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Note

Simple preparations of alkyl and cycloalkyl α-glycosides of maltose, cellobiose, and lactose

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This paper is dedicated to Dr. Yukio Ito

Abstract—Alkyl, cycloalkyl, allyl, 4-pentenyl, and benzyl α-glycosides of maltose, cellobiose, and lactose were prepared (17–77% yield; α/β = 70/30–96/4) via a direct reaction of the free disaccharides with a binary AcBr–AcOH mixture, followed by glycosidation with alcohol using $FeCl_3$ in $MeNO_2$ or CH_2Cl_2, Zemplén deacetylation, and resolution of the anomeric mixture of glycosides by chromatography. Using MeCN as solvent for the glycosidation step, the corresponding β-biosides were also prepared (16–61% yield; α/β = 25/75–5/95).

Keywords: α-Glycosidation; Iron(III) chloride; Glycosyl bromide; Disaccharide

Methyl, allyl, 4-pentenyl, and benzyl glycosides of such disaccharides as maltose (**1**), cellobiose (**2**), and lactose (**3**), are of diverse use as starting materials for various syntheses. Longer-chain alkyl biosides are widely used as nonionic surfactants[1] and are known to form liquid crystalline phases.[2] They are used as sugar acceptors for enzymatic glycosylation[3] and as the lipophile-carrying head-moiety of artificial bioactive sugar clusters.[4] Several biosides are probe-guests combining to receptor proteins[5] and artificial receptors.[6,7] Some long-chain alkyl maltosides enhance the nasal insulin absorption[8] and the bioavailability of calcitonin.[9]

We present here convenient preparations of alkyl, cycloalkyl, allyl, 4-pentenyl, and benzyl α-glycosides of the common disaccharides, **1**, **2**, and **3**, directly from the respective free bioses, as shown in Figure 1. The procedure consists of (*i*) direct reaction of the bioses with a binary AcBr–AcOH system for 0.5 h, (*ii*) condensation of the alcohol with the crude biosyl bromides in the presence of $FeCl_3$ (1–2 mol amount to the starting bioses) in $MeNO_2$ or CH_2Cl_2 for 1 h, (*iii*) deacetylation with methanolic NaOMe, and (*iv*) chromatographic resolution of the anomeric mixture of glycosides formed. When MeCN was used as the solvent in the glycosidation step for 1 h, as shown in Figure 2, the corresponding β-biosides were obtained.

The Fischer method has been used to prepare alkyl α-glycosides directly from glycoses, but its application to a disaccharide (biose) such as **1** is difficult,[10] because of concurrent alcoholysis of the interglycosidic linkage.[11–13] For example,[13] the reaction of **1** with MeOH containing HCl (1%) at 20–25 °C for 4 days affords the corresponding disaccharide glycosides (biosides) in ~35% yield (α/β = ~50/50). The direct glycosidation of **3** with neat 4-penten-1-ol by refluxing at 110 °C for 9 h with 10-camphorsulfonic acid[14] was reported to give an anomeric mixture of the corresponding biosides, but their yields were not given. At present, alkyl α-biosides are best prepared indirectly; thus, the in situ anomerizing

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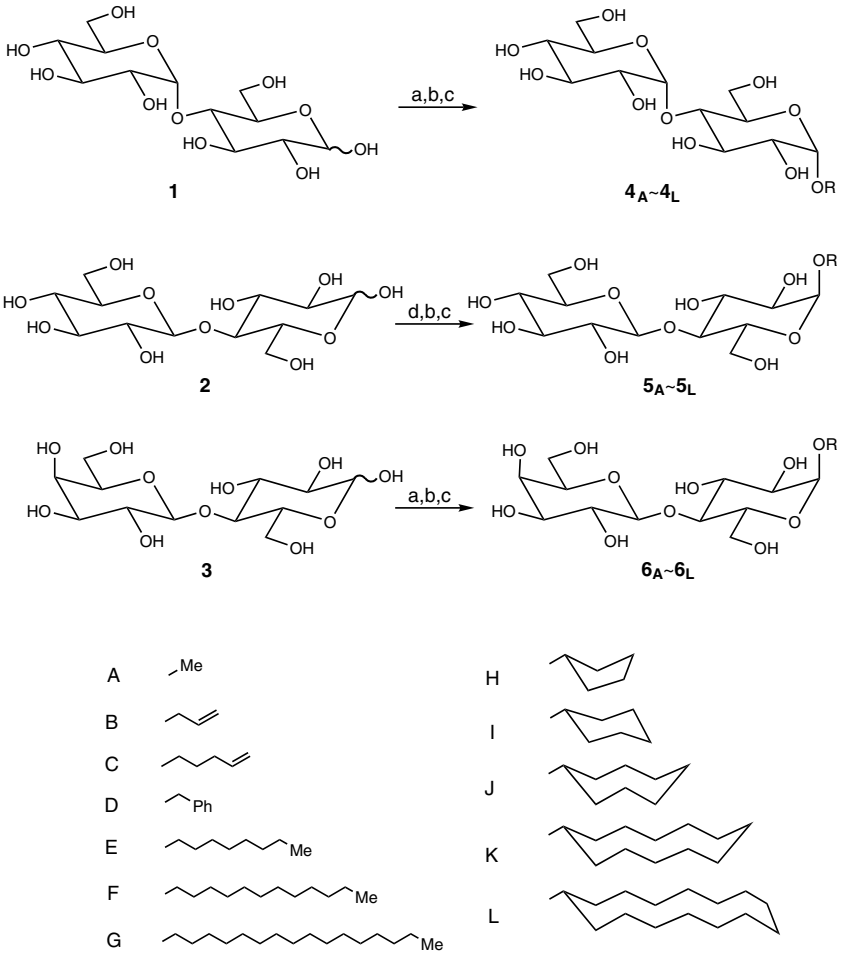

Figure 1. Preparation of α-biosides: (a) AcBr/AcOH, room temperature (rt, ca. 25 °C), 0.5 h; (b) ROH+$FeCl_3$/$MeNO_2$ or CH_2Cl_2, rt, 1 h; (c) NaOMe/MeOH, rt, overnight; (d) AcBr/AcOH, 60 °C, 0.5 h.

glycosylation starting from the respective biose octaacetates is the most useful for obtaining alkyl α-biosides.[15] However, the α-biosylation in the presence of $SnCl_4$ in CH_2Cl_2[15–19] takes more than 4 h. Other methods, starting from 1-thio sugar derivatives,[20,21] 1-*O*-(2,4,6-trimethylbenzoyl)sugars,[22] 1-OH sugar derivatives,[23] and β-glycosides,[24] as well as enzymic methods,[25] require preparation of the particular donors. In contrast, alkyl β-biosides are readily prepared by the standard Koenigs–Knorr method.[1] Such β-biosides are also prepared by short reactions (2 h) using octaacetates and alcohol in the presence of $SnCl_4$[15,17] or $BF_3{\cdot}Et_2O$[19] in CH_2Cl_2.

Direct reaction of the free disaccharides, **1** and **3** with AcBr[26,27] is an old reaction, but is not frequently used, probably because of the difficultly controllable violent evolution of HBr.[28] Some years ago, we reported that direct preparation of the glycosyl bromides from free disaccharides **1** and **3** could be carried out at room temperature using a binary AcBr–AcOH mixture.[29,30] However, this reaction with **2**, which is sparingly soluble in the system, took over 5 h at room temperature. In this study, we found that this went to completion within 0.5 h at 60 °C. It was also found that reactions of **1** and **3** finished within 0.5 h at room temperature (~25 °C). This binary AcBr–AcOH system is more efficient than the ternary Ac_2O–HBr–AcOH system for the direct acetobromination of free bioses; the latter takes more than 2 h for completion.[31,32]

As the condensation reagent for the subsequent glycosidation using biosyl bromides, we used $FeCl_3$, since it was used as an α-glycosidation reagent for the condensation between biose octaacetates and alcohols in $CHCl_3$ at the reflux temperature,[33] but not for the Koenigs–Knorr reaction using the glycosyl bromides, which are expected to be more reactive than the glycosyl acetates. This reagent catalyzes the anomerization of methyl hepta-*O*-acetyl-β-cellobioside,[34] the α-glycosidation of fully acetylated sugars,[35] the Ferrier reaction,[36] the Fischer reaction,[37] the formation of 1,6-anhydro sugars,[38] and the synthesis of β-glucosaminides.[39] we thus considered that $FeCl_3$ would be a good substitute for the standard

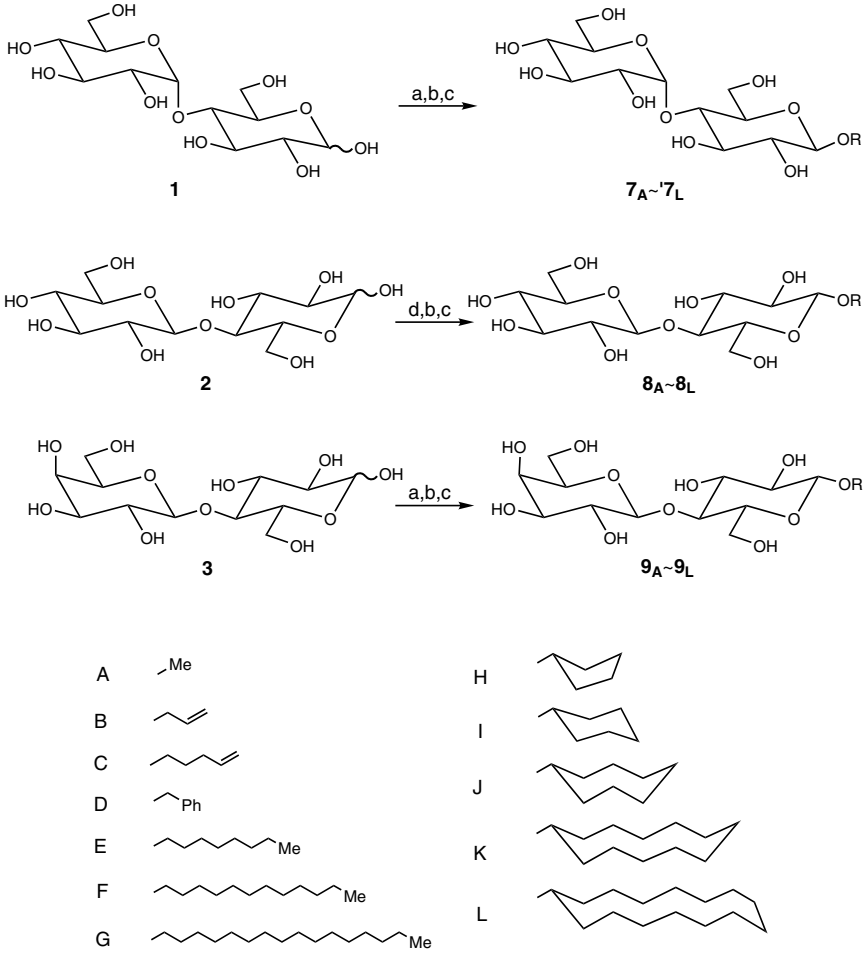

Figure 2. Preparation of β-biosides: (a) AcBr/AcOH, room temperature (rt, ca. 25 °C), 0.5 h; (b) ROH+$FeCl_3$/MeCN, rt, 1 h; (c) NaOMe/MeOH, rt, overnight; (d) AcBr/AcOH, 60 °C, 0.5 h.

reagents of the Koenigs–Knorr method. As shown in Table 1, the reactive biosyl bromides were converted within 1 h at room temperature in $MeNO_2$ or CH_2Cl_2 containing 1.0–1.5 mol of $FeCl_3$ relative to the starting bioses. For lower alcohols, $MeNO_2$ as solvent gave α-biosides with acceptable yields and α-selectivity. For higher ones, such as 1-hexadecanol and cyclopentadecanol, CH_2Cl_2, in which they dissolve well, gave better results. The condensation with allyl alcohol in $MeNO_2$ containing only 1.0 mol amount of $FeCl_3$ to the starting sugars proceeded smoothly to give **4B**, **5B**, and **6B** in ~70% yield, whereas, in CH_2Cl_2 with a 1.5 mol amount of $FeCl_3$, the yields were slightly low (<50%). Longer reaction time (3 h) in $MeNO_2$ slightly diminished the yield of biosides (~60%); but the selectivities were raised (α/β = ~95/5), whereas shorter ones (0.5 h) in $MeNO_2$ gave similar yields (65–70%) but with lower selectivities (α/β = ~80/20). The reactions with other metal salts such as $CoBr_2$[40] and $ZnCl_2$[41] for 3 h resulted similar yields, but with lower selectivities (α/β = 60/40–40/60). In the case of benzyl alcohol, the yields of **4D**, **5D**, and **6D** were low (~20%). When CH_2Cl_2 was used as the solvent, yields were improved (>50%), but the α-selectivities were low (α/β = ~60/40). For the *n*-octyl α-biosides, **4E**, **5E**, and **6E**, the yields of the biosides using $PhCF_3$[42] as solvent were comparable to those using $MeNO_2$ but the selectivities were very low (α/β = ~50/50).

When the glycosidation was conducted in MeCN at room temperature for 1 h, as shown in Figure 2, the corresponding β-biosides were formed selectively (α/β = 25/75–5/95), in spite of a depression of the yields (Table 1). It seems that MeCN weakens the promoting effects of $FeCl_3$, both for condensation and anomerization. In most cases, the amount of $FeCl_3$ could be increased to 2.0 mol to the starting bioses without significantly by raising the content of the α anomers. However, especially in synthesis of the lactosides of cycloalkanols, the anomeric ratios of the products were sensitive to the reaction time; thus extension of the reaction time to only 1.5 h raised the content of the α anomers. The β-biosides were thus obtained selectively in ~40% yield

Table 1. Results of preparations of disaccharides

Alcohol	$FeCl_3$/mol amount	Solvent	Yield/% (α/β)		
			Maltosides	Cellobiosides	Lactosides
Methanol	1.5	N	60 (95/5)	56 (87/13)	52 (89/11)
Methanol	2.0	A	26 (11/89)	33 (5/95)	27 (9/92)
Allylalcohol	1.0	N	71 (87/13)	77 (89/11)	65 (90/10)
Allylalcohol	2.0	A	52 (14/86)	61 (17/83)	58 (20/80)
4-Penten-l-ol	1.5	N	26 (70/30)	28 (73/27)	30 (75/25)
4-Penten-l-ol	1.5	A	39 (13/87)	43 (17/83)	45 (16/84)
Benzylalcohol	1.5	N	22 (86/14)	17 (94/6)	19 (92/8)
Benzylalcohol	2.0	A	34 (9/91)	58 (7/93)	57 (7/93)
1-Octanol	1.5	N	65 (93/7)	65 (96/4)	67 (92/8)
1-Octanol	2.0	A	39 (9/91)	30 (8/92)	34 (20/80)
1-Dodecanol	1.5	N	69 (91/9)	57 (91/9)	60 (98/11)
1-Dodecanol	2.0	A	34 (18/82)	40 (18/82)	31(19/81)
1-Hexadecanol	1.5	D	56 (95/5)	62 (85/15)	50 (95/5)
1-Hexadecanol	2.0	A	49 (5/95)	21 (5/95)	27 (20/80)
Cyclopentanol	1.5	N	63 (87/13)[a]	71 (88/12)	52 (87/13)
Cyclopentanol	2.0	A	20 (17/83)	32 (17/83)	40 (23/77)[b]
Cyclohexanol	1.5	N	69 (84/16)	66 (86/14)	73 (87/13)
Cyclohexanol	2.0	A	25 (22/78)	30 (10/90)	34 (23/77)[b]
Cyclooctanol	1.0	N	21 (86/14)	22 (94/6)	26 (86/14)
Cyclooctanol	2.0	A	16 (17/83)	19 (20/80)	22 (25/75)
Cyclododecanol	1.5	N	50 (88/12)	56 (91/9)	51 (95/5)
Cyclododecanol	2.0	A	26 (5/95)	26 (17/83)	43 (22/78)[b]
Cyclopentadecanol	1.5	D	74 (87/13)	65 (92/8)	55 (91/9)
Cyclopentadecanol	2.0	A	32 (17/83)	24 (6/94)	25 (5/95)[b]

[a] $FeCl_3$ (1.0 mol amount) was used.
[b] $FeCl_3$ (1.5 mol amount) was used.

at best, except for the allyl β-biosides, **7B**, **8B**, and **9B**, (50–60% yield; α/β = ~20/80).

1. Experimental

1.1. General methods

The solvent systems for column chromatography on silica gel (Kanto Kagaku, No 37047; gradient elusion) and thin-layer chromatography (TLC) (Merck, DC-Plastikfolien Kieselgel 60 F 254, Art. 5735) were $CHCl_3$–MeOH (CM) and PhMe–butanone (TK), and that for column chromatography on Dowex 1 × 2 was a pyridine–MeOH (PM) system.

Solvents were evaporated from solutions obtained at 35–45 °C under diminished pressure, unless otherwise noted. The melting points were determined on a Yanaco Micro Melting Point Apparatus (Yanagimoto). Optical rotations were measured on a Jasco DIP-180 digital polarimeter at room temperature. The ^1H and ^{13}C NMR spectra were recorded with a Varian XL-400 spectrometer, along with measurements of H,H-COSY, C,H-COSY, and DEPT spectra. Spectral assignments were made by auxiliary measurements of HOHAHA, HMQC, HMBC, GHMQC, and differential NOE spectra. HRMS were recorded with a Jeol JMS-AX505HA spectrometer or a Jeol JMS-700 spectrometer. The ^1H NMR data of the biosides prepared are given in Tables 2 and 3 and their ^{13}C NMR data are in Tables 4 and 5.[†]

1.2. Synthesis of biosides

A mixture of **1** or **3** (monohydrate, 1.0 g, 2.8 mmol), AcBr (3.6 mL, 44.4 mmol), and AcOH (19 mL) was stirred at room temperature (~25 °C) for 0.5 h to give a homogeneous solution. The mixture was concentrated below 25 torr at 30 °C, co-evaporated three times with dry PhMe (5 mL), and evacuated below 25 torr at 50 °C for 15 min to give a foam [HRMS (FAB) Found: from **1**, *m/z* 721.0964 and from **3**, *m/z* 721.0990. Calcd for $C_{26}H_{35}BrNaO_{11}$ $[M+Na]^+$: 721.0955]. To the crude bromide, the solvent (10 mL), alcohol (5.6 mmol), and $FeCl_3$ were added with vigorous stirring at room temperature for 1 h. To the mixture, aq KBr (10%, 25 mL) and then PhMe (60 mL) were added under stirring. The organic phase was washed with aq KBr (10%, 25 mL, twice), aq $NaHCO_3$ (5%, 25 mL), and H_2O (25 mL, twice). The organic layer was evaporated to dryness. The resultant mixture was dissolved in MeOH (30 mL) containing methanolic NaOMe (7%, 2 mL) and the solution stirred at room temperature overnight. After the addition of AcOH (0.2 mL), the mixture was

[†] Note added in proof: the supplementary NMR data are available at http://kitasato-u.ac.jp/medicinal.

Table 2. ^{1}H NMR data of selected α-biosides determined at 400 MHz (M = CD_3OD, W = D_2O)

Compounds (Solv.)	**4A** (W)	**4E** (W)	**4F** (M)	**4L** (M)	**5A** (W)	**5E** (W)	**5F** (M)	**5L** (M)	**6A** (W)	**6E** (W)	**6F** (M)	**6L** (M)
H-1^{I}	4.78	4.86	4.77	4.89	4.78	4.85	4.77	4.89	4.77	4.86	4.78	4.88
$J_{1,2}$	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	3.5	4.0	4.0
H-2^{I}	3.56	3.56	3.45	3.43	3.58	3.57	3.45	3.44	3.57	3.58	3.46	3.44
$J_{2,3}$	10.0	9.0	10.0	10.0	10.0	9.5	9.5	10.0	9.5	9.0	9.5	9.5
H-3^{I}	3.89	3.92	3.88	3.86	3.76	3.80	3.76	3.75	3.75	3.82	3.77	3.75
$J_{3,4}$	9.0	9.0	9.0	9.5	9.0	8.5	9.0	9.0	10.0	9.0	8.5	10.0
H-4^{I}	3.62	3.66	3.51	3.53	3.61	3.64	3.54	3.36	3.61	3.67	3.54	3.55
$J_{4,5}$	9.0	9.5	10.0	9.5	10.0	9.5	9.5	9.5	10.0	9.0	10.0	10.0
H-5^{I}	3.73	3.64	3.62	3.70	3.78	3.70	3.68	3.77	3.73	3.72	3.69	3.79
$J_{5,6a}$	4.5	6.0	4.5	2.0	4.0	5.5	2.0	2.0	5.0	5.5	2.0	2.0
$J_{5,6b}$	2.0	2.0	2.0	6.0	2.0	3.0	4.5	4.0	2.0	3.5	4.0	4.0
H-6a^{I}	3.77	3.76	3.81	3.77	3.82	3.79	3.80	3.76	3.81	3.78	3.81	3.80
H-6b^{I}	3.85	3.83	3.83	3.86	3.89	3.91	3.88	3.91	3.89	3.91	3.86	3.89
$J_{6a,b}$	12.0	13.0	12.0	12.0	12.0	11.0	12.0	12.0	12.0	10.0	12.0	12.0
H-1^{II}	5.36	5.28	5.15	5.15	4.48	4.50	4.40	4.41	4.40	4.42	4.35	4.36
$J_{1,2}$	4.0	4.0	4.0	4.0	8.0	8.0	8.0	8.0	8.0	8.0	7.5	7.5
H-2^{II}	3.53	3.56	3.45	3.45	3.29	3.32	3.24	3.24	3.50	3.55	3.55	3.55
$J_{2,3}$	10.0	9.5	10.0	9.5	10.0	9.0	8.5	9.0	10.0	10.0	9.5	9.5
H-3^{II}	3.65	3.66	3.63	3.61	3.48	3.49	3.38	3.88	3.62	3.65	3.48	3.49
$J_{3,4}$	9.0	9.5	9.0	9.0	9.0	9.5	9.0	9.0	3.5	3.5	3.0	3.0
H-4^{II}	3.38	3.41	3.27	3.26	3.39	3.38	3.32	3.33	3.88	3.90	3.82	3.82
$J_{4,5}$	9.5	9.5	10.0	9.5	9.0	9.0	10.0	9.5	1.0	1.0	1.0	1.0
H-5^{II}	3.68	3.66	3.69	3.67	3.46	3.46	3.35	3.37	3.66	3.70	3.59	3.59
$J_{5,6a}$	5.5	5.0	6.0	5.5	6.0	5.5	5.0	5.5	4.0	3.5	4.5	4.0
$J_{5,6b}$	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	7.0	8.0	7.5	6.0
H-6a^{II}	3.73	3.76	3.68	3.65	3.70	3.70	3.67	3.67	3.70	3.72	3.70	3.70
H-6b^{II}	3.82	3.79	3.83	3.84	3.90	3.89	3.88	3.88	3.77	3.78	3.79	3.79
$J_{6a,b}$	12.0	12.0	11.5	12.0	11.5	11.0	11.5	11.5	13.0	12.0	11.5	12.0

Aglycon; **4A**: 3.38 (s, Me); **4E**: 0.85 (t, J = 6.5 Hz, Me); **4F**: 0.90 (t, J = 7.0 Hz, Me); **5A**: 3.40 (s, Me); **5E**: 0.84 (t, J = 6.5 Hz, Me); **5F**: 0.90 (t, J = 7.0 Hz, Me); **6A**: 3.53 (s, Me); **6E**: 0.85 (t, J = 6.0 Hz, Me); **6F**: 0.90 (t, J = 6.0 Hz, Me).

evaporated to dryness and chromatographed with the CM system (100:1 → 1:10) to give first the β anomer and then α anomer. Accompanying bioses as impurities, if any, were separated by chromatography on a Dowex 1 × 2 (OH form, 100–200 mesh) with the PM system (10:1 → 1:10).[43] Further purification was by recrystallization from the specified solvents or by repeated chromatography. The α/β values in Tables 1–3 are based on the weights of the isolated anomers and those of fractions containing both anomers whose anomeric ratios were determined from their ^{1}H NMR spectra. The R_f values of the β anomers of each anomeric pair of biosides were greater than those of the corresponding α anomers by TLC using the CM system.

The acetobromination of **2** was performed under more-vigorous conditions as follows: a mixture of **2** (1.0 g, 2.9 mmol), AcBr (19 mL, 0.23 mmol), and AcOH (19 mL) was stirred at 60 °C for 0.5 h (compound **2** from Sigma needed longer warming, for 1 h) to afford a homogeneous solution, which was evaporated to dryness as before to give a crystalline solid [HRMS (FAB) Found: *m/z* 721.0963. Calcd for $C_{26}H_{35}BrNaO_{11}$ $[M+Na]^+$: 721.0955].

The physical constants (melting points and specific rotations in the specified solvents in the literature for) of **4A**,[10,11,13,20,21] **7A**,[11–13] **5A**,[12,21] **8A**,[12] **6A**,[21] **9A**,[44] **9B**,[45] **7D**,[46] **8D**,[47] **9D**,[48] **7E**,[49] **8E**,[50,51] **7F**,[49,52–54] **8F**,[50,53] **8G**,[50] **4I**,[10] **8I**,[55] all showed correct *m/z* value by HRMS (FAB), agreement with the reported data within experimental error.

1.2.1. Allyl α-D-glucopyranosyl-(1 → 4)-α-D-glucopyranoside (4B). Glass; $[\alpha]_D^{25}$ + 158 (*c* 0.8, H_2O); HRMS (FAB) Calcd for $C_{15}H_{26}NaO_{11}$ $[M+Na]^+$: 405.1373. Found: *m/z* 405.1381.

1.2.2. Allyl α-D-glucopyranosyl-(1 → 4)-β-D-glucopyranoside (7B). Glass; $[\alpha]_D^{25}$ + 70 (*c* 0.8, H_2O); HRMS (FAB) Calcd for $C_{15}H_{26}NaO_{11}$ $[M+Na]^+$: 405.1373. Found: *m/z* 405.1384.

1.2.3. Allyl β-D-glucopyranosyl-(1 → 4)-α-D-glucopyranoside (5B). Glass; $[\alpha]_D^{25}$ + 82 (*c* 0.7, H_2O); HRMS (FAB) Calcd for $C_{15}H_{26}NaO_{11}$ $[M+Na]^+$: 405.1373. Found: *m/z* 405.1371.

1.2.4. Allyl β-D-glucopyranosyl-(1 → 4)-β-D-glucopyranoside (8B). Glass; $[\alpha]_D^{25}$ − 22 (*c* 0.8, H_2O); HRMS (FAB) Calcd for $C_{15}H_{26}NaO_{11}$ $[M+Na]^+$: 405.1373. Found: *m/z* 405.1376.

Table 3. ^{1}H NMR data of selected β-biosides determined at 400 MHz (M = CD_3OD, P = C_5H_5N with CD_3OD, W = D_2O)

Compounds (Solv.)	**7A** (W)	**7E** (W)	**7F** (M)	**7L** (M)	**8A** (W)	**8E** (W)	**8F** (P)	**8L** (P)	**9A** (W)	**9E** (M)	**9F** (P)	**9L** (P)
H-1^{I}	4.35	4.37	4.28	4.33	4.36	4.37	4.80	4.90	4.37	4.28	4.78	4.88
$J_{1,2}$	8.0	8.0	8.0	7.5	8.0	8.0	8.0	8.0	8.0	8.0	8.0	8.0
H-2^{I}	3.25	3.28	3.23	3.20	3.26	3.30	4.03	4.00	3.27	3.24	4.03	4.00
$J_{2,3}$	9.5	9.0	9.0	8.5	9.5	9.0	9.0	9.0	9.0	8.0	8.5	8.5
H-3^{I}	3.73	3.72	3.62	3.62	3.60	3.59	4.27	4.29	3.60	3.52	4.27	4.28
$J_{3,4}$	9.0	9.0	9.0	9.0	9.5	9.0	9.0	9.0	10.0	9.0	9.0	9.0
H-4^{I}	3.59	3.62	3.54	3.56	3.58	3.61	4.33	4.35	3.61	3.57	4.33	4.35
$J_{4,5}$	10.0	9.5	9.5	9.0	9.0	10.0	9.5	9.0	10.0	9.0	9.0	9.0
H-5^{I}	3.55	3.48	3.37	3.35	3.57	3.50	3.90	3.93	3.58	3.40	3.87	3.89
$J_{5,6a}$	4.5	4.5	4.5	3.5	4.5	5.0	2.5	2.5	4.0	5.0	3.0	3.0
$J_{5,6b}$	2.0	2.0	2.0	2.5	2.0	2.0	4.0	4.0	2.0	2.0	4.0	4.0
H-6a^{I}	3.73	3.77	3.81	3.66	3.77	3.82	4.49	4.48	3.77	3.84	4.49	4.47
H-6b^{I}	3.90	3.87	3.88	3.87	3.95	3.89	4.56	4.57	3.95	3.90	4.56	4.56
$J_{6a,b}$	12.0	12.0	12.0	11.0	12.5	12.0	12.0	12.0	12.0	12.5	12.0	12.0
H-1^{II}	5.36	5.34	5.17	5.16	4.46	4.50	5.19	5.20	4.41	4.47	5.14	5.15
$J_{1,2}$	4.0	4.0	4.0	4.0	8.0	8.0	8.0	8.5	8.0	7.5	8.0	8.0
H-2^{II}	3.54	3.55	3.45	3.45	3.27	3.30	4.09	4.08	3.50	3.56	4.54	4.52
$J_{2,3}$	10.0	9.5	9.5	9.5	9.5	9.0	8.5	8.5	10.0	10.0	9.0	10.0
H-3^{II}	3.64	3.65	3.65	3.58	3.46	3.45	4.21	4.21	3.63	3.49	4.17	4.16
$J_{3,4}$	9.0	9.5	9.0	9.0	9.0	9.5	9.0	9.0	3.5	3.5	3.5	3.0
H-4^{II}	3.37	3.39	3.27	3.26	3.37	3.39	4.17	4.16	3.88	3.82	4.49	4.49
$J_{4,5}$	10.0	9.5	9.5	9.0	9.0	10.0	9.0	9.0	1.0	1.0	1.0	1.0
H-5^{II}	3.67	3.67	3.69	3.69	3.44	3.47	4.01	4.00	3.68	3.59	4.15	4.13
$J_{5,6a}$	5.0	5.0	6.5	4.0	5.5	5.5	6.0	6.0	4.0	4.0	5.0	4.5
$J_{5,6b}$	2.0	2.0	2.0	2.5	2.0	2.0	2.5	2.5	7.5	7.0	7.0	6.0
H-6a^{II}	3.73	3.74	3.75	3.80	3.69	3.71	4.29	4.27	3.70	3.70	4.37	4.36
H-6b^{II}	3.82	3.81	3.89	3.87	3.88	3.89	4.53	4.52	3.75	3.78	4.46	4.44
$J_{6a,b}$	12.0	12.5	11.0	12.0	12.5	12.5	12.0	11.5	12.0	11.0	11.0	11.0

Aglycon; **7A**: 3.53 (s, Me); **7E**: 0.84 (t, J = 7.0 Hz, Me); **7F**: 0.91 (t, J = 6.5 Hz, Me); **8A**: 3.53 (s, Me); **8E**: 0.84 (t, J = 6.5 Hz, Me); **8F**: 0.89 (t, J = 7.0 Hz, Me); **9A**: 3.53 (s, Me); **9E**: 0.89 (t, J = 6.5 Hz, Me); **9F**: 0.88 (t, J = 6.0 Hz, Me).

Table 4. ^{13}C NMR data of selected α-biosides determined at 100 MHz (M = CD_3OD, W = D_2O)

Compounds (Solv.)	**4A** (W)	**4E** (W)	**4F** (M)	**4L** (M)	**5A** (W)	**5E** (W)	**5F** (M)	**5L** (M)	**6A** (W)	**6E** (W)	**6F** (M)	**6L** (M)
C-1^{I}	101.7	101.1	100.0	98.4	101.7	100.9	99.9	98.9	101.7	101.0	98.7	198.4
C-2^{I}	73.7	73.8	73.2	73.0	73.7	73.8	73.3	73.9	73.58	73.8	72.1	73.4
C-3^{I}	76.2	76.2	74.9	74.7	74.7	74.5	73.5	73.7	74.4	74.5	72.3	73.2
C-4^{I}	79.5	80.7	81.8	81.6	81.3	81.2	81.0	81.5	81.1	80.8	79.8	80.9
C-5^{I}	72.7	73.1	72.3	72.3	72.9	73.1	72.1	72.7	72.9	73.2	70.9	72.2
C-6^{I}	63.20	63.0	62.1	61.8	62.6	62.6	61.8	62.2	62.6	62.6	60.7	61.8
C-1^{II}	102.3	103.2	102.9	102.8	105.2	105.2	104.6	105.0	105.6	105.6	103.9	105.1
C-2^{II}	74.4	74.6	74.3	74.1	75.8	75.8	74.9	75.4	73.63	73.6	71.4	72.6
C-3^{II}	75.5	75.8	75.1	74.9	78.2	78.4	77.9	78.3	75.2	75.4	73.6	74.8
C-4^{II}	72.0	71.7	71.5	71.4	72.1	72.2	71.4	71.8	71.2	71.3	69.1	70.3
C-5^{II}	75.3	75.5	74.7	74.6	78.8	78.7	78.1	78.6	78.0	78.0	76.0	77.0
C-6^{II}	63.15	63.1	62.7	62.6	63.3	63.4	62.4	62.9	63.7	63.8	61.3	62.5

Aglycon; **4A**: 57.7 (Me); **4E**: 16.5, 25.2, 28.5, 31.8 (2C), 31.9, 34.4, 71.1 (*n*-octyl); **4F**: 14.4, 23.7, 27.3, 30.5, 30.6 (2C), 30.7 (2C), 30.8 (2C), 33.1, 69.3 (*n*-dodecyl); **4L**: 24.0, 24.4, 27.5 (3C), 27.67, 27.74 (3C), 27.9, 28.2, 28.3, 32.5, 34.1, 78.1 (cyclopentadecyl); **5A**: 57.8 (Me); **5E**: 16.4, 25.1, 28.5, 31.8 (2C), 31.9, 34.4, 71.2 (*n*-octyl); **5F**: 14.4, 23.7, 27.3, 30.5, 30.6 (2C), 30.7 (2C), 30.75, 30.77, 33.1, 69.3 (*n*-dodecyl); **5L**: 24.7, 25.1, 28.2 (3C), 28.3, 28.4 (3C), 28.6, 28.9, 29.0, 33.2, 34.7, 78.8 (cyclopentadecyl); **6A**: 57.8 (Me); **6E**: 16.4, 25.2, 28.5, 31.8, 31.88, 31.93, 34.4, 71.2 (*n*-octyl); **6F**: 13.3, 22.5, 26.2, 29.3, 29.4(2C), 29.5, 29.56, 29.59(2C), 31.9, 68.2 (*n*-dodecyl); **6L**: 24.2, 24.6, 27.7 (3C), 27.8, 27.9 (3C), 28.1, 28.4, 28.5, 32.7, 34.2, 78.3 (cyclopentadecyl).

1.2.5. Allyl β-D-galactopyranosyl-(1 → 4)-α-D-glucopyranoside (6B). Glass; $[\alpha]_D^{25}$ + 106 (*c* 1.1, H_2O); HRMS (FAB) Calcd for $C_{15}H_{26}NaO_{11}$ $[M+Na]^+$: 405.1373. Found: *m*/*z* 405.1366.

1.2.6. 4-Pentenyl α-D-glucopyranosyl-(1 → 4)-α-D-glucopyranoside (4C). Glass; $[\alpha]_D^{25}$ + 146 (*c* 0.8, H_2O); HRMS (FAB) Calcd for $C_{17}H_{30}NaO_{11}$ $[M+Na]^+$: 433.1686. Found: *m*/*z* 433.1681.

Table 5. ^{13}C NMR data of selected β-biosides determined at 100 MHz (M = CD_3OD, P = C_5H_5N with CD_3OD, W = D_2O)

Compounds (Solv.)	**7A** (W)	**7B** (W)	**7C** (M)	**7D** (M)	**8E** (W)	**8F** (W)	**8G** (P)	**8H** (P)	**8I** (W)	**8J** (M)	**8K** (P)	**8L** (P)
C-1^{I}	105.8	105.0	104.2	103.0	105.7	105.1	104.5	103.3	105.8	104.2	104.5	103.2
C-2^{I}	75.7	75.6	74.6	74.7	75.5	75.5	74.86	75.01	75.5	74.7	74.9	75.0
C-3^{I}	78.9	79.0	77.8	77.8	77.0	77.2	76.9	76.9	77.1	76.4	76.7	76.7
C-4^{I}	79.4	79.9	81.2	81.2	81.3	81.5	81.4	81.6	81.1	80.7	81.9	82.0
C-5^{I}	77.2	77.3	76.5	76.4	77.4	77.4	76.7	76.6	77.4	76.4	76.6	76.5
C-6^{I}	63.4	63.4	62.7	62.7	62.7	62.9	62.2	62.4	62.7	61.9	62.2	62.3
C-1^{II}	102.2	102.6	102.8	102.7	105.2	105.3	105.1	105.1	105.6	105.1	105.8	105.8
C-2^{II}	74.3	74.4	74.1	74.1	75.8	75.9	74.91	74.96	73.6	72.5	72.6	72.6
C-3^{II}	75.5	75.4	75.0	75.0	78.2	78.3	78.3	78.3	75.2	74.8	75.2	75.2
C-4^{II}	72.0	71.9	71.4	71.5	72.1	72.1	71.6	71.6	71.2	70.3	70.2	70.3
C-5^{II}	75.4	75.6	74.7	74.7	78.6	78.7	78.6	78.6	78.0	77.0	77.3	77.3
C-6^{II}	63.2	63.2	62.1	62.1	63.2	63.3	62.5	62.5	63.7	62.5	62.2	62.2

Aglycon; **7A**: 59.8 (Me); **7E**: 16.4, 25.1, 28.2, 31.7, 31.81, 31.84, 34.3, 73.1 (*n*-octyl); **7F**: 14.5, 23.8, 27.1, 30.5, 30.6, 30.76 (3C), 30.80 (2C), 33.1, 70.9 (*n*-dodecyl); **7L**: 24.0, 24.3, 27.7 (2C), 27.76, 27.82, 27.9 (2C), 27.97, 28.03, 28.48, 28.52, 32.9, 34.3, 79.8 (cyclopentadecyl); **8A**: 59.9 (Me); **8E**: 16.4, 25.2, 28.3, 31.9 (3C), 34.4, 73.2 (*n*-octyl); **8F**: 14.5, 23.1, 26.6, 29.8, 30.0, 30.10 (3C), 30.14, 30.5 32.3, 70.2 (*n*-dodecyl); **8L**: 23.3, 23.6, 27.0 (3C), 27.27 (4C), 27.33, 27.85, 27.92, 32.4, 34.0, 78.8 (cyclopentadecyl); **9A**: 59.9 (Me); **9E**: 14.4, 23.7, 27.1, 30.4, 30.5, 30.8, 33.0, 71.0 (*n*-octyl); **9F**: 14.4, 23.1, 26.6, 29.8, 30.0, 30.07 (3C), 30.10, 30.4, 32.3, 70.1; **9L**: 23.3, 23.6, 27.0 (3C), 27.2 (4C), 27.3, 27.8, 27.9, 32.4, 33.9, 78.8 (cyclopentadecyl).

1.2.7. 4-Pentenyl α-D-glucopyranosyl-(1 → 4)-β-D-glucopyranoside (7C). Glass; $[\alpha]_D^{25}$ + 59 (*c* 1.5, H_2O); HRMS (FAB) Calcd for $C_{17}H_{30}NaO_{11}$ $[M+Na]^+$: 433.1686. Found: *m*/*z* 433.1691.

1.2.8. 4-Pentenyl β-D-glucopyranosyl-(1 → 4)-α-D-glucopyranoside (5C). Glass; $[\alpha]_D^{25}$ + 72 (*c* 1.0, H_2O); HRMS (FAB) Calcd for $C_{17}H_{30}NaO_{11}$ $[M+Na]^+$: 433.1686. Found: *m*/*z* 433.1675.

1.2.9. 4-Pentenyl β-D-glucopyranosyl-(1 → 4)-β-D-glucopyranoside (8C). Glass; $[\alpha]_D^{25}$ − 16 (*c* 1.0, H_2O); HRMS (FAB) Calcd for $C_{17}H_{30}NaO_{11}$ $[M+Na]^+$: 433.1686. Found: *m*/*z* 433.1697.

1.2.10. 4-Pentenyl β-D-galactopyranosyl-(1 → 4)-α-D-glucopyranoside (6C). Glass; $[\alpha]_D^{25}$ + 89 (*c* 1.1, H_2O); HRMS (FAB) Calcd for $C_{17}H_{30}NaO_{11}$ $[M+Na]^+$: 433.1686. Found: *m*/*z* 433.1664.

1.2.11. 4-Pentenyl β-D-galactopyranosyl-(1 → 4)-β-D-glucopyranoside (9C). Glass; $[\alpha]_D^{26}$ + 2 (*c* 0.5, H_2O); HRMS (FAB) Calcd for $C_{17}H_{30}NaO_{11}$ $[M+Na]^+$: 433.1686. Found: *m*/*z* 433.1703.

1.2.12. Benzyl α-D-glucopyranosyl-(1 → 4)-α-D-glucopyranoside (4D). Glass; $[\alpha]_D^{25}$ + 162 (*c* 0.4, H_2O); HRMS (FAB) Calcd for $C_{19}H_{28}NaO_{11}$ $[M+Na]^+$: 455.1529. Found: *m*/*z* 455.1537.

1.2.13. Benzyl β-D-glucopyranosyl-(1 → 4)-α-D-glucopyranoside (5D). Glass; $[\alpha]_D^{25}$ + 85 (*c* 0.5, H_2O); HRMS (FAB) Calcd for $C_{19}H_{28}NaO_{11}$ $[M+Na]^+$: 455.1529. Found: *m*/*z* 455.1553.

1.2.14. Benzyl β-D-galactopyranosyl-(1 → 4)-α-D-glucopyranoside (6D). Glass; $[\alpha]_D^{24}$ + 118 (*c* 0.7, H_2O); HRMS (FAB) Calcd for $C_{19}H_{28}NaO_{11}$ $[M+Na]^+$: 455.1529. Found: *m*/*z* 455.1552.

1.2.15. *n*-Octyl α-D-glucopyranosyl-(1 → 4)-α-D-glucopyranoside (4E). Glass; $[\alpha]_D^{23}$ + 138 (*c* 1.1, MeOH); HRMS (FAB) Calcd for $C_{20}H_{38}NaO_{11}$ $[M+Na]^+$: 477.2312. Found: *m*/*z* 477.2324.

1.2.16. *n*-Octyl β-D-glucopyranosyl-(1 → 4)-α-D-glucopyranoside (5E). Glass; $[\alpha]_D^{26}$ + 61 (*c* 0.6, MeOH); HRMS (FAB) Calcd for $C_{20}H_{38}NaO_{11}$ $[M+Na]^+$: 477.2312. Found: *m*/*z* 477.2352.

1.2.17. *n*-Octyl β-D-galactopyranosyl-(1 → 4)-α-D-glucopyranoside (6E). Glass; $[\alpha]_D^{27}$ + 87 (*c* 0.9, MeOH); HRMS (FAB) Calcd for $C_{20}H_{38}NaO_{11}$ $[M+Na]^+$: 477.2312. Found: *m*/*z* 477.2310.

1.2.18. *n*-Octyl β-D-galactopyranosyl-(1 → 4)-β-D-glucopyranoside (9E). Glass; $[\alpha]_D^{25}$ + 3 (*c* 0.8, MeOH); HRMS (FAB) Calcd for $C_{20}H_{38}NaO_{11}$ $[M+Na]^+$: 477.2312. Found: *m*/*z* 477.2340.

1.2.19. *n*-Dodecyl α-D-glucopyranosyl-(1 → 4)-α-D-glucopyranoside (4F). Glass; $[\alpha]_D^{25}$ + 122 (*c* 0.9, C_5H_5N); HRMS (FAB) Calcd for $C_{24}H_{46}NaO_{11}$ $[M+Na]^+$: 533.2938. Found: *m*/*z* 533.2909.

1.2.20. *n*-Dodecyl β-D-glucopyranosyl-(1 → 4)-α-D-glucopyranoside (5F). Crystals (from MeOH); mp 150–153 °C; $[\alpha]_D^{24}$ + 46 (*c* 0.5, C_5H_5N); HRMS (FAB) Calcd for $C_{24}H_{46}NaO_{11}$ $[M+Na]^+$: 533.2938. Found: *m*/*z* 533.2939. Anal. Calcd for $C_{24}H_{46}O_{11}\cdot H_20$: C, 54.53, H, 9.15. Found: C, 54.83, H, 8.86.

1.2.21. *n*-Dodecyl β-D-galactopyranosyl-(1 → 4)-α-D-glucopyranoside (6F). Crystals (from MeOH); mp

160–162 °C; $[\alpha]_D^{24}$ + 64 (*c* 0.7, C_5H_5N); HRMS (FAB) Calcd for $C_{24}H_{46}NaO_{11}$ $[M+Na]^+$: 533.2938. Found: *m/z* 533.2924. Anal. Calcd for $C_{24}H_{46}O_{11}\cdot 0.5H_20$: C, 55.48, H, 9.12. Found: C, 55.21, H, 8.98.

1.2.22. *n*-Dodecyl β-D-galactopyranosyl-(1 → 4)-β-D-glucopyranoside (9F). Crystals (from MeOH); mp 106–111 °C; $[\alpha]_D^{25}$ + 8 (*c* 0.6, C_5H_5N); HRMS (FAB) Calcd for $C_{24}H_{46}NaO_{11}$ $[M+Na]^+$: 533.2938. Found: *m/z* 533.2937. Anal. Calcd for $C_{24}H_{46}O_{11}\cdot 0.5H_20$: C, 55.48, H, 9.12. Found: C, 55.20, H, 8.84.

1.2.23. *n*-Hexadecyl α-D-glucopyranosyl-(1 → 4)-α-D-glucopyranoside (4G). Crystallized spontaneously[‡]; mp 195–202 °C; $[\alpha]_D^{25}$ + 98 (*c* 0.5, C_5H_5N); HRMS (FAB) Calcd for $C_{28}H_{54}NaO_{11}$ $[M+Na]^+$: 589.3564. Found: *m/z* 589.3574.

1.2.24. *n*-Hexadecyl α-D-glucopyranosyl-(1 → 4)-β-D-glucopyranoside (7G). Crystals (from MeOH); mp 111–116 °C; $[\alpha]_D^{24}$ + 45 (*c* 0.5, C_5H_5N); HRMS (FAB) Calcd for $C_{28}H_{54}NaO_{11}$ $[M+Na]^+$: 589.3564. Found: *m/z* 589.3533. Anal. Calcd for $C_{28}H_{54}O_{11}$: C, 59.34, H, 9.60. Found: C, 59.12, H, 9.58.

1.2.25. *n*-Hexadecyl β-D-glucopyranosyl-(1 → 4)-α-D-glucopyranoside (5G). Crystals (from MeOH); mp 119–126 °C; $[\alpha]_D^{25}$ + 43 (*c* 0.5, C_5H_5N); HRMS (FAB) Calcd for $C_{28}H_{54}NaO_{11}$ $[M+Na]^+$: 589.3564. Found: *m/z* 589.3586. Anal. Calcd for $C_{28}H_{54}O_{11}\cdot 0.5H_20$: C, 58.41, H, 9.63. Found: C, 58.53, H, 9.57.

1.2.26. *n*-Hexadecyl β-D-galactopyranosyl-(1 → 4)-α-D-glucopyranoside (6G). Crystals (from MeOH), mp 172–176 °C; $[\alpha]_D^{23}$ + 58 (*c* 0.9, pyridine); HRMS (FAB) Calcd for $C_{28}H_{54}NaO_{11}$ $[M+Na]^+$: 589.3564. Found: *m/z* 589.3527. Anal. Calcd for $C_{28}H_{54}O_{11}\cdot H_2O$: C, 57.51, H, 9.65. Found: C, 57.77, H, 9.36.

1.2.27. *n*-Hexadecyl β-D-galactopyranosyl-(1 → 4)-β-D-glucopyranoside (9G). Crystals (from MeOH), mp 175–178 °C; $[\alpha]_D^{25}$ + 9 (*c* 0.3, pyridine+Me_2SO (1:1)); HRMS (FAB) Calcd for $C_{28}H_{54}NaO_{11}$ $[M+Na]^+$: 589.3564. Found: *m/z* 589.3565. Anal. Calcd for $C_{28}H_{54}O_{11}\cdot H_20$: C, 57.51, H, 9.65. Found: C, 57.57, H, 9.47.

1.2.28. Cyclopentyl α-D-glucopyranosyl-(1 → 4)-α-D-glucopyranoside (4H). Glass; $[\alpha]_D^{25}$ + 156 (*c* 0.8, H_2O); HRMS (FAB) Calcd for $C_{17}H_{30}NaO_{11}$ $[M+Na]^+$: 433.1686. Found: *m/z* 433.1680.

[‡] Glasses obtained crystallized spontaneously but, on the addition of a small amount of MeOH or EtOH, began to liquefy. The addition of EtOAc, Me_2CO, or Et_2O to them did not afford crystals.

1.2.29. Cyclopentyl α-D-glucopyranosyl-(1 → 4)-β-D-glucopyranoside (7H). Glass; $[\alpha]_D^{25}$ + 67 (*c* 1.5, H_2O); HRMS (FAB) Calcd for $C_{17}H_{30}NaO_{11}$ $[M+Na]^+$: 433.1686. Found: *m/z* 433.1686.

1.2.30. Cyclopentyl β-D-glucopyranosyl-(1 → 4)-α-D-glucopyranoside (5H). Glass; $[\alpha]_D^{25}$ + 75 (*c* 1.0, H_2O); HRMS (FAB) Calcd for $C_{17}H_{30}NaO_{11}$ $[M+Na]^+$: 433.1686. Found: *m/z* 433.1680.

1.2.31. Cyclopentyl β-D-glucopyranosyl-(1 → 4)-β-D-glucopyranoside (8H). Glass; $[\alpha]_D^{25}$ − 22 (*c* 1.0, H_2O); HRMS (FAB) Calcd for $C_{17}H_{30}NaO_{11}$ $[M+Na]^+$: 433.1686. Found: *m/z* 433.1688.

1.2.32. Cyclopentyl β-D-galactopyranosyl-(1 → 4)-α-D-glucopyranoside (6H). Glass; $[\alpha]_D^{25}$ + 106 (*c* 1.1, H_2O); HRMS (FAB) Calcd for $C_{17}H_{30}NaO_{11}$ $[M+Na]^+$: 433.1686. Found: *m/z* 433.1689.

1.2.33. Cyclopentyl β-D-galactopyranosyl-(1 → 4)-β-D-glucopyranoside (9H). Glass; $[\alpha]_D^{26}$ + 1 (*c* 0.5, H_2O); HRMS (FAB) Calcd for $C_{17}H_{30}NaO_{11}$ $[M+Na]^+$: 433.1686. Found: *m/z* 433.1672.

1.2.34. Cyclohexyl α-D-glucopyranosyl-(1 → 4)-β-D-glucopyranoside (7I). Glass; $[\alpha]_D^{25}$ + 74 (*c* 0.9, H_2O); HRMS (FAB) Calcd or $C_{18}H_{32}NaO_{11}$ $[M+Na]^+$: 447.1842. Found: *m/z* 447.1853.

1.2.35. Cyclohexyl β-D-glucopyranosyl-(1 → 4)-α-D-glucopyranoside (5I). Glass; $[\alpha]_D^{26}$ + 69 (*c* 0.9, H_2O); HRMS (FAB) Calcd for $C_{18}H_{32}NaO_{11}$ $[M+Na]^+$: 447.1842. Found: *m/z* 447.1824.

1.2.36. Cyclohexyl β-D-galactopyranosyl-(1 → 4)-α-D-glucopyranoside (6I). Glass; $[\alpha]_D^{26}$ + 102 (*c* 1.3, H_2O); HRMS (FAB) Calcd for $C_{18}H_{32}NaO_{11}$ $[M+Na]^+$: 447.1842. Found: *m/z* 447.1846.

1.2.37. Cyclohexyl β-D-galactopyranosyl-(1 → 4)-β-D-glucopyranoside (9I). Glass; $[\alpha]_D^{25}$ + 5 (*c* 1.0, H_2O); HRMS (FAB) Calcd for $C_{18}H_{32}NaO_{11}$ $[M+Na]^+$: 447.1842.

1.2.38. Cyclooctyl α-D-glucopyranosyl-(1 → 4)-α-D-glucopyranoside (4J). Glass; $[\alpha]_D^{24}$ + 124 (*c* 0.6, MeOH); HRMS (FAB) Calcd for $C_{20}H_{36}NaO_{11}$ $[M+Na]^+$: 475.2155. Found: *m/z* 475.2179.

1.2.39. Cyclooctyl α-D-glucopyranosyl-(1 → 4)-β-D-glucopyranoside (7J). Glass; $[\alpha]_D^{26}$ + 51 (*c* 1.1, MeOH); HRMS (FAB) Calcd for $C_{20}H_{36}NaO_{11}$ $[M+Na]^+$: 475.2155. Found: *m/z* 475.2163.

1.2.40. Cyclooctyl β-D-glucopyranosyl-(1 → 4)-α-D-glucopyranoside (5J). Glass; $[\alpha]_D^{26}$ + 55 (*c* 0.7, MeOH); HRMS (FAB) Calcd for $C_{20}H_{36}NaO_{11}$ $[M+Na]^+$: 475.2155. Found: *m/z* 475.2176.

1.2.41. Cyclooctyl β-D-glucopyranosyl-(1 → 4)-β-D-glucopyranoside (8J). Glass; $[\alpha]_D^{25}$ − 5 (*c* 1.1, MeOH); HRMS (FAB) Calcd for $C_{20}H_{36}NaO_{11}$ $[M+Na]^+$: 475.2155. Found: *m/z* 475.2155.

1.2.42. Cyclooctyl β-D-galactopyranosyl-(1 → 4)-α-D-glucopyranoside (6J). Crystallized spontaneously[1]; mp 120–125 °C; $[\alpha]_D^{28}$ + 72 (*c* 0.5, MeOH); HRMS (FAB) Calcd for $C_{20}H_{36}NaO_{11}$ $[M+Na]^+$: 475.2155. Found: *m/z* 475.2148.

1.2.43. Cyclooctyl β-D-galactopyranosyl-(1 → 4)-β-D-glucopyranoside (9J). Glass; $[\alpha]_D^{25}$ + 7 (*c* 0.9, MeOH); HRMS (FAB) Calcd for $C_{20}H_{36}NaO_{11}$ $[M+Na]^+$: 475.2155. Found: *m/z* 475.2141.

1.2.44. Cyclododecyl α-D-glucopyranosyl-(1 → 4)-α-D-glucopyranoside (4K). Glass; $[\alpha]_D^{24}$ + 115 (*c* 0.5, pyridine); R_f = 0.46 ($CHCl_3$–MeOH = 2:1); HRMS (FAB) Calcd for $C_{24}H_{44}NaO_{11}$ $[M+Na]^+$: 531.2781. Found: *m/z* 531.2771.

1.2.45. Cyclododecyl α-D-glucopyranosyl-(1 → 4)-β-D-glucopyranoside (7K). Crystals (from MeOH); mp 195–197 °C; $[\alpha]_D^{25}$ + 48 (*c* 0.9, pyridine); HRMS (FAB) Calcd for $C_{24}H_{44}NaO_{11}$ $[M+Na]^+$: 531.2781. Found: *m/z* 531.2784. Anal. Calcd for $C_{24}H_{44}O_{11}\cdot 0.5H_20$: C, 55.69, H, 8.76. Found: C, 55.97, H, 8.53.

1.2.46. Cyclododecyl β-D-glucopyranosyl-(1 → 4)-α-D-glucopyranoside (5K). Crystals (from MeOH), mp 206–207 °C; $[\alpha]_D^{23}$ + 38 (*c* 1.2, pyridine); HRMS (FAB) Calcd for $C_{24}H_{44}NaO_{11}$ $[M+Na]^+$: 531.2781. Found: *m/z* 531.2801. Anal. Calcd for $C_{24}H_{44}O_{11}\cdot 0.5H_20$: C, 55.69, H, 8.76. Found: C, 55.70, H, 8.64.

1.2.47. Cyclododecyl β-D-glucopyranosyl-(1 → 4)-β-D-glucopyranoside (8K). Crystals (from MeOH), mp 231–238 °C; $[\alpha]_D^{23}$ − 12 (*c* 1.0, pyridine); HRMS (FAB) Calcd for $C_{24}H_{44}NaO_{11}$ $[M+Na]^+$: 531.2781. Found: *m/z* 531.2787. Anal. Calcd for $C_{24}H_{44}O_{11}\cdot 0.5H_20$: C, 55.69, H, 8.76. Found: C, 55.70, H, 8.64.

1.2.48. Cyclododecyl β-D-galactopyranosyl-(1 → 4)-α-D-glucopyranoside (6K). Crystals (from MeOH), mp 207–209 °C; $[\alpha]_D^{25}$ + 56 (*c* 0.6, pyridine); HRMS (FAB) Calcd for $C_{24}H_{44}NaO_{11}$ $[M+Na]^+$: 531.2781. Found: *m/z* 531.2751. Anal. Calcd for $C_{24}H_{44}O_{11}\cdot 0.5H_2O$: C, 55.69, H, 8.76. Found: C, 55.49, H, 8.53.

1.2.49. Cyclododecyl β-D-galactopyranosyl-(1 → 4)-β-D-glucopyranoside (9K). Prisms (from MeOH), mp 212–213 °C; $[\alpha]_D^{25}$ + 5 (*c* 0.6, pyridine); HRMS (FAB) Calcd for $C_{24}H_{44}NaO_{11}$ $[M+Na]^+$: 531.2781. Found: *m/z* 531.2788. Anal. Calcd for $C_{24}H_{44}O_{11}$: C, 56.68, H, 8.72. Found: C, 56.28, H, 8.78.

1.2.50. Cyclopentadecyl α-D-glucopyranosyl-(1 → 4)-α-D-glucopyranoside (4L). Glass; $[\alpha]_D^{26}$ + 91 (*c* 0.8, pyridine); HRMS (FAB) Calcd for $C_{27}H_{50}NaO_{11}$ $[M+Na]^+$: 573.3251. Found: *m/z* 573.3272.

1.2.51. Cyclopentadecyl α-D-glucopyranosyl-(1 → 4)-β-D-glucopyranoside (7L). Glass; $[\alpha]_D^{23}$ + 41 (*c* 1.1, pyridine); HRMS (FAB) Calcd for $C_{27}H_{50}NaO_{11}$ $[M+Na]^+$: 573.3251. Found: *m/z* 573.3268.

1.2.52. Cyclopentadecyl β-D-glucopyranosyl-(1 → 4)-α-D-glucopyranoside (5L). Glass; $[\alpha]_D^{27}$ + 44 (*c* 0.9, pyridine); HRMS (FAB) Calcd for $C_{27}H_{50}NaO_{11}$ $[M+Na]^+$: 573.3251. Found: *m/z* 573.3224.

1.2.53. Cyclopentadecyl-β-D-glucopyranosyl-(1 → 4)-β-D-glucopyranoside (8L). Crystals (from MeOH), mp 198–206 °C; $[\alpha]_D^{24}$ − 12 (*c* 0.8, pyridine); HRMS (FAB) Calcd for $C_{27}H_{50}NaO_{11}$ $[M+Na]^+$: 573.3251. Found: *m/z* 573.3258. Anal. Calcd for $C_{27}H_{50}O_{11}\cdot 0.5H_2O$: C, 57.02, H, 9.22. Found: C, 56.97, H, 9.06.

1.2.54. Cyclopentadecyl-β-D-galactopyranosyl-(1 → 4)-α-D-glucopyranoside (6L). Crystallized spontaneously[‡]; mp 121–123 °C; $[\alpha]_D^{25}$ + 53 (*c* 0.8, pyridine); HRMS (FAB) Calcd for $C_{27}H_{50}NaO_{11}$ $[M+Na]^+$: 573.3251. Found: *m/z* 573.3250.

1.2.55. Cyclopentadecyl-β-D-galactopyranosyl-(1 → 4)-β-D-glucopyranoside (9L). Crystals (from MeOH); mp 154–158 °C; $[\alpha]_D^{25}$ + 5 (*c* 0.7, pyridine); HRMS (FAB) Calcd for $C_{27}H_{50}NaO_{11}$ $[M+Na]^+$: 573.3251. Found: *m/z* 573.3245. Anal. Calcd for $C_{27}H_{50}O_{11}\cdot 0.5H_20$: C, 57.94, H, 9.18. Found: C, 58.00, H, 9.08.

References

1. VanAken, T.; Foxall-VanAken, S.; Castleman, S.; Ferguson-Miller, S. *Methods Enzymol.* **1986**, *125*, 27–35.
2. Vill, V.; Hashim, R. *Curr. Opin. Coll. Interface Sci.* **2002**, *7*, 395–409.
3. Izumi, M.; Shen, G.-J.; Wacowich-Sgarbi, S.; Nakatani, T.; Plettenburg, O.; Wong, C.-H. *J. Am. Chem. Soc.* **2001**, *123*, 10909–10918.
4. Yi, Y.; Zhou, Z.; Ning, J.; Kong, F.; Li, J. *Synthesis* **2003**, *22*, 491–496.
5. Meyar, B.; Peters, T. *Angew. Chem., Int. Ed.* **2003**, *42*, 864–890.
6. Droz, A. S.; Neidlein, U.; Anderson, S.; Seiler, P.; Diederich, F. *Helv. Chim. Acta* **2001**, *84*, 2243–2289.

7. Lecollinet, G.; Dominey, A. P.; Velasco, T.; Davis, A. P. *Angew. Chem., Int. Ed.* **2002**, *41*, 4093–4096.
8. Pillion, D. J.; Ahsan, F.; Arnold, J. J.; Balusubramanian, B. M.; Piraner, O.; Meezan, E. *J. Pharm. Sci.* **2002**, *91*, 1456–1462.
9. Ahasan, F.; Arnold, J.; Meezan, E.; Pillion, D. J. *Pharm. Res.* **2001**, *18*, 1742–1746.
10. Matsubara, S. *Bull. Chem. Soc. Jpn.* **1961**, *34*, 718–722.
11. Zurabyan, S. E.; Bílik, V.; Bauer, S. *Chem. Zvesti* **1969**, *23*, 923–927.
12. Piekarska, B. *Roczn. Chem.* **1975**, *49*, 1919–1925.
13. Cheetham, N. W. H.; Sirimanne, P. *Carbohydr. Res.* **1981**, *96*, 126–128.
14. Grande, D.; Baskaran, S.; Chaikof, E. L. *Polym. Mater. Sci. Eng.* **2001**, *84*, 141–142.
15. Banoub, J.; Bundle, D. R. *Can. J. Chem.* **1987**, *57*, 2085–2090.
16. Mazur, A. W.; Hiler, G. D., Jr. *Carbohydr. Res.* **1987**, *168*, 146–150.
17. Vill, V.; Böcker, T.; Thiem, J.; Fischer, F. *Liq. Cryst.* **1989**, *6*, 349–356.
18. Böcker, T.; Thiem, J. *Tenside Surf. Det.* **1989**, *26*, 318–324.
19. VonMinden, H. M.; Brandenburg, K.; Saydel, U.; Koch, M. H. J.; GaramusV; Willumeit, R.; Vill, V. *Chem. Phys. Lipids* **2000**, *106*, 157–179.
20. Dick, W. E., Jr.; Weisleder, D.; Hodge, J. E. *Carbohydr. Res.* **1971**, *18*, 115–123.
21. Gi, G. T.; Ishihara, H.; Tejima, S. *Chem. Pharm. Bull.* **1978**, *26*, 1570–1575.
22. Helferich, B.; Piel, W. *Justus Liebigs Ann. Chem.* **1959**, *623*, 124–128.
23. Klots, W.; Schmidt, R. R. J. *Carbohydr. Chem.* **1994**, *13*, 1093–1101.
24. Inouye, Y.; Onodera, K.; Karasawa, I.; Nishisawa, Y. *Nippon Nogei Kagaku Kaishi* **1952**, *26*, 631–634.
25. Totani, K.; Yasutake, N.; Ohi, H.; Murata, T.; Usui, T. *Arch. Biochem. Biophys.* **2001**, *385*, 70–77.
26. Ditmar, R. *Monatsh. Chem.* **1902**, *23*, 865–876.
27. Fischer, E.; Fischer, H. *Chem. Ber.* **1910**, *43*, 2521–2536.
28. Ito, Y.; Koto, S.; Umezawa, S. *Bull. Chem. Soc. Jpn.* **1962**, *35*, 1618–1622.
29. Koto, S.; Morishima, N.; Irisawa, T.; Hashimoto, Y.; Yamazaki, M.; Zen, S. *Nippon Kakgaku Kaishi*, **1982**, 1651–1656.
30. Koto, S.; Morishima, N.; Shichi, S.; Haigoh, H.; Hirooka, M.; Okamoto, M.; Higuchi, T.; Shimizu, K.; Hashimoto, Y.; Iriawa, T.; Kawasaki, H.; Takahashi, Y.; Yamazaki, M.; Mori, Y.; Kudo, K.; Ikegaki, T.; Suzuki, S.; Zen, S. *Bull. Chem. Soc. Jpn.* **1992**, *65*, 3257–3274.
31. Kartha, C. P. R.; Jennings, H. J. *J. Carbohydr. Chem.* **1990**, *9*, 777–781.
32. Larsen, K.; Olsen, C. E.; Motawia, M. S. *Carbohydr. Res.* **2003**, *338*, 199–202.
33. Zemplén, G.; Csürös, Z. *Chem. Ber.* **1931**, *64*, 993–1000.
34. Ikemoto, N.; Kim, O. K.; Lo, L.-C.; Satyanarayana, V.; Chang, M.; Nakanishi, K. *Tetrahedron Lett.* **1992**, *33*, 4295–4298.
35. Chatterjee, S. K.; Nuhn, P. *Chem. Commun.* **1998**, 1729–1730.
36. Masson, C.; Soto, J.; Bessodes, M. *Synlett* **2000**, *22*, 1281–1282.
37. Ferrieres, V.; Bertho, J.-N.; Plusquellec, D. *Carbohydr. Res.* **1998**, *311*, 23–35.
38. Miranda, P. O.; Brouard, I.; Padrón, J. I.; Bermejo, J. *Tetrahedron Lett.* **2003**, *44*, 3931–3934.
39. Kiso, M.; Anderson, L. *Carbohydr. Res.* **1985**, *136*, 309–323.
40. Koto, S.; Morishima, N.; Zen, S. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 1543–1547.
41. Watanabe, Y.; Nakamoto, C.; Yamamoto, T.; Ozaki, S. *Tetrahedron* **1994**, *50*, 6523–6536.
42. Yamada, H.; Hayashi, T. *Carbohydr. Res.* **2002**, *337*, 581–585.
43. Rosevear, P.; VanAken, T.; Baxter, J.; Ferguson-Miller, S. *Biochemistry* **1980**, *19*, 4108–4115.
44. Ali, M. A.; Hough, L.; Richardson, A. C. *Carbohydr. Res.* **1991**, *216*, 271–287.
45. Youssef, R. H.; Silwanis, B. A.; El-Sokkary, R. I.; Nematella, A. S.; Nashed, M. A. *Carbohydr. Res.* **1993**, *240*, 287–293.
46. Fischer, H.; Kögl, F. *Justus Liebigs Ann. Chem.* **1924**, *436*, 219–228.
47. Edwards, R. G.; Hough, L.; Richardson, A. C. *Carbohydr. Res.* **1977**, *55*, 129–148.
48. Jung, K.-H.; Hoch, M.; Schmidt, R. R. *Liebigs Ann. Chem.* **1989**, 1099–1106.
49. Boyd, B. J.; Drummond, C. J.; Krodkiewska, I.; Grieser, F. *Langmuir* **2000**, *16*, 7359–7367.
50. Hori, R. *Yakugaku Zasshi* **1958**, *78*, 999–1002.
51. Ma, Y.-D.; Takada, A.; Sugiura, M.; Fukuda, T.; Miyamoto, T.; Watanabe, J. *Bull. Soc. Chem. Jpn.* **1994**, *67*, 346–351.
52. DeGrip, W. J.; Bovee-Geurts, P. H. M. *Chem. Phys. Lipids* **1979**, *23*, 321–335.
53. Landauer, P.; Ruess, K.-P.; Liefländer, M. *Biochem. Biophys. Res. Commun.* **1982**, *106*, 848–855.
54. Koeltzow, D. E.; Urfer, A. D. J. *Am. Oil Chem. Soc.* **1984**, *61*, 1651–1655.
55. Brandon, R. E.; Schroeder, L. R.; Johnson, D. C. *ACS Symp. Ser.* **1975**, *22*, 125–146.