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manno- versus *gluco*-Selectivity in reductions of 2-keto-β-D-*arabino*-hexopyranosides

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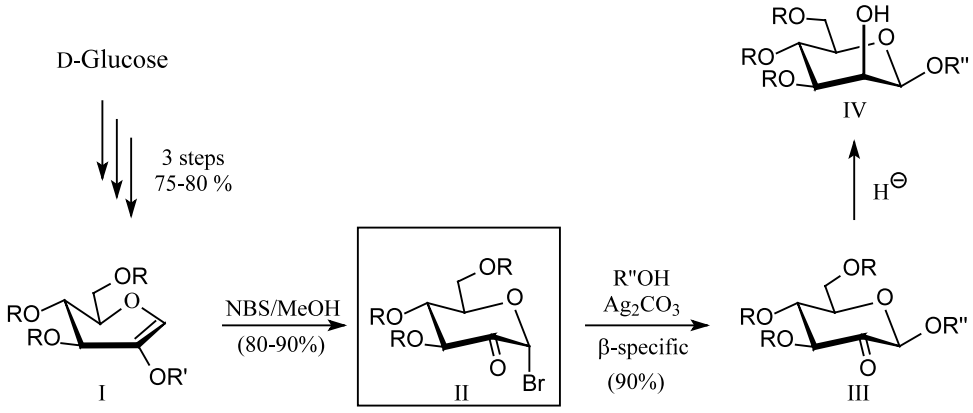
Abstract—Tri-*sec*-butylborohydrides (L- or K-Selectride) reduce the carbonyl group in acylated 2-keto-β-D-*arabino*-hexopyranosides to β-D-mannosides in an essentially stereospecific fashion, whereas borane reduction gives the 2-epimeric β-D-glucosides with high preference. As preparative yields are in the 70–85% range, the *ulosyl donor approach* can thus be utilized for the straightforward construction of oligosaccharides containing either β-D-Man or β-D-Glc units. © 2003 Elsevier Science Ltd. All rights reserved.

1. Introduction

The 2-ulosyl donor approach for the expedient synthesis of β-D-mannosides, introduced in 1985,[1] has successfully been employed for the construction of various β-D-mannose-containing oligosaccharides up to the hexasaccharide level.[1–5] Central to this procedure are the ready preparation of variously blocked α-D-*arabino*-2-ketohexosyl bromides II from D-glucose,[1,4–7] their essentially β-specific glycosidation (→III) — the electron-withdrawing 2-keto group suppresses oxocarbenium ion formation at the anomeric center implementing direct S_N2 displacement of the bromine — and *manno*-selective reduction of the resulting β-D-2-keto-glycosides (II→III). Aside of its preparative simplicity, the procedure has the additional advantage of providing the β-D-mannosides with a free 2-OH group, i.e. mannosyl acceptors ready for further glycosidation towards the various oligosaccharides with β-D-Man-(1→2)-D-Man linkages.

As the glycos-*ulosyl* bromides are accessible from D-glucose in four simple, high yielding steps—the first three to the hydroxyglucal ester I can be combined into one successive operation and its conversion to the ulosyl bromide II is straightforward[4–7]—not only is their access amenable to large-scale preparation, but to stereochemically uniform glycosidation as well. Only the reduction with sodium borohydride III→IV is somewhat capricious, as preparatively useful 20:1 to 50:1 *manno*/*gluco*-selectivities are only obtained in cases with benzyl protection or at least an *O*-benzyl group



R = Ac, Bz, Piv, Bn, ClBn; R' = Ac, Bz, Piv; R" = alkyl, glycosyl

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next to the carbonyl function. β-D-Ulosides carrying an acyl group at *O*-3 give *manno*-preferences in the range of 2:1 to 5:1 only, apparently due to complexation of the borohydride with the ester and pyranoid carbonyl groups, thereby making hydride delivery less uniform. Since ulosyl bromides with acyl blocking groups such as acetyl, benzoyl or pivaloyl, and, hence, the β-D-ulosides derived therefrom, are more readily accessible than their benzylated analogs, a study of various hydride reducing agents towards a substantial improvement of the *manno*-selectivities appeared opportune, as well as an evaluation of conceivable possibilities to turn β-D-*arabino*-hexosuloside reductions *gluco*-selective. In this paper we report on both of these objectives, near *manno*-specificity being attained by the use of sterically demanding borohydrides such as L- or K-Selectride, whilst reduction with borane, notably, reverses the selectivity towards the *gluco*-epimers.

2. Results and discussion

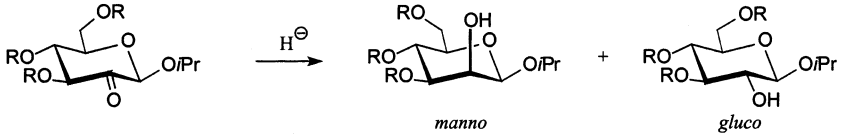
2.1. *manno*-Selective hydride reductions of β-D-*arabino*-2-oxoglycosides

To evaluate comparatively the *manno*-selectivities attainable with β-D-*arabino*-2-ketohexosides, the isopropyl hexosiduloses **1**–**3**, featuring benzyl, benzoyl and pivaloyl protecting groups, and each accessible from the respective ulosyl bromide in high yield (85–90%), were employed as model compounds. The results obtained with a series of different borohydride reagents are shown in Table 1.

As observed previously,[7] a standard $NaBH_4$ reduction of isopropyl β-D-*arabino*-hexosidulose **1** carrying only *O*-benzyl blocking groups provides the respective β-D-mannoside **4** in a stereochemically uniform course and excellent yield, a result which is not further improved by using lithium tri-*sec*-butylborohydride in THF at −78°C (entries 1–4 in Table 1). With ulosides **2** and **3**, however, carrying *O*-benzoyl and *O*-pivaloyl protection instead, the steric outcome of the respective $NaBH_4$ reductions and those with $LiB(iBu)_3H$ or its K-analog are distinctly different: 2:1 to 3:1 selectivities in favor of the mannosides with $NaBH_4$ (entries 5/6 and 12/13), versus high, essentially full, *manno*-stereoselectivities with the sterically bulky, *sec*-butyl-substituted borohydrides (entries 10/11 and 16/17).

A number of other hydride reagents have also been evaluated, with clearly less favourable results. Neither $Zn(BH_4)_2$, useful for the reduction of a variety of functionalised ketones,[8] nor its tetrabutylammonium analog showed any substantial improvement in the

Table 1. Stereoselectivities of hydride reductions of isopropyl β-D-*arabino*-hexosid-2-uloses

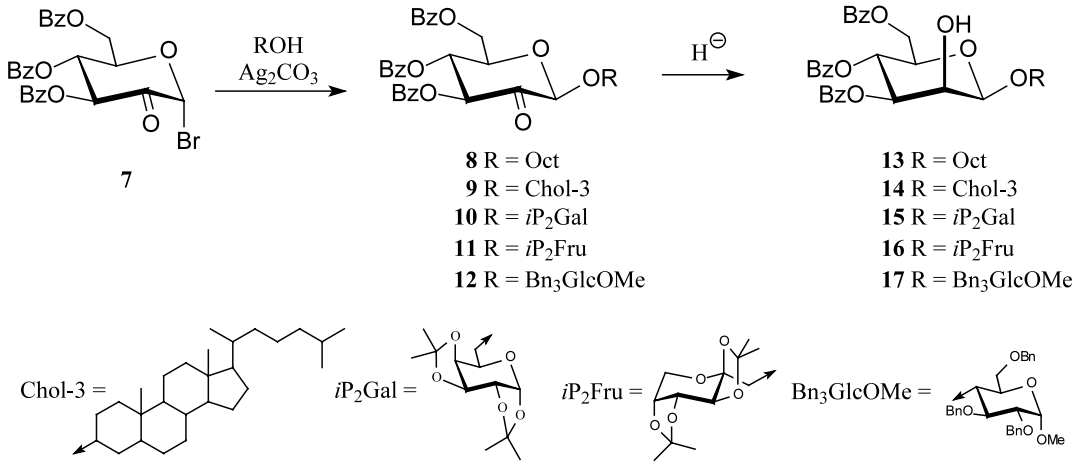


1 R = Bn
2 R = Bz
3 R = Piv

4 R = Bn
5 R = Bz
6 R = Piv

Entry	Uloside	Reagent[b]	Solvent	Temp. (°C)	Time (min)	Ratio[a] *manno*/*gluco*	β-D-Mannoside (isol. yield,%)
1	**1** (R = Bn)	$NaBH_4$	$MeOH/CH_2Cl_2$ (1:1)[7]	rt	120	50:1	91 (**4**)
2	**1** (R = Bn)	$NaBH_4$	$MeOH/CH_2Cl_2$ (1:1)	rt	20	50:1	90 (**4**)
3	**1** (R = Bn)	$LiB(iBu)_3H$	THF	−78	1	50:1	86 (**4**)
4	**1** (R = Bn)	$KB(iBu)_3H$	THF	−78	1	50:1	89 (**4**)
5	**2** (R = Bz)	$NaBH_4$	$MeOH/CH_2Cl_2$ (1:1)	rt	20	3:1	[d]
6	**2** (R = Bz)	$NaBH_4$	CH_2Cl_2[7]	rt	22 h	5:2	[d]
7	**2** (R = Bz)	$Zn(BH_4)_2$	DME	0	45	1:1	[d]
8	**2** (R = Bz)	Bu_4NBH_4	THF	rt	1	2:1	[d]
9	**2** (R = Bz)	Bu_4NBH_4	$THF/Ac_2O/DMSO$[c]	0	1	10:1	[d]
10	**2** (R = Bz)	$LiB(iBu)_3H$	THF	−78	1	50:1	85 (**5**)
11	**2** (R = Bz)	$KB(iBu)_3H$	THF	−78	1	50:1	79 (**5**)
12	**3** (R = Piv)	$NaBH_4$	Dioxane/water (9:1)[7]	rt	30	3:1	[d]
13	**3** (R = Piv)	$NaBH_4$	$MeOH/CH_2Cl_2$ (1:1)	rt	20	5:1	[d]
14	**3** (R = Piv)	Bu_4NBH_4	THF	rt	1	6:1	[d]
15	**3** (R = Piv)	Bu_4NBH_4	$THF/Ac_2O/DMSO$[c]	0	1	10:1	[d]
16	**3** (R = Piv)	$LiB(iBu)_3H$	THF	−78	1	50:1	87 (**6**)
17	**3** (R = Piv)	$KB(iBu)_3H$	THF	−78	1	50:1	89 (**6**)

[a] A 50:1 ratio signifies that no *gluco* isomer was detectable by ^1H NMR or TLC. All other ratios were determined by ^1H NMR.
[b] $LiB(iBu)_3H$ and $KB(iBu)_3H$ refers to lithium and potassium triisobutyl borohydride (i.e. L- and K-Selectride), respectively.
[c] Conditions recommended in Ref. 9: stirring a 2:1 $DMSO/Ac_2O$ mixture for 16 h, then coevaporation with toluene, followed by addition to a THF solution of the uloside and addition of Bu_4NBH_4.
[d] Mixture of *manno* and *gluco* isomers not separated.



manno-selectivities (Table 1, entries 7, 8 and 14). Conditions propagated recently for reaching high *manno*-selectivities in a number of disaccharide-ulosides,[9] i.e. exposure of the uloside to DMSO/acetic anhydride ('activated' DMSO), followed by reduction with tetrabutylammonium borohydride in THF (entries 9 and 15), indeed showed some improvement (~10:1 in favour of the β-D-mannosides), yet not comparable to the results obtained with the sterically bulky selectrides, which have the additional advantage of combining low reaction temperature (−78°C) with exceedingly short reaction times (1 min).

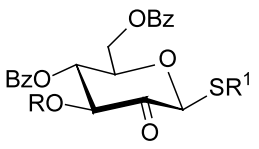
The essentially *manno*-specific course in the selectride reductions of acylated isopropyl ulosides **2** and **3** prompted experiments towards the general applicability in systems with larger anomeric residues. As clearly borne out by examples **8**–**12**, featuring octyl **8**, cholestanyl **9**, and a number of unwieldy glycoside residues **10**–**12**, the 2:1 to 3:1 *manno*-selectivities of their $NaBH_4$ reductions are transformed into essentially stereospecific formation of the desired β-D-mannosides **13**–**17** when employing K- or L-Selectride in THF (Table 2).

Table 2. Stereoselectivities (^{1}H NMR) obtained on reduction of ulosides **8**–**12** with $NaBH_4$ and K- or L-Selectride

Educt	Ratio *manno*/*gluco*		β-D-Mannosides (isol. yield,%)
	$NaBH_4$	Selectride	
8	3:1	50:1	**13**[a]
9	5:2	50:1	**14** (82)
7 (via **10**)	3:1	50:1	**15** (79)
7 (via **11**)	3:2	50:1	**16** (80)
7 (via **12**)	3:2	50:1	**17** (76)

[a] Not isolated.

The same steric outcome is observed for anomerically thiated glycosiduloses of type **18**–**20**, providing the respective 1-thio-β-D-mannosides **21**–**23** in excellent yield. These are not only useful mannosyl acceptors but donors as well as their *S*-aglycones can subsequently be activated under appropriate conditions.[10]



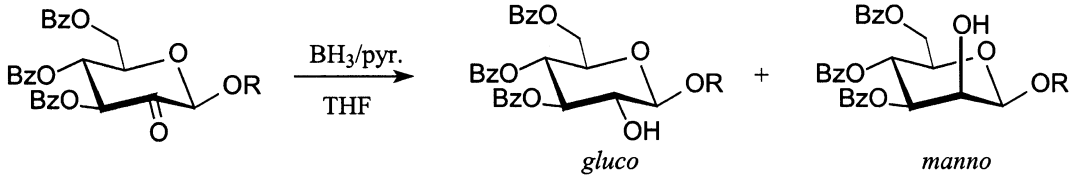
	R	R^1
18	Bz	C_6H_5
19	Bn	Et
20	Bn	C_6H_5

	R	R^1	*manno*/*gluco*-ratio $NaBH_4$	*manno*/*gluco*-ratio Selectride	isol. yield (%)
21	Bz	C_6H_5	3:1	50:1	85
22	Bn	Et	15:1	50:1	78
23	Bn	C_6H_5	15:1	50:1	82

Thus, at last, the most readily accessible acylated 2-oxoglycosides of β-D-*arabino*-configuration—generated either via the ulosyl bromide approach or via oxidation of 2-OH-free β-D-glucosides[11]—can be turned to preparative use for the expedient generation of oligosaccharides with β-D-mannose units.

2.2. *gluco*-Selective borane reductions of 2-oxo-β-D-*arabino*-hexopyranosides

In the course of these studies, the reduction of the 2-keto group in β-D-*arabino*-hexosiduloses with diborane or various borane complexes was also evaluated, in as much as this type of reductants has been used for the straightforward conversion of 2-ketoximes into 2-aminosugars,[1,12,13] yet not for simple carbonyl reductions in sugars. To our surprise, when employing a five molar excess of the borane–pyridine complex for reduc-

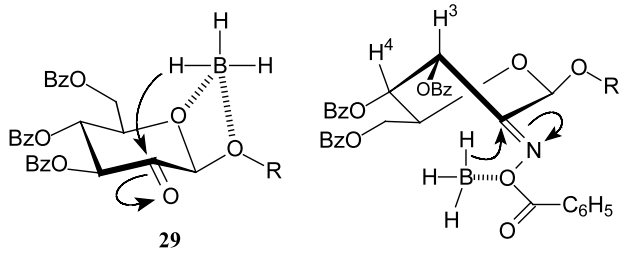


	R	ratio *gluco*/*manno*	glucoside (yield, %)
2 R = *i*Pr	**24**	*i*Pr	11:1	
8 R = Oct	**25**	Oct	7:1	
9 R = Chol-3	**26**	Chol-3	10:1	76
10 R = iP_2Gal	**27**	iP_2Gal	8:1	72
12 R = Bn_3GlcOMe	**28**	Bn_3GlcOMe	>20:1	80

tion of β-D-*arabino*-uloside in THF solution at ambient temperature, a reversal in the carbonyl reduction selectivities as compared to those with ionic borohydrides is observed: β-D-Glucosides are obtained with preferences that make the procedure preparatively useful. This steric course is exemplified by the borane reductions of ulosides **2**, **8**–**10** and **12** which give *gluco*/*manno* ratios from 7:1 to better than 20:1 and allow the isolation of the major product in yields of 70–80%.

As these β-D-glucosides are obtained with free 2-OH groups, they are ideal glucosyl acceptors for the generation of oligosaccharides carrying 2-*O*-linked glucosyl residues.

In trying to rationalize this sterically reverse borane reduction course of 2-keto-β-D-*arabino*-hexopyranosides, a preferential complexation of the neutral borane with the upper side (β-face) of the molecule appears most likely, such that not only the carbonyl oxygen is involved but due to the Lewis acid nature of borane the pyranoid ring oxygen and the anomeric oxygen as well. This pre-orientation of the reducing agent to the uloside, as depicted in formula **29**, obviously results in the preferential delivery of the hydride to the carbonyl carbon from the β-face to yield the β-D-glucosides.



29 **30**

(R = Me, iP_2Gal, Bn_3GlcMe)

It has to be noted though that the borane–tetrahydrofuran reduction of the *O*-benzoyloximino derivatives of β-D-*arabino*-ulosides, i.e. compounds of type **30**, reliably proceed with high *manno*-selectivity,[1,13] to provide (after subsequent *N*-acetylation) *N*-acetyl-β-D-mannosaminides in excellent yields—a procedure that has successfully been used for the straightforward generation of oligosaccharides with β-D-ManNAc units.[1,13] Thus, the initial coordination of the borane with the benzoyloximino derivatives of β-D-*arabino*-hexulosides obviously occurs from the α-face, conceivably by complexation with the oxygen of the *N*-OBz group as outlined in **30**, which not only preforms the benzoylborane ($BzOBH_2$) as a good leaving group, but provides the predisposition for delivering the hydride from the bottom face. This sort of complexation may be facilitated by the fact, that the pyranoid ring in the oximino derivatives is substantially distorted, the unusually small $J_{3,4}$ coupling constants of 3.5–4.5 Hz[1,13] indicating a twist type conformation as depicted in **30**. By contrast, the 2-oxo-hexosides **29** invariably show $J_{3,4}$ values around 8–9 Hz, hence adopt the usual $^4C_1$ chair geometry.

3. Experimental

3.1. General remarks

Reactions were carried out under Ar. All solvents were of reagent grade and were further dried. All other reagents were used as received. Melting points are uncorrected and were measured on a Büchi SMP-20. Optical rotations were measured on a Perkin–Elmer 241 polarimeter at 20°C using a cell of 1 dm path length. Mass spectra were recorded on Varian MAT 311 and MAT 212 spectrometers. Microanalyses were determined on a Perkin–Elmer 240 elemental analyzer. Analytical thin layer chromatography (TLC) was performed on precoated Merck plastic sheets (0.2 mm silica gel 60 F_{254}) with detection by UV (254 nm) and/or spraying with H_2SO_4 (50%) and heating. Column chromatography was carried out on Fluka silica gel 60 (70–230 mesh); eluents are given in brackets. ^1H and ^{13}C NMR spectra were recorded on Bruker WM-300, AC-300 and AVANCE 500 spectrometers. The structures of all new compounds were confirmed by COSY, TOCSY, selective TOCSY, and/or decoupling experiments. Chemical shifts are reported relative to sodium 2,2,3,3-tetradeutero-3-trimethylsilyl propionate (D_2O) or Me_4Si (all other solvents) as internal reference. Coupling constants are listed separately if an assignment was possible. In the listings of ^1H and ^{13}C NMR data for the individual compounds, signals originating from blocking groups are omitted if well separated from the

hexopyranoside hydrogen and carbon signals, e.g. those originating from benzyl and/or benzoyl moieties.

3.2. Preparation of 2-keto-β-D-*arabino*-hexopyranosides

3.2.1. Isopropyl 3,4,6-tri-*O*-pivaloyl-β-D-*arabino*-hexopyranosid-2-ulose, 3. To a solution of *i*-PrOH (185 μL, 2.4 mmol) in CH_2Cl_2 (15 mL) was added Ag_2CO_3 (330 mg, 1.2 mmol) and molecular sieve (3 Å, 500 mg) and the mixture was stirred for 30 min at rt. 3,4,6-Tri-*O*-pivaloyl-β-D-*arabino*-hexopyranos-2-ulosyl bromide[6] (600 mg, 1.2 mmol) was then added and stirring was continued for 1 h. After filtration through Celite the solvent was evaporated in vacuo and the residue was crystallized by trituration with Et_2O: 540 mg (95%) of uloside **3** as a microcrystalline solid; mp 121–128°C; $[\alpha]_D^{20} = -22.2$ (*c* 1, $CHCl_3$); $R_f = 0.3$ (CCl_4/EtOAc, 4:1). ^1H NMR (300 MHz, $CDCl_3$): δ 1.19, 1.22, 1.24 (3s, 27 H, 3 ($C(CH_3)_3$), 1.23, 1.31 (2d, each 3H, two CH_3), 4.04 (m, 1H, $CH(CH_3)_2$), 4.16 (m, 2H, 5-H, 6-H), 4.31 (m, 1H, 6-H′), 5.05 (s, 1H, 1-H), 5.36 (dd, 1H, 4-H), 5.49 (d, 1 H, 3-H); $J_{3,4} = 10.1$, $J_{4,5} = 9.1$, $J_{CH3,CH} = 6.2$ Hz. Partial presence of the monohydrate of **3** was indicated by substantially highfield-shifted minor signals for 1-H (5.05→4.52) and 3-H (5.49→5.10). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 21.8, 23.2 ($2CH_3$), 27.0, 27.1 ($3C(CH_3)_3$), 38.8, 38.9, 39.1 ($3C(CH_3)_3$), 62.4 (C-6), 69.6 (C-4), 72.7 (C-5), 72.9 ($CH(CH_3)_2$), 76.4 (C-3), 98.4 (C-1), 176.2, 177.4, 178.1 (3PivCO), 191.9 (C-2). MS (FD, 15 mA): *m*/*z* 472 [M^+], 473 [M^++1]. Anal. calcd for $C_{24}H_{40}O_9$ (472.57): C, 61.00; H, 8.53. Found: C, 61.05; H, 8.61.

3.2.2. Octyl 3,4,6-tri-*O*-benzoyl-β-D-*arabino*-hexopyranosid-2-ulose, 8. A suspension of *n*-octanol (1.25 mL, 8 mmol), silver alumosilicate[14] (8.00 g, 24.6 mmol) and molecular sieve (3 Å, 1 g) in CH_2Cl_2 (100 mL) was stirred at 0°C and under exclusion of light for 10 min, followed by the addition of ulosyl bromide **7**[6] (4.42 g, 8 mmol). After stirring for another 2 min (TLC monitoring) the mixture was filtered through Celite. The filtrate was washed with 10% aqueous $Na_2S_2O_3$ (20 mL), water (20 mL) and dried (Na_2SO_4). Removal of the solvent in vacuo and trituration with di-isopropyl ether yielded 4.05 g (84%) of **8** as colorless crystals; mp 82–84°C; $[\alpha]_D^{20} = -34.5$ (*c* 1.2, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ 0.86 (t, 3H, CH_3), 1.12–1.46, 1.66 (m, 12H, $6CH_2$), 3.68 (dt, 1H, CH_2O), 3.92 (dt, 1H, CH_2O), 4.52 (ddd, 1H, 5-H), 4.58 (dd, 1H, 6-H), 4.71 (dd, 1H, 6-H′), 5.15 (s, 1H, 1-H), 5.94 (dd, 1H, 4-H), 5.98 (d, 1H, 3-H); $J_{3,4} = 9.5$, $J_{4,5} = 9.6$, $J_{5,6} = 5.6$, $J_{5,6'} = 3.3$, $J_{6,6'} = 11.8$. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 14.2 (CH_3), 22.8, 25.9, 29.3, 29.4, 29.5, 31.9 ($6CH_2$), 63.6 (C-6), 70.6 (CH_2O), 70.9 (C-4), 73.1 (C-5), 76.9 (C-3), 99.8 (C-1), 191.8 (C-2). MS (FD, 20 mA): *m*/*z* 603 (M^++H). Anal. calcd for $C_{35}H_{38}O_9$ (602.68): C, 69.75; H, 6.36. Found: C, 69.74; H, 6.18.

3.2.3. 5α-Cholestan-3β-yl 3,4,6-tri-*O*-benzoyl-β-D-*arabino*-hexopyranosid-2-ulose, 9. A suspension of 5α-cholestan-3β-ol (3.89 g, 10.0 mmol), silver alumosilicate[14] (10.0 g, 30.8 mmol) and molecular sieve (4 Å, 5 g) in CH_2Cl_2 (30 mL) was stirred at rt for 20 min, followed by the addition of ulosyl bromide **7**[6] (5.53 g, 10.0 mmol). After stirring for 6 h (TLC monitoring), the mixture was diluted with CH_2Cl_2 (100 mL), filtered through Celite, and the filtrate was concentrated to dryness to afford 8.36 g (97%) of **9** as a colorless solid; $[\alpha]_D^{20} = -23.2$ (*c* 1.0, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ 0.50–2.00 (m, 46H, $H_{cholestanyl}$), 3.73 (m, 1H, 3-$H_{cholestanyl}$), 4.50 (ddd, 1H, 5-H), 4.59 (dd, 1H, 6-H_a), 4.68 (dd, 1H, 6-H_b), 5.24 (s, 1H, 1-H), 5.89 (dd, 1H, 4-H), 5.95 (d, 1H, 3-H); $J_{3,4} = 10.1$, $J_{4,5} = 8.4$, $J_{5,6a} = 6.0$, $J_{5,6b} = 3.5$, $J_{6a,b} = 11.8$ Hz. The presence of the monohydrate form (~15%) in the product was indicated by substantial highfield shift for 1-H ($\delta = 4.76$ ppm), 3-H (5.50), and 5-H (4.10). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 12.2–56.6 ($26C_{cholestanyl}$), 63.7 (C-6), 71.3 (C-4), 72.9 (C-5), 77.0 (C-3), 79.8 (C-3′), 98.2 (C-1), 191.8 (C-2). Anal. calcd for $C_{54}H_{68}O_9$ (861.13): C, 75.30; H, 7.96. Found: C, 75.24; H, 8.06.

3.2.4. 6-*O*-(3,4,6-Tri-*O*-benzoyl-β-D-*arabino*-hexopyranos-2-ulosyl)-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose, 10. A mixture of 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose[15] (210 mg, 0.8 mmol), molecular sieve (3 Å), silver carbonate (1.1 g, 4 mmol), and CH_2Cl_2 (20 mL) was stirred at rt under exclusion of light for 15 min. Ulosyl bromide **7**[6] (390 mg, 0.7 mmol) was added and stirring continued for 3 h. After addition of CH_2Cl_2 (20 mL) and filtration through Celite, the solution was washed with 10% aqueous $Na_2S_2O_3$ (20 mL) and water (2×20 mL). Drying (Na_2SO_4) and concentration of the solution afforded 425 mg (83%) **10** as a colorless foam. ^1H NMR (300 MHz, $CDCl_3$): δ 1.30–1.53 (4s, 3H, each, $4CH_3$), 3.70–4.74 (m, 9H, 2-H, 3-H, 4-H, 5-H, 6-H_2, 5′-H, 6′-H_2), 5.40 (s, 1H, 1′-H), 5.57 (d, 1H, 1-H), 5.93 (dd, 1H, 4′-H), 5.99 (d, 1H, 3′-H); $J_{1,2} = 4.7$, $J_{3',4'} = 10.0$, $J_{4',5'} = 10.1$ Hz. Partial presence of the monohydrate of **10** was indicated by substantially highfield-shifted minor signals for 1′-H (5.40→4.81) and 3′-H (5.99→5.61). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 24.3–27.4 ($2C(CH_3)_2$), 62.2 (C-6′), 68.4 (C-6), 67.8–68.2, 69.2–73.0 (C-2, C-3, C-4, C-5, C-4′, C-5′), 76.7 (C-3′), 96.2 (C-1), 99.3 (C-1′), 108.6–109.6 ($2C(CH_3)_2$), 191.6 (C-2′). MS (FD, 20 mA): *m*/*z* 733 [M^++H], 717 [M^+-CH_3]. Anal. calcd for $C_{39}H_{40}O_{14}$ (732.75): C, 63.93; H, 5.50. Found: C, 63.59; H, 5.40.

When starting from the ulosyl iodide[6] and employing silver alumosilicate[14] instead of silver carbonate, the reaction time is reduced to 30 s.

3.2.5. Methyl 4-*O*-(3,4,6-tri-*O*-benzoyl-β-D-*arabino*-hexopyranos-2-ulosyl)-2,3,6-tri-*O*-benzyl-α-D-glucopyranoside, 12. To a stirred solution of methyl 2,3,6-tri-*O*-benzyl-α-D-glucopyranoside[16] (145 mg, 0.31 mmol) in CH_2Cl_2 (1.5 mL) was added molecular sieve (4 Å, 200 mg) and silver alumosilicate (500 mg, 1.6 mmol). A solution of ulosyl bromide **7**[6] (258 mg, 0.47 mmol) in CH_2Cl_2 (1 mL) was then injected and stirring continued at rt for 16 h. The suspension was diluted with CH_2Cl_2 (10 mL), filtered through Celite and freed from the solvent in vacuo. The crude product was purified by flash chromatography on silica gel (2.5×20

cm) with CH_2Cl_2/EtOAc (5:1) to afford 225 mg (77%) **12** as a colorless foam. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.37 (s, 3H, CH_3O), 3.52 (m, 2H, 2-H, 5-H), 3.72 (dd, 1H, 6-H_a), 3.80–4.10 (m, 4H, 3-H, 4-H, 5′-H, 6-H_b), 4.29 (dd, 1H, 6′-H_a), 4.37 (dd, 1H, 6′-H_b), 4.60 (d, 1H, 1-H), 4.42–4.98 (m, 6H, $3C_6H_5CH_2$), 5.13 (s, 1H, 1′-H), 5.57 (d, 1H, 3′-H), 5.82 (dd, 1H, 4′-H); $J_{5,6a}=1.3$, $J_{3',4'}=10.1$, $J_{4',5'}=9.9$, $J_{5',6'a}=4.2$, $J_{5',6'b}=3.2$, $J_{6'a,b}=12.2$ Hz. Partial presence of the monohydrate of **12** was indicated by a set of lower intensity signals (ca. 10%), of which singlet for 1′-H (4.68 ppm) and the doublet for 3′-H (5.23) were substantially shifted. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 55.3 (CH_3O), 62.6 (C-6′), 68.2 (C-6), 70.6 (C-4′), 72.3 (C-5′), 73.4-75.3 ($3C_6H_5CH_2$), 77.1 (C-3′), 77.5–80.6 (C-2, C-3, C-4, C-5), 98.2 (C-1), 100.8 (C-1′), 191.8 (C-2′). MS (FD, 20 mA): m/z 936 [M^+], 845 [$M^+-C_6H_5CH_2$].

On using the respective ulosyl iodide[6] instead of bromide **7**, the glycosidation is complete within 3 min.

3.2.6. Ethyl 4,6-di-*O*-benzoyl-3-*O*-benzyl-1-thio-β-D-*arabino*-hexopyranosid-2-ulose, 19. A solution of 4,6-di-*O*-benzoyl-3-*O*-benzyl-1-thio-α-D-*arabino*-hexopyranos-2-ulosyl bromide[4] (2.20 g, 4 mmol), tetramethylurea (1 mL) and ethanethiol (0.5 mL, 8 mmol) in CH_2Cl_2 (35 mL) was stirred for 6 h, followed by dilution with CH_2Cl_2 (300 mL) washing with 2N HCl and 5% $NaHCO_3$ solution (3×) to yield after drying ($MgSO_4$) and removal of the solvent in vacuo, a residue which crystallized on trituration with ethanol: 1.54 g (74%) of **19**; mp 132–134°C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.27 (t, 3H, SCH_2CH_3), 2.63–2.82 (m, 2H, SCH_2CH_3), 4.28 (m, 1H, 5-H), 4.29 (d, 1H, 3-H), 4.47 (dd, 1H, 6-H), 4.63 (dd, 1H, 6-H′), 4.60, 4.76 (2d, 2H, $PhCH_2$), 5.25 (s, 1H, 1-H), 5.68 (dd, 1H, 4-H); $J_{3,4}=9.0$, $J_{4,5}=9.3$, $J_{5,6}=3.3$, $J_{5,6'}=5.9$, $J_{6,6'}=12.2$ Hz. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 14.9 (SCH_2CH_3), 24.2 (SCH_2CH_3), 63.5 (C-6), 72.4 (C-4), 73.0 ($PhCH_2$), 76.3 (C-5), 81.7 (C-3), 86.5 (C-1), 197.0 (C-2). Anal. calcd for $C_{29}H_{28}O_7S$ (520.60): C, 66.91; H, 5.42. Found: C, 66.87; H, 5.36.

3.2.7. Phenyl 4,6-di-*O*-benzoyl-3-*O*-benzyl-1-thio-β-D-*arabino*-hexopyranosid-2-ulose, 20. A solution of 4,6-di-*O*-benzoyl-3-*O*-benzyl-1-thio-α-D-*arabino*-hexopyranos-2-ulosyl bromide[4] (2.37 g, 4.3 mmol), thiophenol (0.88 mL, 8.6 mmol), and 1,1,3,3-tetramethylurea (1.1 mL, 9 mmol) in CH_2Cl_2 (35 mL) was stirred for 30 min at ambient temperature. After dilution with CH_2Cl_2 (300 mL), the solution was washed with 2N HCl, 5% $NaHCO_3$ solution, and three times with water. After drying ($MgSO_4$) the solvent was evaporated giving an amorphous residue, which crystallized to yield 2.01 g (82%) of **18** as a colorless, uniform (TLC in CH_2Cl_2/EtOAc, 20:1) syrup. ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.30 (m, 2H, 3-H, 5-H), 4.47 (dd, 1H, 6-H), 4.59, 4.94 (2d, 2H, $PhCH_2$), 4.66 (dd, 1H, 6H′), 5.40 (s, 1H, 1-H), 5.64 (dd, 1H, 4-H); $J_{3,4}=9.3$, $J_{4,5}=9.4$, $J_{5,6}=7.1$, $J_{5,6'}=2.7$, $J_{6,6'}=12.1$, $J_{PhCH2}=12.3$ Hz. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 63.70 (C-6), 72.63 (C-4), 73.02 ($PhCH_2$), 76.62 (C-5), 81.73 (C-3), 89.51 (C-1), 196.25 (C-2). Anal. calcd for $C_{33}H_{28}O_7S$ (568.64): C, 69.70; H, 4.96. Found: C, 69.60; H, 4.89.

3.3. *manno*-Selective hydride reduction of 2-keto-β-D-*arabino*-hexopyranosides

3.3.1. General procedures

3.3.1.1. K- or L-Selectride reduction (procedure A). A 1 M THF solution of K- or L-Selectride (1 mL, 1 mmol) was added under Ar to a cold (−78°C) solution of the 2-uloside (1 mmol) in THF (3 mL). After 1 min the reaction was stopped by addition of acetic acid (0.2 mL), CH_2Cl_2 (30 mL) was added for dilution, followed by washing of the mixture with 2 M HCl (30 mL) and satd aq. $NaHCO_3$ (30 mL), drying ($MgSO_4$) and removal of the solvent under diminished pressure.

3.3.1.2. $NaBH_4$ reduction (procedure B). $NaBH_4$ (150 mg, 4 mmol) was added at rt to a solution of the 2-uloside (1 mmol) in a mixture of CH_2Cl_2/MeOH 1:1 (10 mL) and stirred for 20 min. After quenching with water (5 mL) and acetic acid (0.2 mL), the mixture was diluted with CH_2Cl_2 (30 mL) followed by washing with 2 M HCl (30 mL) and satd aq. $NaHCO_3$ (30 mL), drying ($MgSO_4$) and evaporation of the solvent in vacuo.

3.3.2. Isopropyl 3,4,6-tri-*O*-benzoyl-β-D-mannopyranoside, 5. A solution of isopropyl 3,4,6-tri-*O*-benzoyl-β-D-*arabino*-2-ketohexoside[6] **2** (535 mg, 1 mmol) in THF (3 mL) was exposed to L-Selectride in THF (1 min) according to procedure A. The residue obtained on work-up was purified by flash elution from a silica gel column with CH_2Cl_2/EtOAc (50:1), to give, after removal of the solvents from the appropriate fraction ($R_f=0.18$ in eluent), a syrupy residue which crystallized on trituration with ether: 455 mg (85%) of **5** as colorless crystals; mp 136–137°C; $[\alpha]_D^{20}=-66.9$ (c 0.8, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.21, 1.27 (2d, each 3H, $CH(CH_3)_2$), 2.56 (d, 1H, 2-OH), 4.03 (ddd, 1H, 5-H), 4.10 (qq, 1H, $OCH(CH_3)_2$), 4.33 (m, 1H, 2-H), 4.51 (dd, 1H, 6-H), 4.63 (dd, 1H, 6-H′), 4.87 (d, 1H, 1-H), 5.40 (dd, 1H, 3-H), 5.95 (dd, 1H, 4-H); $J_{1,2}=0.9$, $J_{2,3}=3.2$, $J_{3,4}=9.8$, $J_{4,5}=9.6$, $J_{5,6}=5.9$, $J_{5,6'}=3.5$ $J_{6,6'}=11.9$ Hz. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 21.7, 23.3 ($CH(CH_3)_2$), 63.8 (C-6), 67.3 (C-4), 69.7 (C-2), 71.9 ($CH(CH_3)_2$), 72.2 (C-5), 73.9 (C-3), 97.6 (C-1). MS (FD, 20 mA): m/z 535 [M^++H], 534 [M^+], 491 [$M^+-C_3H_7$]. Anal. calcd for $C_{30}H_{30}O_9$ (534.56): C, 67.41; H, 5.66. Found: C, 67.19; H, 5.56.

Longer exposure of **2** to the Selectride resulted in partial 3-*O*→2-*O*-benzoyl migration to the 2,4,6-tri-*O*-benzoyl isomer (^{1}H NMR); on exceedingly long contact with silica gel, e.g. slow elution from a column, causes partial elimination of benzoic acid from the 3,4-positions, i.e. formation of the respective 2,6-dihydropyran-3-one, clearly detectable in the ^{1}H NMR.

3.3.3. Isopropyl 3,4,6-tri-*O*-pivaloyl-β-D-mannopyranoside, 6. Uloside **3** (472 mg, 1 mmol) was reacted with L-Selectride according procedure A. Column chromatography of the resulting residue on silica gel (toluene/EtOAc, 8:1) yielded the β-D-mannoside **6** (420 mg, 89%); $R_f=0.54$ (toluene/EtOAc, 4:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.16–1.22 (m, 33H, $2CH_3$, $3C(CH_3)_3$),

2.39 (brs, 1H, 2-OH), 3.67 (m, 1H, 5-H), 3.96–4.10 (m, 2H, 6-H, OC*H*$(CH_3)_2$), 4.04 (d, 1H, 2-H), 4.25 (dd, 1H, 6-H′), 4.68 (d, 1H, 1-H), 4.95 (dd, 1H, 3-H), 5.36 (t, 1H, 4-H); $J_{1,2}=1.1$, $J_{2,3}=3.1$, $J_{3,4}=9.7$, $J_{4,5}=9.6$, $J_{5,6'}=2.3$, $J_{6,6'}=12.0$ Hz. ^{13}C NMR (125 MHz, $CDCl_3$): δ 21.6, 23.3 ($2CH_3$), 27.1 ($3C(CH_3)_3$), 38.1–38.9 ($3C(CH_3)_3$), 62.7 (C-6), 65.7 (C-4), 69.3 (C-2), 71.5 ($CH(CH_3)_2$), 72.7 (C-5), 73.1 (C-3), 97.3 (C-1), 176.7–178.3 (3PivCO). MS (FD/15 mA): *m*/*z* 474 [M$^+$], 475 [M$^+$+1]. Anal. calcd for $C_{24}H_{42}O_9$ (474.59): C, 60.74; H, 8.92. Found: C, 60.71; H, 8.92.

3.3.4. 5α-Cholestan-3β-yl 3,4,6-tri-*O*-benzoyl-β-D-mannopyranoside, 14. Reduction of uloside **9** (200 mg, 0.23 mmol) with K-Selectride was conducted according to procedure A and the product obtained was purified by column chromatography on silica gel (toluene/EtOAc, 15:1) to yield 163 mg (82%) of **14**. $R_f=0.84$ (toluene/EtOAc, 8:1); mp 160–162°C; $[\alpha]_D^{20}=-31.2$ (*c* 1.0, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.57–2.00 (m, 46H, $H_{cholestanyl}$), 2.49 (brs, 1H, 2-OH), 3.72 (m, 1H, 3-$H_{cholestanyl}$), 4.03 (ddd, 1H, 5-H), 4.31 (brs, 1H, 2-H), 4.54 (dd, 1H, 6-H), 4.60 (dd, 1H, 6-H′), 4.90 (d, 1H, 1-H), 5.38 (dd, 1H, 3-H), 5.89 (t, 1H, 4-H); $J_{1,2}=0.6$, $J_{2,3}=3.0$, $J_{3,4}=J_{4,5}=9.8$, $J_{5,6}=6.4$, $J_{5,6'}=3.6$, $J_{6,6'}=11.9$ Hz. ^{13}C NMR (125 MHz, $CDCl_3$): δ 12.5–56.9, 79.0 ($C_{cholestanyl}$), 64.3 (C-6), 67.9 (C-4), 71.1 (C-2), 72.6 (C-5), 74.3 (C-3), 97.7 (C-1). MS (ESI): *m*/*z* 885.5 [(M+Na)$^+$]. Anal. calcd for $C_{54}H_{70}O_9$ (863.14): C, 75.14; H, 8.17. Found: C, 75.24; H, 7.82.

3.3.5. 6-*O*-(3,4,6-Tri-*O*-benzoyl-β-D-mannopyranosyl)-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose, 15. A suspension of 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose[15] (262 mg, 1.0 mmol), silver alumosilicate[14] (1.0 g, 3.1 mmol) and powdered molecular sieve (4 Å, 400 mg) in CH_2Cl_2 (5 mL) was stirred at rt and under exclusion of light for 30 min. A solution of bromide **7**[6] (615 mg, 1.1 mmol) in CH_2Cl_2 (2 mL) was added and the solution was stirred for another 20 min. Dilution with CH_2Cl_2 (5 mL), filtration and evaporation of the solvent afforded 740 mg of crude uloside **10** as a colorless foam. This was dissolved in THF (3 mL) and reduced with K-Selectride according procedure A. The residue obtained was subjected to column chromatography on silica gel (toluene/EtOAc, 5:1) to furnish **15** (580 mg, 79%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.31 (s, 6H, $2CH_3$), 1.43, 1.51 (2s, each 3H, $2CH_3$), 2.35 (brs, 1H, 2′-OH), 3.85 (m, 1H, 6-H), 4.07 (m, 4H, 5-H, 6-H′, 2′-H, 5′-H), 4.16 (dd, 1H, 4-H), 4.31 (dd, 1H, 2-H), 4.51 (dd, 1H, 6′-H), 4.58 (dd, 1H, 3-H), 4.63 (dd, 1H, 6′-H′), 4.91 (d, 1H, 1′-H), 5.41 (dd, 1H, 3′-H), 5.54 (d, 1H, 1-H), 5.97 (dd, 1H, 4′-H); $J_{1,2}=5.0$, $J_{2,3}=2.5$, $J_{3,4}=7.8$, $J_{4,5}=1.8$, $J_{5,6b}=3.0$, $J_{6a,b}=11.2$, $J_{1',2'}=0.7$, $J_{2',3'}=3.1$, $J_{3',4'}=9.8$, $J_{4',5'}=9.7$, $J_{5',6a}=5.1$, $J_{5',6'b}=3.4$, $J_{6'a,b}=11.8$ Hz. ^{13}C NMR (75 MHz, $CDCl_3$): δ 23.3, 24.9, 26.0 ($4CH_3$), 63.6 (C-6′), 67.1 (C-4′), 68.0, 72.1 (C-5, C-5′), 68.9 (C-2′), 69.2 (C-6), 70.4 (C-2), 70.7 (C-3), 71.3 (C-4), 73.6 (C-3′), 96.2 (C-1), 100.1 (C-1′), 108.7, 109.5 ($2(CH_3)_2C$).

3.3.6. 2,3:4,5-Di-*O*-isopropylidene-1-*O*-(3,4,6-tri-*O*-benzoyl-β-D-mannopyranosyl)-α-D-fructopyranose, 16. A suspension of ulosyl bromide **7**[6] (277 mg, 0.5 mmol), Ag_2CO_3 (138 mg, 0.5 mmol) and molecular sieve (3 Å, 500 mg) in CH_2Cl_2 (5 mL) was stirred for 30 min followed by addition of 2,3:4,5-di-*O*-isopropylidene-β-D-fructopyranose (130 mg, 0.5 mmol) and stirring was continued for 4 h. After filtration through Celite the filtrate was evaporated in vacuo to give crude uloside **11** (470 mg, 85%) as a colorless foam, which as such was subjected to reduction with L-Selectride by procedure A. The resulting syrup was purified by elution from a silica gel column with toluene/EtOAc (4:1): 295 mg (80%) of **16**; $R_f=0.39$ (toluene/EtOAc, 2:1); $[\alpha]_D^{20}=-42.3$ (*c* 1.0, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.31, 1.41, 1.42, 1.55 (4s, each 3H, $4CH_3$), 2.60 (brs, 1H, 2b-OH), 3.75 (d, 1H, 6a-H), 3.88 (d, 1H, 1a-H), 3.92 (dd, 1H, 6a-H′), 3.99 (d, 1H, 1a-H′), 4.03 (ddd, 1H, 5b-H), 4.21 (dd, 1H, 5a-H), 4.40 (d, 1H, 3a-H), 4.45 (d, 1H, 2b-H), 4.50 (dd, 1H, 6b-H), 4.58 (dd, 1H, 4a-H), 4.62 (dd, 1H, 6b-H′), 4.97 (d, 1H, 1b-H), 5.57 (dd, 1H, 3b-H), 5.98 (t, 1H, 4b-H); $J_{1a,1a'}=11.7$, $J_{3a,4a}=2.7$, $J_{4a,5a}=7.9$, $J_{5a,6a'}=1.8$, $J_{6a,6a'}=12.9$, $J_{1b,2b}=0.5$, $J_{2b,3b}=3.0$, $J_{3b,4b}=9.9$, $J_{4b,5b}=9.8$, $J_{5b,6b}=5.4$, $J_{5b,6b'}=3.2$, $J_{6b,6b'}=12.0$ Hz. ^{13}C NMR (125 MHz, $CDCl_3$): δ 24.4, 25.9, 26.2, 27.0 ($4CH_3$), 61.7 (C-6a), 63.9 (C-6b), 67.3 (C-4b), 69.4 (C-2b), 70.2 (C-1a), 70.4, 70.5 (C-3a, C-4a), 71.3 (C-5a), 72.9 (C-5b), 74.3 (C-3b), 100.5 (C-1b), 102.6 (C-2a), 109.2, 109.5 ($2C(CH_3)_2$). MS (ESI): *m*/*z* 757.3 [(M+Na)$^+$], 773.2 [(M+K)$^+$]. Anal. calcd for $C_{39}H_{42}O_{14}$ (734.76): C, 63.75; H, 5.76. Found: C, 63.60; H, 5.87.

3.3.7. Methyl 4-*O*-(3,4,6-tri-*O*-benzoyl-β-D-mannopyranosyl)-2,3,6-tri-*O*-benzyl-α-D-glucopyranoside, 17. A suspension of methyl 2,3,6-tri-*O*-benzyl-α-D-glucopyranoside[16] (474 mg, 1.0 mmol), powdered molecular sieve (4 Å, 600 mg) and silver alumosilicate[14] (1.6 g, 5.1 mmol) in CH_2Cl_2 (5 mL) was stirred at rt for 30 min. A solution of ulosyl bromide **7**[6] (837 mg, 1.5 mmol) in CH_2Cl_2 (4 mL) was added and the mixture was stirred at rt for 16 h. Dilution with CH_2Cl_2 (15 mL), filtration through Celite and evaporation of the solvent afforded a hard foam (1.16 g), which was dissolved in THF (5 mL) and reacted with K-Selectride according procedure A. Column chromatography on silica gel (toluene/EtOAc, 5:1), evaporation of the appropriate fractions ($R_f=0.11$ in eluent), and crystallization from ether/hexane afforded 710 mg (76%) of **17**; mp 127°C; $[\alpha]_D^{20}=-10.2$; $[\alpha]_{365\,nm}^{20}=-57.5$ (*c* 0.7, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.67 (d, 1H, 2′-OH), 3.37 (s, 3H, CH_3O), 3.52 (dd, 1H, 2-H), 3.56 (ddd, 1H, 5′-H), 3.65–3.78, 3.99 (m, 5H, 3-H, 4-H, 5-H, 6-H_2), 4.14 (m, 1H, 2′-H), 4.25 (dd, 1H, 6′-H_a), 4.40 (dd, 1H, 6′-H_b), 4.45 (d, 1H, $C_6H_5CH_2$), 4.60 (d, 1H, 1-H), 4.62, 4.66, 4.76 (3d, 1H, each, $3C_6H_5CH_2$), 4.83 (brs, 1H, 1′-H), 4.91 (2d, 1H, each, $2C_6H_5CH_2$), 5.08 (dd, 1H, 3′-H), 5.84 (dd, 1H, 4′-H); $J_{1,2}=3.6$, $J_{2,3}=9.2$, $J_{1',2'}=<0.5$, $J_{2',3'}=2.9$, $J_{2',OH}=2.7$, $J_{3',4'}=10.0$, $J_{4',5'}=9.9$, $J_{5',6'a}=4.8$, $J_{5',6'b}=3.3$, $J_{6'a,b}=12.2$, $J_{CH2}=11.5$, 11.7, 12.1 Hz. Anal. calcd for $C_{55}H_{54}O_{16}$ (939.03): C, 70.35; H, 5.80. Found: C, 70.26; H, 5.77.

3.3.8. Phenyl 3,4,6-tri-*O*-benzoyl-1-thio-β-D-mannopyranoside, 21. Uloside **18**[6] (250 mg, 0.43 mmol) was subjected to K-Selectride reduction according to procedure A. The resulting residue was then purified by elution from a silica gel column with hexane/EtOAc (2:1). Removal of the

solvent from the appropriate eluents in vacuo gave a residue which crystallized from an EtOAc solution on addition of *n*-hexane: 215 mg (85%) of **21** as colorless crystals of mp 170–172°C; $R_f = 0.45$ (hexane/EtOAc, 2:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.80 (brs, 1H, 2-OH), 4.12 (ddd, 1H, 5-H), 4.52 (dd, 1H, 6-H), 4.63 (m, 2H, 2-H, 6-H′), 5.09 (d, 1H, 1-H), 5.40 (dd, 1H, 3-H), 5.91 (t, 1H, 4-H); $J_{1,2} = 0.9$, $J_{2,3} = 3.2$, $J_{3,4} = J_{4,5} = 10.0$, $J_{5,6} = 7.2$, $J_{5,6'} = 2.8$, $J_{6,6'} = 12.2$ Hz. ^{13}C NMR (125 MHz, $CDCl_3$): δ 63.9 (C-6), 66.9 (C-4), 70.9 (C-2), 75.0 (C-3), 76.8 (C-5), 87.5 (C-1). MS (ESI): m/z 607.2 $[M+Na]^+$. Anal. calcd for $C_{33}H_{28}O_8S$ (584.64): C, 67.80; H, 4.83. Found: C, 67.59; H, 5.19.

3.3.9. Ethyl 4,6-di-*O*-benzoyl-3-*O*-benzyl-1-thio-β-D-mannopyranoside, 22. A solution of 520 mg (1.0 mmol) of thio-uloside **19** in THF (3 mL) was treated with K-Selectride according to procedure A. After work-up, the resulting residue was subjected to column chromatography on silica gel (CH_2Cl_2/EtOAc, 95:5) to yield after removal of the solvent from the appropriate fractions (R_f 0.42 in the eluent) and crystallization of the residue from EtOH 405 mg (78%) of **22**; mp 142–143°C; $[\alpha]_D^{20} = -52.4$ (c 1.1, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.29 (t, 3H, SCH_2CH_3), 2.72 (m, 2H, SCH_2CH_3), 2.76 (s, 1H, 2-OH), 3.73 (dd, 1H, 3-H), 3.88 (ddd, 1H, 5-H), 4.23 (broad s, 1H, 2-H), 4.42 (dd, 1H, 6-H), 4.54 (dd, 1H, 6-H′), 4.53, 4.69 (2d, 2H, $PhCH_2$), 4.71 (s, 1H, 1-H), 5.63 (dd, 1H, 4-H); $J_{1,2}$ = undetectable, $J_{2,3} = 3.3$, $J_{3,4} = 9.4$, $J_{4,5} = 9.7$, $J_{5,6} = 6.5$, $J_{5,6'} = 3.3$, $J_{6,6'} = 12.0$, $J_{PhCH2} = 12.3$ Hz. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 15.1 (SCH_2CH_3), 24.7 (SCH_2CH_3), 64.1 (C-6), 68.6 (C-4), 69.3 (C-2), 71.3 ($PhCH_2$), 76.2 (C-5), 78.7 (C-3), 83.8 (C-1). Anal. calcd for $C_{29}H_{30}O_7S$ (522.61): C, 66.65; H, 5.78; S, 6.13. Found: C, 66.60; H, 5.80; S, 6.01.

When conducting the reduction of thio-uloside **19** (1.40 g, 2.69 mmol) with $NaBH_4$ following procedure B, a 15:1 mixture (^{1}H NMR) of β-D-mannoside **22** and the respective β-D-glucoside was obtained, which was subjected to column chromatography on silica gel (eluent: CH_2Cl_2/EtOAc, 95:5). The mannoside **22** eluted first (R_f 0.42 in the eluent) to yield after removal of the solvent and crystallization of the residue from EtOH 1.18 g (84%) identical with **22** described above. The minor fraction eluted next ($R_f = 0.57$), upon analogous work-up gave 70 mg (5%) of ethyl 4,6-di-*O*-benzoyl-3-*O*-benzyl-1-thio-β-D-glucopyranoside of mp 108–109°C; $[\alpha]_D^{20} = -24.4$ (c 1.2, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.29 (t, 3H, SCH_2CH_3), 2.73 (m, 2H, SCH_2CH_3), 3.74 (m, 2H, 2-H, 3-H), 3.91 (ddd, 1H, 5-H), 4.35 (dd, 1H, 6-H), 4.45 (d, 1H, 1-H), 4.53 (dd, 1H, 6-H′), 4.72, 4.80 (2d, 2H, $PhCH_2$), 5.41 (dd, 1H, 4-H); $J_{1,2} = 9.3$, $J_{3,4} = 9.2$, $J_{4,5} = 9.7$, $J_{5,6} = 5.8$, $J_{5,6'} = 3.0$, $J_{6,6'} = 12.1$, $J_{PhCH2} = 12.1$ Hz.

3.3.10. Phenyl 4,6-di-*O*-benzoyl-3-*O*-benzyl-1-thio-β-D-mannopyranoside, 23. Thio-uloside **20** (570 mg, 1.0 mmol) was dissolved in THF (3 mL) and exposed to K-Selectride as described in procedure A. Subsequent purification of the product by elution from a silica gel column with CH_2Cl_2/EtOAc (95:5), removal of the solvents from the appropriate fractions and crystallization of the residue by trituration with ethanol gave 470 mg (82%) of **23**; mp 119–121°C; $[\alpha]_D^{20} = -85.8$ (c 1.0, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.88 (s, 1H, 2-OH), 3.74 (dd, 1H, 3-H), 3.93 (ddd, 1H, 5-H), 4.40 (broad s, 1H, 2-H), 4.43 (dd, 1H, 6-H), 4.55, 4.70 (2d, 2H, $PhCH_2$), 4.59 (dd, 1H, 6-H′), 4.88 (s, 1H, 1-H), 5.63 (dd, 1H, 4-H); $J_{1,2}$ = undetectable, $J_{2,3} = 3.3$, $J_{3,4} = 9.4$, $J_{4,5} = 9.7$, $J_{5,6} = 7.7$, $J_{5,6'} = 2.8$, $J_{6,6'} = 12.0$, $J_{PhCH2} = 12.2$ Hz. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 64.2 (C-6), 68.5 (C-4), 69.8 (C-2), 71.6 ($PhCH_2$), 76.4 (C-5), 78.8 (C-3), 87.0 (C-1). Anal. calcd for $C_{33}H_{30}O_7S$ (570.65): C, 69.45; H, 5.30; S, 5.62. Found: C, 69.40; H, 5.20; S, 5.49.

Reduction of thio-uloside **20** (1.88 g, 3.3 mmol) with $NaBH_4$ according procedure B gave an approximate 12:1 mixture (^{1}H NMR) of the *manno*-isomer **23** and the corresponding glucoside. Separation was effected by elution from a silica gel column with CH_2Cl_2/EtOAc (95:5). The product eluted first (R_f 0.30 in eluent) was the mannoside which crystallized on trituration with ethanol: 1.57 g (83%), identical with **23** described above. The product eluted next ($R_f = 0.53$), on similar work-up and crystallization from ethanol afforded 104 mg (5.5%) of phenyl 4,6-di-*O*-benzoyl-3-*O*-benzyl-1-thio-β-D-glucopyranoside; mp 146–148°C; $[\alpha]_D^{20} = -24.1$ (c 1.2, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.56 (broad s, 1H, OH), 3.54 (dd, 1H, 2-H), 3.67 (dd, 1H, 3-H), 3.85 (ddd, 1H, 5-H), 4.25 (dd, 1H, 6-H), 4.52 (d, 1H, 1-H), 4.54 (dd, 1H, 6-H′), 4.62, 4.70 (2d, 2H, $PhCH_2$), 5.29 (dd, 1H, 4-H); $J_{1,2} = 9.6$, $J_{2,3} = 8.9$, $J_{3,4} = 9.6$, $J_{4,5} = 9.7$, $J_{5,6} = 5.7$, $J_{5,6'} = 2.7$, $J_{6,6'} = 12.1$, $J_{PhCH2} = 11.5$ Hz. Anal. calcd for $C_{33}H_{30}O_7S$ (570.65): C, 69.45; H, 5.30; S, 5.62. Found: C, 69.39; H, 5.27; S, 5.55.

3.4. *gluco*-Selective borane reduction of 2-keto-β-D-*arabino*-hexopyranosides

3.4.1. Isopropyl 3,4,6-tri-*O*-benzoyl-β-D-glucopyranoside, 24. Isopropyl uloside **2**[6] (2.00 g, 3.7 mmol), dissolved in THF (15 mL), was added dropwise to a cooled (−78°C) solution of BH_3–pyridine (1.80 mL, 18 mmol) in THF (50 mL). The mixture was stirred for 1 h, warmed up to rt, and quenched with water (5 mL). After removal of the solvents the syrupy residue was diluted with CH_2Cl_2 (50 mL), followed by vigorous stirring with 2N HCl (20 mL) for 30 min, separation of the layers and washing of the organic phase with satd $NaHCO_3$ solution (10 mL) and water (10 mL). Drying (Na_2SO_4) and evaporation of the solvent led to a crude product, comprising (^{1}H NMR) an 11:1 mixture of glucoside **24** and mannoside. Purification by elution from a silica gel column (3×15 cm) with CH_2Cl_2/acetone (30:1) gave a hard foam, which crystallized on trituration with ether: 1.50 g (75%) of **24**; mp 129–131°C; $[\alpha]_D^{20} = -52.1$ (c 0.8, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.24, 1.28 (2d, 3H, each, $CH(CH_3)_2$), 2.58 (d, 1H, 2-OH), 3.78 (ddd, 1H, 2-H), 4.05 (m, 2H, 5-H, $CH(CH_3)_2$), 4.47 (dd, 1H, 6-H), 4.58 (dd, 1H, 6-H′), 4.63 (d, 1H, 1-H), 5.55 (dd, 1H, 4-H), 5.63 (dd, 1H, 3-H); $J_{1,2} = 7.7$; $J_{2,3} = 9.4$; $J_{2,OH} = 2.5$; $J_{3,4} = 9.5$; $J_{4,5} = 9.5$; $J_{5,6} = 5.8$; $J_{5,6'} = 3.5$; $J_{6,6'} = 12.1$ Hz. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 22.0,

23.4 ($2CH_3$), 63.5 (C-6), 69.7 (C-4), 72.6 (C-2), 72.0, 72.8 (C-5, $CH(CH_3)_2$), 74.9 (C-3), 101.5 (C-1). Anal. calcd for $C_{30}H_{30}O_9$ (534.56): C, 67.41; H, 5.66. Found: C, 67.49; H, 5.65.

The presence of the C-2 epimeric mannoside in the reaction mixture was indicated by a low intensity 0.9 Hz d at $\delta = 4.87$ for the anomeric proton.

3.4.2. Octyl 3,4,6-tri-*O*-benzoyl-β-D-glucopyranoside, 25. A solution of BH_3–pyridine (1.3 mL, 13 mmol) in THF (5 mL) was added dropwise to a cooled (−78°C) solution of octyl uloside **8** (1.60 g, 2.65 mmol) in THF (50 mL). After stirring for 30 min the mixture was allowed to warm up to rt, stirred for another h and quenched with water (5 mL). Removal of the solvents in vacuo afforded a residue, which was dissolved in CH_2Cl_2 (60 mL) vigorously stirred with 2N HCl (20 mL) for 30 min, followed by washing of the organic layer with satd $NaHCO_3$ solution (20 mL), and finally with 10% aq. NaCl (2×10 mL). Drying (Na_2SO_4) and concentration to dryness furnished a syrup, consisting (^{1}H NMR) of an approximate 8:1 mixture of **25** and its *manno*-epimer **13**. Separation was achieved by elution from silica gel (5×18 cm) with cyclohexane/EtOAc (4:1). Processing of the fractions with $R_f = 0.27$ afforded 1.10 g (69%) of a syrupy **25**. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.88 (t, 3H, CH_3), 1.26 (m, 10H, $5CH_2$), 1.65 (m, 2H, CH_2CH_2O), 2.68 (brd, 1H, 2-OH), 3.61 (dt, 1H, CH_2O), 3.82 (ddd, 1H, 2-H), 3.93 (dt, 1H, CH_2O), 4.06 (ddd, 1H, 5-H), 4.47 (dd, 1H, 6-H), 4.57 (d, 1H, 1-H), 4.59 (dd, 1H, 6-H′), 5.57 (dd, 1H, 4-H), 5.63 (dd, 1H, 3-H); $J_{1,2} = 7.6$, $J_{2,3} = 9.4$, $J_{2,OH} = 2.3$, $J_{3,4} = 9.4$, $J_{4,5} = 9.3$, $J_{5,6} = 3.6$ and 5.5, $J_{6,6'} = 12.0$ Hz. Anal. calcd for $C_{35}H_{40}O_9$ (604.73): C, 69.52; H, 6.67. Found: C, 68.97; H, 6.59.

3.4.3. 5α-Cholestan-3β-yl 3,4,6-tri-*O*-benzoyl-β-D-glucopyranoside, 26. To a cooled (−78°C) solution of cholestanyl uloside **9** (3.90 g, 4.5 mmol) in THF (50 mL) was added dropwise a solution of BH_3–pyridine (2.30 mL, 23 mmol) in THF (15 mL). The mixture was stirred for 1 h, allowed to warm up to rt, and was quenched with water (5 mL). After removal of the solvents the syrupy residue was diluted with CH_2Cl_2 (60 mL). The organic layer was stirred vigorously for 30 min in a two-phase system with 2N HCl (20 mL). Washing with 2N HCl (20 mL), satd $NaHCO_3$/NaCl solution (1:1, 40 mL), drying (Na_2SO_4) and evaporation of the solvent led to a syrup, containing the *gluco*- and *manno*-isomers in an approximate 10:1 ratio (^{1}H NMR). Silica gel chromatography (4.5×22 cm column) with toluene/EtOAc (50:1) as eluted the glucoside first ($R_f = 0.35$ in eluent) to give on processing the appropriate fractions and crystallisation of the residue from MeOH, 2.70 g (69%) of **26** as colorless needles; mp 99–101°C; $[\alpha]_D^{20} = -20.8$ (*c* 1.3, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.50–2.00 (m, 46H, $H_{cholestanyl}$), 2.57 (d, 1H, 2-OH), 3.67 (m, 1H, 3-$H_{cholestanyl}$), 3.79 (ddd, 1H, 2-H), 4.06 (ddd, 1H, 5-H), 4.49 (dd, 1H, 6-H_a), 4.55 (dd, 1H, 6-H_b), 4.66 (d, 1H, 1-H), 5.52 (dd, 1H, 4-H), 5.62 (dd, 1H, 3-H); $J_{1,2} = 7.8$, $J_{2,3} = 9.4$, $J_{2,OH} = 2.5$, $J_{3,4} = 9.5$, $J_{4,5} = 9.6$, $J_{5,6a} = 6.0$, $J_{5,6b} = 3.7$, $J_{6a,b} = 12.0$ Hz. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 11.7–56.2 ($26C_{cholestanyl}$), 63.2 (C-6), 69.6 (C-4), 71.7 (C-5), 72.3 (C-2), 74.6 (C-3), 79.2 (C-3′), 101.0 (C-1). Anal. calcd for $C_{54}H_{70}O_9$ (863.15): C, 75.14; H, 7.17. Found: C, 74.93; H, 7.36.

The second fraction ($R_f = 0.25$) contained mannoside **14**, which crystallized from MeOH: 180 mg (5%) as colorless needles, identical in physical data with the product described earlier (vide supra).

3.4.4. 6-*O*-(3,4,6-Tri-*O*-benzoyl-β-D-glucopyranosyl)-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose, 27. A suspension of 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose[15] (1.57 g, 6 mmol), silver alumosilicate[14] (6.20 g, 19 mmol) and powdered molecular sieve (4 Å, 2.5 g) in CH_2Cl_2 (30 mL) was stirred at rt and under exclusion of light for 30 min. A solution of bromide **7**[6] (3.69 g, 6.67 mmol) in CH_2Cl_2 (15 mL) was added and the solution was stirred for another 20 min. Dilution with CH_2Cl_2 (25 mL), filtration and evaporation of the solvent afforded 4.68 g of crude product as a colorless foam, which was dissolved in THF (20 mL). This solution was added dropwise during 15 min to a cooled (−78°C) solution of BH_3/pyridine (2.4 mL, 24 mmol) in THF (20 mL). The mixture was allowed to warm up to rt, quenched with water (10 mL) and evaporated to dryness. The residue, comprising an approximat 8:1 mixture of **27** and its *manno*-isomer **15** (^{1}H NMR) was subjected to column chromatography on silica gel (eluent: CH_2Cl_2/acetone, 15:1). Processing of the fractions containing **27** ($R_f = 0.36$ in eluent) in the usual manner gave 3.25 g (74%, based on ulosyl bromide **7**) as a colorless foam. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.31 (s, 6H, $2CH_3$), 1.44, 1.52 (2s, 3H, each, $2CH_3$), 3.42 (brs, 1H, 2′-OH), 3.80–3.90 (m, 2H, 2′-H, 6-H_a), 4.00–4.13 (m, 3H, 5-H, 6-H_b, 5′-H), 4.19 (dd, 1H, 4-H), 4.31 (dd, 1H, 2-H), 4.45 (dd, 1H, 6′-H_a), 4.58 (m, 2H, 3-H, 6′-H_b), 4.70 (d, 1H, 1′-H), 5.54 (d, 1H, 1-H), 5.56 (dd, 1H, 4′-H), 5.67 (dd, 1H, 3′-H); $J_{1,2} = 5.0$, $J_{2,3} = 2.3$, $J_{3,4} = 7.8$, $J_{4,5} = 1.8$, $J_{1',2'} = 7.8$, $J_{2',3'} = 9.5$, $J_{3',4'} = 9.6$, $J_{4',5'} = 9.7$, $J_{5',6'a} = 5.4$, $J_{6'a,b} = 11.9$ Hz. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 23.3, 24.9, 26.0 ($4CH_3$), 63.4 (C-6′), 69.6 (C-4′), 69.9 (C-6), 70.4 (C-2), 70.7 (C-3), 71.1 (C-4), 68.0, 72.3, 72.4 (C-2′, C-5′, C-5), 74.7 (C-3′), 96.2 (C-1), 104.3 (C-1′). Anal. calcd for $C_{39}H_{42}O_{14}$ (734.75): C, 63.75; H, 5.76. Found: C, 64.71; H, 5.85.

3.4.5. Methyl 4-*O*-(3,4,6-tri-*O*-benzoyl-β-D-glucopyranosyl)-2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (methyl 2,3,6-tri-*O*-benzyl-3′,4′,6′-tri-*O*-benzoyl-α-cellobioside), 28. A suspension of methyl 2,3,6-tri-*O*-benzyl-α-D-glucopyranoside[16] (2.05 g, 4.3 mmol), powdered molecular sieve (4 Å, 2.50 g) and silver alumosilicate[14] (6.90 g, 22 mmol) in CH_2Cl_2 (15 mL) was stirred at rt for 30 min. A solution of ulosyl bromide **7** (3.60 g, 6.46 mmol) in CH_2Cl_2 (15 mL) was added and the mixture was stirred at rt for 16 h. Dilution with CH_2Cl_2 (50 mL), filtration through Celite and evaporation of the solvent afforded a hard foam (4.97 g), which was dissolved in THF (50 mL) and cooled (−78°C). BH_3–pyridine (1.80 mL, 18 mmol) in THF (15 mL) was added dropwise and after stirring for 30 min the mixture was allowed to warm up to rt and quenched with water (4.5 mL).

Evaporation of the solvents in vacuo yielded a syrup, which was dissolved in CH_2Cl_2 (100 mL) and stirred vigorously with 2N HCl (25 mL) for 30 min. The organic layer was washed with satd $NaHCO_3$ solution (100 mL) and water (2×50 mL), dried (Na_2SO_4), and freed from the solvent. The residue, consisting of an approximate 10:1 mixture of *gluco*- (**28**) and *manno*-isomers (**17**) was subjected to chromatography on silica gel (5×30 cm, eluent: toluene/EtOAc, 5:1).

The major product with $R_f = 0.15$ (in eluent) was eluted first to afford after removal of the solvents from the appropriate fractions 2.91 of **28** (72%, based on bromide **7**) as a colorless foam; $[\alpha]_D^{20} = -2.7$; $[\alpha]_{365\ nm}^{20} = -32.5$ (*c* 1, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.35 (s, 3H, CH_3O), 3.47–3.53 (m, 1H, 5′-H), 3.51 (dd, 1H, 2-H), 3.58 (d, 1H, 2′-OH), 3.63–3.69 (m, 2H, 2′-H, 6-H_a), 3.79 (m, 1H, 5-H), 3.97 (dd, 1H, 3-H), 4.04 (dd, 1H, 6-H_b), 4.05 (dd, 1H, 4-H), 4.16 (dd, 1H, 6′-H_a), 4.31 (dd, 1H, 6′-H_b), 4.49 (d, 1H, $C_6H_5CH_2$), 4.57 (d, 1H, 1-H), 4.58 (d, 1H, $C_6H_5CH_2$), 4.67 (d, 1H, 1′-H), 4.73, 4.74, 4.90, 5.00 (4d, 1H, each, $4C_6H_5CH_2$), 5.33 (dd, 1H, 3′-H), 5.47 (dd, 1H, 4′-H); $J_{1,2} = 4.0$, $J_{2,3} = 9.1$, $J_{3,4} = 9.2$, $J_{4,5} = 9.4$, $J_{5,6b} = 3.7$, $J_{6a,b} = 11.3$, $J_{CH2} = 11.4$, 12.1, 12.2, $J_{1',2'} = 7.8$; $J_{2',3'} = 9.5$, $J_{2',OH} = 3.2$, $J_{3',4'} = 9.6$, $J_{4',5'} = 9.7$, $J_{5',6'a} = 4.7$, $J_{5',6'b} = 3.3$, $J_{6'a,b} = 12.2$ Hz. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 55.5 (CH_3O), 63.5 (C-6′), 68.7 (C-6), 69.7 (C-4′, C-5), 72.2 (C-5′), 73.6 (C-2′), 73.7, 73.9, 75.3 ($3C_6H_5CH_2$), 75.6 (C-3′), 77.5 (C-4), 79.4 (C-2), 80.8 (C-3), 98.6 (C-1), 103.3 (C-1′). MS (FD, 20 mA): *m*/*z* 938 [M$^+$], 937 [M$^+$–H], 936 [M$^+$–2H], 847 [M$^+$–C_7H_7], 846 [M$^+$–C_7H_7–H]. Anal. calcd for $C_{55}H_{54}O_{16}$ (939.03): C, 70.35; H, 5.80. Found: C, 70.37; H, 5.68.

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