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Synthesis of trehalose mimics by bismuth(III) triflate or bis(trifluoromethane)sulfonimide-catalyzed 1-*C*-methyl-D-hexopyranosylation

Takashi Yamanoi,[a,*] Ryo Inoue,[a,b] Sho Matsuda,[a] Kaname Katsuraya[c] and Keita Hamasaki[b]

[a]*The Noguchi Institute, 1-8-1 Kaga, Itabashi-ku, Tokyo 173-0003, Japan*
[b]*Department of Applied Chemistry, Shibaura Institute of Technology, 3-7-5 Toyosu, Koto-ku, Tokyo 135-8548, Japan*
[c]*School of Home Economics, Wayo Women's University, Chiba 272-8533, Japan*

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Abstract—We investigated the ketopyranosylation of 2,3,4,6-tetra-*O*-benzyl-1-*C*-methyl-D-hexopyranoses with the benzylated D-aldohexopyranoses in order to produce novel non-reducing disaccharides as trehalose mimics. It was found that 5 mol % of bismuth(III) triflate or bis(trifluoromethane)sulfonimide efficiently catalyzed the ketopyranosylation that produced various non-reducing disaccharides.

1. Introduction

The 1-*C*-alkyl-sugars, which have alkyl groups at their anomeric carbon centers, are considered to be a novel class of artificial ketoses, which replace naturally occurring aldoses. Their glycosylated compounds, that is, 1-*C*-alkyl-glycosides, are expected to show biological functions that are different from those of natural compounds.[1] Therefore, considerable attention has been paid to efficient glycosidation methods for synthesizing 1-*C*-alkyl-*O*-glycosides.[2] We have also studied the synthesis of 1-*C*-alkyl-D-glucopyranosides by Lewis acid- or Brønsted acid-catalyzed O-glycosidation.[3] Our investigation into the 1-*C*-alkyl-D-glucopyranosylation showed that 5 mol % of Tf_2NH was an efficient activator for a dehydration–condensation O-glycosidation using 1-*C*-alkyl-2,3,4,6-tetra-*O*-benzyl-D-glucopyranoses as the ketosyl donors.[3a,c]

Another interesting finding was that the ketopyranosylation showed high α-stereoselectivity. This feature was expected to be useful for synthesizing mimics of trehalose (α-D-glucopyranosyl α-D-glucopyranoside), as this natural non-reducing disaccharide is composed of two glucose molecules linked with each other by an α-glucopyranosidic linkage.[4] Thus we attempted the dehydrative glycosidation to synthesize trehalose mimics into which 1-*C*-methyl-D-hexopyranoses were incorporated. As a result of the preliminary experiment, the fully benzylated α-D-glucopyranosyl 1-*C*-methyl-α-D-glucopyranoside derivative was successfully obtained in 47% yield by the reaction of 2,3,4,6-tetra-*O*-benzyl-1-*C*-methyl-α-D-glucopyranose **1** with 2,3,4,6-tetra-*O*-benzyl-D-glucopyranose **2** in the presence of 5 mol % Tf_2NH in CH_3CN.[3a,c]

To the best of our knowledge, this was the first example of synthesizing a non-reducing disaccharide into which a 1-*C*-methyl-D-hexopyranose was incorporated. Interestingly, the non-reducing disaccharide synthesized was obtained as a single isomer and both of its glycosidic linkages were α-configured. In addition, since trehalose is well known for its various biological activities such as the suppressive effect on osteoporosis progress,[5] this reaction was expected to have the potential for synthesizing various types of trehalose mimics, which show novel useful functions. Therefore, we made a further investigation into the glycosidation conditions of **1** with **2** and applied the reaction to the synthesis of several non-reducing disaccharides composed of a 2,3,4,6-tetra-*O*-benzyl–1-*C*-methyl-D-hexopyranose and a benzylated D-aldohexopyranose. Our investigation included not only the stereoselectivity of the glycosidation, but also a search for other effective activators of **1**, because Tf_2NH is a moisture-sensitive compound. The detailed results are described below.

* Corresponding author. Tel./fax: +81 3 5944 3213; e-mail: tyama@noguchi.or.jp

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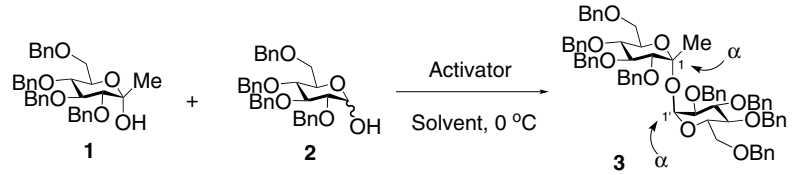


Scheme 1.

2. Results and discussion

We first investigated the glycosidation conditions of **1** with **2** using 5 mol % of Tf_2NH to afford **3** in the presence of Ca_2SO_4 (Scheme 1). These results are summarized in Table 1. Remarkably, the reaction in CH_2Cl_2 at 0 °C for 3 h increased the yield of **3** up to 87% (entry 2). This was due to the high solubility of **2** in CH_2Cl_2. Lewis acids, which were expected to be resistant to water, ytterbium(III) triflate ($Yb(OTf)_3$), scandium(III) triflate ($Sc(OTf)_3$), and bismuth(III) triflate ($Bi(OTf)_3$)[6] were used. The reactions using $Sc(OTf)_3$ and $Bi(OTf)_3$ in CH_2Cl_2 at 0 °C for 3 h gave **3** in high yields of 80% and 89%, respectively (entries 4 and 6). $Bi(OTf)_3$ was an efficient activator for the 1-*C*-methyl-glucopyranosylation,[7] while bismuth(III) trichloride ($BiCl_3$) did not work at all (entry 7). This was attributable to the weaker Lewis acidity of $BiCl_3$. Compound **3** was produced as a single isomer under the stated reaction conditions and both of its glycosidic linkages were determined as being α by analysis of the NMR spectra (NOE interaction of CH_3 and H-2, and H-1′ δ 5.34 (d, $J = 3.4$ Hz)).

Next we examined the synthesis of several non-reducing disaccharides into which **1** was incorporated (Scheme 2). As the acceptors for the 1-*C*-methyl-glucopyranosylation, 2,3,4,6-tetra-*O*-benzyl-D-mannopyranose **4**, 2-azido-3,4,6-tri-*O*-benzyl-2-deoxy-D-glucopyranose **5**, and 2,3,4,6-tetra-*O*-benzyl-D-galactopyranose **6** were utilized. Both Tf_2NH and $Bi(OTf)_3$ were used as the activators. These results are shown in Table 2. The reactions using 5 mol % of Tf_2NH in CH_2Cl_2 at 0 °C for 3 h successfully gave the corresponding disaccharides **7**–**9** in good yields of 64%, 90%, and 83%, respectively (entries 3, 5, and 7). The reaction using **4** gave benzyl 2,3,4,6-tetra–*O*-benzyl-1-*C*-methyl-α-D-glucopyranoside **12**[8] as a major by-product (Scheme 3). The reactions using 5 mol % of $Bi(OTf)_3$ as the activator also afforded **7**–**9** in 75%, 84%, and 89%, respectively (entries 4, 6, and 8).

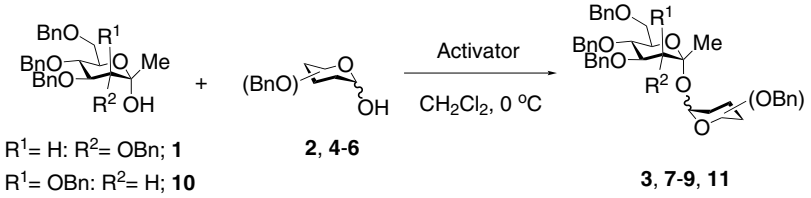
Compound **7** was obtained as a single isomer (entries 3 and 4), while **8** and **9** were formed in isomeric ratios of 78/22, 58/42 and of 87/13, 76/24, respectively (entries 5–8). The anomeric configurations of all the formed ketopyranosidic linkages of **7**–**9** were α, which were also determined by the observation of the NOE interactions between the CH_3 group and the H-2 of the 1-*C*-methyl-D-glucopyranosyl rings. The high α-stereoselectivities of the 1-*C*-methyl-D-glucopyranosylation corresponded to our former results.[3a–c] As the measurement, from the NMR, spectra of $J_{C1'-H1'}$ of **7** indicated 168 Hz, its mannopyranosidic linkage was determined to be α.[9] The two anomeric protons of H-1′ of **8** and **9** were observed as doublet peaks at δ 5.26 ($J = 3.4$ Hz, α) and δ 4.61 ($J = 6.9$ Hz, β), and at δ 5.36 ($J = 1.4$ Hz, α) and δ 4.70 ($J = 6.9$ Hz, β), respectively.

Table 1. Synthesis of trehalose mimic **3** by reaction of **1** with **2** under several reaction conditions

Entry[a]	Activator	Solvent	Yield (%)
1	Tf_2NH	CH_3CN	47
2	Tf_2NH	CH_2Cl_2	87
3	$Yb(OTf)_3$	CH_2Cl_2	21
4	$Sc(OTf)_3$	CH_2Cl_2	80
5	$Sc(OTf)_3$	$PhCH_3$	61
6	$Bi(OTf)_3$	CH_2Cl_2	89
7	$BiCl_3$	CH_2Cl_2	Trace

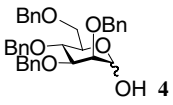
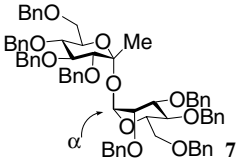
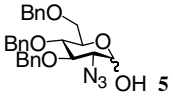
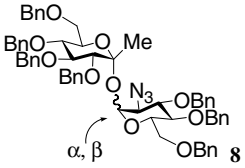
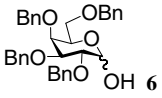
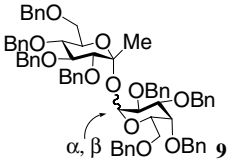
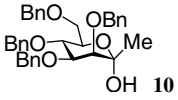
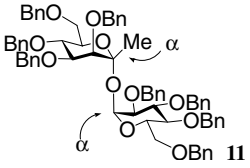
[a] Molar ratio: **1**:**2**:activator = 1:0.67:0.05, reaction time: 3 h, reaction temperature: 0 °C.

In order to investigate the relationship between the α/β-anomer ratios of the acceptors and those of the aldopyranosidic linkages of the products, we measured the α/β-anomer ratios of the aldohexopyranoses **2**, **4**–**6** in the CH_2Cl_2 solvent based on the NMR spectra. Compounds **2** and **4**–**6** were dissolved in CD_2Cl_2 and the NMR spectra measured about 30 min later showed that **2** and **4** contained the β-anomers of ca. 15–20%, and that **5** and **6** contained the β-anomers of ca. 40%. In spite of the presence of the β-anomers, the ketopyranosylations of **2** and **4** did not form the products having β-aldopyranosidic linkages at all. This suggested that the α-anomers of **2** and **4** predominantly worked as the reactive acceptors. The ketopyranosylations of **5** and **6** formed small amounts of **8** and

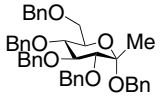


Scheme 2.

Table 2. Synthesis of various trehalose mimics **3**, **7**–**9**, **11** by the reaction of **1** (or **10**) with **2**, **4**–**6**

Entry[a]	1-C-Methylated donor	Aldopyranose of acceptor	Activator (5 mol %)	Product	Yield (%)	α/β Ratio of aldopyranosidic linkage[b]
1	**1**	**2**	Tf_2NH	**3**	87	α Only
2	**1**	**2**	$Bi(OTf)_3$	**3**	89	α Only
3	**1**	 **4**	Tf_2NH	 **7**	64	α Only
4	**1**	**4**	$Bi(OTf)_3$	**7**	75	α Only
5	**1**	 **5**	Tf_2NH	 **8**	90	78/22
6	**1**	**5**	$Bi(OTf)_3$	**8**	84	58/42
7	**1**	 **6**	Tf_2NH	 **9**	83	87/13
8	**1**	**6**	$Bi(OTf)_3$	**9**	89	76/24
9	 **10**	**2**	Tf_2NH	 **11**	37	α Only
10	**10**	**2**	$Bi(OTf)_3$	**11**	80	α Only

[a] Molar ratio: donor:acceptor:activator = 1:0.67:0.05, solvent: CH_2Cl_2, reaction time: 3 h, reaction temperature: 0 °C.
[b] All the 1-*C*-methyl-hexopyranosidic linkages of **3**, **7**–**9**, and **11** were α.


12

Scheme 3.

9 with β-aldopyranosidic linkages, which showed that their β-anomers partly participated in the ketopyranosylations though the α-anomers were preferentially used as the reactive acceptors.

Similarly, we investigated the synthesis of a non-reducing disaccharide by the reaction of 2,3,4,6-tetra-*O*-benzyl-1-*C*-methyl-α-D-mannopyranose **10** with **2** under similar reaction conditions (Scheme 2). The reaction using 5 mol % of Tf_2NH gave the corresponding **11** in 37% yield (entry 9). Both of its glycosidic linkages were α. The reaction using 5 mol % of $Bi(OTf)_3$ successfully increased the yield of **11** to 80% (entry 10).

3. Conclusion

Several types of non-reducing disaccharides, into which 1-*C*-methyl-α-D-hexopyranoses were incorporated, were synthesized as the trehalose mimics. It was found that 5 mol % of $Bi(OTf)_3$ or Tf_2NH effectively promoted the 1-*C*-methyl-hexopyranosylations of the benzylated D-hexopyranoses to afford the desired non-reducing disaccharides in excellent

yields. The stereoselectivities of the glycosidic linkages during the ketopyranosylation were also clarified.

4. Experimental

4.1. General

The NMR spectra were measured using an ECA-600 (JEOL) spectrometer at 600 MHz (^{1}H), and 150 MHz (^{13}C). The ^{1}H NMR chemical shifts are referenced to the internal standard TMS ($\delta_H = 0.00$). The ^{13}C NMR chemical shifts are referenced to the solvent signal ($\delta_C = 77.0$ for the central line of $CDCl_3$). The ESI-MS spectra were recorded using a Mariner (Applied Biosystems) spectrometer. Optical rotations were recorded using a JASCO DIP-360 digital polarimeter. All reactions were monitored by thin-layer chromatography (TLC) using Merck silica gel 60 F254 precoated plates (0.25 mm).

4.2. General synthesis of 3 by the ketopyranosylation of 1 with 2

To a stirred solution of $Bi(OTf)_3$ (4.4 mg, 0.0067 mmol) and **2** (48.3 mg, 0.0893 mmol) in CH_2Cl_2 (3.5 mL) was added **1** (79.3 mg, 0.134 mmol) at 0 °C in the presence of Drierite (ca. 100 mg) under an Ar atmosphere. The resulting mixture was stirred for 3 h. The reaction was then quenched by the addition of a satd $NaHCO_3$ solution (5 mL). The reaction mixture was extracted with ethyl acetate, and the organic layer was washed with water and a satd NaCl solution. After the organic layer was dried over Na_2SO_4, the solvent was evaporated under reduced pressure. The crude product was purified by preparative silica gel TLC (ethyl acetate/hexane = 1/3) to give **3** as a colorless oil (85.3 mg, 89%).

4.2.1. 2,3,4,6-Tetra-*O*-benzyl-α-D-glucopyranosyl 2,3,4,6-tetra-*O*-benzyl-1-*C*-methyl-α-D-glucopyranoside 3. Colorless oil; $[\alpha]_D^{23} = +70$ (*c* 2.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 1.49 (3H, s, CH_3), 3.29 (1H, d, $J = 9.6$ Hz, H-2), 3.33–3.39 (3H, m, H-6a, H-6b, H-6′a), 3.55–3.58 (1H, m, H-6′b), 3.56 (1H, dd, $J = 10.3$ Hz, $J = 3.4$ Hz, H-2′), 3.64 (1H, dd, $J = 9.6$ Hz, $J = 10.3$ Hz H-4), 3.68 (1H, t, $J = 9.6$ Hz, H-4′), 4.03 (1H, t, $J = 10.3$ Hz, H-3), 4.05 (1H, t, $J = 9.6$ Hz, H-3′), 4.17–4.19 (1H, m, H-5′), 4.29–4.28 (1H, m, H-5), 5.34 (1H, d, $J = 3.4$ Hz, H-1′); ^{13}C NMR ($CDCl_3$): δ 22.7 (CH_3), 68.3 (C-6′), 68.5 (C-6), 70.0 (C-5′), 71.0 (C-5), 78.0 (C-4′), 78.5 (C-4), 80.1 (C-2′), 81.8 (C-3), 82.7 (C-3′), 85.1 (C-2′), 90.2 (C-1′), 101.0 (C-1); HRMS (ESI): *m*/*z* calcd for $C_{69}H_{72}O_{11}Na^+$: 1099.4967; found: 1099.5006.

4.2.2. 2,3,4,6-Tetra-*O*-benzyl-α-D-mannopyranosyl 2,3,4,6-tetra-*O*-benzyl-1-*C*-methyl-α-D-glucopyranoside 7. Colorless oil; $[\alpha]_D^{23} = +59$ (*c* 0.83, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 1.46 (3H, s, CH_3), 3.23 (1H, d, $J = 9.6$ Hz, H-2), 3.29–3.31 (1H, m, H-5), 3.44 (1H, d, $J = 10.3$ Hz, H-6a), 3.52–3.54 (2H, m, H-6b, H-2′), 3.56 (1H, dd, $J = 8.9$ Hz, $J = 10.3$ Hz, H-4), 3.61 (1H, d, $J = 10.3$ Hz, H-6′a), 3.70–3.72 (1H, m, H-6′b), 3.74 (1H, dd, $J = 8.9$ Hz, $J = 10.3$ Hz, H-3), 3.96 (1H, dd, $J = 2.8$ Hz, $J = 10.3$ Hz, H-3′), 4.00 (1H, t, $J = 9.6$ Hz, H-4′), 4.07–4.10 (1H, m, H-5′), 5.24 (1H, d, $J = 2.1$ Hz, H-1′); ^{13}C NMR ($CDCl_3$): δ 23.0 (CH_3), 68.6 (C-6), 69.1 (C-6′), 71.6 (C-5′), 72.2 (C-5), 75.23 (C-4′ or C-2′ or *C*H_2Ph), 75.25 (C-4′ or C-2′ or *C*H_2Ph), 75.36 (C-4′ or C-2′ or *C*H_2Ph), 75.37 (C-4′ or C-2′ or *C*H_2Ph), 78.2 (C-4), 79.7 (C-3′), 82.9 (C-3), 84.6 (C-2), 90.7 (C-1′), 101.2 (C-1, $J_{C1-H1} = 168$ Hz); HRMS (ESI): *m*/*z* calcd for $C_{69}H_{72}O_{11}Na^+$: 1099.4967; found: 1099.5009.

4.2.3. 2-Azido-3,4,6-tri-*O*-benzyl-2-deoxy-α and β-D-glucopyranosyl 2,3,4,6-tetra-*O*-benzyl-1-*C*-methyl-α-D-glucopyranoside 8. Colorless oil (α,β-mixture); α-form; ^{1}H NMR ($CDCl_3$): δ 1.47 (3H, s, CH_3), 5.26 (1H, d, $J = 3.4$ Hz, H-1′), 3.29 (1H, d, $J = 9.6$ Hz, H-2); ^{13}C NMR ($CDCl_3$): δ 23.0 (CH_3), 90.6 (C-1′), 101.2 (C-1); β-form; ^{1}H NMR ($CDCl_3$): δ 1.49 (3H, s, CH_3), 4.61 (1H, d, $J = 6.9$ Hz, H-1′), 3.30–3.39 (1H, m, H-2); ^{13}C NMR ($CDCl_3$): δ 22.3 (CH_3), 95.7 (C-1′), 102.6 (C-1); HRMS (ESI): *m*/*z* calcd for $C_{62}H_{65}O_{10}N_3Na^+$: 1034.4562; found: 1034.4598 (α, β-mixture).

4.2.4. 2,3,4,6-Tetra-*O*-benzyl-α and β-D-galactopyranosyl 2,3,4,6-tetra-*O*-benzyl-1-*C*-methyl-α-D-glucopyranoside 9. α-Form; Colorless oil; $[\alpha]_D^{23} = +74$ (*c* 0.95, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 1.47 (3H, s, CH_3), 3.26 (1H, d, $J = 9.6$ Hz, H-2), 3.28–3.33 (2H, m, H-6), 3.47 (1H, dd, $J = 6.2$ Hz, $J = 9.6$ Hz, H-6′a) 3.55 (1H, dd, $J = 7.6$ Hz, $J = 8.9$ Hz, H-6′b), 3.63 (1H, dd, $J = 9.6$ Hz, $J = 10.3$ Hz, H-4), 3.93 (1H, dd, $J = 8.9$ Hz, $J = 9.6$ Hz, H-3), 4.02 (1H, d, $J = 0.7$ Hz, H-3′ or H-4′), 4.06–4.07 (2H, m, H-2′, H-3′ or H-4′), 4.31–4.33 (1H, m, H-5), 4.34–4.37 (1H, m, H-5′), 5.36 (1H, d, $J = 1.4$ Hz, H-1′); ^{13}C NMR ($CDCl_3$): δ 22.8 (CH_3), 68.4 (C-6), 69.0 (C-6′), 69.2 (C-5′), 70.9 (C-5), 74.9 (C-3′ or C-4′), 76.8 (C-2′ or C-3′ or C-4′), 78.4 (C-4), 78.6 (C-2′ or C-3′ or C-4′), 83.0 (C-3), 85.1 (C-2), 90.9 (C-1′), 100.8 (C-1); HRMS (ESI): *m*/*z* calcd for $C_{69}H_{72}O_{11}Na^+$: 1099.4967; found: 1099.4985. β-Form; colorless oil; $[\alpha]_D^{23} = +48$ (*c* 0.70, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 1.45 (3H, s, CH_3), 3.34 (1H, d, $J = 9.6$ Hz, H-2), 3.45–3.53 (4H, m, H-3′ or H-4′, H-5′, H-6a, H-6b), 3.60–3.66 (2H, m, H-6′), 3.70 (1H, t, $J = 9.6$ Hz, H-4), 3.80–3.84 (2H, m, H-2′, H-3′, or H-4′), 4.19 (1H, t, $J = 9.6$ Hz, H-3), 4.32–4.37 (3H, m, CH_2Ph, H-5), 4.70 (1H, d, $J = 6.9$ Hz, H-1′); ^{13}C NMR ($CDCl_3$): δ 22.4 (CH_3), 68.6 (C-6′), 69.0 (C-6), 72.1 (C-5), 73.6 (C-5′), 73.8 (C-2′ or C-3′ or C-4′), 78.7 (C-4), 79.0 (C-2′ or C-3′ or C-4′), 82.4 (C-2′ or C-3′ or C-4′), 82.9 (C-3), 84.5 (C-2), 97.6 (C-1′), 102.3 (C-1); HRMS (ESI): *m*/*z* calcd for $C_{69}H_{72}O_{11}Na^+$: 1099.4967; found: 1099.4975.

4.2.5. 2,3,4,6-Tetra-*O*-benzyl-α-D-glucopyranosyl 2,3,4,6-tetra-*O*-benzyl-1-*C*-methyl-α-D-mannopyranoside 11. Colorless oil; $[\alpha]_D^{23} = +57$ (*c* 0.81, $CHCl_3$); ^{1}H NMR ($CDCl_3$): ^{1}H NMR ($CDCl_3$): δ 1.46 (3H, s, CH_3), 3.50–3.51 (2H, m, H-6′), 3.54–3.58 (3H, m, H-6a, H-4′, H-2′), 3.66 (1H, t, $J = 9.6$ Hz, H-4), 3.72 (1H, dd, $J = 3.4$ Hz, $J = 10.3$ Hz, H-6b), 3.77–3.78 (1H, m, H-5), 3.89 (1H, dd, $J = 8.9$ Hz, $J = 9.6$ Hz, H-3′), 3.94 (1H, dd, $J = 9.6$ Hz, $J = 10.3$ Hz, H-3), 4.16 (1H, dd, $J = 2.1$ Hz, $J = 9.6$ Hz, H-2), 4.18–4.21 (1H, m, H-5′), 5.42 (1H, d, $J = 3.4$ Hz, H-1′); ^{13}C NMR ($CDCl_3$): δ 22.5 (CH_3), 68.5 (C-6), 69.3 (C-6′), 70.5 (C-5), 72.9 (C-5′), 74.8 (C-3), 77.9 (C-4), 79.1 (C-2′), 80.1

(C-4′), 80.7 (C-2), 81.8 (C-3′), 89.9 (C-1′), 102.0 (C-1); HRMS (ESI): *m/z* calcd for $C_{69}H_{72}O_{11}Na^{+}$: 1099.4967; found: 1099.4999.

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