# Efficient Generation of β-L-Rhamnosidic Linkages by the 2-Ulosyl Donor Approach: Synthesis of a Trisaccharide with a Central β-L-Rhamnose Unit

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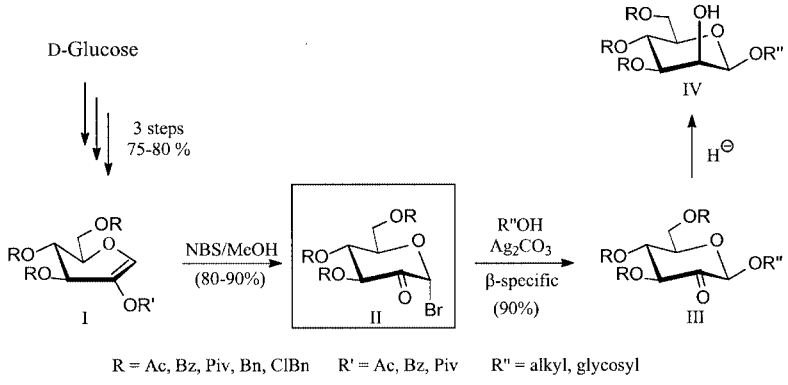
Practical procedures for the production of variously blocked 6-deoxy-α-L-*arabino*-2-ketohexosyl bromides from L-rhamnose have been developed. These compounds are highly useful as indirect β-L-rhamnosyl donors: they undergo β-specific glycosidations under Koenigs-Knorr conditions, and the 2-keto group of the resulting 6-deoxy-β-L-hexosiduloses is reduced with high β-L-*rhamno* selectivity. The straightforward application of this 2-ulosyl donor approach for the synthesis of β-L-rhamnose-containing di- and trisaccharides is demonstrated.


## Introduction

The 2-ulosyl donor approach, introduced in 1985,[1] has proven to be highly expedient for the generation of β-D-mannosidic linkages, as evidenced by the straightforward synthesis of various β-D-mannose-containing oligosaccharides up to the hexasaccharide level.[1−5] Central to this procedure is the ready preparation of variously blocked α-D-*arabino*-2-ketohexosyl bromides of type II from D-glucose,[1,4−7] their essentially β-specific glycosidation (→ III) − the nonparticipating electron-withdrawing 2-keto group suppresses oxycarbenium ion formation at the anomeric center thereby resulting in direct $S_N2$ displacement of the bromine − and *manno*-selective reduction of the resulting β-D-2-keto-glycosides III → IV (Scheme 1). When selectrides are used rather than borohydride only, the carbonyl reduction is also essentially *manno*-specific.[8] Besides its preparative simplicity, the procedure has the further advantage of providing the β-D-mannosides with free 2-OH groups (i.e., mannosyl acceptors ready for further glycosidation towards the oligosaccharides with β-D-Man-(1→2)-D-Man linkages).




Scheme 1. The ulosyl donor approach to β-D-mannosides

Numerous bacterial antigens contain β-L-rhamnopyranose units,[9] and the 6-deoxy-L enantiomers of II, ulosyl bromides of types **1**−**5**, should, if reasonably readily accessible, provide an expedient two-step procedure for their

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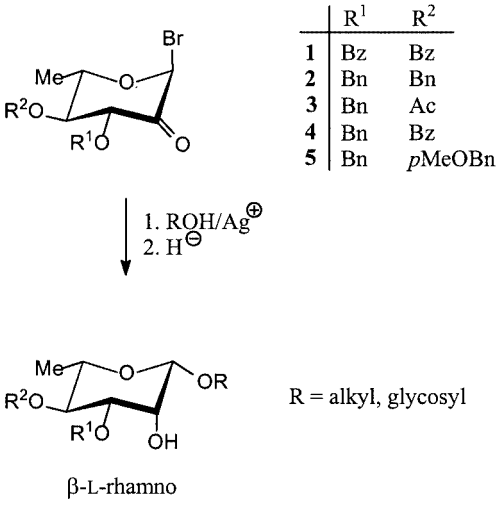
straightforward synthesis. As a consequence, we opted to evaluate this concept and here we present practical syntheses of a series of differently *O*-protected L-ulosyl bromides **1**−**5**, as well as illustrations of their utility as indirect β-L-rhamnosyl donors:[10]




| | $R^1$ | $R^2$ |
|---|---|---|
| **1** | Bz | Bz |
| **2** | Bn | Bn |
| **3** | Bn | Ac |
| **4** | Bn | Bz |
| **5** | Bn | *p*MeOBn |

Scheme 2

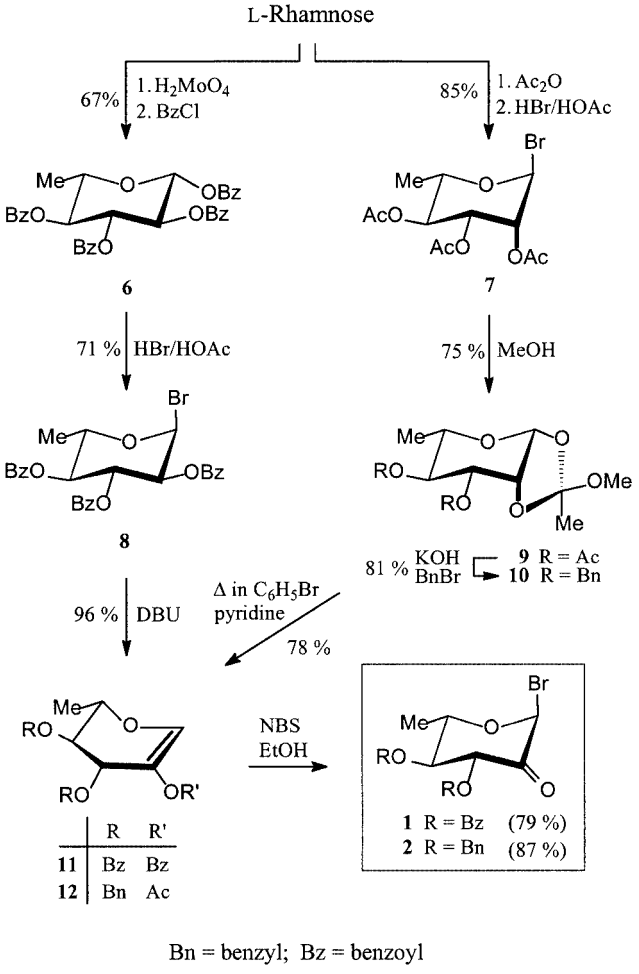
## Results and Discussion

The practical preparation of the indirect β-L-rhamnosyl donors **1**−**5** was based on L-rhamnose as a suitable, readily available starting material, and on the 2-acyloxy-L-rhamnals of type **11** or **12** as key intermediates, these being expected to provide the desired ulosyl bromides smoothly through brief treatment with NBS/methanol.[1,6]

The preparation of the 3,4-*O*-benzoyl-protected α-L-rhamnosulosyl bromide **1** (Scheme 3) started with the molybdate-promoted C-2-epimerization of L-rhamnose to provide 6-deoxy-L-glucose,[11] the resulting mixture of the two epimers (≈ 3:1 in favor of the *gluco* isomer) being readily separable upon benzoylation, as the β-L-*gluco*-tetrabenzoate **6** crystallizes exceedingly well (65%). Subsequent conversion into the known[12] glucosyl bromide by treatment with HBr/HOAc (→**8**), followed by DBU-induced elimination of HBr, smoothly gave the 2-benzoyloxy-L-rhamnal (**11**), which provided the desired ulosyl bromide **1** in crystalline form and in satisfactory overall yield (39% for the five steps from L-rhamnose) simply on treatment with NBS/methanol in dichloromethane (30 min, 25 °C).

The 3,4-di-*O*-benzyl-blocked ulosyl bromide **2** similarly required a seven-step sequence from L-rhamnose (although four of these steps were combinable into two one-pot operations). This approach involved conversion into the aceto-bromo derivative **7**[13] and then, by treatment with methanol/lutidine,[14] into orthoester **9**, in which the exchange of acetyl for benzyl blocking groups **9** → **10** could be performed in a one-pot operation by use of benzyl bromide/KOH in THF. The subsequent thermal fragmentation[1,6] (**10** → **12**) was satisfactorily effected by heating at reflux in bromobenzene (≈ 160 °C) in the presence of catalytic amounts of pyridine for 5 h (81%). Final treatment of 2-acetoxy-L-rhamnal (**12**) with NBS/ethanol gave ulosyl bromide **2** (87%), thus providing an overall yield of 35% for the seven steps from L-rhamnose.

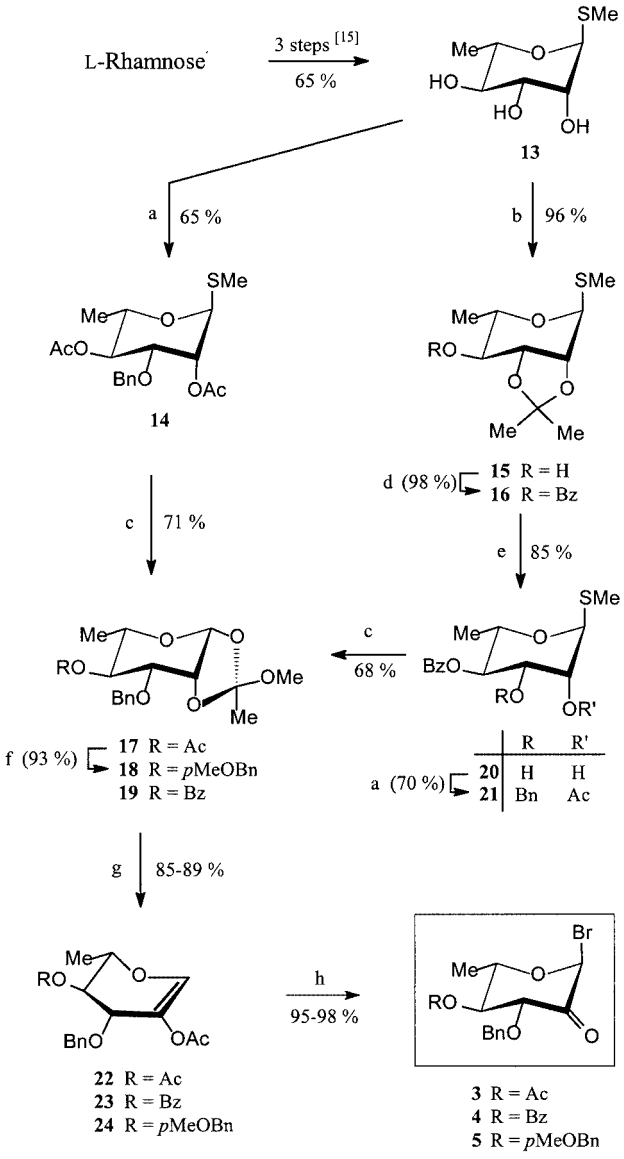
For the synthesis of naturally occurring β-L-rhamnose oligosaccharides both with (1→3)- and with (1→4)-intersaccharidic linkages, ulosyl donors with differentiated blocking groups at *O*-3 and *O*-4 were required. These were provided in the form of 3-*O*-benzyl ulosyl bromides **3** −**5**, bearing either an acyl or a *p*-methoxybenzyl moiety at *O*-4, by similar use of the respective orthoesters and 2-acetoxy-rhamnals as the key intermediates, by starting with methyl 1-thio-α-L-rhamnoside (**13**) and its 2,3-*O*-isopropylidene derivative **15**, readily accessible in three steps − acetylation,[13] $BF_3$-induced thiation with methyl sulfide, and deacetylation [14] (→ **13**) − and in four (isopropylidenation[14] of **13**) steps, respectively, a preparative advantage being that




Scheme 3. Conversion of L-rhamnose into β-L-rhamnosyl donors **1** and **2**

the sequences are easily adaptable to 100 g scale preparations and allow overall yields in the 65% range.

For the preparation of the 4-*O*-acetyl- and 4-*O*-(*p*-methoxybenzyl)-blocked ulosyl bromides (Scheme 4), the thio-rhamnoside **13** was first converted by 2,3-*O*-stannylation-di-



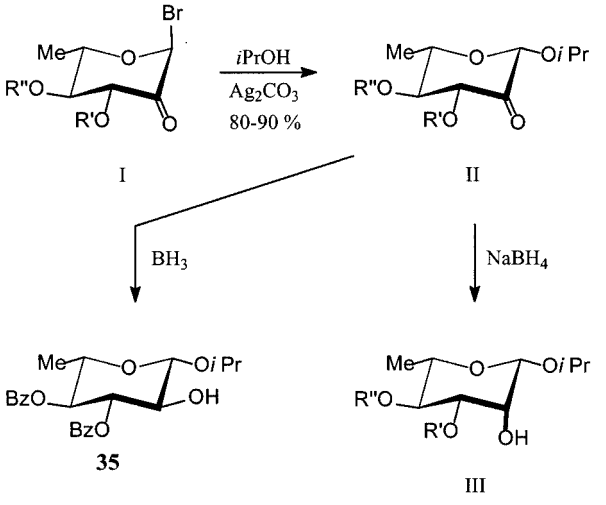

Scheme 4. Reagents and conditions: a) $Bu_3SnO$/toluene, reflux, then BnBr/DMF, finally $Ac_2O$/pyr.;[16] b) $Me_2(OMe)_2$, reflux;[15] c) $Br_2/CH_2Cl_2$, then MeOH/2,6-lutidine, 65 °C; d) BzCl/pyr.; e) 90% TFA, room temp.; f) *p*MeOBnCl/KOH; g) reflux in PhBr with catal. amounts of pyridine; h) NBS/MeOH or EtOH, 15 min, 0 °C

4rected selective benzylation and acetylation[16] into the easily crystallizing 2,4-di-*O*-acetyl-3-*O*-benzyl glycoside **14** (65%), and subsequently, by *S*-bromination and methanolysis, into the orthoester **17**, in which the 4-*O*-protecting acetyl group could be directly exchanged for a *p*-methoxybenzyl residue (**17** → **18**). An alternate route from S-rhamnoside **13** to another orthoester differently blocked at *O*-3 and *O*-4, the 3-*O*-benzyl-4-*O*-benzoyl derivative **19**, involved a straightforward six-step sequence performable in a 38% overall yield: benzoylation of its 2,3-*O*-isopropylidene derivative **15** → **16**, TFA-promoted removal of the isopropylidene group ("deacetonation" → **20**), selective benzylation at O-3 via the 2,3-*O*-stannylidene derivative, followed by acetylation (→ **21**) and methanolysis of the anomeric SMe group upon *S*-bromination (→ **19**).

As observed for orthoester **10**, the analogues **17**−**19** also underwent thermal fragmentation, simply on being heated at reflux in bromobenzene (b.p. 165 °C) for 5 h, providing the respective 2-acetoxy-L-rhamnals **22** −**24** through elimination of methanol, yields being in the 85−90% range. Their conversion into the ulosyl bromides **3** −**5** proved to be similarly efficient − yields were nearly quantitative − being smoothly effected by treatment with *N*-bromosuccinimide/methanol (or ethanol) in dichloromethane at ambient temperature or 0 °C, the initial bromonium ion addition at C-2 being followed by liberation of the carbonyl function through loss of the acetyl group as methyl acetate.

### Model Glycosidations of Ulosyl Donors 1 −5 and Uloside Reductions

The utility of ulosyl bromides **1**−**5** as indirect β-L-rhamnosyl donors was first examined with 2-propanol as model acceptor. Under standard Koenigs−Knorr conditions ($Ag_2CO_3$ in dichloromethane at 25 °C), glycosidation was consistently complete within 15−30 min, and no α-anomeric products were detectable in the reaction mixture by TLC or $^1H$ NMR spectroscopy. The glycosidation of the ulosyl bromides **1**−**5** is therefore essentially β-specific − not unexpected in view of the strongly electron-withdrawing effect of the carbonyl function, favoring direct $S_N2$ displacement of the bromide through suppression of carboxonium ion formation at the anomeric center. The β-L-ulosides **25**−**29** were therefore isolable in yields of 80−90% (Scheme 5).




| I → II → III | | | R' | R" | *rhamno* : 6-deoxy-*gluco* | overall yield |
|---|---|---|---|---|---|---|
| **1** | **25** | **30** | Bz | Bz | 3 : 1 | 60%[a] |
| **2** | **26** | **31** | Bn | Bn | > 25 : 1 | 76% |
| **3** | **27** | **32** | Bn | Ac | > 25 : 1 | 78% |
| **4** | **28** | **33** | Bn | Bz | > 25 : 1 | 81% |
| **5** | **29** | **34** | Bn | *p*MeOBn | > 25 : 1 | 80% |

*a*: Due to partial 3-*O* → 2-*O*-benzoyl migration during workup, the product was isolated as the tribenzoate.

Scheme 5

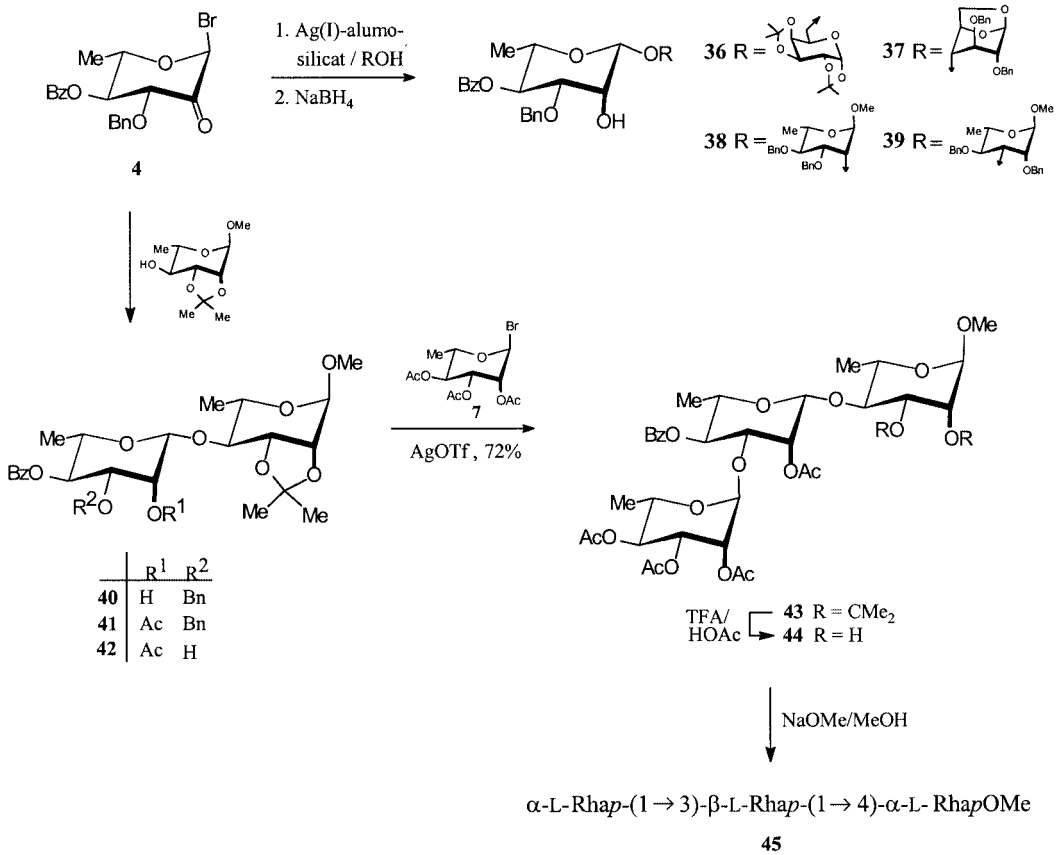
The *rhamno*/6-deoxy-*gluco* selectivities obtained in the carbonyl reductions of the glycosiduloses confirmed previous findings[6−8] that the outcomes depend on the nature of the 3-*O*-protection: uloside **25**, on treatment with $NaBH_4$ in dichloromethane/methanol (2 h, 0 °C → room temperature), gave a 3:1 mixture of the L-*rhamno* (**30**) and 6-deoxy-L-*gluco* epimers, whereas use of the bulkier and more reactive tri-*sec*-butylborohydride (L-selectride) gave a sizably improved *rhamno* selectivity in the 25:1 range. Both reductions, though, were impeded by partial 3-*O*→2-*O*-benzoyl migration during workup, resulting in product mixtures best resolved either by de-*O*-benzoylation or by benzoylation.

As the hydride reductions of the 3-*O*-benzylated ulosides **26**−**29** were already taking an essentially stereospecific course with sodium borohydride as the reductant − no 2-epimers were detectable in the reaction mixture either by $^1H$ NMR or by TLC (Scheme 5) − recourse to more bulky hydrides for enhancement of selectivity was not necessary. When diborane was used as the reducing agent, however, the reduction became *gluco*-selective, as also previously observed in the D-hexosidulose series.[8] Uloside **25**, for example, on treatment with the borane/pyridine complex in THF at −78 °C for 30 min, underwent a high-yield conversion (80%) to the 6-deoxy-β-L-glucoside **35**. The ulosyl donor approach thus not only shows promise for the generation of β-L-rhamnosidic linkages but, through changing the reducing agent, for the acquisition of 6-deoxy-β-L-glucosides as well.

### Di- and Trisaccharides with β-L-Rhamnose Units

Given the viability of ulosyl bromides **1**−**5** as donors for the generation at least of simple β-L-rhamnosides − both steps required in the glycosidation/reduction procedure proceed in an essentially stereospecific manner − their utility for the synthesis of oligosaccharides had to be probed next. A series of glycosyl acceptors were evaluated for glycosylation with ulosyl bromide **4**, with employment of, instead of silver carbonate, the more reactive[6] silver alumo-silicate catalyst [silver(I) immobilized on porous silica alumina],[17] as glycosidic OH groups were deemed to be less reactive than that of 2-propanol.

Primary OH groups in glycoside acceptors, such as in diacetone-galactose, were most readily glycosylated with ulosyl bromide **4**, providing the galactosyl β-L-rhamnoside **36** in 85% yield after in situ reduction (Scheme 6). Similarly, the axially disposed 4-OH of a 1,6-anhydro-D-glucose readily underwent the two-step glycosidation/reduction procedure to provide the L-rhamnosyl-β(1→4)-D-glucose derivative **37** in crystalline form (78%). In an analogous manner, rhamnobiosides with β(1→2)-, β(1→3)-, and β(1→4)-intersaccharidic linkages could be effectively prepared by starting from ulosyl bromide **4** and the corresponding L-rhamnoside acceptors protected except for a free 2-OH




Scheme 6. Synthesis of a rhamnotrisaccharide with a central β-L-rhamnose unit

(→ **38**, 79%), 3-OH (→ **39**, 77%), and 4-OH group (→ **40**, 80%) (Scheme 6).

Aside from the efficient generation of β-L-rhamnopyranosidic linkages, the ulosyl donor approach has the advantage of providing the di- or oligosaccharide with a free rhamnosyl-2-OH, thus ready for further glycosylation. Thanks to the differentiated group pattern at *O*-3 and *O*-4, though, further glycosyl residues may also be introduced at these positions. This option was demonstrated with the synthesis of the 3-*O*-rhamnosylated rhamnosyl-β(1→4)-rhamnoside **45**, a trisaccharide sequence found in the repeating units of *Klebsiella* and *Azotobacter vinelandii* polysaccharides[18] as well as various lipopolysaccharides:[19] the readily accessible rhamnobioside **40** was converted by acetylation (→ **41**) and hydrogenolysis into an acceptor **42** with a free 3-OH (91% for the two steps). Silver triflate-promoted glycosylation with acetobromo-rhamnose (**7**) smoothly gave the protected rhamnotrisaccharide **43** (82%), which afforded the target **45** on standard removal of the blocking groups. Thus, by utilization of ulosyl bromide in combination with two simple rhamnose derivatives a simple synthesis of a rhamnotrisaccharide with a central β-L-rhamnose unit could be carried out.

## Conclusion

The results described amply demonstrate the potential of the *ulosyl donor* approach for the generation of β-L-rhamnosidic linkages − an approach that compares favorably with existing methodologies,[20] in its β-specific glycosylation even meeting Ziegler's strategy of intramolecular β-L-rhamnosylation through pre-linked donor and acceptor substrates.[20f]

## Experimental Section

**General Remarks:** All solvents were of reagent grade and were further dried. All other reagents were used as received. Melting points are uncorrected and were measured with a Büchi SMP-20 machine. Optical rotations were measured with a Perkin−Elmer 241 polarimeter at 20 °C in a cell of 1-dm path length. Mass spectra were recorded with 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 by 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 with Bruker WM 300, AC 300, and AVANCE 500 spectrometers. Chemical shifts are reported relative to sodium 2,2,3,3-tetradeuterio-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 spectroscopic data for the individual compounds, signals originating from blocking groups, such as those originating from benzyl and/or benzoyl moieties, are omitted if well separated from the hexopyranoid hydrogen and carbon signals.

**Preparation of the 6-Deoxy-β-L-*arabino*-2-ketohexosyl Bromides**

**3,4-Di-*O*-benzoyl-ulosyl Bromide (1)**

**1,2,3,4-Tetra-*O*-benzoyl-6-deoxy-β-L-glucopyranose (β-L-Quinovose-tetrabenzoate) (6):** A solution of L-rhamnose monohydrate (50.0 g, 28 mmol) and molybdic acid (565 mg, 3.3 mmol) in water (250 mL) was stirred at 95 °C for 3 h. The reaction mixture was filtered, neutralized by addition of an anion-exchange resin (Amberlite® IRA 410; $OH^-$ form), and concentrated in vacuo to a syrup, which was coevaporated twice with EtOH (50 mL). The resulting syrup (49.0 g), an approximate 2:1 mixture of 6-deoxy-L-glucose and L-rhamnose ($^1H$ NMR), was dissolved in pyridine (125 mL), diluted with $CHCl_3$ (250 mL), cooled (0 °C), and benzoyl chloride (175 mL, 1.5 mol) was added dropwise. The solution was stirred for 2 h, and was then warmed to room temperature, diluted with $CHCl_3$ (200 mL), and washed consecutively with water (200 mL), HCl (2 N, 3 × 200 mL), and water (200 mL). The organic layer was stirred with charcoal (6.5 g), filtered through Celite, and dried ($Na_2SO_4$). Removal of the solvent in vacuo provided a crystalline residue, which was triturated with diethyl ether (600 mL) and filtered, to provide **6** (73.6 g) as colorless crystals. The mother liquor was taken to dryness and the residue was crystallized from MeOH (400 mL) to give additional **6** (29.6 g); overall yield: 103.1 g (65%, based on L-rhamnose). M.p. 177−179 °C; $[\alpha]_D^{20} = +16.0$ ($c = 0.9$, $CHCl_3$). $^1H$ NMR (300 MHz, $CDCl_3$): δ = 1.33 (d, 3 H, 6-$H_3$), 4.09 (qd, 1 H, 5-H), 5.37 (dd, 1 H, 4-H), 5.74 (dd, 1 H, 2-H), 5.89 (dd, 1 H, 3-H), 6.14 (d, 1 H, 1-H) ppm; $J_{1,2} = 8.2$, $J_{2,3} = J_{3,4} = J_{4,5} = 9.6$, $J_{5,6} = 6.2$ Hz. MS (FD, 10 mA): $m/z$ = 580 [$M^+$]. $C_{34}H_{28}O_9$ (580.6): calcd. C 70.34, H 4.86; found C 70.24, H 4.90.

**2,3,4-Tri-*O*-benzoyl-6-deoxy-α-L-glucopyranosyl Bromide (8):** A solution of **6** as obtained above (100.0 g, 0.17 mol) in $CHCl_3$ (125 mL) was treated with a solution of HBr in AcOH (33%, 300 mL, 1.69 mol), and the mixture was stirred at room temperature for 5 h. Dilution with $CHCl_3$ (350 mL), pouring onto crushed ice (500 mL) containing $Na_2S_2O_3$ (5 g), washing of the organic layer with saturated aqueous $NaHCO_3$ solution (4 × 400 mL) and water (2 × 500 mL), followed by drying ($Na_2SO_4$) and concentration in vacuo gave a crystalline residue, which was triturated with $Et_2O$ (200 mL) and collected after standing for 6 h at −27 °C, affording **8** (69.0 g, 71%) as colorless crystals. M.p. 160 °C. $[\alpha]_D^{20} = -117.8$ ($c = 1.0$, $CHCl_3$). ref.[12] M.p. 158−160 °C; $[\alpha]_D^{20} = -108$ ($c = 3.3$, $CHCl_3$). $^1H$ NMR (300 MHz, $CDCl_3$): δ = 1.39 (d, 3 H, 6-$H_3$), 4.48 (qd, 1 H, 5-H), 5.28 (dd, 1 H, 2-H), 5.45 (dd, 1 H, 4-H), 6.19 (dd, 1 H, 3-H), 6.83 (d, 1 H, 1-H) ppm; $J_{1,2} = 4.0$, $J_{2,3} = J_{3,4} = J_{4,5} = 9.8$, $J_{5,6} = 6.3$ Hz. $^{13}C$ NMR (75 MHz, $CDCl_3$): δ = 17.1 (C-6), 70.5 (C-3), 71.1 (C-5), 71.9 (C-2), 72.7 (C-4), 87.4 (C-1) ppm. MS (FI): $m/z$ = 459 [$M^+$ − Br]. $C_{27}H_{23}BrO_7$ (539.3): calcd. C 60.13, H 4.28; found C 60.16, H 4.21.

**(1,5-Anhydro-2,3,4-tri-*O*-benzoyl-6-deoxy-L-*arabino*-hex-1-enitol (3,4-Di-*O*-benzoyl-2-benzoyloxy-L-rhamnal) (11):** DBU (3.2 g, 21.2 mmol) was added to a cooled solution (0 °C) of **8** (10.0 g, 17.6 mmol) in 1,2-dichloroethane (30 mL). The mixture was stirred in the dark for 0.5 h and warmed to room temperature The reaction mixture was then diluted with $CH_2Cl_2$ (250 mL), and washed with HCl (2 N, 2 × 100 mL), water (2 × 100 mL) and saturated aqueous $NaHCO_3$ solution (100 mL). The organic layer was dried ($Na_2SO_4$) and the solvents were evaporated to give a faintly red syrup that crystallized from EtOH (40 mL), affording **11** (7.7 g, 96%) as colorless crystals. M.p. 95−96 °C. $[\alpha]_D^{20} = +179.0$ ($c = 1.0$, $CHCl_3$). $^1H$ NMR (500 MHz, $CDCl_3$): δ = 1.57 (d, 3 H, 6-$H_3$), 4.56 (m, 1 H, 5-H), 5.56 (dd, 1 H, 4-H), 6.11 (dd, 1 H, 3-H), 6.89 (d, 1 H, 1-H) ppm; $J_{3,4} = 4.3$, $J_{4,5} = 5.7$, $J_{5,6} = 6.8$ Hz. $^{13}C$ NMR (75 MHz,

$CDCl_3$): δ = 16.1 (C-6), 67.6 (C-3), 72.1 (C-4), 72.8 (C-5), 126.3−133.6 (3 $C_6H_5$, C-2), 139.9 (C-1) ppm. MS (FD, 0−10 mA): *m*/*z* = 458 [$M^+$]. $C_{27}H_{22}O_7$ (458.46): calcd. C 70.73, H 4.84; found C 70.68, H 4.82.

The D enantiomer of **11**, prepared from 2,3,4-tri-*O*-benzoyl-6-deoxy-D-glucosyl bromide (D-**8**) had m.p. 93−95 °C and $[\alpha]_D$ = −182 (*c* = 1.0, $CHCl_3$).[21]

**3,4-Di-*O*-benzoyl-6-deoxy-α-L-*arabino*-hexopyranos-2-ulosyl Bromide (1):** A solution of 2-benzoyloxy-rhamnal (**11**, 5.00 g, 10.9 mmol) and MeOH (0.53 mL, 0.42 g, 13.1 mmol) in $CH_2Cl_2$ (50 mL) was stirred over freshly desiccated molecular sieves (3 Å). After 15 min the mixture was cooled to 0 °C and treated with NBS (2.33 g, 13.1 mmol), stirred at room temperature for 35 min, and then diluted with $CH_2Cl_2$ (200 mL) and successively washed with 10% aqueous $Na_2S_2O_3$ solution (3 × 150 mL) and water (2 × 150 mL). Drying ($Na_2SO_4$) and concentration gave a colorless syrup that slowly crystallized in vacuo (finally at $10^{-2}$ mbar to remove the methyl benzoate formed). The crude product was dissolved in diethyl ether, triturated with *n*-hexane to turbidity, and kept for 16 h at −27 °C to give **1** (3.55 g, 75%) as colorless crystals. M.p. 123−124 °C. $[\alpha]_D^{20}$ = −195.2 (*c* = 1.1, $CHCl_3$). $^1$H NMR (300 MHz, $CDCl_3$): δ = 1.44 (d, 3 H, 6-$H_3$), 4.65 (qd, 1 H, 5-H), 5.64 (dd, 1 H, 4-H), 6.44 (d, 1 H, 3-H), 6.46 (s, 1 H, 1-H) ppm; $J_{3,4} = J_{4,5}$ = 10.3, $J_{5,6}$ = 6.3 Hz. $^{13}$C NMR (75 MHz, $CDCl_3$): δ = 17.0 (C-6), 71.5 (C-5), 72.8 (C-4), 73.1 (C-3), 83.8 (C-1), 189.1 (C-2) ppm. MS (FD, 0−20 mA): *m*/*z* = 435, 433 [$M^+$ + H], 434, 432 [$M^+$], 353 [$M^+$ − Br]. $C_{20}H_{17}BrO_6$ (433.3): calcd. C 56.36, H 3.96, Br 2.22; found C 56.27, H 3.91, Br 2.30.

The D enantiomer of **1**, prepared in analogous fashion from 2,3,4-tri-*O*-benzoyl-6-deoxy-D-glucosyl bromide (D-**8**)[21] via 2-benzoyloxy-D-glucal (D-**11**), had m.p. 125−126 °C, $[\alpha]_D^{22}$ = +191.4 (*c* = 1, $CHCl_3$), and identical NMR spectroscopic data.[22]

**3,4-Di-*O*-benzyl-ulosyl Bromide (2)**

**3,4-Di-*O*-benzyl-1,2-*O*-[1-(*exo*-methoxy)ethylidene]-β-L-rhamnopyranose (10):** Benzyl bromide (4.5 mL, 3.4 g, 39 mmol) and powdered KOH (9.8 g, 177 mmol) were added to a solution of 3,4-di-*O*-acetyl-1,2-*O*-[1-(*exo*-methoxy)ethylidene]-β-L-rhamnopyranose (**9**, 4.0 g, 13 mmol), prepared in 72% yield by treatment of acetobromo-L-rhamnose (**7**) with MeOH/lutidine,[15] in dry THF (150 mL), and the mixture was stirred under reflux for 2 h. Subsequent dilution with $CH_2Cl_2$ (250 mL), extraction and washing with water (4 × 250 mL) and saturated aqueous $NaHCO_3$ solution (2 × 250 mL), drying ($Na_2SO_4$), and evaporation to dryness gave a crystalline residue, which was recrystallized from 2-propanol to afford **10** (4.4 g, 81%) as colorless crystals. M.p. 109−111 °C. $[\alpha]_D^{20}$ = +0.9 (*c* = 1.0, $CHCl_3$). ref.[15] 68%; m.p. 109−111 °C; $[\alpha]_D^{20}$ = +0.6 (*c* = 1.0, $CHCl_3$). $^1$H NMR (300 MHz, $CDCl_3$): δ = 1.32 (d, 3 H, 6-$H_3$), 1.73 (s, 3 H, C$H_3$), 3.28 (s, 3 H, OC$H_3$), 3.34 (qd, 1 H, 5-H), 3.49 (dd, 1 H, 4-H), 3.68 (dd, 1 H, 3-H), 4.38 (dd, 1 H, 2-H), 4.67 and 4.96 (2 d, 1 H, 3-BnC$H_2$), 4.78 (s, 2 H, 4-BnC$H_2$), 5.27 (d, 1 H, 1-H) ppm; $J_{1,2}$ = 2.4, $J_{2,3}$ = 4.1, $J_{3,4} = J_{4,5}$ = 9.1, $J_{5,6}$ = 6.1, $^2J_{C,H_2}$ = 10.8 Hz. $^{13}$C NMR (75 MHz, $CDCl_3$): δ = 17.9 (C-6), 24.5 (*C*$H_3$), 49.8 (O*C*$H_3$), 70.2 (C-5), 72.2 (3-*C*$H_2$), 75.6 (4-*C*$H_2$), 77.2 (C-2), 79.0 (C-3), 79.5 (C-4), 97.3 (C-1), 123.8 (C-1′) ppm. MS (FD, 0−20 mA): *m*/*z* = 401 [$M^+$ + H], 400 [$M^+$], 370 [$M^+$ − MeOH], 309 [$M^+$ − $PhCH_2$], 91 [$PhCH_2^+$]. $C_{23}H_{28}O_6$ (400.47): calcd. C 68.98, H 7.05; found C 69.09, H 7.00.

**2-*O*-Acetyl-1,5-anhydro-3,4-di-*O*-benzyl-6-deoxy-L-*arabino*-hex-1-enitol (12):** A solution of orthoester **10** (1.0 g, 2.5 mmol) in bromobenzene (20 mL) containing pyridine (0.3 mL) was stirred under reflux for 5 h. Evaporation in vacuo and purification of the residue by elution from a silica gel column (toluene/EtOAc, 20:1) afforded **12** (0.72 g, 78%) as a colorless syrup. $[\alpha]_D^{20}$ = −8.7 (*c* = 1.1, $CHCl_3$). $^1$H NMR (300 MHz, $CDCl_3$): δ = 1.39 (d, 3 H, 6-$H_3$), 2.06 (s, 3 H, AcC$H_3$), 3.59 (dd, 1 H, 4-H), 4.12 (m, 1 H, 5-H), 4.47 (d, 1 H, 3-H), 4.55, 4.77 (2 d, each 1 H, BnC$H_2$), 4.63 (m, 2 H, BnC$H_2$), 6.54 (d, 1 H, 1-H) ppm; $J_{1,3}$ = 0.6, $J_{3,4}$ = 5.5, $J_{4,5}$ = 7.7, $J_{5,6}$ = 6.6, $^2J_{C,H_2}$ = 11.6 Hz. $^{13}$C NMR (75 MHz, $CDCl_3$): δ = 16.9 (C-6), 20.6 (Ac*C*$H_3$), 72.1, 73.3 (2 Bn*C*$H_2$), 74.3 (C-5), 75.9 (C-3), 78.8 (C-4), 127.7−130.0 (2 Bn$CH_2$), 137.8 (C-2), 138.2 (C-1), 169.7 (Ac*C*O) ppm. MS (FD, 0−20 mA): *m*/*z* = 368 [$M^+$], 369 [$M^+$ + H], 43 [$Ac^+$]. $C_{22}H_{24}O_5$ (368.43): calcd. C 71.72, H 6.57; found C 71.77, H 6.61.

**3,4-Di-*O*-benzyl-6-deoxy-α-L-*arabino*-hexopyranos-2-ulosyl Bromide (2):** A solution of 2-acetoxyrhamnal **12** (185 mg, 0.5 mmol) in $CH_2Cl_2$ (5 mL) was treated with MeOH (25 μL, 1.9 mg, 0.6 mmol), stirred for 20 min over freshly desiccated molecular sieves (3 Å), and cooled to 0 °C. NBS (110 mg, 0.6 mmol) was then added and stirring was continued for 15 min, followed by immediate workup by dilution with cold $CH_2Cl_2$ (25 mL) and successive washings with cold 10% aqueous $Na_2S_2O_3$ solution (2 × 10 mL) and ice-water (2 × 10 mL). Drying ($MgSO_4$) and concentration in vacuo provided **2** (177 mg, 87%) as a colorless syrup with $[\alpha]_D^{20}$ = −229.2 (*c* = 1.1, $CHCl_3$). The product is sufficiently pure for glycosidations. $^1$H NMR (300 MHz, $CDCl_3$): δ = 1.35 (d, 3 H, 6-$H_3$), 3.46 (dd, 1 H, 4-H), 4.21 (qd, 1 H, 5-H), 4.62, 4.63 (2 d, each 1 H, BnC$H_2$), 4.87 (d, 1 H, 3-H), 4.90 and 5.00 (2 d, each 1 H, BnC$H_2$), 6.27 (s, 1 H, 1-H) ppm; $J_{3,4} = J_{4,5}$ = 9.6, $J_{5,6}$ = 6.2, $^2J_{C,H_2}$ = 10.9, 11.2 Hz. $^{13}$C NMR (75 MHz, $CDCl_3$): δ = 17.3 (C-6), 72.7 (C-5), 74.2, 75.7 (2 Bn*C*$H_2$), 81.5 (C-3), 82.3 (C-4), 85.7 (C-1), 195.1 (C-2) ppm. MS (FD, 0−20 mA): *m*/*z* = 407, 405 [$M^+$ + H], 406, 404 [$M^+$], 325 [$M^+$ − Br], 315, 313 [$M^+$ − $PhCH_2$], 91 [$PhCH_2^+$].

**4-*O*-Acetyl-3-*O*-benzyl-ulosyl Bromide (3)**

**4-*O*-Acetyl-3-*O*-benzyl-1,2-*O*-[1-(*exo*-methoxy)ethylidene]-β-L-rhamnopyranose (17):** Bromine (0.6 mL, 1.85 g, 11.6 mmol) was added to a cold (0 °C) solution of methyl 2,4-di-*O*-acetyl-3-*O*-benzyl-1-thio-α-L-rhamnopyranoside (**14**,[16] 4.20 g, 11.4 mmol) in $CH_2Cl_2$ (50 mL), and after 15 min stirring, the mixture was concentrated in vacuo. The resulting syrup was dissolved in a mixture of 2,6-lutidine (10 mL) and dry MeOH (2.3 mL, 1.82 g, 57.0 mmol) and the solution was stirred at 60−65 °C for 21 h. Dilution with $CH_2Cl_2$ (300 mL), washings with saturated aqueous $NaHCO_3$ solution (2 × 200 mL) and water (2 × 200 mL), drying ($MgSO_4$), and removal of the solvent in vacuo gave a syrup that crystallized from diethyl ether/*n*-hexane to afford **17** (2.81 g, 71%) as colorless crystals. M.p. 74−75 °C. $[\alpha]_D^{20}$ = +36.0 (*c* = 0.9, $CHCl_3$). $^1$H NMR (300 MHz, $CDCl_3$): δ = 1.20 (d, 3 H, 6-$H_3$), 1.73 (s, 3 H, 1′-C$H_3$), 2.06 (s, 3 H, AcC$H_3$), 3.28 (s, 3 H, OC$H_3$), 3.38 (qd, 1 H, 5-H), 3.66 (dd, 1 H, 3-H), 4.45 (dd, 1 H, 2-H), 4.65, 4.73 (2 d, each 1 H, BnC$H_2$), 5.04 (dd, 1 H, 4-H), 5.33 (d, 1 H, 1-H) ppm; $J_{1,2}$ = 2.4, $J_{2,3}$ = 4.1, $J_{3,4} = J_{4,5}$ = 9.6, $J_{5,6}$ = 6.2, $^2J_{C,H_2}$ = 12.5 Hz. $^{13}$C NMR (75 MHz, $CDCl_3$): δ = 17.5 (C-6), 21.0 (Ac*C*$H_3$), 24.4 (1′-*C*$H_3$), 50.0 (O*C*$H_3$), 69.1 (C-5), 71.8 (Bn*C*$H_2$), 71.8 (C-4), 76.0 (C-3), 76.8 (C-2), 97.4 (C-1), 124.2 (C-1′), 169.8 (AcCO) ppm. MS (FD, 0−5 mA): *m*/*z* = 352 [$M^+$]. $C_{18}H_{24}O_7$ (352.38): calcd. C 61.35, H 6.86; found C 61.06, H 6.61.

**2,4-Di-*O*-acetyl-1,5-anhydro-3-*O*-benzyl-6-deoxy-L-*arabino*-hex-1-enitol (22):** Pyridine (450 μL) was added to a solution of orthoester **17** (1.06 g, 3.0 mmol) in bromobenzene (30 mL), and the mixture was heated at reflux for 2.5 h. Subsequent concentration in vacuo, elution of the resulting syrup from a silica gel column (toluene/

EtOAc, 30:1), and removal of the solvents from the respective eluate gave **22** (0.86 g, 89%) as a colorless syrup. $[\alpha]_D^{20} = -13.7$ ($c$ = 1.1, $CHCl_3$). $^1H$ NMR (300 MHz, $CDCl_3$): δ = 1.38 (d, 3 H, 6-$H_3$), 2.03, 2.07 (2 s, each 3 H, Ac$CH_3$), 4.21−4.26 (m, 2 H, 3-H, 5-H), 4.62 (s, 2 H, Bn$CH_2$), 5.13 (d, 1 H, 4-H), 6.56 (s, 1 H, 1-H) ppm; $J_{1,3} < 0.5$, $J_{3,4} = 4.4$, $J_{4,5} = 5.1$, $J_{5,6} = 6.8$ Hz. $^{13}C$ NMR (75 MHz, $CDCl_3$): δ = 16.0 (C-6), 20.6, 20.9 (2 Ac$CH_3$), 71.0 (Bn$CH_2$), 71.4 (C-4), 72.2 and 72.7 (C-3, C-5), 137.9 (C-1), 138.0 (C-2), 169.5, 170.0 (2 Ac$CO$) ppm. MS (FD, 0−5 mA): $m/z$ = 320 [$M^+$]. $C_{17}H_{20}O_6$ (320.34): calcd. C 63.74, H 6.29; found C 62.84, H 6.25.

**4-*O*-Acetyl-3-*O*-benzyl-6-deoxy-α-L-*arabino*-hexopyranos-2-ulosyl Bromide (3):** Dry EtOH (70 μL, 55.3 mg, 1.2 mmol) and freshly desiccated molecular sieves (3 Å) were added to a solution of 2-acetoxyrhamnal **22** (320.3 mg, 1.0 mmol) in $CH_2Cl_2$ (5 mL), and the mixture was stirred for 15 min and cooled to 0 °C. NBS (213.6 mg, 1.2 mmol) was then added and stirring was continued for 35 min, followed by immediate workup by dilution with cold $CH_2Cl_2$ (30 mL) and successive washings with cold aqueous $Na_2S_2O_3$ solution (10%, 2 × 15 mL) and ice-water (2 × 15 mL). Drying ($MgSO_4$) and removal of the solvent in vacuo gave **3** (357 mg, 98%) as a colorless syrup with $[\alpha]_D^{20} = -203.9$ ($c$ = 1.0, $CHCl_3$). The product is sufficiently pure for glycosidations. $^1H$ NMR (300 MHz, $CDCl_3$): δ = 1.28 (d, 3 H, 6-$H_3$), 2.03 (s, 3 H, Ac$CH_3$), 4.27 (qd, 1 H, 5-H), 4.55, 4.97 (2 d, each 1 H, Bn$CH_2$), 4.72 (dd, 1 H, 3-H), 5.08 (dd, 1 H, 4-H), 6.32 (d, 1 H, 1-H) ppm; $J_{1,2} = 0.4$, $J_{3,4} = J_{4,5} = 10.1$, $J_{5,6} = 6.2$, $^2J_{C,H_2} = 12.0$ Hz. $^{13}C$ NMR (75 MHz, $CDCl_3$): δ = 16.8 (C-6), 20.7 (Ac$CH_3$), 71.4 (C-5), 73.5 (Bn$CH_2$), 73.5 (C-4), 77.6 (C-3), 85.1 (C-1), 169.1 (Ac$CO$), 194.0 (C-2) ppm. MS (FD): $m/z$ = 356, 358 [$M^+$], 277 [$M^+$ − Br], 218 [$M^+$ − AcO].

**4-*O*-Benzoyl-3-*O*-benzyl-ulosyl Bromide (4)**

**Methyl 4-*O*-Benzoyl-2,3-*O*-isopropylidene-1-thio-α-L-rhamnopyranoside (16):** Benzoyl chloride (2.3 mL, 2.8 g, 24.8 mmol) was added dropwise to a *cooled* solution (0 °C) of methyl 2,3-*O*-isopropylidene-1-thio-α-L-rhamnopyranoside[15] (**15**, 3.33 g, 14.2 mmol) in pyridine (10 mL), and the reaction mixture was stirred at room temperature for 17 h. Dilution with $CHCl_3$ (60 mL) and successive washings with water (40 mL), saturated aqueous $NaHCO_3$ solution (2 × 40 mL), and water (40 mL), gave, after drying ($MgSO_4$) and evaporation in vacuo, a syrup, which crystallized from diethyl ether to afford **16** (4.71 g, 98%) as fine, colorless crystals. M.p. 155−156 °C. $[\alpha]_D^{20} = -114.6$ ($c$ = 1.1, $CHCl_3$). $^1H$ NMR (300 MHz, $CDCl_3$): δ = 1.24 (d, 3 H, 6-$H_3$), 1.35, 1.63 (2 s, each 3 H, $C(CH_3)_2$], 2.16 (s, 3 H, SC$H_3$), 4.19 (qd, 1 H, 5-H), 4.25 (br. d, 1 H, 2-H), 4.33 (dd, 1 H, 3-H), 5.19 (dd, 1 H, 4-H), 5.47 (br. s, 1 H, 1-H) ppm; $J_{2,3} = 5.3$, $J_{3,4} = 7.9$, $J_{4,5} = 10.0$, $J_{5,6} = 6.3$ Hz. $^{13}C$ NMR (75 MHz, $CDCl_3$): δ = 13.4 (S$CH_3$), 17.2 (C-6), 26.5, 27.8 [C($CH_3$)$_2$], 64.7 (C-5), 75.4 (C-4), 75.6 (C-3), 76.7 (C-2), 81.3 (C-1), 110.0 [$C(CH_3)_3$] ppm. MS (FD, 0−20 mA): $m/z$ = 338 [$M^+$], 323 [$M^+$ − Me], 292 [$M^+$ − $CH_2S$], 291 [$M^+$ − SMe], 105 [PhCO$^+$], 47 [SMe$^+$]. $C_{17}H_{24}O_5S$ (338.42): calcd. C 60.34, H 6.55; found C 60.18, H 6.53.

**Methyl 4-*O*-Benzoyl-1-thio-α-L-rhamnopyranoside (20):** A suspension of thiorhamnoside **16** (4.0 g, 11.8 mmol) in dry MeOH (30 mL) and trifluoroacetic acid (5 mL) was heated at reflux for 4.5 h. Concentration in vacuo gave a syrup, which was purified by elution from a silica gel column (*n*-hexane/EtOAc, 2:1) to yield **20** (2.98 g, 85%) as a colorless foam: $[\alpha]_D^{20} = -206.5$ ($c$ = 1.0, $CHCl_3$). $^1H$ NMR (300 MHz, $CDCl_3$). δ = 1.29 (d, 3 H, 6-$H_3$), 2.15 (s, 3 H, SC$H_3$), 3.72 (br. s, 2 H, 2-O$H$, 3-O$H$), 4.01 (dd, 1 H, 3-H), 4.12 (dd, 1 H, 2-H), 4.29 (qd, 1 H, 5-H), 5.14 (dd, 1 H, 4-H), 5.23 (d, 1 H, 1-H) ppm; $J_{1,2} = 1.0$, $J_{2,3} = 3.5$, $J_{3,4} = J_{4,5} = 9.5$, $J_{5,6} = 6.3$ Hz. $^{13}C$ NMR (75 MHz, $CDCl_3$): δ = 13.7 (S$CH_3$), 17.5 (C-6), 66.4 (C-5), 70.7 (C-3), 72.3 (C-2), 76.1 (C-4), 85.4 (C-1) ppm. MS (FD, 0−12 mA): $m/z$ = 298 [$M^+$], 251 [$M^+$ − SMe], 105 [PhCO$^+$]. $C_{14}H_{18}O_5S$ (298.35): calcd. C 56.36, H 6.08; found C 55.87, H 6.06.

**Methyl 2-*O*-Acetyl-4-*O*-benzoyl-3-*O*-benzyl-1-thio-α-L-rhamnopyranoside (21):** A suspension of **20** (1.70 g, 5.7 mmol) and *n*-dibutyltin oxide (1.63 g, 6.5 mmol) in benzene (40 mL) was stirred at reflux under a Dean−Stark trap for 5 h. Evaporation in vacuo gave a colorless syrup, which was dissolved in benzene (20 mL). Benzyl bromide (1.25 mL, 10.7 mmol) and *n*-tetrabutylammonium iodide (2.11 g, 5.7 mmol) were then added, and the mixture was stirred at 50 °C for 6 h. The solution was then concentrated and the semicrystalline residue was stirred with EtOAc (20 mL). The solids were removed by filtration and the filtrate was concentrated to a syrup, which was dissolved in pyridine (6 mL) and cooled to 0 °C. Acetic anhydride (6 mL, 63.5 mmol) was added dropwise to this solution, which was then stirred at room temperature for 2 h, treated with dry EtOH at 0 °C, and stirred for 20 min (room temperature). Evaporation in vacuo and purification by elution from a silica gel column with *n*-hexane/EtOAc (5:1) containing 1% triethylamine gave **21** (1.68 g, 70%) as a colorless syrup. $[\alpha]_D^{20} = -27.3$ ($c$ = 1.0, $CHCl_3$). $^1H$ NMR (300 MHz, $CDCl_3$). δ = 1.27 (d, 3 H, 6-$H_3$), 2.15 (s, 3 H, SC$H_3$), 2.19 (s, 3 H, Ac$CH_3$), 3.89 (dd, 1 H, 3-H), 4.22 (qd, 1 H, 5-H), 4.40, 4.60 (2d, 2 H, 3-C$H_2$), 5.16 (d, 1 H, 1-H), 5.33 (dd, 1 H, 4-H), 5.50 (dd, 1 H, 2-H) ppm; $J_{1,2} = 1.4$, $J_{2,3} = 3.4$, $J_{3,4} = J_{4,5} = 9.8$, $J_{5,6} = 6.25$, $^2J_{C,H_2} = 12.3$ Hz. $^{13}C$ NMR (75 MHz, $CDCl_3$): δ = 13.9 (S$CH_3$), 17.6 (6-$H_3$), 21.1 (Ac$CH_3$), 67.2 (C-5), 69.8 (C-2), 71.1 (Bn$CH_2$), 73.0 (C-4), 74.5 (C-3), 83.8 (C-1) ppm. MS (FD, 0−10 mA): $m/z$ = 430 [$M^+$], 383 [$M^+$ − MeS]. $C_{23}H_{26}O_6S$ (430.52): calcd. C 64.17, H 6.09; found C63.65, H 5.95.

**4-*O*-Benzoyl-3-*O*-benzyl-1,2-*O*-[1-(*exo*-methoxy)ethylidene]-β-L-rhamnopyranose (19):** A solution of thiorhamnoside **21** (4.0 g, 9.2 mmol) in dry $CH_2Cl_2$ (60 mL) was cooled to 0 °C, bromine (480 μL, 1.5 g, 9.3 mmol) was added, and the mixture was stirred for 0.5 h. Concentration in vacuo and coevaporation with $CHCl_3$ gave 2-*O*-acetyl-4-*O*-benzoyl-3-*O*-benzyl-α-L-rhamnopyranosyl bromide as a colorless syrup, which was directly subjected to methanolysis by dissolution in $CH_2Cl_2$/2,6-lutidine (1:1, 20 mL), addition of dry MeOH (1.9 mL, 1.5 g, 42.2 mmol), and stirring at 50 °C for 19 h. Dilution with $CH_2Cl_2$ (80 mL), successive washings with saturated aqueous $NaHCO_3$ solution (2 × 60 mL) and water (2 × 60 mL), drying ($MgSO_4$), and evaporation to dryness left a syrup, which crystallized on trituration with 2:1 *n*-hexane/diethyl ether to afford **19** (2.6 g, 68%) as fine, colorless crystals. M.p. 136.5−137 °C. $[\alpha]_D^{20} = +50.5$ ($c$ = 0.8, $CHCl_3$). $^1H$ NMR (300 MHz, $CDCl_3$): δ = 1.25 (d, 3 H, 6-$H_3$), 1.78 (s, 3 H, 1′-C$H_3$), 3.32 (s, 3 H, OC$H_3$), 3.54 (qd, 1 H, 5-H), 3.82 (dd, 1 H, 5-H), 4.52 (dd, 1 H, 2-H), 4.64 and 4.72 (2 d, each 1 H, Bn$CH_2$), 5.32 (dd, 1 H, 4-H), 5.39 (d, 1 H, 1-H) ppm; $J_{1,2} = 2.3$, $J_{2,3} = 4.0$, $J_{3,4} = 9.6$, $J_{4,5} = 9.5$, $J_{5,6} = 6.2$, $^2J_{C,H_1} = 12.6$, 12.7 Hz. $^{13}C$ NMR (75 MHz, $CDCl_3$): δ = 17.6 (C-6), 24.4 (1′-$CH_3$), 49.9 (O$CH_3$), 69.3 (C-5), 71.5 (3-Bn$CH_2$), 72.4 (C-4), 75.6 (C-3), 76.7 (C-2), 97.5 (C-1), 124.2 (C-1′) ppm. MS (FD, 0−12 mA): $m/z$ = 414 [$M^+$], 383 [$M^+$ − OMe]. $C_{23}H_{26}O_7$ (414.46): calcd. C 66.65, H 6.32; found C 66.62, H 6.39.

**2-*O*-Acetyl-1,5-anhydro-4-*O*-benzoyl-3-*O*-benzyl-6-deoxy-L-*arabino*-hex-1-enitol (23):** A solution of orthoester **19** (1.92 g, 4.6 mmol) in bromobenzene (40 mL) was treated with pyridine (700 μL) and stirred under reflux for 3 h. The mixture was concentrated and purified by elution from a silica gel column (toluene/

EtOAc, 30:1) to yield **23** (1.50 g, 85%) as a colorless syrup on evaporation of the respective eluate . $[\alpha]_D^{20}$ = +37.7 (*c* = 1.1, $CHCl_3$). $^1H$ NMR (300 MHz, $CDCl_3$). δ = 1.44 (d, 3 H, 6-$H_3$), 2.04 (s, 3 H, AcC$H_3$), 4.38 (dd, 1 H, 3-H), 4.37−4.41 (m, 1 H, 5-H), 4.64−4.72 (2 d, each 1 H, BnC$H_2$), 5.41 (d, 1 H, 4-H), 6.63 (d, 1 H, 1-H) ppm; $J_{1,3}$ = 0.4, $J_{3,4}$ = 4.3, $J_{4,5}$ = 5.3, $J_{5,6}$ = 6.9, $^2J_{C,H_2}$ = 11.8 Hz. $^{13}C$ NMR (75 MHz, $CDCl_3$): δ = 16.1 (C-6), 20.7 (2 Ac$CH_3$), 71.2 (Bn$CH_2$), 71.9 (C-4), 72.4, 72.8 (C-3, C-5), 127.8−133.4 (2 $C_6H_5$), 137.9 (C-2), 138.1 (C-1) ppm. MS (FD, 0−5 mA): *m*/*z* = 382 [$M^+$], 383 [$M^+$ + H]. $C_{22}H_{22}O_6$ (382.41): calcd. C 69.10, H 5.80; found C 68.96, H 5.74.

**4-*O*-Benzoyl-3-*O*-benzyl-6-deoxy-α-L-*arabino*-hexopyranos-2-ulosyl Bromide (4):** A solution of 2-acetoxyrhamnal **23** (1.36 g, 3.6 mmol) in $CH_2Cl_2$ (25 mL) was treated with dry EtOH (250 μL, 197 mg, 4.3 mmol), stirred for 15 min over freshly desiccated molecular sieves (3 Å), and cooled to 0 °C. NBS (759 mg, 4.3 mmol) was then added to the mixture and stirring was continued for 15 min. The solution was immediately worked up by dilution with cold $CH_2Cl_2$ (50 mL) and successive washings with cold aqueous $Na_2S_2O_3$ solution (10%, 2 × 30 mL) and ice-water (2 × 30 mL). Drying ($MgSO_4$) and concentration in vacuo gave **4** (1.41 g, 95%) as a colorless syrup. The product is sufficiently pure for glycosidations: $[\alpha]_D^{20}$ = −132.5 (*c* = 1.1, $CHCl_3$). $^1H$ NMR (300 MHz, $CDCl_3$): δ = 1.34 (d, 3 H, 6-$H_3$), 4.41 (qd, 1 H, 5-H), 4.59 and 4.94 (2 d, each 1 H, BnC$H_2$), 4.85 (d, 1 H, 3-H), 5.36 (dd, 1 H, 4-H), 6.37 (s, 1 H, 1-H) ppm; $J_{3,4}$ = 10.2, $J_{4,5}$ = 10.1, $J_{5,6}$ = 6.3, $^2J_{C,H_2}$ = 12.1 Hz. $^{13}C$ NMR (75 MHz, $CDCl_3$): δ = 16.8 (C-6), 71.5 (C-5), 73.3 (Bn$CH_2$), 73.9 (C-4), 77.1 (C-3), 85.1 (C-1), 194.1 (C-2) ppm. MS (FD, 0−12 mA): *m*/*z* = 421, 419 [$M^+$ + H], 420, 418 [$M^+$].

**3-*O*-Benzyl-4-*O*-(4-methoxybenzyl)-ulosyl Bromide (5)**

**3-*O*-Benzyl-4-*O*-(4-methoxybenzyl)-1,2-*O*-[1-(*exo*-methoxy)-ethylidene]-β-L-rhamnopyranose (18):** 4-Methoxybenzyl chloride (1.7 mL, 2.0 g, 12.5 mmol), *n*-tetrabutylammonium iodide (20 mg), and powdered KOH (3.1 g, 55.4 mmol) were successively added to a solution of **17** (1.5 g, 4.3 mmol) in dry THF (60 mL), and the mixture was heated at reflux for 3 h. Subsequent dilution with $CH_2Cl_2$ (250 mL), extraction with water (4 × 200 mL) and saturated aqueous $NaHCO_3$ solution (2 × 200 mL), drying of the organic layer ($MgSO_4$), and concentration in vacuo gave a syrup, which was purified by flash chromatography on a short column of silica gel. The nonpolar components were removed first, with *n*-hexane/EtOAc (30:1) containing 1% triethylamine, and the product was then eluted with *n*-hexane/EtOAc (2:1) containing 1% triethylamine. Evaporation of the eluate gave a colorless syrup, which was crystallized from 2-propanol (8 mL) to afford **18** (1.7 g, 93%) as colorless needles. M.p. 98−99 °C. $[\alpha]_D^{20}$ = −0.7 (*c* = 0.9, $CHCl_3$). $^1H$ NMR (300 MHz, $CDCl_3$): δ = 1.30 (d, 3 H, 6-$H_3$), 1.72 (s, 3 H, 1′-C$H_3$), 3.28 (s, 3 H, OC$H_3$), 3.30 (qd, 1 H, 5-H), 3.46 (dd, 1 H, 4-H), 3.66 (dd, 1 H, 3-H), 3.79 (s, 3 H, PhOC$H_3$), 4.38 (dd, 1 H, 2-H), 4.60, 4.87 (2 d, 1 H each, BnC$H_2$), 4.77 (s, 2 H, MeOBnC$H_2$), 5.26 (d, 1 H, 1-H) ppm; $J_{1,2}$ = 2.4, $J_{2,3}$ = 4.1, $J_{3,4}$ = $J_{4,5}$ = 9.1, $J_{5,6}$ = 6.1, $^2J_{C,H_2}$ = 10.5 Hz. $^{13}C$ NMR (75 MHz, $CDCl_3$): δ = 18.0 (C-6), 24.4 (1′-$CH_3$), 49.8 (1′-O$CH_3$), 55.3 (PhO$CH_3$), 70.3 (C-5), 72.3 (Bn$CH_2$), 75.2 (MeOBn$CH_2$), 77.3 (C-2), 79.2, 79.3 (C-3, C-4), 97.4 (C-1), 123.8 (C-1′) ppm. MS (FD, 0−5 mA): *m*/*z* = 430 [$M^+$]. $C_{24}H_{30}O_7$ (430.50): calcd. C 66.96, H 7.02; found C 67.37, H 7.08.

**2-*O*-Acetyl-1,5-anhydro-3-*O*-benzyl-4-*O*-(4-methoxybenzyl)-6-deoxy-L-*arabino*-hex-1-enitol (24):** A solution of orthoester **18** (1.4 g, 3.3 mmol) in bromobenzene (30 mL) was treated with pyridine (500 μL) and stirred under reflux for 3 h. The mixture was concentrated and purified by elution from a silica gel column (toluene/EtOAc, 40:1) to afford **23** (1.1 g, 85%) as a colorless syrup that crystallized in vacuo. M.p. 75−77 °C; $[\alpha]_D^{20}$ = −7.4 (*c* = 1.0, $CHCl_3$). $^1H$ NMR (300 MHz, $CDCl_3$): δ = 1.36 (d, 3 H, 6-$H_3$), 2.04 (s, 3 H, AcC$H_3$), 3.57 (d, 1 H, 4-H), 3.77 (s, 3 H, PhOC$H_3$), 4.08 (qd, 1 H, 5-H), 4.45 (dd, 1 H, 3-H), 4.55, 4.58, 4.63, 4.70 (4 d, 1 H each, BnC$H_2$, MeOBnC$H_2$), 6.53 (s, 1 H, 1-H) ppm; $J_{3,4}$ = 5.5, $J_{4,5}$ = 7.8, $J_{5,6}$ = 6.5, $^2J_{C,H_2}$ = 11.2, 11.6 Hz. $^{13}C$ NMR (75 MHz, $CDCl_3$): δ = 17.0 (C-6), 20.7 (Ac$CH_3$), 55.3 (PhO$CH_3$), 72.2, 73.1 (Bn$CH_2$, MeOBn$CH_2$), 74.5 (C-5), 76.1 (C-3), 78.6 (C-4), 138.3 (C-1), 138.4 (C-2), 169.6 (Ac$CO$) ppm. MS (FD, 0−5 mA): *m*/*z* = 398 [$M^+$], 399 [$M^+$ + H]. $C_{23}H_{26}O_6$ (398.46). Calcd. C, 69.33, H 6.58; found C 69.10, H 6.65.

**3-*O*-Benzyl-4-*O*-(4-methoxybenzyl)-6-deoxy-α-L-*arabino*-hexopyranos-2-ulosyl Bromide (5):** Dry ethanol (88 μL, 70 mg, 1.5 mmol) was added to a solution of 2-acetoxy-rhamnal **24** (500 mg, 1.25 mmol) in $CH_2Cl_2$ (30 mL), and the mixture was stirred for 15 min over freshly desiccated molecular sieves (3 Å) and cooled (0 °C), followed by the addition of NBS (269 mg, 1.5 mmol) and continued stirring for 15 min. Workup (as given for compound **4**) provided **5** (535 mg, 98%) as a colorless syrup with $[\alpha]_D^{20}$ = −196.4 (*c* = 1.0, $CHCl_3$), sufficiently pure for the ensuing glycosidations. $^1H$ NMR (300 MHz, $CDCl_3$): δ = 1.33 (d, 3 H, 6-$H_3$), 3.44 (dd, 1 H, 4-H), 3.79 (s, 3 H, PhOC$H_3$), 4.19 (qd, 1 H, 5-H), 4.57, 4.65, 4.83, 5.01 (4 s, 1 H each, BnC$H_2$, MeOBnC$H_2$), 4.85 (d, 1 H, 3-H), 6.27 (s, 1 H, 1-H) ppm; $J_{3,4}$ = $J_{4,5}$ = 9.6, $J_{5,6}$ = 6.3, $^2J_{C,H_2}$ = 10.6, 11.2 Hz. $^{13}C$ NMR (75 MHz, $CDCl_3$): δ = 17.2 (C-6), 55.3 (PhO$CH_3$), 72.7 (C-5), 74.2, 75.2 (Bn$CH_2$, MeOBn$CH_2$), 81.5 (C-3), 81.9 (C-4), 85.8 (C-1), 195.0 (C-2) ppm. MS (FD): *m*/*z* = 434, 436 [$M^+$].

**Model Glycosidations of Ulosyl Bromides with 2-Propanol**

**Isopropyl 3,4-Di-*O*-benzoyl-6-deoxy-β-L-*arabino*-hexopyranosid-2-ulose (25):** A suspension of 2-propanol (0.88 mL, 0.69 g, 11.5 mmol), $Ag_2CO_3$ (4.46 g, 16.2 mmol) in $CH_2Cl_2$ (80 mL), and molecular sieves (4 Å) was stirred at room temperature for 15−20 min with exclusion of moisture. A solution of ulosyl bromide **1** (5.00 g, 11.5 mmol) in $CH_2Cl_2$ (20 mL) was then added, stirring was continued for 30 min, and the mixture was filtered through Celite, followed by removal of the solvent in vacuo to afford **25** (4.55 g, 96%) as a colorless foam. $^1H$ NMR (300 MHz, $CDCl_3$): δ = 1.20, 1.32 [2 d, each 3 H, C(C$H_3$)$_2$], 1.44 (d, 3 H, 6-$H_3$), 4.10 [qq, 1 H, C$H$(CHMe$_2$], 4.21 (qd, 1 H, 5-H), 5.18 (s, 1 H, 1-H), 5.57 (dd, 1 H, 4-H), 5.88 (d, 1 H, 3-H) ppm; $J_{3,4}$ = 10.2, $J_{4,5}$ = 9.6, $J_{5,6}$ = 5.8, $J_{C,H,CH_3}$ = 6.2, $^1J_1$ = 158.0 Hz. $^{13}C$ NMR (75 MHz, $CDCl_3$): δ = 17.9 (C-6), 22.0, 23.3 [C($CH_3$)$_2$], 71.1 (C-5), 72.7 [$CH$(CMe$_2$)], 75 (C-4), 77.3 (C-3), 98.5 (C-1), 192.2 (C-2) ppm.

**Isopropyl 3,4-Di-*O*-benzyl-6-deoxy-β-L-*arabino*-hexopyranosid-2-ulose (26):** A mixture of 2-propanol (0.70 mL, 0.55 g, 9.1 mmol), $Ag_2CO_3$ (2.51 g, 9.1 mmol) in $CH_2Cl_2$ (50 mL), and molecular sieves (4 Å) was stirred for 20 min at ambient temperature with exclusion of moisture. The ulosyl bromide **2** (1.49 g, 3.7 mmol), dissolved in $CH_2Cl_2$ (12 mL), was added and stirring was continued for 20 min. The mixture was filtered through Celite and removal of the solvent in vacuo provided an amorphous product, that was crystallized from diisopropyl ether to afford **26** (1.28 g, 91%) as colorless needles. M.p. 94−96 °C; $[\alpha]_D^{20}$ = +74.2 (*c* = 1.0, $CHCl_3$). $^1H$ NMR (300 MHz, $CDCl_3$): δ = 1.23, 1.30 [2 d, each 3 H, CH(C$H_3$)$_2$], 1.36 (d, 3 H, 6-$H_3$), 3.49 (dd, 1 H, 4-H), 3.73 (dq, 1 H, 5-H), 4.04 [qq, 1 H, C$H$(CH$_3$)$_2$], 4.18 (dd, 1 H, 3-H), 4.58, 4.64, 4.92, 4.99 (4 d, each 1 H, 2 BnC$H_2$), 4.83 (d, 1 H, 1-H) ppm; $J_{1,3}$ =

0.6, $J_{3,4} = J_{4,5} = 9.1$, $J_{5,6} = 6.1$, $J_{C,H,CH_3} = 6.2$, $^2J_{C,H2} = 11.0$ and 11.4, $^1J_1 = 156.6$ Hz. $^{13}$C NMR (75 MHz, $CDCl_3$): δ = 18.1 (C-6), 21.7, 23.2 [CH($CH_3$)$_2$], 71.9, 72.0 [C-5, CH($CH_3$)$_2$], 73.4, 75.3 (2 Bn$CH_2$), 85.5 (C-4), 85.8 (C-3), 97.7 (C-1), 197.4 (C-2) ppm. MS (FD, 0−12 mA): *m/z* = 384 [M$^+$].

**Isopropyl 4-*O*-Acetyl-3-*O*-benzyl-6-deoxy-β-L-*arabino*-hexopyranosid-2-ulose (27):** A mixture of 2-propanol (161 μL, 126 mg, 2.1 mmol), $Ag_2CO_3$ (580 mg, 2.1 mmol) in $CH_2Cl_2$ (4 mL), and molecular sieves (4 Å) was stirred for 20 min at ambient temperature with exclusion of moisture. Ulosyl bromide **3** (357 mg, 1.0 mmol), dissolved in $CH_2Cl_2$ (3 mL), was then added, stirring was continued for 20 min, the mixture was filtered through Celite, and the solvent was removed in vacuo to give a syrup, which crystallized from diisopropyl ether to afford **27** (302 mg, 90%) as colorless crystals. M.p. 78−80 °C; $[\alpha]_D^{20} = +101.1$ (*c* = 0.9, $CHCl_3$). $^1$H NMR (300 MHz, $CDCl_3$): δ = 1.23, 1.31 [2 d, 6 H, CH(C$H_3$)$_2$], 1.30 (d, 3 H, 6-$H_3$), 2.04 (s, 3 H, AcC$H_3$), 3.81 (qd, 1 H, 5-H), 4.04 [qq, 1 H, C$H$(CH$_3$)$_2$], 4.08 (dd, 1 H, 3-H), 4.52, 4.93 (2 d, 2 H, 3-C$H_2$), 4.86 (d, 1 H, 1-H), 5.05 (dd, 1 H, 4-H) ppm; $J_{1,3} = 0.7$, $J_{3,4} = 9.6$, $J_{4,5} = 9.4$, $J_{5,6} = 6.3$, $^2J_{C,H_2} = 12.2$, $J_{C,H,CH_3} = 6.2$, $^1J_1 = 156.6$ Hz. $^{13}$C NMR (75 MHz, $CDCl_3$): δ = 17.8 (C-6), 20.9 (Ac$CH_3$), 21.7, 23.2 [CH($CH_3$)$_2$], 70.8 (C-5), 72.1 [$CH$(CH$_3$)$_2$], 72.5 (Bn$CH_2$), 76.4 (C-4), 81.9 (C-3), 97.9 (C-1), 197.0 (C-2) ppm. MS (FD): *m/z* = 259 [M$^+$ − Ph], 91 [PhCH$_2^+$], 43 [Ac$^+$]. $C_{18}H_{24}O_6$(336.4): calcd. C 64.27, H 7.19; found C 63.37, H 7.14.

**Isopropyl 4-*O*-Benzoyl-3-*O*-benzyl-6-deoxy-β-L-*arabino*-hexopyranosid-2-ulose (28):** A suspension of 2-propanol (0.55 mL, 0.43 g, 7.2 mmol), $Ag_2CO_3$ (1.99 g, 7.2 mmol) in $CH_2Cl_2$ (35 mL), and molecular sieves (4 Å) was stirred for 20 min at room temperature with exclusion of moisture. A solution of ulosyl bromide **4** (1.38 g, 3.3 mmol) in $CH_2Cl_2$ (15 mL) was then added, stirring was continued for 20 min, the mixture was filtered through Celite, and the solvent was removed in vacuo to provide a syrup that crystallized on trituration with diisopropyl ether to afford **28** (1.22 g, 93%) as colorless needles. M.p. 110 °C; $[\alpha]_D^{20} = +125.7$ (*c* = 0.6, $CHCl_3$). $^1$H NMR (300 MHz, $CDCl_3$): δ = 1.25, 1.32 [2 d, each 3 H, CH(C$H_3$)$_2$], 1.36 (d, 3 H, 6-$H_3$), 3.96 (qd, 1 H, 5-H), 4.07 [qq, 1 H, C$H$(CH$_3$)$_2$], 4.22 (dd, 1 H, 3-H), 4.57, 4.92, 4.92 (d, 1 H, 1-H), 5.32 (dd, 1 H, 4-H) ppm; $J_{1,3} = 0.5$, $J_{3,4} = J_{4,5} = 9.4$, $J_{5,6} = 6.2$, $J_{C,H,CH_3} = 6.2$, $^2J_{C,H_2} = 12.4$, $^1J_1 = 157.1$ Hz. $^{13}$C NMR (75 MHz, $CDCl_3$): δ = 18.0 (C-6), 21.7, 23.2 [CH($CH_3$)$_2$], 71.1 (C-5), 72.1 [$CH$(CH$_3$)$_2$], 72.4 (Bn$CH_2$), 77.0 (C-4), 81.4 (C-3), 98.0 (C-1), 197.1 (C-2) ppm. MS (FD, 0−12 mA): *m/z* = 398 [M$^+$], 399 [M$^+$ + H]. $C_{23}H_{26}O_6$ (398.5): calcd. C 69.33, H 6.58; found C 69.15, H 6.54.

**Isopropyl 3-*O*-Benzyl-4-*O*-(4-methoxybenzyl)-6-deoxy-β-L-*arabino*-hexopyranosid-2-ulose (29):** A suspension of 2-propanol (230 μL, 180 mg, 3.0 mmol), $Ag_2CO_3$ (830 mg, 3.0 mmol) in $CH_2Cl_2$ (15 mL), and molecular sieves (4 Å) was stirred at room temperature for 20 min with exclusion of moisture. The ulosyl bromide **5** (535 mg, 1.2 mmol), dissolved in $CH_2Cl_2$ (5 mL), was added and stirring was continued for 25 min. The mixture was filtered through Celite and removal of the solvent in vacuo gave a syrup that crystallized from diisopropyl ether to afford **29** (435 mg, 95%) as fine needles. M.p. 85−86 °C; $[\alpha]_D^{20} = +67.1$ (*c* = 1.0, $CHCl_3$). $^1$H NMR (300 MHz, $CDCl_3$): δ = 1.22, 1.30 (2 d, 6 H, CH(C$H_3$)$_2$], 1.33 (d, 3 H, 6-$H_3$), 3.47 (dd, 1 H, 4-H), 3.70 (dq, 1 H, 5-H), 3.80 (s, 3 H, OC$H_3$), 4.03 [qq, 1 H, C$H$(CH$_3$)$_2$], 4.17 (dd, 1 H, 3-H), 4.57, 4.59, 4.84, and 5.00 (4 d, each 1 H, BnC$H_2$ and MeOBnC$H_2$), 4.81 (d, 1 H, 1-H) ppm; $J_{1,3} = 0.5$, $J_{3,4} = 9.1$, $J_{4,5} = 9.1$, $J_{5,6} = 6.2$, $J_{C,H,CH_3} = 6.2$, $^2J_{C,H_2} = 10.6$ and 11.5, $^1J_1 = 156.3$ Hz. $^{13}$C NMR (75 MHz, $CDCl_3$): δ = 18.1 (C-6), 21.7, 23.2 [CH($CH_3$)$_2$], 55.3 (O$CH_3$), 71.9 (C-5, $CH$(CH$_3$)$_2$], 73.4, 73.9 (Bn$CH_2$, MeOBn$CH_2$), 85.1 (C-3), 85.9 (C-4), 97.7 (C-1), 197.5 (C-2) ppm. MS (FD, 0−12 mA): *m/z* = 414 [M$^+$], 415 [M$^+$ + H]. $C_{24}H_{30}O_6$ (414.50): calcd. C 69.55, H 7.30; found C 69.09, H 7.31.

**Uloside Reductions**

**Isopropyl 2,3,4-Tri-*O*-benzoyl-β-L-rhamnopyranoside (30):** A solution of K-Selectride in THF (1 M, 0.97 mL, 0.97 mmol) was added to a cold (−78 °C) solution of uloside **25** (400 mg, 0.97 mmol) in THF (3 mL). After 1 min the reaction was stopped by addition of acetic acid (0.2 mL) and $CH_2Cl_2$ (30 mL), followed by washing of the mixture with HCl (2 M, 30 mL) and satd. aqueous $NaHCO_3$ (30 mL), drying ($MgSO_4$), and evaporation of the solvent in vacuo. The resulting residue was diluted in $CH_2Cl_2$ (5 mL) and benzoylated over 3 h with pyridine (1 mL), benzoyl chloride (0.5 mL), and DMAP (50 mg). The mixture was diluted with $CH_2Cl_2$ (30 mL), washed with HCl (2 M, 30 mL) and $NaHCO_3$ (30 mL), dried ($MgSO_4$), and concentrated to a syrup, which was subjected to column chromatography on silica gel (hexane/EtOAc, 3:1) to yield **30** (78%) as colorless needles. M.p. 133−134 °C. $[\alpha]_D^{20} = +218.6$ (*c* = 0.9, $CHCl_3$). $^1$H NMR (500 MHz, $CDCl_3$): δ = 1.19, 1.21 [2 d, 6 H, CH(C$H_3$)$_2$], 1.44 (d, 3 H, 6-$H_3$), 3.84 (m, 1 H, H-5), 4.07 [m, 1 H, C$H$(CH$_3$)$_2$], 4.96 (d, 1 H, H-1), 5.57 (dd, 1 H, H-3), 5.60 (t, 1 H, H-4), 5.86 (dd, 1 H, 2-H) ppm; $J_{1,2} = 0.9$, $J_{2,3} = 3.1$, $J_{3,4} = 10.0$, $J_{4,5} = 9.1$, $J_{5,6} = 6.2$, $J_{C,H,CH_3} = 6.2$ Hz. $^{13}$C NMR (125 MHz, $CDCl_3$): δ = 18.1 (C-6), 21.9, 23.3 [CH($CH_3$)$_2$], 70.8 (C-2), 71.1 (C-5), 71.6 [$CH$(CH$_3$)$_2$], 72.1 (C-4), 72.3 (C-3), 97.0 (C-1) ppm. MS (FD, 0−20 mA): *m/z* = 518 [M$^+$], 519 [M$^+$ + H], 122 [PhCO$_2$H$^+$], 105 [PhCO$^+$], 43 [$C_3H_7^+$]. $C_{30}H_{30}O_8$ (518.56): calcd. C 69.49, H 5.83; found C 69.45, H 5.81.

When $NaBH_4$ in $CH_2Cl_2$ was used for reduction of **25**, a 3:1 mixture of **30** and its L-*gluco* epimer was obtained, allowing the isolation of the major product in 60% yield only.

**Isopropyl 3,4-Di-*O*-benzyl-β-L-rhamnopyranoside (31):** L-Selectride (1 M in THF, 1 mL, 1 mmol) was added to a cooled (−78 °C) stirred solution of uloside **33** (385 mg, 1 mmol) in THF (3 mL), and after 1 min the reaction was stopped by the addition of AcOH (0.2 mL). After dilution with $CH_2Cl_2$ (15 mL), the mixture was washed with HCl (2 N, 2 × 20 mL) and satd. $NaHCO_3$ (2 × 20 mL) and dried ($MgSO_4$), and the solvents were evaporated in vacuo to give a syrup, which was subjected to column chromatography on silica gel (toluene/EtOAc, 4:1) to yield **31** (313 mg, 81%) as a colorless syrup on evaporation of the eluate. $[\alpha]_D^{20} = +29.8$ (*c* = 0.9, $CHCl_3$). $^1$H NMR (500 MHz, $CDCl_3$): δ = 1.16, 1.25 [2 d, each 3 H, CH(C$H_3$)$_2$], 1.33 (d, 3 H, 6-$H_3$), 2.80 (br. s, 1 H, 2-O$H$), 3.30 (m, 1 H, 5-H), 3.53 (m, 2 H, 3-H, 4-H), 4.03 [m, 1 H, C$H$(CH$_3$)$_2$], 4.05 (m, 1 H, 2-H), 4.46 (d, 1 H, 1-H), 4.63, 4.66, 4.77, 4.93 (4 d, each H, 2 BnC$H_2$), 7.25−7.40 (m, 10 H, 2 $C_6H_5$); $J_{1,2} = 0.8$, $J_{5,6} = 6.2$, $J_{C,H,CH_3} = 6.2$ Hz. $^{13}$C NMR (125 MHz, $CDCl_3$): δ = 17.9 (C-6), 21.6, 23.4 [CH($CH_3$)$_2$], 69.0 (C-2), 70.8 [$CH$(CH$_3$)$_2$], 71.3 (Bn$CH_2$), 71.4 (C-5), 75.3 (Bn$CH_2$), 79.6, 81.6 (C-3 and C-4), 97.4 (C-1), 127.7−138.4 (2 $C_6H_5$) ppm. MS (FD, 0−12 mA): *m/z* = 387 [M$^+$ + H], 386 [M$^+$]. $C_{23}H_{30}O_5$ (386.49): calcd. C 71.48, H 7.82; found C 70.51, H 7.78.

With $NaBH_4$ as reducing agent, **31** was isolated in 76% yield.

**Isopropyl 4-*O*-Acetyl-3-*O*-benzyl-β-L-rhamnopyranoside (32):** Subjection of **27** to reduction with $NaBH_4$ (100 mg) in $CH_2Cl_2$/MeOH (1:1, 20 mL) at 0 °C, and stirring for 1 h, followed by dilution with $CH_2Cl_2$ (120 mL) and workup (as described for compound **32**) provided a crude syrup, that was purified by elution from a silica gel column (*n*-hexane/EtOAc, 3:1) to give **32** (238 mg, 70%) as a color-

less syrup. $[\alpha]_D^{20} = +77.0$ ($c = 1.0$, $CHCl_3$). $^1H$ NMR (300 MHz, $CDCl_3$): δ = 1.18, 1.27 [2 d, each 3 H, $CH(CH_3)_2$], 1.23 (d, 3 H, 6-$H_3$), 2.03 (s, 3 H, 4-Ac$CH_3$), 2.52 (br. s, 1 H, 2-OH), 3.36 (qd, 1 H, 5-H), 3.47 (dd, 1 H, 3-H), 4.04 [qq, 1 H, $CH(CH_3)_2$], 4.07 (d, 1 H, 2-H), 4.51 (d, 1 H, 1-H), 4.54, 4.72 (2 d, each 1 H, Bn$CH_2$), 5.09 (dd, 1 H, 4-H) ppm; $J_{1,2} = 0.5$, $J_{2,3} = 3.3$, $J_{3,4} = 9.5$, $J_{4,5} = 9.6$, $J_{5,6} = 6.2$, $^2J_{C,H2} = 12.4$, $J_{C,H,CH_3} = 6.2$, $^1J_1 = 155.4$ Hz. $^{13}C$ NMR (75 MHz, $CDCl_3$): δ = 17.5 (C-6), 21.0 (4-Ac$CH_3$), 21.5, 23.4 [$CH(CH_3)_2$], 68.7 (C-2), 70.1 (C-5), 71.0 [$CH(CH_3)_2$], 71.0 (3-Bn$CH_2$), 72.3 (C-4), 78.5 (C-3), 97.5 (C-1), 169.9 (4-Ac$CO$) ppm. MS (FD): $m/z$ = 338 [$M^+$], 91 [$PhCH_2^+$], 43 [$MeCO^+$]. $C_{18}H_{26}O_6$(338.40): calcd. C 63.89, H 7.74; found C 63.16, H 7.63.

**Isopropyl 4-*O*-Benzoyl-3-*O*-benzyl-β-L-rhamnopyranoside (33):** $NaBH_4$ (0.75 g, 19.8 mmol) was added to a stirred, cooled (0 °C) solution of uloside **28** (1.00 g, 2.5 mmol) in $CH_2Cl_2$/MeOH (1:1, 60 mL), and stirring was continued for 2 h. Dilution with $CH_2Cl_2$ (70 mL), successive washings with water (70 mL), aqueous citric acid solution (1%, 2 × 70 mL), and water (70 mL), and drying ($MgSO_4$), followed by concentration in vacuo, gave a syrupy product that was purified by elution from a silica gel column (toluene/EtOAc, 6:1) to afford **33** (0.72 g, 71%) as a colorless syrup. $[\alpha]_D^{20} = +87.7$ ($c = 1.0$, $CHCl_3$). $^1H$ NMR (300 MHz, $CDCl_3$): δ = 1.20 (d, 3 H, CH$CH_3$), 1.28 (d, 6 H, 6-$H_3$, CH$CH_3$), 2.57 (br. s, 1 H, 2-O$H$), 3.52 (qd, 1 H, 5-H), 3.63 (dd, 1 H, 3-H), 4.07 [qq, 1 H, $CH(CH_3)_2$], 4.13 (br. d, 1 H, 2-H), 4.53 (d, 1 H, $CH_aC_6H_5$), 4.57 (d, 1 H, 1-H), 4.69 (d, 1 H, $CH_bC_6H_5$), 5.38 (dd, 1 H, 4-H) ppm; $J_{1,2} = 0.7$, $J_{2,3} = 3.1$, $J_{3,4} = J_{4,5} = 9.5$, $J_{5,6} = 6.2$, $J_{C,H,CH_3} = 6.1$, $^2J_{C,H_2} = 12.5$, $^1J_1 = 154.6$ Hz. $^{13}C$ NMR (75 MHz, $CDCl_3$): δ = 17.6 (C-6), 21.6, 23.4 [$CH(CH_3)_2$], 68.8 (C-2), 70.4 (C-5), 70.9 (Bn$CH_2$), 71.0 [$CH(CH_3)_2$], 73.0 (C-4), 78.1 (C-3), 97.6 (C-1) ppm. MS (FD, 0−12 mA): $m/z$ = 400 [$M^+$], 401 [$M^+ + H$]. $C_{23}H_{28}O_6$ (400.47): calcd. C 68.98, H 7.05; found C 68.08, H 6.99.

**Isopropyl 3-*O*-Benzyl-4-*O*-(4-methoxybenzyl)-β-L-rhamnopyranoside (34):** $NaBH_4$ (290 mg, 7.7 mmol) was added to a cooled (0 °C), stirred solution of uloside **29** (400 mg, 0.97 mmol) in $CH_2Cl_2$/MeOH (1:1, 20 mL), and stirring was continued for 1 h. Dilution with $CH_2Cl_2$ (40 mL), successive washings with water (40 mL), aqueous citric acid solution (1%, 2 × 40 mL), and water (2 × 40 mL), and drying ($MgSO_4$), followed by evaporation in vacuo, gave a syrup, that was purified by elution from a silica gel column (toluene/EtOAc, 5:1) to yield **34** (292 mg, 73%) as a colorless syrup on evaporation of the eluate. $[\alpha]_D^{20} = +40.4$ ($c = 1.1$, $CHCl_3$). $^1H$ NMR (300 MHz, $CDCl_3$): δ = 1.15, 1.25 [2 d, each 3 H, $CH(CH_3)_2$], 1.32 (d, 3 H, 6-$H_3$), 2.48 (br. s, 1 H, 2-O$H$), 3.28 (qd, 1 H, 5-H), 3.51−3.53 (m, 2 H, 3-H, 4-H), 3.78 (s, 3 H, $C_7H_6OCH_3$), 3.98−4.07 [m, 2 H, 2-H, $CH(CH_3)_2$], 4.45 (d, 1 H, 1-H), 4.58, 4.67, 4.78, 4.86 (4d, 4 H, 2 $CH_2$) ppm; $J_{1,2} = 0.7$, $J_{4,5} = 9.2$, $J_{5,6} = 6.1$, $J_{C,H,CH_3} = 6.2$, $^2J_{C,H_2} = 10.5$, 12.0, $^1J_1 = 155.3$ Hz. $^{13}C$ NMR (75 MHz, $CDCl_3$): δ = 17.9 (C-6), 21.6, 23.4 [$CH(CH_3)_2$], 55.3 ($C_7H_6OCH_3$), 69.1 (C-2), 70.7 [$CH(CH_3)_2$], 71.3 ($CH_2$), 71.4 (C, 5), 75.1 ($CH_2$), 79.3, 81.6 (C-3, C-4), 97.4 (C-1) ppm. MS (FD, 0−20 mA): $m/z$ = 416 [$M^+$]. $C_{24}H_{32}O_6$ (416.51): calcd. C 69.21, H 7.74; found C 68.35, H 7.70.

**Isopropyl 3,4-Di-*O*-benzoyl-β-L-glucopyranoside (35):** A solution of $BH_3$/pyridine (0.5 mL, 4 mmol) in THF (2.5 mL) was added dropwise to a cooled (−78 °C) solution of uloside **25** (400 mg, 0.97 mmol) in THF (10 mL). After stirring for 30 min the mixture was allowed to warm up to room temp., stirred for another hour, and quenched with water (2 mL). Removal of the solvents in vacuo afforded a residue, which was dissolved in $CH_2Cl_2$ (30 mL) and vigorously stirred with HCl (2 N, 10 mL) for 30 min, followed by washing of the organic layer with satd. $NaHCO_3$ solution (30 mL), and finally with aqueous NaCl (10%, 2 × 10 mL). Drying ($MgSO_4$) and concentration to dryness furnished a syrup, which was purified by elution from silica gel (hexane/EtOAc, 3:1) to yield a 10:1 mixture ($^1H$ NMR) of L-glucoside **35** and the corresponding L-rhamnoside (326 mg, 81%). $^1H$ NMR (500 MHz, $CDCl_3$): δ = 1.23, 1.29 [2 d, each 3 H, $CH(CH_3)_2$], 1.32 (d, 3 H, 6-$H_3$), 2.70 (br. s, 1 H, 2-OH), 3.73 (dd, 1 H, 2-H), 3.77 (m, 1 H, 5-H), 4.08 [m, 1 H, $CH(CH_3)_2$], 4.57 (d, 1 H, 1-H), 5.24 (t, 1 H, 4-H), 5.54 (t, 1 H, 3-H) ppm; $J_{1,2} = 7.8$, $J_{2,3} = J_{3,4} = J_{4,5} = 9.6$, $J_{5,6} = 6.2$ Hz. $^{13}C$ NMR (125 MHz, $CDCl_3$): δ = 14.6 (C-6), 22.3, 23.8 [$CH(CH_3)_2$], 70.7 (C-5), 72.6 [$CH(CH_3)_2$], 73.3 (C-2), 74.2 (C-4), 75.4 (C-3), 101.5 (C-1) ppm.

### Di- and Trisaccharides Containing β-L-Rhamnose Units

**General Glycosidation Procedure for Ulosyl Bromides with Glycoside Acceptors:** A suspension of acceptor (0.225 mmol), silver alumosilicate catalyst (170 mg, 0.5 mmol), and molecular sieves (4 Å) in dry $CH_2Cl_2$ (1.5 mL) was stirred for 20−30 min at room temperature with exclusion of moisture. The ulosyl bromide (0.45 mmol), dissolved in dry $CH_2Cl_2$ (1.0 mL), was added dropwise over 30−45 min and stirring was continued until no donor could be observed in the reaction mixture by TLC. The mixture was filtered through Celite and the solvent was removed in vacuo to obtain the 2-ulose. Subsequent treatment with $NaBH_4$ (47 mg, 1.25 mmol) in $CH_2Cl_2$/MeOH (1:1, 20 mL) at 0 °C, followed by stirring for 60 min, and evaporation in vacuo, provided a crude product that was dissolved in $CH_2Cl_2$ (60 mL), washed successively with aqueous citric acid solution (1%, 25 mL) and water (2 × 25 mL), and dried ($MgSO_4$). Concentration of the solution and chromatographic purification by elution from a silica gel column yielded the β-linked disaccharide.

**Silver Alumosilicate Catalyst:**[17] A slurry of silica-alumina SHPV catalyst (a porous aluminosilicate with a BET surface 473 $m^2/g$; AKZO Chemie, Amsterdam, 20 g) in NaOH ( N, 250 mL) was stirred at 100 °C for 1 h. The material was then filtered, washed with water (5 × 50 mL), and stirred with an aqueous solution of $AgNO_3$ (0.2 M, 400 mL) in the dark for 16 h at ambient temperature. Filtration and washing of the residue with water (2 × 30 mL) and acetone (200 mL), followed by drying in vacuo for about 3 d at 90 °C, gave the active material.

**6-*O*-(4-*O*-Benzoyl-3-*O*-benzyl-β-L-rhamnopyranosyl)-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (36):** Glycosidation of 1,2:4,5-di-*O*-isopropylidene-D-galactose[23] with ulosyl bromide **4** (30 min) and subsequent $NaBH_4$ reduction according to the General Procedure, followed by chromatography (*n*-hexane/$Et_2O$, 1:2) gave **36** (115 mg, 85%) as a colorless syrup; $[\alpha]_D^{20} = +8.2$ ($c = 0.8$, $CHCl_3$). $^1H$ NMR (300 MHz, $CDCl_3$): β-*rhamnosyl-H*: δ = 1.28 (d, 3 H, 6′-$H_3$), 2.70 (br. s, 1 H, 2′-O$H$), 3.54 (qd, 1 H, 5′-H), 3.60 (dd, 1 H, 3′-H), 4.23 (d, 1 H, 2′-H), 4.53, 4.69 (2 d, each 1 H, Bn$CH_2$), 4.54 (d, 1 H, 1′-H), 5.38 (dd, 1 H, 4′-H) ppm; $J_{1',2'} \leq 0.5$, $J_{2',3'} = 2.9$, $J_{3',4'} = J_{4',5'} = 9.5$, $J_{5',6'} = 6.2$, $^2J_{C,H_2} = 12.5$, $^1J_{1'} = 157.6$ Hz. α-*galactosyl-H*: δ = 1.33, 1.37, 1.46, 1.53 (4s, 12 H, 4 $CH_3$), 3.81 (dd, 1 H, 6-$H_a$), 3.97 (dd, 1 H, 6-$H_b$), 4.09 (ddd, 1 H, 5-H), 4.32 (dd, 1 H, 2-H), 4.38 (dd, 1 H, 4-H), 4.63 (dd, 1 H, 3-H), 5.52 (d, 1 H, 1-H) ppm; $J_{2,3} = 5.0$, $J_{2,3} = 2.4$, $J_{3,4} = 8.0$, $J_{4,5} = 1.8$, $J_{5,6a} = 8.7$, $J_{5,6b} = 5.7$, $^2J_{6a,b} = 9.4$, $^1J_1 = 179.6$ Hz. $^{13}C$ NMR (75 MHz, $CDCl_3$): β-*rhamnosyl-C*: δ = 17.5 (C-6′), 67.8 (C-2′), 70.6 (C-5′), 70.9 (Bn$CH_2$), 72.7 (C-4′), 77.7 (C-3′), 100.3 (C-1′). α-*galactosyl-C*: δ = 24.5, 24.9, 26.0, 26.1 (4 $CH_3$), 65.7 (C-5), 67.6 (C-6), 70.5 (C-3), 70.6 (C-2, C-4), 96.2 (C-1), 108.7, 109.2 (2 $C(CH_3)_2$] ppm. MS (FD, 0−20 mA): $m/z$ = 600 [$M^+$]. $C_{32}H_{40}O_{11}$ (600.66): calcd. C 63.99, H 6.71; found C 63.83, H 6.73.

**1,6-Anhydro-2,3-di-*O*-benzyl-4-*O*-(4-*O*-benzoyl-3-*O*-benzyl-β-L-rhamnopyranosyl)-β-D-glucopyranose (37):** Treatment of 1,6-anhydro-2,3-di-*O*-benzyl-β-D-glucopyranose[24] with ulosyl bromide **4** according to the General Procedure (vide supra, glycosylation time: 2.5 h), followed by purification on a silica gel column (toluene/EtOAc, 2:1) and crystallization from 2-propanol gave 120 mg (78%) of **37** as fine, colorless needles. M.p. 177 °C; $[\alpha]_D^{20} = +33.5$ ($c$ = 1.0, $CHCl_3$). $^1H$ NMR (300 MHz, $CDCl_3$): δ = 1.25 (d, 3 H, 6′-$H_3$), 2.60 (br. s, 1 H, 2′-O*H*), 3.32−3.42 (m, 1 H, 5′-H), 3.39 (d, 1 H, 2-H), 3.47 (dd, 1 H, 3′-H), 3.61 (dd, 1 H, 3-H), 3.68 (dd, 1 H, 6-$H_a$), 3.74 (d, 1 H, 4-H), 3.90 (d, 1 H, 6-$H_b$), 4.05 (d, 1 H, 2′-H), 4.43 (s, 1 H, 1′-H), 4.48−4.72 (m, 7 H, 5-H, 3 BnC$H_2$), 5.35 (dd, 1 H, 4′-H), 5.46 (s, 1 H, 1-H) ppm; $J_{2,3}$ = 3.7, $J_{3,4}$ = 4.1, $J_{5,6a}$ = 5.5, $J_{6a,b}$ = 7.2, $J_{2',3'}$ = 3.0, $J_{3',4'} = J_{4',5'}$ = 9.5, $J_{5',6'}$ = 6.2, $^1J_1$ = 172.4, $^1J_{1'}$ = 157.8 Hz. $^{13}C$ NMR (75 MHz, $CDCl_3$): δ = 17.6 (C-6′), 66.8 (C-6), 68.0 (C-2′), 70.6 (C-5′), 70.9, 72.0 (2 Bn*C*$H_2$), 72.6 (C-4′), 73.1 (Bn*C*$H_2$), 76.6 (C-5), 77.3 (C-3), 77.6 (C-3′), 78.1 (C-4), 79.1 (C-2), 99.0 (C-1′), 100.8 (C-1) ppm. MS (FD): $m/z$ = 682 [$M^+$]. $C_{40}H_{42}O_{10}$ (682.77): calcd. C 70.37, H 6.20; found C 69.97, H 6.18.

**Methyl 3,4-Di-*O*-benzyl-2-*O*-(4-*O*-benzoyl-3-*O*-benzyl-β-L-rhamnopyranosyl)-α-L-rhamnopyranoside (38):** Ulosyl bromide **4**, dissolved in $CH_2Cl_2$, was injected into a suspension of methyl 3,4-di-*O*-benzyl-α-L-rhamnopyranoside[25] and silver alumosilicate catalyst as described in the General Procedure (vide supra, glycosylation time: 80 min), followed by elution from a silica gel column (toluene/EtOAc, 2:1) to give **38** (125 mg, 79%) as a colorless syrup. $[\alpha]_D^{20} = +50.1$ ($c$ = 0.8, $CHCl_3$). $^1H$ NMR (300 MHz, $CDCl_3$): δ = 1.29 (d, 3 H, 6′-$H_3$), 1.32 (d, 3 H, 6-$H_3$), 2.60 (br. s, 1 H, 2′-O*H*), 3.34 (s, 3 H, 1-OC$H_3$), 3.46−3.59 (m, 2 H, 4-H, 5′-H), 3.58 (dd, 1 H, 3′-H), 3.68 (qd, 1 H, 5-H), 3.87 (dd, 1 H, 3-H), 4.26 (d, 1 H, 2′-H), 4.39 (dd, 1 H, 2-H), 4.53, 4.54, 4.58, 4.72, 4.83, 4.89 (6 d, each 1 H, 3 BnC$H_2$), 4.66 (s, 1 H, 1′-H), 4.70 (s, 1 H, 1-H), 5.46 (dd, 1 H, 4′-H) ppm; $J_{1,2}$ = 2.0, $J_{2,3}$ = 3.3, $J_{3,4}$ = 8.9, $J_{4,5}$ = 9.4, $J_{5,6}$ = 6.2, $J_{2',3'}$ = 2.9, $J_{3',4'} = J_{4',5'}$ = 9.4, $J_{5',6'}$ = 6.2, $^2J_{C,H_2}$ = 10.9, 11.4, 12.7, $^1J_1$ = 166.6, $^1J_{1'}$ = 158.1 Hz. $^{13}C$ NMR (75 MHz, $CDCl_3$): δ = 17.7 (C-6′), 18.1 (C-6), 54.8 (1-OC$H_3$), 67.7 (C-5), 68.2 (C-2′), 70.4 (Bn*C*$H_2$), 70.9 (C-5′), 71.1 (Bn*C*$H_2$), 71.6 (C-2), 72.8 (C-4′), 75.2 (Bn*C*$H_2$), 77.5 (C-3′), 78.2 (C-3), 79.8 (C-4), 97.4 (C-1′), 98.4 (C-1) ppm. MS (FD): $m/z$ = 698 [$M^+$]. $C_{41}H_{46}O_{10}$ (698.81): calcd. C 70.47, H 6.64; found C 70.32, H 6.75.

**Methyl 2,4-Di-*O*-benzyl-3-*O*-(4-*O*-benzoyl-3-*O*-benzyl-β-L-rhamnopyranosyl)-α-L-rhamnopyranoside (39):** Treatment of methyl 2,4-di-*O*-benzyl-α-L-rhamnopyranoside[25] with ulosyl bromide **4** according to the General Procedure (vide supra, glycosylation time: 100 min), followed by chromatography on silica gel (*n*-hexane/EtOAc, 2:1) gave **39** (120 mg, 77%) as a colorless syrup. $[\alpha]_D^{20}$ = +19.5 ($c$ = 0.9, $CHCl_3$). $^1H$ NMR (300 MHz, $CDCl_3$): δ = 1.21 (d, 3 H, 6′-$H_3$), 1.36 (d, 3 H, 6-$H_3$), 2.45 (br. s, 1 H, 2′ O*H*), 3.33 (s, 3 H, 1-OC$H_3$), 3.26−3.40 (m, 1 H, 5′-H), 3.45 (dd, 1 H, 3′-H), 3.55−3.73 (m, 3 H, 4-H, 5-H, 2-H), 3.98 (d, 1 H, 2′-H), 4.23 (dd, 1 H, 3-H), 4.33 (s, 1 H, 1′-H), 4.50, 4.59, 4.61, 4.67, 4.77, 5.01 (6 d, each 1 H, 3 BnC$H_2$), 4.73 (d, 1 H, 1-H), 5.35 (dd, 1 H, 4′-H) ppm; $J_{1,2}$ = 1.7, $J_{2,3}$ = 3.2, $J_{3,4}$ = 8.7, $J_{5,6}$ = 6.0, $J_{2',3'}$ = 3.0, $J_{3',4'} = J_{4',5'}$ = 9.6, $J_{5',6'}$ = 6.1, $^2J_{C,H_2}$ = 10.6, 12.5, 12.6, $^1J_1$ = 167.1, $^1J_{1'}$ = 156.3 Hz. $^{13}C$ NMR (75 MHz, $CDCl_3$): δ = 17.6 (C-6′), 18.1 (C-6), 54.7 (1-OC$H_3$), 67.7 (C-5), 68.4 (C-2′), 70.6 (C-5′), 70.8, 72.5 (2 Bn*C*$H_2$), 72.9 (C-4′), 74.6 (C-2), 74.9 (Bn*C*$H_2$), 76.9 (C-3), 77.9 (C-3′), 79.6 (C-4), 97.3 (C-1′), 98.6 (C-1) ppm. MS (FD): $m/z$ = 698 [$M^+$]. $C_{41}H_{46}O_{10}$ (698.81): calcd. C 70.47, H 6.64; found C 70.46, H 6.70.

**Methyl 2,3-*O*-Isopropylidene-4-*O*-(4-O-benzoyl-3-*O*-benzyl-β-L-rhamnopyranosyl)-α-L-rhamnopyranoside (40):** Glycosylation of methyl 2,3-*O*-isopropylidene-α-L-rhamnopyranoside[27] with ulosyl bromide **4** according to the General Procedure (vide supra, glycosylation time: 15 min), followed by elution from a silica gel column (*n*-hexane/EtOAc, 3:2), gave **40** (100 mg, 80%) as a colorless syrup. $[\alpha]_D^{20}$ = +29.8 ($c$ = 0.9, $CHCl_3$). $^1H$ NMR (300 MHz, $CDCl_3$): β-*rhamnosyl-H*: δ = 1.29 (d, 3 H, 6′-$H_3$), 2.60 (br. s, 1 H, 2′-O*H*), 3.52−3.57 (m, 1 H, 5′-H), 3.62 (dd, 1 H, 3′-H), 4.20 (d, 1 H, 2′-H), 4.54, 4.70 (2 d, each 1 H, BnC$H_2$), 4.69 (d, 1 H, 1′-H), 5.38 (dd, 1 H, 4′-H) ppm; $J_{1',2'} \leq 0.5$, $J_{2',3'}$ = 3.4, $J_{3',4'} = J_{4',5'}$ = 9.4, $J_{5',6'}$ = 6.1, $^2J_{C,H_2}$ = 12.4, $^1J_{1'}$ = 156.8 Hz. α-*rhamnosyl-H*: δ = 1.31 (d, 3 H, 6-$H_3$), 1.34, 1.53 (2s, 6 H, 2 C$H_3$), 3.36 (s, 3 H, 1-OC$H_3$), 3.49 (dd, 1 H, 4-H), 3.74 (qd, 1 H, 5-H), 4.12 (d, 1 H, 2-H), 4.34 (dd, 1 H, 3-H), 4.84 (d, 1 H, 1-H) ppm; $J_{2,3}$ = 6.0, $J_{3,4}$ = 7.2, $J_{4,5}$ = 9.8, $J_{5,6}$ = 6.1, $^1J_1$ = 166.1 Hz. $^{13}C$ NMR (75 MHz, $CDCl_3$): β-*rhamnosyl-C*: δ = 17.7 (C-6′), 68.0 (C-2′), 70.8 (C-5′), 70.9 (Bn*C*$H_2$), 72.8 (C-4′), 78.1 (C-3′), 97.7 (C-1′). α-*rhamnosyl-C:* δ = 17.5 (C-6), 26.1, 28.0 (2 C$H_3$), 54.8 (1-OC$H_3$), 64.3 (C-5), 75.9 (C-2), 76.6 (C-3), 81.7 (C-4), 98.2 (C-1), 109.1 [*C*$(CH_3)_2$] ppm. MS (FD, 0−12 mA): $m/z$ = 558 [$M^+$]. $C_{30}H_{38}O_{10}$ (558.63): calcd. C 64.50, H 6.86; found C 64.04, H 6.83.

**Methyl 2,3-*O*-Isopropylidene-4-*O*-(2-*O*-acetyl-4-*O*-benzoyl-3-*O*-benzyl-β-L-rhamnopyranosyl)-α-L-rhamnopyranoside (41):** $Ac_2O$ (2 mL, 2.16 g, 21.2 mmol) was added dropwise to a cooled solution (0 °C) of rhamnobioside **40** (930 mg, 1.7 mmol) in pyridine (15 mL). The reaction mixture was stirred at room temperature for 12 h, cooled (0 °C), and treated with dry EtOH (0.64 mL). Stirring was continued for 0.5 h, during which the mixture was allowed to warm to room temperature. Concentration in vacuo and purification by elution from a silica gel column (*n*-hexane/EtOAc, 4:1) gave **41** (920 mg, 92%) as a colorless foam. $[\alpha]_D^{20}$ = +54.5 ($c$ = 1.1, $CHCl_3$). $^1H$ NMR (300 MHz, $CDCl_3$): δ = 1.27 (d, 3 H, 6-$H_3$), 1.32 (d, 3 H, 6′-$H_3$), 1.34, 1.55 (2 s, 6 H, 2 C$H_3$), 2.22 (s, 3 H, AcC$H_3$), 3.35 (s, 3 H, 1-OC$H_3$), 3.41 (dd, 1 H, 4-H), 3.59 (qd, 1 H, 5′-H), 3.64−3.75 (m, 1 H, 5-H), 3.67 (dd, 1 H, 3′-H), 4.11 (d, 1 H, 2-H), 4.32 (dd, 1 H, 3-H), 4.42, 4.66 (2 d, 2 H, BnC$H_2$), 4.84 (s, 2 H, 1-H, 1′-H), 5.30 (dd, 1 H, 4′-H), 5.72 (d, 1 H, 2′-H) ppm; $J_{2,3}$ = 5.8, $J_{3,4}$ = 7.2, $J_{4,5}$ = 9.8, $J_{5,6}$ = 6.2, $J_{2',3'}$ = 3.0, $J_{3',4'} = J_{4',5'}$ = 9.7, $J_{5',6'}$ = 6.2, $^2J_{C,H_2}$ = 12.7 Hz. $^{13}C$ NMR (75 MHz, $CDCl_3$): δ = 17.6 (C-6, C-6′), 21.2 (Ac*C*$H_3$), 26.2, 28.1 (2 C$H_3$), 54.8 (1-OC$H_3$), 64.0 (C-5), 67.0 (C-2′), 70.6 (Bn*C*$H_2$), 71.0 (C-5′), 72.8 (C-4′), 75.9 (C-2), 76.2 (C-3′), 76.8 (C-3), 82.0 (C-4), 98.1, 98.4 (C-1, C-1′), 109.2 [*C*$(CH_3)_2$] ppm. MS (FD): $m/z$ = 601 [$M^+$ + H]. $C_{32}H_{40}O_{11}$ (600.66): calcd. C 63.99, H 6.71; found C 63.89, H 6.64.

**Methyl 2,3-*O*-Isopropylidene-4-*O*-(2-*O*-acetyl-4-*O*-benzoyl-β-L-rhamnopyranosyl)-α-L-rhamnopyranoside (42):** A cooled (0 °C) solution of **41** (738 mg, 1.2 mmol) in EtOAc (140 mL) was hydrogenated over $Pd(OH)_2$/C (20%, 350 mg) for 17 h, during which the mixture was warmed to room temperature. Filtration through Celite and concentration provided a residue, which was eluted from a silica gel column (*n*-hexane/EtOAc, 1:1) to yield **42** (620 mg, 99%) as a colorless syrup. $[\alpha]_D^{20}$ = +3.0 ($c$ = 0.9, $CHCl_3$). $[\alpha]_{365}^{20}$ = +17.8 ($c$ = 0.9, $CHCl_3$). $^1H$ NMR (300 MHz, $CDCl_3$): δ = 1.26 (d, 3 H, 6-$H_3$), 1.35 (d, 3 H, 6′-$H_3$), 1.34, 1.55 (2 s, 6 H, 2 C$H_3$), 2.20 (s, 3 H, AcC$H_3$), 2.75 (br. s, 1 H, 3′-O*H*), 3.35 (s, 3 H, 1-OC$H_3$), 3.42 (dd, 1 H, 4-H), 3.67 (m, 2 H, 5-H, 5′-H), 3.95 (dd, 1 H, 3′-H), 4.11 (d, 1 H, 2-H), 4.30 (dd, 1 H, 3-H), 4.84 (s, 1 H, 1-H), 4.87 (d, 1 H, 1′-H), 5.10 (dd, 1 H, 4′-H), 5.52 (d, 1 H, 2′-H) ppm; $J_{2,3}$ = 5.8, $J_{3,4}$ = 7.2, $J_{4,5}$ = 9.8, $J_{5,6}$ = 6.2, $J_{1',2'}$ = 0.8, $J_{2',3'}$ = 3.0, $J_{3',4'} = J_{4',5'}$ = 9.6 Hz. $^{13}C$ NMR (75 MHz, $CDCl_3$): δ = 17.5 (C-6, C-6′),

21.0 (Ac*C*H$_3$), 26.2, 28.0 (2 C*H*$_3$), 54.8 (1-O*C*H$_3$), 64.1 (C-5), 70.6 (C-5′), 71.0 (C-2′), 71.5 (C-3′), 75.1 (C-4′), 75.9 (C-2), 76.7 (C-3), 82.3 (C-4), 98.0 (C-1), 98.6 (C-1′), 109.1 [*C*(CH$_3$)$_2$] ppm. MS (FD): *m*/*z* = 495 [M$^+$ − Me]. $C_{25}H_{34}O_{11}$ (510.54): calcd. C 58.82, H 6.71; found C 58.18, H 6.83.

**Methyl 2,3-*O*-Isopropylidene-4-*O*-[2-*O*-acetyl-4-*O*-benzoyl-3-*O*-(2,3,4-tri-*O*-acetyl-α-L-rhamnopyranosyl)-β-L-rhamnopyranosyl]-α-L-rhamnopyranoside (43):** A solution of rhamnobioside **42** (150 mg, 0.3 mmol), acetobromo-rhamnose **7**[13] (170 mg, 0.5 mmol), and 2,6-di-*tert*-butyl-4-methylpyridine (72 mg, 0.35 mmol) in dry $CH_2Cl_2$ (3 mL) was stirred at room temperature for 10 min over molecular sieves (4 Å) with exclusion of moisture. The solution was cooled to −45 °C, treated with AgOTf (75 mg, 0.3 mmol), and stirred for 100 min, during which the mixture was warmed to −5 °C. The mixture was filtered through Celite, diluted with $CH_2Cl_2$ (60 mL), and washed with saturated aqueous $NaHCO_3$ solution (2 × 25 mL) and water (2 × 25 mL). Drying ($MgSO_4$) and concentration in vacuo provided a residue, which was purified by elution from a silica gel column with $CHCl_3$/*n*-hexane (15:1) to afford **43** (190 mg, 82%) as a colorless syrup. $[\alpha]_D^{20}$ + = 7.3 (*c* = 1.0, $CHCl_3$). $^1$H NMR (300 MHz, $CDCl_3$): δ = 1.21 (d, 3 H, 6′′-H$_3$), 1.26 (d, 3 H, 6-H$_3$), 1.34 (d, 3 H, 6′-H$_3$), 1.35, 1.56 (2 s, 6 H, 2 C*H*$_3$), 1.82, 1.88, 2.03, 2.26 (4 s, 12 H, 4 AcC*H*$_3$), 3.35 (s, 3 H, 1-OC*H*$_3$), 3.42 (dd, 1 H, 4-H), 3.60−3.71 (m, 2 H, 5-H, 5′-H), 3.98 (qd, 1 H, 5′′-H), 4.05 (dd, 1 H, 3′-H), 4.12 (d, 1 H, 2-H), 4.33 (dd, 1 H, 3-H), 4.84 (s, 2 H, 1-H, 1′′-H), 4.93 (d, 1 H, 2′′-H), 4.93 (s, 1 H, 1′-H), 4.95 (dd, 1 H, 4′′-H), 5.09 (dd, 1 H, 3′′-H), 5.36 (dd, 1 H, 4′-H), 5.56 (d, 1 H, 2′-H) ppm; $J_{2,3}$ = 5.7, $J_{3,4}$ = 7.2, $J_{4,5}$ = 9.8, $J_{5,6}$ = 6.4, $J_{2',3'}$ = 3.0, $J_{3',4'}$ = $J_{4',5'}$ = 9.7, $J_{5',6'}$ = 6.2, $J_{2'',3''}$ = 3.4, $J_{3'',4''}$ = 10.0, $J_{4'',5''}$ = 9.8, $J_{5'',6''}$ = 6.2, $^1J_1$ = 163.9, $^1J_{1'}$ = 153.1, $^1J_{1''}$ = 171.8 Hz. $^{13}$C NMR (75 MHz, $CDCl_3$): δ = 17.4, 17.5 (C-6, C-6′, C-6′′), 20.4, 20.5, 20.8, 21.0 (4 Ac*C*H$_3$), 26.2, 28.1 [C(*C*H$_3$)$_2$], 54.8 (1-O*C*H$_3$), 63.9 (C-5), 67.3 (C-5′′), 68.3 (C-3′′), 69.5 (C-2′′), 69.8 (C-2′), 70.7 (C-5′) 70.8 (C-4′′), 73.6 (C-4′), 75.8, 75.9 (C-2, C-3′), 76.7 (C-3), 82.0 (C-4), 98.0 (C-1), 98.1 (C-1′), 99.0 (C-1′′), 109.1 [*C*(CH$_3$)$_2$] ppm. MS (FD): *m*/*z* = 782 [M$^+$], 750 [M$^+$ − MeOH]. $C_{37}H_{50}O_{18}$ (782.79): calcd. C 56.77, H 6.44; found C 56.74, H 6.40.

**Methyl 4-*O*-[3-*O*-(α-L-Rhamnopyranosyl)-β-L-rhamnopyranosyl]-α-L-rhamnopyranoside (45):** Trisaccharide **43** (110 mg, 0.14 mmol) was stirred in a solution of 2% trifluoroacetic acid in 96% AcOH (2 mL) at 35 °C for 3.5 h. Removal of the solvent in vacuo and coevaporation with toluene (3 × 5 mL) delivered a colorless foam, which was purified by elution from a silica gel column with *n*-hexane/EtOAc (3:1). The intermediate product (**44**, 84 mg) was directly subjected to saponification with NaOMe (cat. amount) in dry MeOH (4 mL). The mixture was stirred for 3 days at room temperature and neutralized by addition of ion-exchange resin (Amberlite® IRC-86, H$^+$-form). Filtration and concentration in vacuo provided a residue, which was purified by elution from a silica gel column with $CHCl_3$/MeOH (3:1) to afford **45** (51 mg, 75%) as an amorphous powder. $[\alpha]_D^{20}$ = −56.2 (*c* = 1.4, MeOH). $^1$H NMR (300 MHz, $D_2O$): δ = 1.30 (d, 3 H, 6′′-H$_3$), 1.31−1.35 (m, 6 H, 6-H$_3$, 6′-H$_3$), 3.40 (s, 3 H, 1-OC*H*$_3$), 3.47 (dd, 2 H, 4′-H, 4′′-H), 3.49 (qd, 1 H, 5′-H), 3.58 (dd, 1 H, 4-H), 3.67 (dd, 1 H, 3′-H), 3.77 (qd, 1 H, 5-H), 3.82 (dd, 1 H, 3-H), 3.86 (dd, 1 H, 3′′-H), 3.80−3.90 (m, 1 H, 5′′-H), 4.00 (dd, 1 H, 2-H), 4.08 (dd, 1 H, 2′′-H), 4.12 (d, 1 H, 2′-H), 4.71 (d, 1 H, 1-H), 4.76 (s, 1 H, 1′-H), 5.04 (s, 1 H, 1′′-H) ppm; $J_{1,2}$ = 1.6, $J_{2,3}$ = 3.4, $J_{3,4}$ = $J_{4,5}$ = 9.4, $J_{5,6}$ = 6.4, $J_{2',3'}$ = 3.0, $J_{3',4'}$ = $J_{4',5'}$ = 9.8, $J_{1'',2''}$ = 1.4, $J_{2'',3''}$ = 3.4, $J_{3'',4''}$ = $J_{4'',5''}$ = 9.8, $J_{5'',6''}$ = 6.4, $^1J_1$ = 170.9, $^1J_{1'}$ = 161.1, $^1J_{1''}$ = 170.9 Hz. $^{13}$C NMR (75 MHz, $D_2O$): δ = 17.4, 17.4, 17.5 (C-6, C-6′, C-6′′), 55.6 (1-O*C*H$_3$), 67.6 (C-5), 69.8, 69.9, 70.1, 70.9 (C-2, C-3, C-3′′, C-5′′), 70.9 (C-2′′), 71.3 (C-2′), 71.9, 72.7, 72.8 (C-4′, C-4′′, C-5′), 81.2 (C-3′), 83.3 (C-4), 101.0 (C-1′), 101.4 (C-1), 103.2 (C-1′′) ppm. MS (FD): *m*/*z* = 471 [M$^+$ + H], 147 [Rha$^+$-OH].

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