCl_3$): δ 5.30 (dd, $J=10.0$, 3.3 Hz, 1 H, H-3), 5.22 (t, $J=9.9$ Hz each, 1 H, H-4), 5.15–5.13 (m, 1 H, H-2), 4.89 (br s, 1 H, H-1), 4.24-4.20 (m, 1 H, H-6$_a$), 4.10–4.01 (m, 2 H, H-5, H-6$_b$), 3.67–3.60 (m, 1 H, CH), 2.11, 2.05, 2.01, 1.95 (4 s, 12 H, 4 COCH$_3$), 1.60–1.43 (m, 2 H), 1.17 (d, $J=6.2$ Hz, 3 H), 0.88 (d, $J=6.2$ Hz, 3 H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 170.6, 170.0, 169.8, 169.7 (4 COCH$_3$), 95.1 (C-1), 74.9, 70.1, 69.1, 68.4, 66.3, 62.5, 24.8, 20.8, 20.6 (3 C) (4 COCH$_3$), 20.4, 9.4; ESI-MS: 427.1 $[M+Na]^+$.

4.2.14. 3-Pentyl 2,3,4,6-tetra-O-acetyl-α-D-Mannopyranoside (29)

^{1}H NMR (200 Hz, $CDCl_3$): δ 5.32 (dd, $J=10.0$, 3.3 Hz, 1 H, H-3), 5.18 (t, $J=9.9$ Hz each, 1 H, H-4), 5.10–5.08 (m, 1 H, H-2), 4.79 (br s, 1 H, H-1), 4.24–3.92 (m, 3 H, H-5, H-6$_{ab}$), 3.64–3.55 (m, 1 H, CH), 2.07, 2.00, 1.98, 1.95 (4 s, 12 H, 4 COCH$_3$), 1.70–1.40 (m, 10 H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 170.5, 170.0, 169.7, 169.5 (4 COCH$_3$), 96.4 (C-1), 80.2, 70.1, 69.1, 68.5, 66.4, 62.5, 23.4, 23.0, 20.8, 20.6 (3 C) (4 COCH$_3$), 10.1 (2 C); ESI-MS: 441.1 $[M+Na]^+$.

4.2.15. 2-Octyl 2,3,4,6-tetra-O-acetyl-α-D-Mannopyranoside (30)

^{1}H NMR (200 Hz, $CDCl_3$): δ 5.29 (dd, $J=10.0$, 3.3 Hz, 1 H, H-3), 5.20 (t, $J=9.9$ Hz each, 1 H, H-4), 5.13–5.12 (m, 1 H, H-2), 4.86 (br s, 1 H, H-1), 4.28–3.97 (m, 3 H, H-5, H-6$_{ab}$), 3.72-3.62 (m, 1 H, CH), 2.11, 2.05, 2.00, 1.95 (4 s, 12 H, 4 COCH$_3$), 1.50-1.16 (m, 10 H), 1.09 (d, $J=6.1$ Hz, 3 H, CH$_3$), 0.83 (t, $J=6.6$ Hz, 3 H, CH$_3$); ^{13}C NMR (50 MHz, $CDCl_3$): δ 170.6, 170.1, 169.9, 169.7 (4 COCH$_3$), 95.1 (C-1), 73.7, 70.3, 69.1, 68.5, 66.3, 62.6, 36.3, 31.7, 25.7, 22.6, 21.0, 20.8, 20.7 (3 C) (4 COCH$_3$), 18.9, 14.0; ESI-MS: 483.2 $[M+Na]^+$.

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References

[1] P. Wang, C. Bertozzi (Eds.), Glycochemistry: Principles, Synthesis and Applications, Marcel Dekker Inc, New York, 2000.
[2] B. Ernst, G.W. Hart, P. Sinay (Eds.), Carbohydrates in Chemistry and Biology, Part I: Chemistry of Saccharides, vol. 1, Wiley-VCH, Weinheim, 2000.
[3] A.V. Demchenko, Handbook of Chemical Glycosylation, Wiley-VCH, Weinheim, 2008.
[4] W. Koenigs, E. Knorr, Ber. Dtsch. Chem. Ges. 34 (1901) 957–981.
[5] X. Zhu, R.R. Schmidt, Angew. Chem. Int. Ed. Engl. 48 (2009) 1900–1934.
[6] S. Hanessian (Ed.), Preparative Carbohydrate Chemistry, Mercel Dekker Inc, New York, 1997.
[7] E. Fischer, Ber. Dtsch. Chem. Ges. 26 (1893) 2400–2412.
[8] R. Velty, T. Benvegnu, M. Gelin, E. Privat, D. Plusquellec, Carbohydr. Res. 299 (1997) 7–14.
[9] D. Balzer, H. Luders, Nonionic Surfactants - Alkyl polyglucosides, Marcel Dekker Inc, New York, 2000.
[10] B. Roy, B. Mukhopadhyay, Tetrahedron Lett. 48 (2007) 3783–3787.
[11] U. Aich, D. Loganathan, Carbohydr. Res. 342 (2007) 704–709.
[12] L.F. Bornaghi, S.-A. Poulsen, Tetrahedron Lett. 46 (2005) 3485–3488.
[13] S. Brochette, G. Descotes, A. Bouchu, Y. Queneau, N. Monnier, C. Petrier, J. Mol. Catal. A: Chem. 123 (1997) 123–130.
[14] Y. Kuroiwa, M. Sekine, S. Tomono, D. Takahashi, K. Toshima, Tetrahedron Lett. 51 (2010) 6294–6297.
[15] J. Auge, G. Sizun, Green Chem. 11 (2009) 1179–1183.
[16] T.-J. Park, M. Weiwer, X. Yuan, S.N. Baytas, E.M. Munoz, S. Murugesan, R.J. Linhardt, Carbohydr. Res. 342 (2007) 614–620.
[17] S.D. Mitragotri, D.M. Pore, U.V. Desai, P.P. Wadgaonkar, Catal. Commun. 9 (2008) 1822–1826.
[18] D.J. Upadhyaya, A. Barge, R. Stefania, G. Cravotto, Tetrahedron Lett. 48 (2007) 8318–8322.
[19] B. Wang, Y. Gu, G. Song, T. Yang, L. Yang, J. Suo, J. Mol. Catal. A: Chem. 233 (2005) 121–126.
[20] M. Matsui, M. Okada, Chem. Pharm. Bull. 18 (1970) 2129–2131.
[21] W. Klotz, R.R. Schmidt, Liebigs Ann. Chem. (1993) 683–690.
[22] K. Tori, S. Seo, Y. Yoshimura, H. Arita, Y. Tomita, Tetrahedron Lett. 2 (1977) 179–182.
[23] P.J. Garegg, I. Kvarnstrom, Acta Chem. Scand. B. Org. Chem. Biochem. B30 (1976) 655–658.
[24] B.G. Wilson, B. Fraser-Raid, J. Org. Chem. 60 (1995) 317–320.
[25] G. Balavoine, S. Berteina, A. Gref, J.-C. Fischer, A. Lubineau, J. Carbohydr. Chem. 14 (1995) 1217–1236.
[26] S. Seo, Y. Tomita, K. Tori, Y. Yoshimura, J. Am. Chem. Soc. 100 (1978) 3331–3339.
[27] J.N. BeMiller, E.R. Doyle, Carbohydr. Res. 20 (1971) 23–30.
[28] P. Sharma, M. Alam, M.V. Chari, J. Nat. Prod. 52 (1989) 395–397.
[29] M. Poláková, M. Beláňová, L. Petruš, K. Mikušová, Carbohydr. Res. 345 (2010) 1339–1347.
[30] S.K. Mamidyala, M.G. Finn, J. Org. Chem. 74 (2009) 8417–8420.
[31] R. Kasai, M. Okihara, J. Asakawa, K. Mizutani, O. Tanaka, Tetrahedron 35 (1979) 1427–1432.
[32] P. Seroka, M. Plosinski, J. Czub, P. Sowinski, J. Pawlak, Magn. Reson. Chem. 44 (2006) 132–138.
[33] S. Malik, K.J. Shah, K.P. Ravindranathan Kartha, Carbohydr. Res. 345 (2010) 867–871.
[34] M.T. Campos-Val Des, J.R. Marino-albernas, V. Verez-Bencomo, J. Carbohydr. Chem. 6 (1987) 509–514.
[35] J.-i. Kadokawa, T. Nagaoka, J. Ebana, H. Tagaya, K. Chiba, Carbohydr. Res. 327 (2000) 341–344.