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Note

Preparation of partially benzylated mono-, di-, and trisaccharides by selective cleavage of the β-fructofuranosidic linkage in fully benzylated sucrose and sucrose-related oligosaccharides under acidic conditions

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Abstract—Several partially benzylated mono-, di-, and trisaccharides having an anomeric hydroxyl group were successfully prepared by selective cleavage of the β-fructofuranosidic linkage in fully benzylated sucrose and sucrose-related oligosaccharides derived from lactosucrose, raffinose, melezitose, stachyose, and nystose under acidic conditions using 1:10 75% aqueous sulfuric acid–dioxane at room temperature for 1 h.

Keywords: Partially benzylated sugars; Acidic hydrolysis; β-Fructofuranosidic linkage; Sucrose-related oligosaccharides; Benzylated oligosaccharides

Partially benzylated sugars are significant reagents in synthetic carbohydrate chemistry. In particular, partially benzylated sugar derivatives having a free anomeric hydroxyl group are often used as glycosyl donors in glycosidation studies.[1] Partially benzylated sugar derivatives can be produced by cleaving the glycosidic bonds of fully benzylated oligosaccharides. Our recent study showed that fully benzylated cyclomaltohexaose was hydrothermolyzed into 2,3,6-tri-*O*-benzyl-D-glucopyranose and partially benzylated maltooligosaccharides.[2]

Ness et al. reported that acidic hydrolysis of fully benzylated sucrose **1**[3] using 2 M sulfuric acid–acetic acid at 65 °C for 6 h gave 2,3,4,6-tetra-*O*-benzyl-D-glucopyranose (**2**) and 1,3,4,6-tetra-*O*-benzyl-D-fructofuranose (**3**) in 76% and 17% yields, respectively.[4] Their study indicated that the β-fructofuranosidic linkage in fully benzylated sucrose could be easily cleaved under acidic conditions, though more appropriate hydrolysis conditions were necessary for increasing the yield of **3**.

Our attention focused on sucrose-related oligosaccharides, such as commercially available lactosucrose, raffinose, melezitose, stachyose, and nystose, which are otherwise effective for the development of bifidobacteria.[5] As they have the β-fructofuranosidic linkage and consist of sucrose and one or two more sugar moieties (glucose, galactose, or fructose), we expected that the selective cleavage of the β-fructofuranosidic linkages in the fully benzylated derivatives of these sucrose-related oligosaccharides (**4**–**8**) under acidic conditions could produce the partially benzylated disaccharides Galβ1→4Glu **9**, Galα1→6Glu **10**, Gluα1→3Fru **11**, and trisaccharide Galα1→6Galα1→6Glu **12** in addition to the partially benzylated monosaccharides **2**, **3**, and 3,4,6-tri-*O*-benzyl-D-fructofuranose (**13**) (see Scheme 1). They are all synthetically useful sugar derivatives having a free anomeric hydroxyl group. For example, some of them are appropriate reagents for preparing glycosphingolipids and their analogs.[6]

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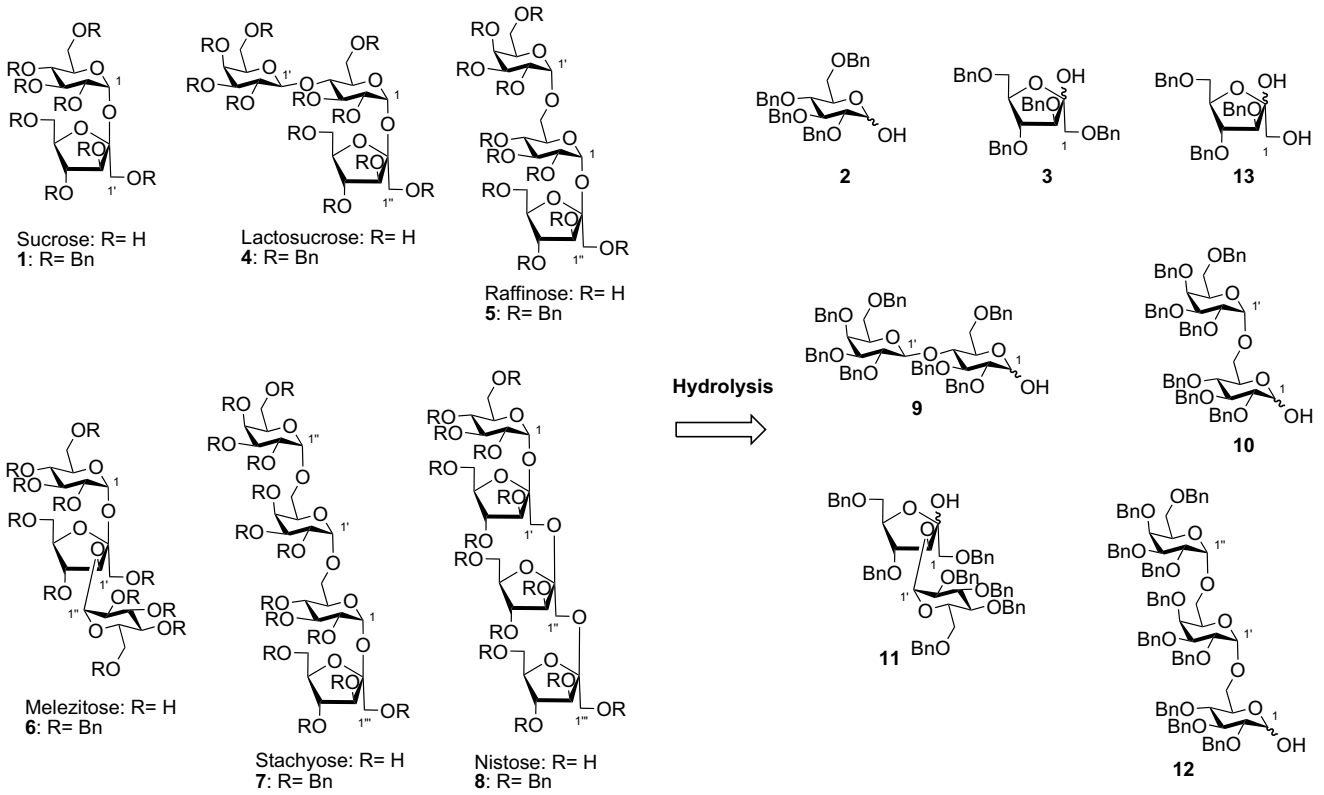

Scheme 1.

This paper describes the effective preparation of the partially benzylated mono-, di-, and trisaccharide derivatives **2**, **3**, **9**–**13** by selective cleavage of the β-fructofuranosidic linkage in the fully benzylated sucrose-related oligosaccharides **4**–**8** under acidic conditions.

Preparation of fully benzylated sucrose and sucrose-related oligosaccharides: As the benzylation of sucrose using benzyl bromide, silver oxide, and barium oxide in dimethylformamide gave **1** in only 29% yield,[3a] we introduced benzyl groups into sucrose, lactosucrose, raffinose, melezitose, stachyose, and nystose by a different benzylation method using benzyl bromide and sodium hydride in DMF.[3b] The benzylation method could successfully produce **1**, and **4**–**8** in yields of 79%, 67%, 78%, 89%, 53%, and 84%, respectively. The purity and the hydration of these commercial sucrose-related oligosaccharides likely influence the benzylation yields. The results are summarized in Table 1.

Hydrolysis of fully benzylated sucrose and sucrose-related oligosaccharides: First, we investigated the acidic conditions for hydrolyzing **1** into **2**[†] and **3**. Conditions[‡] using 1:1 3 M HCl–THF at reflux for 1 day scarcely promoted the hydrolysis of **1**. In contrast, conditions[$] using 1:10 75% aqueous sulfuric acid–1,4-dioxane at room temperature for 1 h smoothly hydrolyzed **1** to **2** and **3** in yields of 94% and 85%, respectively. The method was applicable to the hydrolysis of **1** on a multigram scale (see Section 1).

Table 1. Benzylation of sucrose, and sucrose-related oligosaccharides

Entry[a]	Starting material	Product	Yield (%)
1[b]	Sucrose	**1**	79
2[c]	Lactosucrose[d]	**4**	67
3[c]	Raffinose[e]	**5**	78
4[c]	Melezitose[f]	**6**	89
5[g]	Stachyose[h]	**7**	53
6[g]	Nystose	**8**	84

[a] Reaction was done using NaH and benzyl bromide in DMF overnight.
[b] NaH (32 equiv), benzyl bromide (9.2 equiv).
[c] NaH (44 equiv), benzyl bromide (15 equiv).
[d] The purity was ca. 90%.
[e] 5 Hydrate was used.
[f] 1 Hydrate was used.
[g] NaH (56 equiv), benzyl bromide (28 equiv).
[h] 4 Hydrate was used.

[†] It was reported that 2 M H_2SO_4–AcOH at 90 °C for 24 h hydrolyzed methyl 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranoside into **2** in 30% yield.[7]

[‡] It was reported that 3 M HCl–THF under reflux for 48 h could hydrolyze benzyl 2-acetamido-2-deoxy-3,4,6-tri-*O*-benzyl-2-deoxy-β-D-glucopyranoside into 2-amino-2-deoxy-3,4,6-tri-*O*-benzyl-2-deoxy-D-glucopyranose.[8]

[$] It was reported that 1:10 75% aq H_2SO_4–1,4-dioxane at 100 °C for 3 h could hydrolyze fully benzylated cyclomaltoheptaose into 2,3,6-tri-*O*-benzyl-D-glucopyranose in 43% yield.[9]

Table 2. Preparation of mono-, di-, and trisaccharide units **2**, **3**, **9**–**13** by the acidic hydrolysis of **1**, **4**–**8**

Entry[a]	Fully benzylated sucrose-related oligosaccharide	Partially benzylated product (yield/%)	
		Di- or trisaccharide unit	Monosaccharide unit
1	**1**	—	**2** (94) **3** (85)
2	**4**	**9** (85)	**3** (91)
3	**5**	**10** (92)	**3** (90)
4	**6**	**11** (77)	**2** (94)
5	**7**	**12** (92)	**3** (86)
6	**8**	—	**2** (78) **3** (88) **13** (54)

[a] Reaction conditions: 75% aq H_2SO_4–1,4-dioxane (v/v = 1/10); room temperature; 1 h.

Next, the hydrolysis of **4**–**7** under the same acidic conditions was examined in order to observe whether only the β-fructofuranosidic linkage in **4**–**7** is selectively cleaved, while the other aldopyranosidic linkages remain uncleaved under the reaction conditions. Treatment of **4** by 1:10 75% aqueous H_2SO_4–1,4-dioxane at room temperature for 1 h similarly produced the partially benzylated mono- and disaccharides **3** and **9** in 91% and 85% yields. Similar reaction conditions promoted the acidic hydrolysis of **5** to **3** and **10** in 90% and 92% yields. The acidic hydrolysis of **6** similarly produced **2** and **11** in 94% and 77% yields. The reaction using **7** afforded **3** and **12** in 86% and 92% yields, respectively. This means that hydrolysis under these conditions selectively cleaved the β-fructofuranosidic linkages without cleaving the other aldopyranosidic linkages of **4**–**7**.

The same treatment of **8** produced **2**, **3**, and **13** in 78%, 88%, and 54% yields, respectively. We found that all the three β-fructofuranosidic linkages in **8** were smoothly cleaved under these conditions. These results are shown in Table 2.

In summary, we were able to prepare the partially benzylated mono-, di-, and trisaccharides **2**, **3**, **9**–**13** having a free anomeric hydroxyl group by selective cleavage of the β-fructofuranosidic linkage in the fully benzylated sucrose-related oligosaccharides **4**–**8** under acidic conditions using 1:10 75% aqueous H_2SO_4–dioxane at room temperature for 1 h. This method is expected to be applicable to the hydrolysis of other benzylated sucrose-related oligosaccharides containing a β-fructofuranosidic linkage.

1. Experimental

1.1. General

Lactosucrose (purity ca. 90%) was a gift from Hayashibara Biochemical Laboratories, Inc. Sucrose and raffinose·$5H_2O$ were purchased from Wako Pure Chemicals Industries, Ltd. Melezitose·H_2O, stachyose·$4H_2O$, and nystose·$3H_2O$ were purchased from Tokyo Chemical Industry Co., Ltd. The ^1H and ^{13}C NMR spectra were recorded on an ECA-600 spectrometer (JEOL) in $CDCl_3$ using TMS as the internal standard. Optical rotations were recorded on a JASCO DIP-360 digital polarimeter. HRMS was obtained on a Mariner spectrometer (PerSeptive Biosystems Inc.). Preparative TLC was performed on E. Merck Silica Gel 60GF254. Column chromatography was conducted using Silica Gel 60 N (40–50 μm, Kanto Chemical Co., Inc.).

1.2. Benzylation of sucrose and sucrose-related oligosaccharides

1.2.1. 1,3,4,6-Tetra-*O*-benzyl-β-D-fructofuranosyl 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranoside (1). To a soln of sucrose (2.2 g, 6.4 mmol) and benzyl bromide (7.0 mL, 59 mmol) in DMF (80 mL) was added NaH (4.9 g, 0.21 mol) at 0 °C. The reaction mixture was then stirred overnight at room temperature. Methanol (5 mL) was slowly dropped into the reaction mixture, and then water (20 mL) was added. The mixture was then extracted with CH_2Cl_2 and dried over anhyd Na_2SO_4. Concentration led to a crude product which was purified by silica gel chromatography (8:1→4:1, hexane–EtOAc) to give **1**[3] (5.4 g, 79%) as a colorless oil; $[\alpha]_D^{27}$ +34.7 (*c* 1.2, $CHCl_3$); lit.[3a] $[\alpha]_D^{20}$ +31.6; lit.[3b] $[\alpha]_D^{20}$ +38.4. ^1H NMR ($CDCl_3$, 600 MHz): δ 3.37 (1H, dd, *J* 2.06 Hz, *J* 11.00 Hz, H_a-6), 3.49 (1H, dd, *J* 3.44 Hz, *J* 6.87 Hz, H-2), 3.50 (1H, dd, *J* 3.44 Hz, *J* 11.00 Hz, H_b-6), 3.54 (1H, d, *J* 11.00 Hz, H_a-1′), 3.64 (1H, t, *J* 9.62 Hz, H-4), 3.67 (1H, dd, *J* 3.44 Hz, *J* 10.31 Hz, H_a-6′), 3.72 (1H, dd, *J* 5.50 Hz, *J* 10.31 Hz, H_b-6′), 3.74 (1H, d, *J* 11.00 Hz, H_b-1′), 3.93 (1H, t, *J* 9.62 Hz, H-3), 4.06 (1H, m, H-5), 4.11 (1H, m, H-5′), 4.18 (1H, t, *J* 7.56 Hz, H-4′), 4.43 (1H, d, *J* 7.56 Hz, H-3′), 5.72 (1H, d, *J* 3.44 Hz, H-1); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 68.41 (C-6), 70.53 (C-5), 71.20 (C-1′), 71.37 (C-6′), 72.15 (*C*H_2Ph), 72.49 (*C*H_2Ph), 72.96 (*C*H_2Ph), 73.19 (*C*H_2Ph), 73.34 (*C*H_2Ph), 73.38 (*C*H_2Ph), 74.78 (*C*H_2Ph), 75.48 (*C*H_2Ph), 77.58 (C-4), 79.57 (C-5′), 79.79 (C-2), 81.90 (C-3), 82.39 (C-4′), 83.86 (C-3′), 89.89 (C-1), 104.58 (C-2′). HRESIMS: calcd for $C_{68}H_{70}O_{11}\cdot Na^+$: 1085.4810; found: *m*/*z* 1085.4843.

1.2.2. 1,3,4,6-Tetra-*O*-benzyl-β-D-fructofuranosyl 2,3,6-tri-*O*-benzyl-4-*O*-(2,3,4,6-tetra-*O*-benzyl-β-D-galactopyranosyl)-α-D-glucopyranoside (4). The same procedure as for **1** but using lactosucrose (563 mg, 1.11 mmol), benzyl bromide (2.0 mL, 17.2 mmol) in DMF (40 mL) and NaH (1.18 g, 49.1 mmol) was applied resulting in **4** (1.12 g, 67%) as a colorless oil; $[\alpha]_D^{27}$ +16.7 (*c* 1.1, $CHCl_3$). ^1H NMR ($CDCl_3$, 600 MHz): δ 3.32–3.40

(4H, m, H-3′, H-5′, H_a-6′, H_a-6), 3.45 (1H, dd, *J* 3.44 Hz, *J* 9.62 Hz, H-2), 3.51 (1H, d, *J* 11.00 Hz, H_a-1″), 3.54 (1H, t, *J* 8.94 Hz, H_b-6), 3.63 (1H, dd, *J* 4.12 Hz, *J* 10.31 Hz, H_a-6″), 3.69–3.75 (3H, m, H_b-1″, H_b-6″, H-2′), 3.79 (1H, dd, *J* 3.44 Hz, *J* 10.31 Hz, H_b-6′), 3.84 (1H, t, *J* 8.94 Hz, H-3), 3.90–3.93 (2H, m, H-4, H-4′), 4.08–4.10 (2H, m, H-5, H-4″), 4.13 (1H, m, H-5″), 4.34 (1H, d, *J* 7.56 Hz, H-1′), 4.45 (1H, d, *J* 3.44 Hz, H-3″), 5.66 (1H, d, *J* 3.44 Hz, H-1). ^{13}C NMR ($CDCl_3$, 150 MHz): δ 68.17 (C-6, C-6′), 70.66 (C-5), 71.17 (C-1″), 71.78 (C-6″), 72.51 (*C*H_2Ph), 72.56 (*C*H_2Ph), 72.75 (*C*H_2Ph), 72.79 (*C*H_2Ph), 72.96 (C-5′), 73.05 (*C*H_2Ph), 73.20 (*C*H_2Ph), 73.32 (*C*H_2Ph), 73.37 (*C*H_2Ph), 73.70 (C-4′), 74.68 (*C*H_2Ph), 75.01 (*C*H_2Ph), 75.26 (*C*H_2Ph), 77.35 (C-4), 79.05 (C-2), 79.76 (C-5″), 79.87 (C-2′), 80.10 (C-3), 82.52 (C-3′), 83.09 (C-4″), 83.79 (C-3″), 90.09 (C-1), 103.02 (C-1′), 104.51 (C-2″). HRESIMS: calcd for $C_{95}H_{98}O_{16}{\cdot}Na^+$: 1517.6747; found: *m*/*z* 1517.6702. Anal. Calcd for $C_{95}H_{98}O_{16}{\cdot}H_2O$: C, 75.37; H, 6.66. Found: C, 75.37; H, 6.69.

1.2.3. 1,3,4,6-Tetra-*O*-benzyl-β-D-fructofuranosyl 2,3,4-tri-*O*-benzyl-6-*O*-(2,3,4,6-tetra-*O*-benzyl-α-D-galactopyranosyl)-α-D-glucopyranoside (5). The same procedure as for **1** was followed starting from raffinose·5H_2O (780 mg, 1.55 mmol), benzyl bromide (3.3 mL, 28 mmol) in DMF (60 mL) and NaH (1.18 g, 49 mmol). This led to **5** (1.8 g, 78%) as a colorless oil; $[\alpha]_D^{27}$ +39.6 (*c* 1.2, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 600 MHz): δ 3.30 (1H, dd, *J* 3.44 Hz, *J* 9.62 Hz, H-2), 3.46 (1H, dd, *J* 5.50 Hz, *J* 8.94 Hz, H_a-6′), 3.50–3.55 (4H, m, H_a-1″, H_a-6″, H_b-6′, H_a-6), 3.65–3.70 (2H, m, H_b-1″, H_b-6″), 3.72 (1H, dd, *J* 2.75 Hz, *J* 12.37 Hz, H_b-6), 3.78 (1H, t, *J* 9.62 Hz, H-4), 3.87–3.92 (4H, m, H-3, H-3′, H-4′, H-5′), 4.01 (1H, dd, *J* 3.44 Hz, *J* 7.56 Hz, H-2′), 4.02 (1H, m, H-5), 4.09 (1H, m, H-5″), 4.15 (1H, t, *J* 7.56 Hz, H-4″), 4.37 (1H, m, H-3″), 5.10 (1H, d, *J* 3.44 Hz, H-1′), 5.63 (1H, d, *J* 3.44 Hz, H-1); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 65.73 (C-6), 68.79 (C-6′), 69.20 (C-5′), 71.21 (C-1″ or C-6″), 71.25 (C-1″ or C-6″), 71.32 (C-4′), 71.94 (*C*H_2Ph), 72.40 (*C*H_2Ph), 72.55 (*C*H_2Ph), 72.81 (*C*H_2Ph), 72.85 (*C*H_2Ph), 73.17 (*C*H_2Ph), 73.35 (*C*H_2Ph × 2), 74.76 (*C*H_2Ph), 74.80 (*C*H_2Ph), 75.07 (C-5), 75.30 (*C*H_2Ph), 76.68 (C-2′), 77.46 (C-4), 78.13 (C-3′), 79.49 (C-5″), 80.13 (C-2), 81.81 (C-3), 82.42 (C-4″), 83.74 (C-3″), 89.93 (C-1), 98.06 (C-1′), 104.51 (C-2″). HRESIMS: calcd for $C_{95}H_{98}O_{16}{\cdot}Na^+$: 1517.6747; found: *m*/*z* 1517.6774. Anal. Calcd for $C_{95}H_{98}O_{16}$: C, 76.28; H, 6.60. Found: C, 76.37; H, 6.73.

1.2.4. 1,4,6-Tri-*O*-benzyl-3-*O*-(2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl)-β-D-fructofuranosyl 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranoside (6). The same procedure as for **1** was followed starting from melezitose·H_2O (545 mg, 1.1 mmol), benzyl bromide (2.0 mL, 17 mmol) in DMF (40 mL) and NaH (1.14 g, 48 mmol) resulting in **6** (1.38 g, 89%) as a colorless oil; $[\alpha]_D^{27}$ +47.8 (*c* 0.87, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 600 MHz): δ 3.32 (1H, d, *J* 9.62 Hz, H_a-6), 3.44 (2H, m, H_a-1′, H_a-6″), 3.50 (1H, dd, *J* 3.44 Hz, *J* 9.62 Hz, H-2), 3.54 (1H, dd, *J* 3.44 Hz, *J* 10.31 Hz, H-2″), 3.54–3.57 (2H, m, H_a-6′, H_b-6), 3.62 (1H, t, *J* 9.62 Hz, H-4), 3.64 (1H, dd, *J* 2.06 Hz, *J* 11.00 Hz, H_b-6″), 3.74 (1H, t, *J* 9.62 Hz, H-4′), 3.76–3.82 (2H, m, H_b-1′, H_b-6′), 3.84 (1H, t, *J* 9.62 Hz, H-3), 3.99 (1H, m, H-5), 4.01 (1H, t, *J* 8.25 Hz, H-4″), 4.05 (1H, t, *J* 9.62 Hz, H-3″), 4.11 (1H, m, H-5″), 4.16 (1H, m, H-5′), 4.54–4.58 (1H, m, H-3′), 5.12 (1H, d, *J* 3.44 Hz, H-1″), 5.48 (1H, d, *J* 3.44 Hz, H-1); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 68.10 (C-6″), 68.56 (C-6), 70.33 (C-1′), 70.54 (C-5), 70.93 (C-5″), 71.72 (C-6′), 72.29 (*C*H_2Ph), 72.93 (*C*H_2Ph), 73.07 (*C*H_2Ph), 73.23 (*C*H_2Ph), 73.28 (*C*H_2Ph), 73.30 (*C*H_2Ph), 73.36 (*C*H_2Ph), 74.54 (*C*H_2Ph), 74.88 (*C*H_2Ph), 75.59 (*C*H_2Ph), 75.79 (*C*H_2Ph), 77.51 (C-4), 77.74 (C-4′), 79.37 (C-5′), 79.57 (C-2 or C-2″), 79.61 (C-2 or C-2″), 81.07 (C-4″), 82.11 (C-3″), 82.39 (C-3), 84.47 (C-3′), 89.78 (C-1), 99.88 (C-1″), 103.81 (C-2′). HRESIMS: calcd for $C_{95}H_{98}O_{16}{\cdot}Na^+$: 1517.6747; found: *m*/*z* 1517.6714. Anal. Calcd for $C_{95}H_{98}O_{16}{\cdot}H_2O$: C, 75.37; H, 6.66. Found: C, 75.37; H, 6.38.

1.2.5. 1,3,4,6-Tetra-*O*-benzyl-β-D-fructofuranosyl 2,3,4-tri-*O*-benzyl-6-*O*-[2,3,4-tri-*O*-benzyl-6-*O*-(2,3,4,6-tetra-*O*-benzyl-α-D-galactopyranosyl)-α-D-galactopyranosyl]-α-D-glucopyranoside (7). The same procedure as for **1** was followed starting from stachyose·4H_2O (262 mg, 0.39 mmol), benzyl bromide (1.3 mL, 11 mmol) in DMF (10 mL) and NaH (0.54 g, 22 mmol) resulting in **7** (363 mg, 53%) as a colorless oil; $[\alpha]_D^{26}$ +69.8 (*c* 1.0, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 600 MHz): δ 3.26 (1H, dd, *J* 3.44 Hz, *J* 9.62 Hz, H-2), 3.47–3.58 (4H, m, H_a-1‴, H_a-6, H-6″), 3.66–3.71 (5H, m, H_b-1‴, H-6‴, H-6′), 3.74 (1H, d, *J* 12.37 Hz, H_b-6), 3.80 (1H, t, *J* 10.31 Hz, H-4), 3.88–3.92 (5H, m, H-3, H-3′, H-5′, H-3″, H-5″), 3.97–4.04 (5H, m, H-5, H-2′, H-4′, H-2″, H-4″), 4.10–4.15 (2H, m, H-4‴, H-5‴), 4.43 (1H, m, H-3‴), 4.83 (1H, d, *J* 3.44 Hz, H-1″), 5.10 (1H, d, *J* 3.44 Hz, H-1′), 5.62 (1H, d, *J* 3.44 Hz, H-1); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 65.95 (C-6), 66.69 (C-6′), 68.85 (C-6″), 68.99 (C-5′), 69.65 (C-5″), 71.31 (C-1‴), 71.56 (C-6‴), 71.72 (C-5), 72.12 (*C*H_2Ph), 72.60 (*C*H_2Ph), 72.68 (*C*H_2Ph), 72.73 (*C*H_2Ph), 72.82 (*C*H_2Ph), 73.05 (*C*H_2Ph), 73.37 (*C*H_2Ph), 73.55 (*C*H_2Ph), 73.69 (*C*H_2Ph), 73.78 (*C*H_2Ph), 74.86 (*C*H_2Ph), 74.97 (*C*H_2Ph × 2), 75.01 (C-4′, C-4″), 75.48 (*C*H_2Ph), 76.37 (C-2″), 76.81 (C-2′), 77.48 (C-4), 78.34 (C-3′ or C-3″), 79.41 (C-3′ or C-3″), 79.78 (C-5‴), 80.31 (C-2), 81.97 (C-3), 82.76 (C-4‴), 83.97 (C-3‴), 90.24 (C-1), 98.47 (C-1′), 98.92 (C-1″), 104.75 (C-2‴); HRESIMS: calcd

for $C_{122}H_{126}O_{21}\cdot Na^+$: 1949.8684; found: *m*/*z* 1949.8634. Anal. Calcd for $C_{122}H_{126}O_{21}$: C, 75.99; H, 6.59. Found: C, 75.94; H, 6.46.

1.2.6. 3,4,6-Tri-*O*-benzyl-1-*O*-[3,4,6-tri-*O*-benzyl-1-*O*-(1,3,4,6-tetra-*O*-benzyl-β-D-fructofuranosyl)-β-D-fructofuranosyl]-β-D-fructofuranosyl 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranoside (8). The same procedure as for **1** was followed starting from nystose·3H_2O (219 mg, 0.3 mmol), benzyl bromide (1 mL, 8.5 mmol) in DMF (10 mL) and NaH (0.41 g, 17 mmol) resulting in **8** (490 mg, 84%) as a colorless oil; $[\alpha]_{365}^{23}$ −11.4 (*c* 1.6, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 600 MHz): δ 3.24 (1H, d, *J* 11.00 Hz, H_a-6), 3.39 (1H, d, *J* 10.31 Hz, H_b-6), 3.44 (1H, dd, *J* 3.44 Hz, *J* 9.62 Hz, H-2), 3.49 (1H, d, *J* 10.31 Hz, H_a-1″ or H_a-1‴), 3.54 (1H, d, *J* 10.31 Hz, H_b-1″ or H_b-1‴), 3.59–3.70 (7H, m, H-4, H-6′, H-6″, H-6‴), 3.84 (1H, d, *J* 10.31 Hz, H_a-1″ or H_a-1‴), 3.91–3.94 (2H, m, H_b-1″ or H_b-1‴, H-3), 4.00–4.09 (7H, m, H-1′, H-4′ or H-4″ or H-4‴, H-5′, H-5″, H-5‴, H-5), 4.12 (1H, t, *J* 5.50 Hz, H-4′ or H-4″ or H-4‴), 4.20 (1H, t, *J* 8.25 Hz, H-4′ or H-4″ or H-4‴), 4.31 (1H, dd, *J* 2.06 Hz, *J* 6.87 Hz, H-3′ or H-3″ or H-3‴), 4.44 (1H, m, H-3′ or H-3″ or H-3‴), 4.56 (1H, m, H-3′ or H-3″ or H-3‴), 5.74 (1H, d, *J* 4.12 Hz, H-1). ^{13}C NMR ($CDCl_3$, 150 MHz): δ 63.59 (C-1′), 64.49 (C-1″ or C-1‴), 70.45 (C-6), 70.65 (C-5), 70.94 (C-6′ or C-6″ or C-6‴), 71.32 (C-6′ or C-6″ or C-6‴), 71.33 (C-6′ or C-6″ or C-6‴), 71.59 (*C*H_2Ph), 71.72 (C-1″ or C-1‴), 72.17 (*C*H_2Ph), 72.36 (*C*H_2Ph), 72.40 (*C*H_2Ph), 72.45 (*C*H_2Ph × 2), 73.04 (*C*H_2Ph), 73.07 (*C*H_2Ph), 73.15 (*C*H_2Ph × 2), 73.27 (*C*H_2Ph), 73.49 (*C*H_2Ph), 74.68 (*C*H_2Ph), 75.43 (*C*H_2Ph), 77.52 (C-4), 78.47 (C-5′ or C-5″ or C-5‴), 78.93 (C-5′ or C-5″ or C-5‴), 79.00 (C-5′ or C-5″ or C-5‴), 79.29 (C-2), 81.50 (C-4′ or C-4″ or C-4‴), 82.10 (C-3), 83.62 (C-3′ or C-3″ or C-3‴ or C-4′ or C-4″ or C-4‴), 83.66 (C-3′ or C-3″ or C-3‴ or C-4′ or C-4″ or C-4‴), 83.69 (C-3′ or C-3″ or C-3‴ or C-4′ or C-4″ or C-4‴), 84.80 (C-3′ or C-3″ or C-3‴), 84.99 (C-3′ or C-3″ or C-3‴), 89.42 (C-1), 104.18 (C-2″ or C-2‴), 104.20 (C-2″ or C-2‴), 104.40 (C-2′). HRESIMS: calcd for $C_{122}H_{126}O_{21}\cdot Na^+$: 1949.8684; found: *m*/*z* 1949.8695. Anal. Calcd for $C_{122}H_{126}O_{21}$: C, 75.99; H, 6.59. Found: C, 76.12; H, 6.68.

1.3. Hydrolysis of fully benzylated sucrose and sucrose-related oligosaccharides

1.3.1. Preparation of 2,3,4,6-tetra-*O*-benzyl-D-glucopyranose (2) and 1,3,4,6-tetra-*O*-benzyl-D-fructofuranose (3) from 1. To a soln of **1** (265 mg, 0.25 mmol) in dioxane (6 mL) was added 75% aq H_2SO_4 (0.5 mL). The reaction mixture was stirred for 1 h at room temperature. A saturated aq $NaHCO_3$ soln (10 mL) was then added, the reaction was extracted with EtOAc, and the organic layer dried over anhyd Na_2SO_4. After concentration, the crude products were purified by silica gel chromatography (4:1→1:1 hexane–EtOAc) to give **2**[7] (127 mg, 94%) as white crystals and **3**[4] (115 mg, 85%) as a colorless syrup. A reaction on a multigram scale was also performed as follows: To a soln of **1** (2.12 g, 2.0 mmol) in dioxane (10 ml) was added 75% aq H_2SO_4 (1 mL), and the reaction mixture was stirred for 1 h at room temperature. Aq $NaHCO_3$ (20 mL) was then added and the mixture was extracted with EtOAc. The organic solvent was dried over anhyd Na_2SO_4. Concentration led to the crude products which were separated by silica gel chromatography (4:1→1:1 hexane–EtOAc) to give **3**[4] (947.4 mg, 94%). **2**[7] (807 mg, 75%) was obtained as white crystals from EtOH. Compound **2** (71:29 α/β mixture); α Form: ^{1}H NMR ($CDCl_3$, 600 MHz): δ 3.50 (1H, dd, *J* 3.44 Hz, *J* 8.94 Hz, H-2), 3.54–3.57 (2H, m, H-4, H_a-6), 3.62 (1H, m, H_b-6), 3.90 (1H, t, *J* 8.94 Hz, H-3), 3.96 (1H, m, H-5), 5.15 (1H, d, *J* 3.44 Hz. H-1); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 68.56 (C-6), 70.27 (C-5), 73.23 (*C*H_2Ph), 73.46 (*C*H_2Ph), 74.98 (*C*H_2Ph), 75.68 (*C*H_2Ph), 77.66 (C-4), 79.97 (C-2), 81.71 (C-3), 91.28 (C-1); β Form: ^{1}H NMR ($CDCl_3$, 600 MHz): δ 3.32 (1H, t, *J* 8.25 Hz, H-2), 3.44 (1H, m, H-5), 3.47 (1H, m, H-4), 3.54–3.59 (2H, m, H-3, H_a-6), 3.62 (1H, m, H_b-6), 4.63 (1H, d, *J* 8.25 Hz, H-1); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 68.87 (C-6), 73.50 (*C*H_2Ph), 74.70 (C-5, *C*H_2Ph), 74.96 (*C*H_2Ph), 75.64 (*C*H_2Ph), 77.78 (C-4), 83.09 (C-2), 84.55 (C-3), 97.45 (C-1). ^{1}H NMR data were in accordance with the lit. data.[7] Compound **3** (23:77 α/β mixture): $[\alpha]_D^{22}$ +6.6→+9.2 (25 h, *c* 1.4, $CHCl_3$); lit.[4] $[\alpha]_D^{20}$ +6.5→+8.7 (25 h, *c* 1.4, $CHCl_3$); α Form: ^{1}H NMR ($CDCl_3$, 600 MHz): δ 3.43 (1H, m, H_a-6), 3.52 (1H, m, H_b-6), 3.58 (1H, d, *J* 10.31 Hz, H_a-1), 3.65 (1H, d, *J* 10.31 Hz, H_b-1), 3.85 (1H, dd, *J* 2.06 Hz, *J* 3.44 Hz, H-4), 3.95 (1H, d, *J* 1.38 Hz, H-3), 4.32 (1H, m, H-5); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 70.06 (C-6), 70.93 (C-1), 71.84 (*C*H_2Ph), 71.89 (*C*H_2Ph), 73.26 (*C*H_2Ph), 73.79 (*C*H_2Ph), 81.78 (C-5), 82.72 (C-4), 86.32 (C-3), 105.34 (C-2); β Form: ^{1}H NMR ($CDCl_3$, 600 MHz): δ 3.43 (1H, dd, *J* 4.12 Hz, *J* 10.31 Hz, H_a-6), 3.49 (2H, d, *J* 2.75 Hz, H-1), 3.52 (1H, dd, *J* 4.81 Hz, *J* 10.31 Hz, H_b-6), 4.02 (1H, m, H-5), 4.10 (1H, t, *J* 4.81 Hz, H-4), 4.15 (1H, d, *J* 4.81 Hz, H-3); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 70.59 (C-6), 71.89 (C-1), 72.09 (*C*H_2Ph), 72.68 (*C*H_2Ph), 73.51 (*C*H_2Ph), 73.59 (*C*H_2Ph), 79.95 (C-5), 83.41 (C-4), 83.65 (C-3), 102.43 (C-2). HRESIMS (α/β mixture): calcd for $C_{34}H_{36}O_6\cdot K^+$: 579.2143; found: *m*/*z* 579.2184.

1.3.2. Preparation of 2,3,6-tri-*O*-benzyl-4-*O*-(2,3,4,6-tetra-*O*-benzyl-β-D-galactopyranosyl)-D-glucopyranose (9) and 3 from 4. The same procedure as for **1** was used starting from **4** (61.5 mg, 0.041 mmol) in dioxane (3 mL) and using 75% aq H_2SO_4 (0.3 mL) and then

stirring for 1 h at room temperature which resulted in **9**[10] (34 mg, 85%) and **3** (20 mg, 91%) both as colorless syrups. Compound **9** (63:37 α/β mixture); α Form: ^{1}H NMR ($CDCl_3$, 600 MHz): δ 3.32–3.35 (2H, m, H-3′, H-5′), 3.37 (1H, dd, *J* 5.50 Hz, *J* 8.94 Hz, H_a-6′), 3.51 (1H, dd, *J* 3.44 Hz, *J* 9.62 Hz, H-2), 3.52–3.56 (2H, m, H_a-6, H_b-6′), 3.74 (H, dd, *J* 7.56 Hz, *J* 9.62 Hz, H-2′), 3.82–3.86 (2H, m, H-3, H_b-6), 3.89–3.96 (3H, m, H-4, H-5, H-4′), 4.35 (1H, d, *J* 7.56 Hz, H-1′), 5.16 (1H, d, *J* 3.44 Hz, H-1); ^{13}C NMR ($CDCl_3$ 150 MHz): δ 68.01 (C-6), 68.16 (C-6′), 70.37 (C-5), 72.55 (*C*H_2Ph), 73.05 (C-5′), 73.09 (*C*H_2Ph), 73.37 (*C*H_2Ph), 73.56 (*C*H_2Ph), 73.69 (C-4′), 74.66 (*C*H_2Ph), 75.17 (*C*H_2Ph), 75.36 (*C*H_2Ph), 76.44 (C-4), 79.05 (C-2), 79.89 (C-2′, C-3), 82.39 (C-3′), 91.34 (C-1), 102.83 (C-1′); β Form: ^{1}H NMR ($CDCl_3$, 600 MHz): δ 4.37 (1H, d, *J* 7.56 Hz, H-1′), 4.65 (1H, m, H-1); ^{13}C NMR ($CDCl_3$ 150 MHz): δ 68.03, 68.21, 72.61, 73.08, 73.09, 73.15, 73.42, 73.65, 73.75, 74.70, 75.23, 75.28, 75.41, 76.40, 79.11, 79.95, 82.45, 97.50 (C-1), 103.45 (C-1′); HRESIMS (α/β mixture): calcd for $C_{61}H_{64}O_{11}{\cdot}Na^+$: 995.4341; found: *m*/*z* 995.4378. The ^{1}H and ^{13}C NMR data were in accordance with the lit. data.[10]

1.3.3. Preparation of 2,3,4-tri-*O*-benzyl-6-*O*-(2,3,4,6-tetra-*O*-benzyl-α-D-galactopyranosyl)-D-glucopyranose (10) and 3 by the hydrolysis of 5. The procedure used for **1** was applied starting from **5** (110 mg, 0.074 mmol) in dioxane (3 mL) to which was added 75% aq H_2SO_4 (0.3 mL). resulting in **10** (66 mg, 92%) and **3** (36 mg, 90%), both as colorless syrups. Compound **10** (61:39 α/β mixture); α Form: ^{1}H NMR ($CDCl_3$, 600 MHz): δ 3.39 (1H, dd, *J* 3.44 Hz, *J* 8.94 Hz, H-2), 3.46–3.55 (4H, m, H-4, H-6, H-5′), 3.73 (1H, dd, *J* 5.50 Hz, *J* 12.37 Hz, H_a-6′), 3.85 (1H, dd, *J* 5.50 Hz, *J* 11.00 Hz, H_b-6′), 3.91 (1H, dd, *J* 2.75 Hz, *J* 10.31 Hz, H-4′), 3.94 (1H, t, *J* 10.31 Hz, H-3′), 3.95 (1H, t, *J* 9.62 Hz, H-3), 4.02 (1H, dd, *J* 3.44 Hz, *J* 10.31 Hz, H-2′), 4.05 (1H, m, H-5), 4.99 (1H, d, *J* 3.44 Hz, H-1′), 5.09 (1H, d, *J* 2.75 Hz, H-1); ^{13}C NMR ($CDCl_3$ 150 MHz): δ 67.59 (C-6′), 69.21 (C-6), 69.50 (C-5′), 70.69 (C-5), 72.53 (*C*H_2Ph), 72.95 (*C*H_2Ph), 73.13 (*C*H_2Ph), 73.36 (*C*H_2Ph), 74.68 (*C*H_2Ph), 74.97 (C-4′, *C*H_2Ph), 75.59 (*C*H_2Ph), 76.67 (C-2′), 77.99 (C-4), 78.43 (C-3′), 80.30 (C-2), 81.75 (C-3), 90.97 (C-1), 98.36 (C-1′); β Form: ^{1}H NMR ($CDCl_3$, 600 MHz): 4.67 (1H, d, *J* 7.56 Hz, H-1), 5.00 (1H, d, *J* 3.44 Hz, H-1′); ^{13}C NMR ($CDCl_3$ 150 MHz): δ 67.78, 69.24, 72.92, 73.09, 73.48, 74.34, 74.65, 74.79, 74.86, 74.97, 75.10, 75.35, 76.63, 77.84, 78.67, 83.47, 84.47, 97.16 (C-1), 98.26 (C-1′); HRESIMS (α/β mixture): calcd for $C_{61}H_{64}O_{11}{\cdot}K^+$: 1011.4080; found: *m*/*z* 1011.4113; Anal. Calcd for $C_{61}H_{64}O_{11}{\cdot}0.5H_2O$: C, 74.60; H, 6.67. Found: C, 74.52; H, 6.48.

1.3.4. Preparation of 1,4,6-tri-*O*-benzyl-3-*O*-(2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl)-D-fructofuranose (11) from 6. The procedure used for **1** was applied to **6** (133 mg, 0.089 mmol) in dioxane (3 mL) to which was added 75% aq H_2SO_4 (0.3 mL) resulting in **11** (66 mg, 77%) as a colorless syrup and **2** (45 mg, 94%) as white crystals. Compound **11** (2:3 α/β mixture); α Form: ^{1}H NMR ($CDCl_3$, 600 MHz): δ 4.81 (1H, d, *J* 3.44 Hz, H-1′); ^{13}C NMR ($CDCl_3$ 150 MHz): δ 67.85, 70.45, 70.49, 70.88 (C-5′), 71.48, 72.97, 73.07, 73.10, 74.70, 74.92, 75.54, 77.38, 79.17, 81.07, 81.94, 82.30, 82.57, 95.04 (C-1′), 105.69 (C-2); β Form: ^{1}H NMR ($CDCl_3$, 600 MHz): 3.44 (1H, dd, *J* 3.44 Hz, *J* 10.31 Hz, H_a-6), 3.49 (1H, m, H_a-6′), 3.54 (1H, d, *J* 10.31 Hz, H_a-1), 3.55–3.58 (2H, m, H-2′, H_b-6), 3.61–3.69 (2H, m, H-4′, H_b-6′), 3.74 (1H, d, *J* 10.31 Hz, H_b-1), 4.00 (1H, t, *J* 9.62 Hz, H-3′), 4.04 (1H, m, H-5′), 4.11 (1H, m, H-5), 4.24 (1H, t, *J* 6.19 Hz, H-4), 4.42 (1H, d, *J* 6.19 Hz, H-3), 5.03 (1H, d, *J* 3.44 Hz, H-1′); ^{13}C NMR ($CDCl_3$ 150 MHz): δ 68.28 (C-6′), 70.31 (C-6), 70.85 (C-5′), 71.24 (C-1), 71.26 (*C*H_2Ph), 73.07 (*C*H_2Ph), 73.41 (*C*H_2Ph), 73.46 (*C*H_2Ph), 73.50 (*C*H_2Ph), 75.02 (*C*H_2Ph), 75.63 (*C*H_2Ph), 77.61 (C-4′), 79.58 (C-5), 79.80 (C-2′), 81.85 (C-3′, C-4), 84.41 (C-3), 97.99 (C-1′), 102.54 (C-2). HRESIMS (α/β mixture): calcd for $C_{61}H_{64}O_{11}{\cdot}Na^+$: 995.4341; found: *m*/*z* 995.4376. Anal. Calcd for $C_{61}H_{64}O_{11}{\cdot}0.5H_2O$: C, 74.60; H, 6.67. Found: C, 74.68; H, 6.64.

1.3.5. Preparation of 2,3,4-tri-*O*-benzyl-6-*O*-[2,3,4-tri-*O*-benzyl-6-*O*-(2,3,4,6-tetra-*O*-benzyl-α-D-galactopyranosyl)-α-D-galactopyranosyl]-D-glucopyranose (12) and 3 from 7. The procedure used for **1** was applied starting from **7** (278 mg, 0.14 mmol) in dioxane (8 mL) to which was added 75% aqueous H_2SO_4 (0.8 mL), resulting in **12** (187 mg, 92%) and **3** (67 mg, 86%) both as colorless syrups. Compound **12** (19:31 α/β mixture); α Form: ^{1}H NMR ($CDCl_3$, 600 MHz): δ 3.34–3.37 (1H, m, H-2), 3.48–3.83 (9H, m, H-6, H-5′, H-6′, H-2″, H-5″, H-6″), 3.90–4.04 (4H, m, H-3, H-4, H-5, H-2′), 4.77–4.82 (1H, m, H-1″), 5.00 (1H, d, *J* 3.44 Hz, H-1′), 5.05 (1H, d, *J* 2.75 Hz, H-1); ^{13}C NMR ($CDCl_3$ 150 MHz): δ 66.77 (C-6), 67.22 (C-6′), 68.70 (C-6″α or C-6″β), 68.90 (C-6″α or C-6″β), 69.17 (C-5′), 69.40 (C-5″), 70.69 (C-5), 75.36 (C-4), 78.21 (C-2′α or C-4″β), 78.23 (C-2′α or C-4″β), 78.73 (C-2″), 80.26 (C-2), 90.95 (C-1), 97.85 (C-1′), 98.23 (C-1″); β Form: ^{1}H NMR ($CDCl_3$, 600 MHz): δ 3.17 (1H, dd, *J* 7.56 Hz, *J* 8.97 Hz, H-2), 3.34–3.37 (1H, m, H-3″), 3.48–3.83 (11H, m, H-3, H-4, H-6, H-5′, H-6′, H-4″, H-5″, H-6″), 3.90–4.04 (3H, m, H-5, H-2′, H-2″), 4.54 (1H, d, *J* 7.56 Hz, H-1), 4.77–4.82 (1H, m, H-1″), 4.90–4.93 (1H, m, H-1′); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 67.33 (C-6), 67.50 (C-6′), 68.70 (C-6″α

or C-6″β), 68.90 (C-6″α or C-6″β), 69.02 (C-5″), 69.37 (C-5′), 75.18 (C-4), 78.21 (C-2′α or C-4″β), 78.23 (C-2′α or C-4″β), 78.24 (C-3″), 78.39 (C-3), 81.63 (C-2′), 83.88 (C-2), 84.53 (C-2″), 97.20 (C-1), 97.49 (C-1′), 98.44 (C-1″); HRESIMS (α/β mixture): calcd for $C_{88}H_{92}O_{16}{\cdot}Na^{+}$: 1427.6278; found: *m*/*z* 1427.6254. Anal. Calcd for $C_{88}H_{92}O_{16}$: C, 75.19; H, 6.60. Found: C, 75.51; H, 6.76.

1.3.6. Preparation of 3,4,6-tri-*O*-benzyl-D-fructofuranose (13), 2 and 3 from 8. The procedure used for **1** was applied starting from **8** (97 mg, 0.05 mmol) in dioxane (3 mL) to which was added 75% aq H_2SO_4 (0.3 mL) resulting in **2** (21 mg, 78%) as white crystals, **3** (24 mg, 88%) and **13** (24 mg, 54%) both as colorless syrups. Compound **13** (8:17 α/β mixture); α Form: ^{1}H NMR ($CDCl_3$, 600 MHz): δ 3.51–3.56 (2H, m, H-1), 3.69 (1H, dd, *J* 7.56 Hz, *J* 11.69 Hz, H_a-6), 3.78 (1H, dd, *J* 4.12 Hz, *J* 11.69 Hz, H_b-6), 4.02–4.04 (2H, m, H-3, H-4), 4.36 (1H, m, H-5); ^{13}C NMR ($CDCl_3$ 150 MHz): δ 64.25 (C-1), 69.63 (C-6), 72.05 (*C*H_2Ph), 72.20 (*C*H_2Ph), 73.30 (*C*H_2Ph), 81.02 (C-5), 82.08 (C-4), 86.36 (C-3), 105.36 (C-2); β Form: ^{1}H NMR ($CDCl_3$, 600 MHz): δ 3.50 (1H, dd, *J* 4.12 Hz, *J* 10.31 Hz, H_a-6), 3.57 (1H, dd, *J* 4.81 Hz, *J* 10.31 Hz, H_b-6), 3.59–3.62 (2H, m, H-1), 4.11 (1H, m, H-5), 4.16–4.17 (2H, m, H-3, H-4); ^{13}C NMR ($CDCl_3$ 150 MHz): δ 65.15 (C-1), 70.67 (C-6), 72.02 (*C*H_2Ph), 72.85 (*C*H_2Ph), 73.52 (*C*H_2Ph), 80.55 (C-5), 83.29 (C-3), 83.49 (C-4), 103.08 (C-2); HRESIMS (α/β mixture): calcd for $C_{27}H_{30}O_6{\cdot}Na^{+}$: 473.1935; found: *m*/*z* 473.1940. Anal. Calcd for $C_{27}H_{30}O_6$: C, 71.98; H, 6.71. Found: C, 72.14; H, 6.88.

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References

1. Toshima, K.; Tatsuta, K. *Chem. Rev.* **1993**, *93*, 1503–1531.
2. Yamanoi, T.; Inoue, N.; Fujimoto, M.; Sasaura, H.; Murota, A. *Heterocycles* **2003**, *60*, 2425–2428.
3. (a) Tate, M. E.; Bishop, C. T. *Can. J. Chem.* **1963**, *41*, 1801–1806; (b) Kasbeck, L.; Kessler, H. *Liebigs Ann./Recueil* **1997**, 169–173.
4. Ness, R. K.; Diehl, H. W.; Fletcher, J. H. G. *Carbohydr. Res.* **1970**, *13*, 23–32.
5. (a) Hino, K.; Kurose, M.; Sakurai, T.; Inoue, S.-I.; Oku, K.; Chaen, H.; Fukuda, S. *J. Appl. Glycosci.* **2007**, *54*, 169–172; (b) Rackis, J. J. In *Physiological Effects of Food Carbohydrates*; Jeanes, A., Hodge, J., Eds.; ACS Symposium Ser. No. 15; American Chemical Society: Washington, DC, 1975; p 207.
6. Yu, R. K.; Yanagisawa, M.; Ariga, T. Glycosphingolipid Structures. In *Comprehensive Glycoscience, From Chemistry to Systems Biology*, 1st ed.; Kamerling, J. P., Boons, G.-J., Lee, Y. C., Suzuki, A., Taniguchi, N., Voragen, A. G. J., Eds.; Elsevier: Oxford, 2007; Vol. 1, pp 73–122.
7. Hardick, D. J.; Hutchinson, D. W.; Trew, S. J.; Wellington, E. M. H. *Tetrahedron* **1992**, *48*, 6285–6296.
8. Harrison, R.; Fletcher, J. H. G. *J. Org. Chem.* **1965**, *30*, 2317–2321.
9. Sato, T.; Nakamura, H.; Ohno, Y.; Endo, T. *Carbohydr. Res.* **1990**, *199*, 31–35.
10. Ishii, K.; Kubo, H.; Yamasaki, R. *Carbohydr. Res.* **2002**, *337*, 11–20.