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Synthesis of novel types of divalent saccharide structures by a ketene acetal Claisen rearrangement

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Dedicated to Prof. Stephen J. Angyal, Sydney, on the occasion of his 90th birthday in recognition of his eminent contribution to carbohydrate chemistry

Abstract—A simple allyl uronate was rearranged to give the branched product, which in turn could be transformed into a spiro-annellated bicyclic compound. More complex allyl uronates of D-and L-arabinose were rearranged to give novel methylene-bridged dimeric saccharide structures.

1. Introduction

Aiming at the specific manipulation of biologically important carbohydrate recognition and bindings sites, considerable efforts have been directed towards the design and chemical synthesis of structural mimetics for significant naturally occurring saccharides. In order to inhibit reaction pathways proceeding subsequent to binding and to generally minimize biological degradation, a particularly high value is attributed to the unique chemical stability of C–C connected derivatives, as it is reflected by the rapidly growing activities in the field of *C*-glycoside synthesis.[1] An approach to enhance binding affinity by displaying a crucial structural unit more than once within the same molecule has recently lead to the development of a variety of oligovalent glycostructures.[2,3] In our contribution, a combination of both features was sought to be realized by the synthesis of divalent molecules, which should be tied together by a carbon–carbon bond.

2. Results and discussion

C–C bond formation as a key synthetic step can be achieved by means of ketene acetal Claisen rearrangement, which has previously been applied successfully to uronic acid derived starting materials.[4] Thus, *C*-allyl branched urinate **2**[5,6] could be obtained by enolization of the allyl ester easily prepared from the corresponding uronic acid **1**[4] (Scheme 1). Prior to further processing of the branching side chain into a second saccharide moiety, the uronate carbonyl group was reduced and the resulting alcohol acetylated by standard synthetic steps to obtain lyxofuranoside **3**. To transform the terminal double bond into the desired hydroxyaldehyde function, the synthetic strategy ingeniously elaborated during the total synthesis of L-hexoses[7,8] was adopted and simplified with respect to the far less demanding present case. Since in these initial studies there was no focus on stereochemistry, epoxidation was easily carried out with *m*-chloroperbenzoic acid to give a high yield of the diastereomeric epoxide mixture **4**. Base induced epoxide opening with thiophenol to **5** enabled introduction of a masked aldehyde function via Pummerer rearrangement[9] of the corresponding sulfoxide, to give a mixture of four stereoisomers of acetoxy thioacetals **6**. Base catalyzed deacetylation proceeded smoothly under the release of the aldehyde and, subsequently, spontaneous formation of a cyclic hemiacetal moiety, to result in the bicyclic structure **7** containing two anomeric centres. The general feasibility of the overall process was thus demonstrated, with future work directed towards the synthesis of fully oxygenated and stereochemically pure derivatives.

The above described procedure employed a ketene acetal rearrangement starting from a simple allyl ester at the beginning of the synthetic sequence followed by

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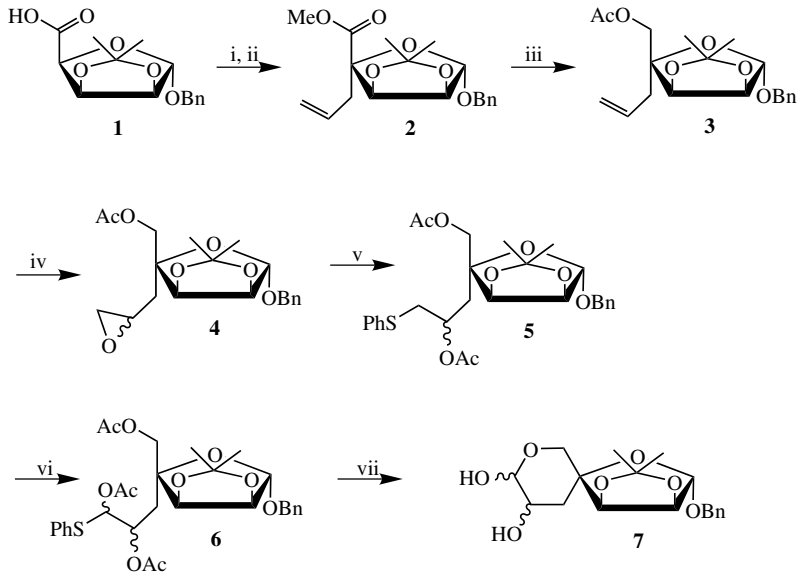
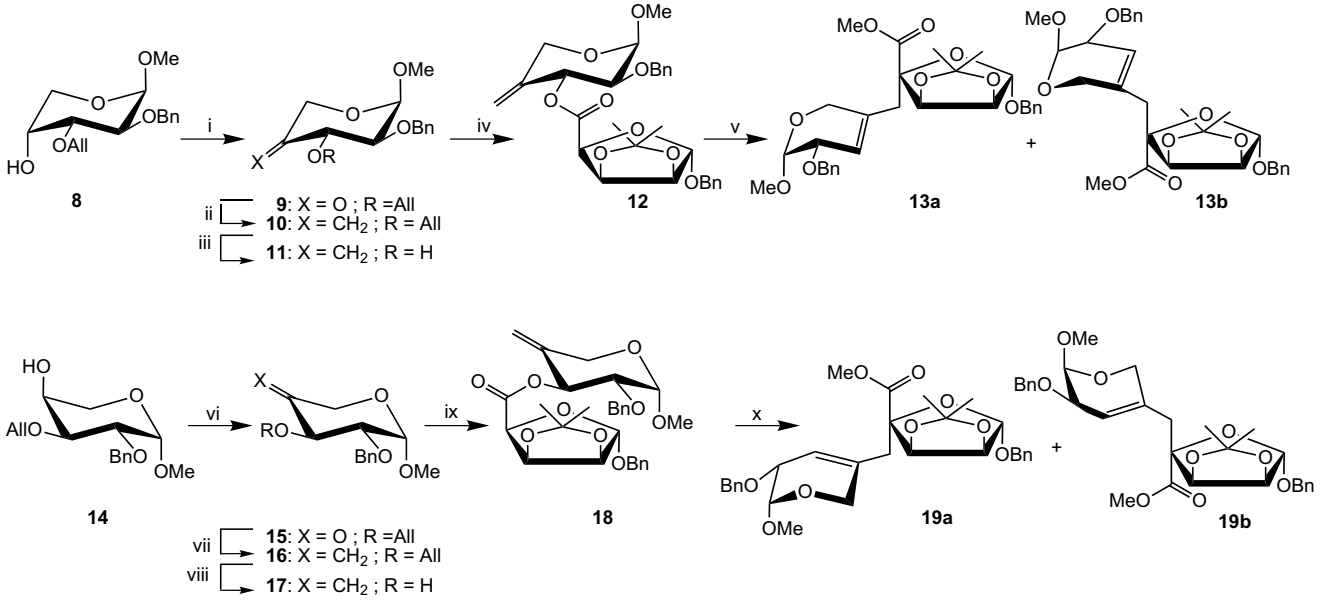


Scheme 1. Reagents and conditions: (i) $(COCl)_2$, cat. DMF, PhH, 0 °C to rt; DMAP, CH_2=$CHCH_2OH$, CH_2Cl_2, 0 °C to rt; 94%; (ii) TMSCl, LDA, THF–HMPA, −100 °C to rt; TBAF, THF; $TMSCHN_2$, PhH–MeOH, 43%; (iii) LAH, THF, reflux; Ac_2O, Py, 83%; (iv) MCPBA, CH_2Cl_2, 87%; (v) PhSH, Bu^{t}OK, Bu^{t}OH–DMF, reflux; Ac_2O, Py, 41%; (vi) MCPBA, CH_2Cl_2, −78 °C; NaOAc, Ac_2O, reflux, 66%; (vii) Na_2CO_3, MeOH, 87%.

several further manipulations to obtain the complex disaccharide structure. Our second approach used the reverse strategy by linking the complete second saccharide unit into the urinate precursor and performing an enolization and Claisen rearrangement at a late stage of the overall process (Scheme 2). Starting from the corresponding 3,4-acetonide,[10] the suitably protected D-arabinopyranoside **8** was prepared via regioselective opening[11] of a stannylene intermediate. Swern oxidation[12] followed by Wittig reaction of ketone **9** gave the exocyclic alkene **10**, from which the allylic hydroxyl function could be selectively released by palladium catalyzed deallylation.[13] The resulting alcohol **11** was reacted with the same uronic acid **1** employed in the previous synthesis to give allyl ester **12**. After enolization and silylation to the corresponding ketene acetal, a 1:1 mixture of both epimeric rearrangement products **13a** and **13b** was formed in a total yield of only 15%. The lack of stereodiscrimination during sigmatropic rearrangement in the present case was rather unexpected, as results previously reported,[5,6] indicated a clear preference of the bond forming process to occur *trans* to the furanoside isoprop- ylidenedioxy moiety.

To rationalize the observed stereochemical ambiguity, as well as the modest total yield, different stereoelec-



Scheme 2. All = allyl. Reagents and conditions: (i) $(COCl)_2$, DMSO, CH_2Cl_2, −40 °C; NEt_3, 68%; (ii) Ph_3PCH_2, Et_2O, 50%; (iii) 10% Pd–C, TsOH, MeOH, reflux, 72%; (iv) **1**, DCC, DMAP, CH_2Cl_2, 0 °C to rt, 70%; (v) TMSCl, LDA, THF–HMPA, −100 °C to rt; TBAF, THF; $TMSCHN_2$, PhH–MeOH, 15%; (vi) same as (i) 56%; (vii) same as (ii), 40%; (viii) same as (iii), 61%; (ix) same as (iv), 91%; (x) same as (v), 40%.

tronic influences may be supposed to direct in opposite ways. Apart from steric crowding, the transition state geometry is of dominant importance. Only very recently for a closely related structure of the starting material[6] could this be proven to predominantly adopt a chair-like conformation. The number of possible transition state structures in this case is restricted by the allyloxy moiety being partially embedded in a pyranoside ring, and hence the configuration at its connecting 3-position could play an important role. An obvious approach to further investigate this matter was to repeat the same starting material synthesis within the oppositely configurated L-*arabino* series. Thus, the corresponding acetonide precursor[14] was likewise transformed into hydroxyl compound **14**, oxidized to ketone **15** and the resultant Wittig product **16** deallylated to alcohol **17**, esterification of which with uronic acid **1** gave allyl ester **18**, suitable for another ketene acetal Claisen rearrangement. Subsequently, the epimeric products **19a** and **19b** were obtained in a significantly increased total yield of 40%. With respect to stereoselectivity, though, only very little improvement could be observed; the D-*lyxo* isomer **19a** being formed in a slightly larger amount. Elucidation of the nature and extent of the respective influences leading to this unexpected behaviour remains a task to be addressed in future research in our laboratories, as well as the possible elaboration of the obtained novel dimers into fully oxygenated disaccharide structures.

3. Experimental

3.1. General

Solvents were purified and dried according to standard procedures. Petroleum ether used refers to bp 50–70 °C. TLC was performed on silica gel 60-coated aluminium sheets (Merck or Macherey-Nagel), with detection by UV at 254 nm and by heating with H_2SO_4 (5% in EtOH). Flash chromatography was carried out on silica gel 60 (0.04–0.063 mm; Merck, Macherey-Nagel or ICN). NMR spectra were recorded on a Bruker AMX-400 NMR spectrometer (^{1}H: 400 MHz; ^{13}C: 100 MHz) with TMS as internal standard. Melting points were determined on a Leitz apparatus and are uncorrected. The optical rotations were measured on a Perkin-Elmer 243 or 341 polarimeter at 20 °C.

3.2. Benzyl 5-*O*-acetyl-2,3-*O*-isopropylidene-4-*C*-(2-propenyl)-α-D-lyxofuranoside 3

A solution of methyl (benzyl-2,3-*O*-isopropylidene-4-*C*-(2-propenyl)-α-D-lyxofuranoside)-uronate **2**[5,6] (361 mg, 1.04 mmol) in anhydrous THF (5 mL) was added dropwise to a suspension of lithium aluminium hydride (20 mg, 0.5 mmol) in THF (5 mL). The mixture was refluxed for 1 h, after cooling diluted with ethyl acetate, excessive hydride hydrolyzed with water and the precipitate dissolved with 2 M sulfuric acid. The organic phase was washed with saturated sodium chloride solution and concentrated to dryness. The residue was acetylated in anhydrous pyridine (10 mL) with acetic anhydride (5 mL) and worked up by standard procedure to give **2** as colourless syrup (11 mg, 83%); $[\alpha]_{578}^{20} = +45.5$ (*c* 1.0, $CHCl_3$); $C_{20}H_{26}O_6$ (362.4); ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.24, 1.50 (2 × s, 2 × 3H, 2 × Me), 2.05 (s, 3H, OAc), 2.38, 2.56 (2 × dd, 2 × 1H, CH_2), 4.08, 4.22, 4.41, 4.71 (4 × d, 4 × 1H, H-5a, H-5b, benzyl–OCH_2, $J_{5a,5b}$ = 11.7 Hz) 4.53, 4.74 (2 × d, 2 × 1H, H-2, H-3, $J_{2,3}$ = 6.1 Hz), 5.05 (m, 2H, =CH_2), 5.11 (s, 1H, H-1), 5.69–5.79 (m, 1H, =CH–) 7.22–7.28 (m, 5H, aryl), ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.93, 23.79, 25.09 (3C, 3 × Me), 39.28 (1C, CH_2), 63.35, 68.72 (2C, C-5, benzyl–OCH_2), 82.63, 85.40 (2C, C-2, C-3), 86.61 (1C, C-4), 106.50 (1C, C-1), 111.89 (1C, *i*Prdn), 117.95 (1C, =CH_2), 126.80–136.30 (7C, =CH–, aryl), 169.52 (1C, acetyl–CO_2).

3.3. Benzyl 5-*O*-acetyl-2,3-*O*-isopropylidene-4-*C*-(2,3-epoxypropyl)-α-D-lyxofuranoside 4

A solution of **3** (109 mg, 0.3 mmol) in anhydrous dichloromethane (5 mL) was stirred with 4-chloroperbenzoic acid (87 mg, 0.5 mmol) at room temperature. For work-up the solution was washed with saturated sodium hydrogencarbonate, concentrated under reduced pressure to dryness and the remainder purified by column chromatography (petroleum ether/ethyl acetate 10:1) to give the diastereomeric mixture (ca. 1:1) of **4** as colourless crystals (98 mg, 87%); $C_{20}H_{26}O_7$ (378.4), EI: *m*/*z* = 363 (M−Me); ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.25, 1.42 (2 × s, 2 × 6H, 4 × Me), 1.61, 1.75 (2 × dd, 2 × 1H, 2 × H-1′, $J_{1',1'}$ = 14.5, $J_{1',2'}$ = 5.1, 8.1 Hz), 2.04, 2.05 (2 × s, 2 × 3H, 2 × OAc), 2.11, 2.18 (2 × dd, 2 × 1H, 2 × H-1′), 2.35, 2.39 (2 × dd, 2 × 1H, 2 × H-3′, $J_{3',3'}$ = 4.9 Hz), 2.67, 2.73 (2 × dd t, 2 × 1H, 2 × H-3′), 2.96, 3.04 (2 × m, 2 × 1H, 2 × H-2′, $J_{2',3'}$ = 2.5, 4.6 Hz), 4.16, 4.26, 4.29, 4.39, 4.43, 4.44, 4.67, 4.70 (8 × d, 8 × 1H, 2 × H-5a, 2 × H-5b, 2 × benzyl–OCH_2, $J_{5a',5b'}$ = 11.7 Hz) 4.54, 4.68, 4.73, 4.75 (4 × d, 4 × 1H, 2 × H-2, 2 × H-3, $J_{2,3}$ = 5.6 Hz), 5.11, 5.13 (2 × s, 2 × 1H, 2 × H-1), 7.20–7.30 (m, 10H, aryl); ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.93, 19.96 (2C, 2 × acetyl–Me), 23.81, 25.09, 25.11 (4C, 4 × *i*Prdn–Me), 37.81, 37.86 (2C, 2 × C-1′), 45.36, 46.32 (2C, 2 × C-3′), 47.22, 47.26 (2C, 2 × C-2′), 63.61, 63.78, 68.75, 68.98 (4C, 2 × C-5, 2 × benzyl–OCH_2), 82.88, 82.98, 85.39 (4C, 2 × C-2, 2 × C-3), 85.92, 86.35 (2C, 2 × C-4), 106.70, 106.79 (2C, 2 × C-1), 112.02, 112.12 (2C, 2 × *i*Prdn), 126.75–136.18 (12C, aryl), 169.55 (2C, 2 × acetyl–CO_2).

3.4. Benzyl 5-*O*-acetyl-2,3-*O*-isopropylidene-4-*C*-(2-acetyloxy-3-phenylthiopropyl)-α-D-lyxofuranoside 5

A solution of **4** (89 mg, 235 μmol) in *tert*-butanol (2 mL) was treated with a solution of thiophenol (30 μL, 0.3 mmol) and potassium *tert*-butylate (45 mg, 0.4 mmol) in dimethylformamide (1 mL) and then heated under reflux for 12 h. For work-up the mixture was diluted with water, the organic phase washed with saturated sodium chloride solution and dried under reduced pressure. The remainder was acetylated with pyridine (5 mL) and acetic acid anhydride (5 mL) at room temperature and after work-up purified by column chromatography (petroleum ether/ethyl acetate 5:1) to give the diastereomeric mixture **5** (51 mg, 41%) as a yellow

syrup; $C_{28}H_{34}O_8S$ (530.6); EI: m/z = 530 (M^+); ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.24, 1.25, 1.30, 1.43 (4 × s, 4 × 3H, 4 × Me), 1.88, 1.89, 2.03, 2.05 (4 × s, 4 × 3H, 4 × OAc), 2.03, 2.29 (2 × m, 1H, 3H, 2 × CH_2), 2.96, 3.08, 3.20 (3 × m, 2H, 1H, 1H, 2 × SCH_2), 4.01, 4.09, 4.18, 4.23 (4 × d, 4 × 1H, 2 × H-5a, 2 × H-5b, $J_{5a,5b}$ = 11.7 Hz), 4.47 (d, 2H, OCH_2), 4.49, 4.61, 4.74, 4.77 (4 × d, 4 × 1H, 2 × H-2, 2 × H-3, $J_{2,3}$ = 5.9 Hz), 4.65, 4.79 (2 × d, 2 × 1H, OCH_2), 5.11, 5.16 (2 × s, 2 × 1H, 2 × H-1, $J_{1,2}$ = 0 Hz), 5.13, 5.28 (2 × m, 2 × 1H, 2 × H-2′), 7.15–7.40 (m, 20H, aryl); ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.84, 20.86, 20.93, 20.98 (4C, 4 × acetyl–Me), 24.54, 24.88, 25.92, 26.10 (4C, 4 × *i*Prdn–Me), 37.98, 38.38 (2C, 2 × C-l′), 63.67, 64.90 (2C, 2 × C-3′), 69.42, 69.51, 69.59, 70.02 (4C, 2 × C-5, 2 × benzyl–OCH_2), 77.20, 83.74, 84.40, 86.29, 86.34 (6C, 2 × C-2, 2 × C-3, 2 × C-2′), 86.68, 87.08 (2C, 2 × C-4) 107.23, 107.48 (2C, 2 × C-1), 113.03 (2C, 2 × *i*Prdn), 126.30–136.00 (24C, aryl).

3.5. Benzyl 5-*O*-acetyl-2,3-*O*-isopropylidene-4-*C*-(2,3-diacetyloxy-3-phenylthiopropyl)-α-D-lyxofuranoside 6

A solution of **5** (48 mg, 90 μmol) in anhydrous dichloromethane (2 mL) was treated at −78 °C with 3-chloroperbenzoic acid (80%, 20 mg, ca. 90 μmol) in dichloromethane (0.2 mL). After 5 min quenching was done with 1 M aqueous sodium hydroxide. The mixture was diluted with dichloromethane, and the organic phase washed with 1 M aqueous sodium hydroxide, water and saturated sodium chloride solution. The residue obtained after concentration to dryness was dissolved in acetic anhydride (1 mL), after which sodium acetate (45 mg, 0.5 mmol) was added and then heated to reflux overnight. The mixture was co-distilled with toluene to dryness, the residue suspended in dichloromethane, filtered and the filtrate washed with saturated sodium hydrogen carbonate solution, water and saturated sodium chloride solution. The remainder was taken to dryness under diminished pressure and the residue purified by column chromatography (petroleum ether/ethyl acetate 5:1) to give the diastereomeric mixture **6** as yellow syrup (35 mg, 66%); $C_{30}H_{36}O_{10}S$ (588.7); EI: m/z = 573 (M−Me); ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.24–1.46 (8s, 8 × 3H, 8 × Me), 1.97–2.12 (12 × s, 12 × 3H, 12 × OAc), 2.22–2.45 (m, 8H, 4 × CH_2), 4.04–4.89 (24H, 4 × OCH_2, 4 × H-2, 4 × H-3, 4 × H-5a, 4 × H-5b), 5.12, 5.15, 5.17, 5.19 (4 × s, 4 × 1H, 4 × H-1), 5.36, 5.44, 5.54 (3 × m, 1H, 1H, 2H, 4 × H-2′), 6.04, 6.08, 6.20, 6.22 (4 × d, 4 × 1H, 4 × H-3′), 7.26–7.50 (aryl); ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.80–21.05 (acetyl–Me), 24.64–26.06 (*i*Prdn–Me), 34.10, 34.37 (C-1′), 62.89, 63.57, 63.83, 68.46, 69.04, 69.10 (C-5, benzyl–OCH_2), 69.12, 69.62, 81.60–86.30 (C-2, C-3, C-2′, C-3′), 86.35–86.55 (C-4), 107.28, 107.39, 107.44 (C-1), 113.03, 113.10, 113.21 (*i*Prdn), 127.52–133.77 (aryl).

3.6. (2*S*,3*S*,4*R*,5*R*)-2-Benzyloxy-8,9-dihydroxy-3,4-isopropylidenedioxy-1,7-dioxa-spiro[4.5]-decane 7

A solution of compound **6** (30 mg, 0.05 mmol) in methanol (1 mL) was treated with sodium carbonate (13 mg, 0.13 mmol) at 0 °C with gradual warming to room temperature. After deacetylation, the solution was neutralized with Amberlite 120 H^+, the solution taken to dryness under reduced pressure and the residue purified by column chromatography (petroleum ether/ethyl acetate 2:1) to give the diastereomeric mixture **7** as yellow syrup (20 mg, 87%); $C_{18}H_{24}O_7$ (352.4); ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.18, 1.23, 1.39 (*i*Prdn–Me), 1.66, 1.82, 2.09, 2.39 (H-10), 3.63 (H-9), 3.93, 4.09 (H-6), 4.42 (H-3/H-4, benzyl–OCH_2), 4.65 (H-8), 4.72 (H-3/H-4), 4.78 (benzyl–OCH_2), 5.13, 5.15 (H-2); ^{13}C NMR (100 MHz, $CDCl_3$): δ 23.53, 24.84 (*i*Prdn–Me), 36.91 (C-10), 62.97, 66.22, 67.41, 69.02, 69.13 (C-6, C-9, benzyl–OCH_2), 82.76, 83.23, 83.62, 84.91 (C-3, C-4, C-5), 94.18 (C-8), 106.22 (C-2), 112.04 (*i*Prdn), 126.95–127.55 (aryl).

3.7. Methyl 3-*O*-allyl-2-*O*-benzyl-β-D-arabinopyranoside 8

A solution of methyl 2-*O*-benzyl-3,4-*O*-isopropylidene-β-D-arabinopyranoside[10] (1.76 g, 6 mmol) in aqueous acetic acid (80%, 6 mL) was stirred at room temperature overnight and then co-distilled with toluene under reduced pressure to dryness. The residue was dissolved in anhydrous toluene (35 mL) and heated with dibutyltinoxide (1.78 g, 7.1 mmol) under reflux. When a clear solution formed, the mixture was taken to dryness and the residue together with caesium fluoride (1.27 g, 8.4 mmol) suspended in anhydrous dimethylformamide (35 mL) and stirred with allylbromide (1.1 mL, 13 mmol) at room temperature. For work-up, the mixture was diluted with ethyl acetate, washed with water, dried, concentrated and the remainder purified by column chromatography (petroleum ether/ethyl acetate 10:1 to 2:1) to give **8** as a colourless syrup (1.3 g, 73%); $[\alpha]_D^{20} = -158.8$ (c 2.0, $CHCl_3$); $C_{16}H_{22}O_5$ (294.3); EI: m/z = 294 (M^+); ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.38 (s, 3H, OMe), 3.67–3.77 (m, 4H, H-2, H-3, H-5a, H-5b), 4.01 (br s, 1H, H-4), 4.17–4.27 (m, 2H, allyl–OCH_2), 4.64 (d, 1H, H-1, $J_{1,2}$ = 1.5 Hz), 4.65, 4.78 (2 × d, 2 × 1H, benzyl–OCH_2), 5.20, 5.31 (2 × m, 2 × 1H, =CH_2), 5.90–5.99 (m, 1H, =CH–), 7.27–7.37 (m, 5H, aryl); ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.44 (1C, OMe), 61.44, 71.57, 73.51 (3C, C-5, allyl–OCH_2, benzyl–OCH_2), 67.76, 75.65, 76.65 (3C, C-2, C-3, C-4), 99.12 (1C, C-1), 117.27 (1C, =CH_2), 127.78–138.46 (7C, =CH–, aryl).

3.8. Methyl 3-*O*-allyl-2-*O*-benzyl-β-D-*threo*-pent-4-ulopyranoside 9

A solution of oxalyl chloride (1 mL, 11.3 mmol) in anhydrous dichloromethane (10 mL) was cooled to −40 °C under argon and then treated with anhydrous dimethylsulfoxide (1.35 mL, 19 mmol). Compound **8** (1.3 g, 4.4 mmol) dissolved in dichloromethane (1 mL) was added over 6 h at −40 °C with stirring. For work-up the mixture was stirred with triethylamine (7 mL) for 30 min at room temperature, after which the mixture was poured into ice water and extracted with ethyl acetate. The organic phase was dried under reduced pressure and the remainder purified by column chromatography (petroleum ether/ethyl acetate 3:1 + 5% tri-

ethylamine) to give compound **9** as a colourless syrup (826 mg, 68%); $[\alpha]_D^{20} = -160.2$ (*c* 2.0, $CHCl_3$); $C_{16}H_{20}O_5$ (292.3); EI: *m/z* = 292 (M^+); ^1H NMR (400 MHz, $CDCl_3$): δ 3.46 (s, 3H, OMe), 3.73 (dd, 1H, H-2, $J_{2,3}$ = 10.0 Hz), 3.86, 4.01 (2 × d, 2 × 1H, H-5a, H-5b, $J_{5a,5b}$ = 14.8 Hz), 4.17–4.22, 4.40–4.45 (2 × m, 2 × 1H, allyl–OCH_2), 4.33 (d, 1H, H-3), 4.68, 4.86 (2 × d, 2 × 1H, benzyl–OCH_2), 4.74 (d, 1H, H-1, $J_{1,2}$ = 3.4 Hz), 5.21, 5.34 (2 × m, 2 × 1H, $=CH_2$), 5.92–6.02 (m, 1H, =CH–), 7.27–7.37 (m, 5H, aryl); ^{13}C NMR (100 MHz, $CDCl_3$): δ 56.12 (1C, OMe), 66.05, 73.58, 74.10 (3C, 3 × OCH_2), 79.60, 81.87 (2C, C-2, C-3), 98.88 (1C, C-1), 117.71 (1C $=CH_2$), 127.53–137.88 (7C, =CH–, aryl), 203.30 (1C, C-4).

3.9. Methyl 3-*O*-allyl-2-*O*-benzyl-4-deoxy-4-*C*-methylene-β-D-*threo*-pentopyranoside 10

A solution of methyltriphenylphosphoniumbromide (330 mg, 0.9 mmol) in anhydrous diethyl ether (3 mL) was treated under argon with *n*-butyllithium in hexane (1.6 M, 0.6 mL) to form under stirring a clear orange solution within 1 h at room temperature. After dropwise addition of a solution of **9** (180 mg, 0.6 mmol) in diethyl ether (1.5 mL), stirring was continued for 1 h. For work-up the formed viscous suspension was treated with water and extracted with ethyl acetate. The organic phase was taken to dryness under diminished pressure and the residue purified by column chromatography (petroleum ether/ethyl acetate 10:1) to give **10** as a colourless syrup (88 mg, 50%); $[\alpha]_D^{20} = -91.8$ (*c* 2.0, $CHCl_3$); $C_{17}H_{22}O_4$ (290.4); EI: *m/z* = 290 (M^+); ^1H NMR (400 MHz, $CDCl_3$): δ 3.41 (s, 3H, OMe), 3.42 (dd, 1H, H-2, $J_{2,3}$ = 9.0 Hz), 3.89 (d, 1H, H-5a, $J_{5a,5b}$ = 12.2 Hz), 4.19–4.26 (m, 4H, H-3, H-5b, allyl–OCH_2), 4.65 (d, 1H, H-1, $J_{1,2}$ = 3.9 Hz), 4.67, 4.84 (2 × d, 2 × 1H, benzyl–OCH_2), 5.00, 5.20 (2 × s, 2 × 1H, $=CH_2$), 5.18, 5.33 (2 × m, 2 × 1H, $=CH_2$), 5.92–6.02 (m, 1H, =CH–), 7.25–7.38 (m, 5H, aryl); ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.48 (1C, OMe), 63.67, 72.60, 73.67 (3C, C-5, allyl–OCH_2, benzyl–OCH_2), 78.24, 81.28 (2C, C-2, C-3), 99.76 (1C, C-1), 109.79 (1C $=CH_2$), 116.73 (1C, $=CH_2$), 127.73–138.52 (7C, =CH–, aryl), 142.48 (1C, C-4).

3.10. Methyl 2-*O*-benzyl-4-deoxy-4-*C*-methylene-β-D-*threo*-pentopyranoside 11

A solution of **10** (384 mg, 1.3 mmol) in methanol (70 mL) was treated with 4-toluenesulfonic acid (200 mg, 1.1 mmol) and palladium/charcoal (10%, 530 mg) and heated under reflux. After complete turnover, saturated sodium hydrogen carbonate solution was added, filtered and the filtrate extracted with dichloromethane. The organic phase was washed with saturated sodium hydrogen carbonate solution and water and then taken to dryness under reduced pressure. The remainder was purified by column chromatography (petroleum ether/ethyl acetate 10:1 to 5:1) to give **11** as a colourless syrup (236 mg, 72%); $[\alpha]_D^{20} = -118.5$ (*c* 1.0, $CHCl_3$); $C_{14}H_{18}O_4$ (250.3); ^1H NMR (400 MHz, $CDCl_3$): δ 3.32 (dd, 1H, H-2, $J_{2,3}$ = 9.7 Hz), 3.38 (s, 3H, OMe), 3.89, 4.24 (2 × d, 2 × 1H, H-5a, H-5b, $J_{5a,5b}$ = 12.2 Hz), 4.52 (d, 1H, H-3), 4.69 (s, 2H, OCH_2), 4.71 (d, 1H, H-1, $J_{1,2}$ = 3.4 Hz), 5.00, 5.23 (2 × s, 2 × 1H, $=CH_2$), 7.31–7.37 (m, 5H, aryl); ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.45 (1C, OMe), 63.32, 73.01 (2C, C-5, OCH_2) 69.58, 82.64 (2C, C-2, C-3), 98.43 (1C, C-1), 108.60 (1C, $=CH_2$), 128.11–137.93 (6C, aryl), 142.88 (1C, C-4).

3.11. Methyl 3-*O*-allyl-2-*O*-benzyl-β-L-arabinopyranoside 14

The synthesis is analogous to that of compound **8** by employing methyl-2-*O*-benzyl-3,4-*O*-isopropylidene-β-arabinopyranoside[14] (1.2 g, 4 mmol), aqueous acetic acid (80%, 5 mL), dibutyltinoxide (1.25 g, 5 mmol) and toluene (40 mL), dimethylformamide (40 mL), caesium fluoride (870 mg, 5.8 mmol) and allylbromide (0.76 mL, 9 mmol). Column chromatography (petroleum ether/ethyl acetate 5:1); yield (555 mg, 45%); colourless syrup; $[\alpha]_D^{20} = +67.7$ (*c* 1.0, $CHCl_3$); $C_{16}H_{22}O_5$ (294.3); ^1H NMR (400 MHz, $CDCl_3$): 3.31 (s, 3H, OMe), 3.63–3.71 (m, 4H, H-2, H-3, H-5a, H-5b), 3.94 (m, 1H, H-4), 4.10–4.17 (m, 2H, allyl–OCH_2) 4.57 (d, 1H, H-1, $J_{1,2}$ = 4.1 Hz), 4.59, 4.72 (2 × d, 2 × 1H, benzyl–OCH_2), 5.13, 5.24 (2 × m, 2 × 1H, $=CH_2$), 5.80–5.94 (m, 1H, =CH–), 7.19–7.30 (m, 5H, aryl); ^{13}C NMR (100 MHz, $CDCl_3$): δ 54.42 (1C, OMe), 60.39, 70.53 72.48 (3C, C-5, allyl–OCH_2, benzyl–OCH_2), 66.71, 74.57, 75.60 (3C, C-2, C-3, C-4), 98.07 (1C, C-1), 116.25 (1C, $=CH_2$), 126.60–137.41 (7C, =CH–, aryl).

3.12. Methyl 3-*O*-allyl-2-*O*-benzyl-β-L-*threo*-pent-4-ulopyranoside 15

The preparation was done analogously to that of compound **9** by employing compound **14** (536 mg, 1.8 mmol) in dichloromethane (0.5 mL); dichlormethane (4 mL), dimethylsulfoxide (0.54 mL, 7.6 mmol) and oxalylchloride (0.4 mL, 4.6 mmol); triethylamine (2.7 mL); column chromatography (petroleum ether/ethyl acetate 3:1 + 5% triethylamine); yield (300 mg, 56%) colourless syrup; $[\alpha]_D^{20} = +15.3$ (*c* 0.2, $CHCl_3$); $C_{16}H_{20}O_5$ (292.3); ^1H NMR (400 MHz, $CDCl_3$): δ 3.47 (s, 3H, OMe), 3.73 (dd, 1H, H-2, $J_{2,3}$ = 10.2 Hz), 3.87 (d, 1H, H-5a, $J_{5a,5b}$ = 14.8 Hz), 4.11 (d, 1H, H-5b), 4.18–4.23, 4.40–4.45 (2 × m, 2 × 1H, allyl–OCH_2), 4.33 (d, 1H, H-3), 4.69, 4.87 (2 × d, 2 × 1H, benzyl–OCH_2), 4.74 (d, 1H, H-1, $J_{1,2}$ = 3.4 Hz), 5.21, 5.34 (2 × m, 2 × 1H, $=CH_2$), 5.93–6.02 (m, 1H, =CH–), 7.28–7.38 (m, 5H, aryl); ^{13}C NMR (100 MHz, $CDCl_3$): δ 56.57 (1C, OMe), 66.48, 74.04 74.38 (3 C, C-5, allyl–OCH_2, benzyl–OCH_2) 79.99, 82.31 (2C, C-2, C-3), 99.31 (1C, C-1), 118.20 (1C, $=CH_2$), 128.42–138.26 (7C, =CH–, aryl), 203.80 (1C, C-4).

3.13. Methyl 3-*O*-allyl-2-*O*-benzyl-4-deoxy-4-*C*-methylene-β-L-*threo*-pentopyranoside 16

The synthesis is analogous to that of compound **10**. Employed are compound **15** (292 mg, 1 mmol) in diethyl ether (1 mL); methyltriphenylphosphoniumbromide (526 mg, 1.5 mmol) in diethyl ether (5 mL), and

n-butyllithium in hexane (1.6 M, 1 mL); column chromatography (petroleum ether/ethyl acetate 10:1), yield (117 mg, 40%); colourless syrup; $[\alpha]_D^{20} = +19.0$ (*c* 0.2, $CHCl_3$); $C_{17}H_{22}O_4$ (290.4); ^1H NMR (400 MHz, $CDCl_3$): δ 3.34 (s, 3H, OMe), 3.35 (dd, 1H, H-2, $J_{2,3} = 8.1$ Hz), 3.82 (d, 1H, H-5a, $J_{5a,5b} = 11.7$ Hz), 4.12–4.19 (m, 4H, H-3, H-5b, allyl–OCH_2), 4.57 (d, 1H, H-1, $J_{1,2} = 3.6$ Hz), 4.61, 4.77 ($2 \times$ d, $2 \times$ 1H, benzyl–OCH_2), 4.93, 5.11, 5.13, 5.26 ($4 \times$ m, $4 \times$ 1H, $2 \times$ =CH_2), 5.86–5.95 (m, 1H, =CH–), 7.19–7.31 (m, 5H, aryl); ^{13}C NMR (100 MHz, $CDCl_3$): δ 54.46 (1C, OMe), 62.63, 71.58, 72.64 (3C, C-5, allyl–OCH_2, benzyl–OCH_2), 77.20, 80.23 (2C, C-2, C-3), 98.72 (1C, C-1), 108.76, 115.72 (2C, $2 \times$ =CH_2), 126.70–137.48 (7C, =CH–, aryl), 141.43 (1C, C-4).

3.14. Methyl 2-*O*-benzyl-4-deoxy-4-*C*-methylene-β-L-*threo*-pentopyranoside 17

The preparation is analogous to that of compound **11**. Employed are compound **16** (112 mg, 0.4 mmol) in methanol (20 mL), 4-toluenesulfonic acid (60 mg, 0.3 mmol) and palladium/charcoal (10%, 150 mg); column chromatography (petroleum ether/ethyl acetate 5:1); yield (59 mg, 61%) colourless syrup; $[\alpha]_D^{20} = +62.4$ (*c* 0.5, $CHCl_3$); $C_{14}H_{18}O_4$ (250.3); ^1H NMR (400 MHz, $CDCl_3$): δ 3.25 (dd, 1H, H-2, $J_{2,3} = 9.9$ Hz), 3.32 (s, 3H, OMe), 3.83 (d, 1H, H-5a, $J_{5a,5b} = 12.7$ Hz), 4.17 (d, 1H, H-5b), 4.46 (d, 1H, H-3) 4.62 (s, 2H, benzyl–OCH_2) 4.64 (d, 1H, H-1, $J_{1,2} = 3.4$ Hz), 4.94, 5.16 ($2 \times$ br s, $2 \times$ 1H, =CH_2), 7.24–7.30 (m, 5H, aryl); ^{13}C NMR (100 MHz, $CDCl_3$): δ 54.42 (1C, OMe), 62.29, 71.98 (2C, C-5, benzyl–OCH_2) 68.55, 81.62 (2C, C-2, C-3), 97.41 (1C, C-1), 107.56 (1C, =CH_2), 127.07–136.41 (6C, aryl), 141.86 (1C, C-4).

3.15. Methyl 2-*O*-benzyl-4-deoxy-4-*C*-methylene-β-D-*threo*-pentopyranoside-3-yl-(benzyl 2,3-*O*-isopropylidene-α-D-lyxofuranoside)-uronate 12

A solution of compound **11** (212 mg, 0.85 mmol) and (benzyl 2,3-0-isopropylidene-α-D-lyxofuranoside)-uronate[4] (375 mg, 1.27 mmol) in anhydrous dichloromethane (35 mL) was treated with DMAP (21 mg, 0.17 mmol) and DCC (315 mg, 1.6 mmol) under ice cooling. With stirring, the mixture was warmed to room temperature. For work-up the filtrate was concentrated under reduced pressure and the remainder purified by column chromatography (petroleum ether/ethyl acetate 10:1) to give compound **12** (310 mg, 70%) as a colourless syrup; $[\alpha]_D^{20} = -52.3$ (*c* 1.0, $CHCl_3$); $C_{29}H_{34}O_9$ (526.6); ^1H NMR (400 MHz, $CDCl_3$): δ 1.30, 1.40 ($2 \times$ s, 2×3H, $2 \times$ Me), 3.43 (s, 3 H, OMe), 3.55 (dd, 1H, H-2′, $J_{2',3'} = 10.2$ Hz), 3.91, 4.31 ($2 \times$ d, $2 \times$ 1H, H-5′a, H-5′b, $J_{5'a,5'b} = 12.2$ Hz), 4.50 (d, 1H, H-4), 4.54 (d, 1H, OCH_2) 4.65 (s, 2H, OCH_2) 4.69 (d, 1H, H-2, $J_{2,3} = 5.6$ Hz), 4.73 (d, 1H, OCH_2), 4.77 (d, 1H, H-1′, $J_{1',2'} = 3.9$ Hz), 4.97 (br s, 1H, =OCH_2) 5.00 (dd, 1H, H-3, $J_{3,4} = 4.1$ Hz), 5.29 (s, 1H, H-1, $J_{1,2} = 0$ Hz), 5.31 (br s, 1H, =CH_2), 5.86 (d, 1H, H-3′), 7.22–7.37 (m, 10H, aryl); ^{13}C NMR (100 MHz, $CDCl_3$): δ 25.67, 26.39 (2C, $2 \times$ Me), 55.84 (1C, OMe), 63.76, 69.88, 73.54 (3C, C-5′, $2 \times$ benzyl–OCH_2) 73.37, 79.69, 79.98, 80.83, 84.87 (5C, C-2, C-3, C-4, C-2′, C-3′), 99.41 (1C, C-1′), 106.16 (1C, C-1), 110.82 (1C, =CH_2), 113.81 (1C, *i*Prdn), 128.20–138.55 (12C, aryl), 139.85 (1 C, C-4′), 166.63 (1C, C-5).

3.16. Methyl 2-*O*-benzyl-4-deoxy-4-*C*-methylene-β-L-*threo*-pentopyranoside-3-yl-(benzyl 2,3-*O*-isopropylidene-α-D-lyxofuranoside)-uronate 18

The synthesis is analogous to compound **12**. Employed are compound **17** (55 mg, 0.22 mmol), (benzyl 2,3-*O*-isopropylidene-α-D-lyxofuranoside)-uronate[4] (130 mg, 0.44 mmol), anhydrous dichloromethane (40 mL), DMAP (5 mg, 0.04 mmol) and DCC (108 mg, 0.52 mmol); yield of compound **18** after column chromatography (petroleum ether/ethyl acetate 10:1) 106 mg, 91%; colourless syrup; $[\alpha]_D^{20} = +38.7$ (*c* 1.0, $CHCl_3$); $C_{29}H_{34}O_9$ (526.6); ^1H NMR (400 MHz, $CDCl_3$): δ 1.25, 1.42 ($2 \times$ s, 2×3H, $2 \times$ Me), 3.42 (s, 3H, OMe), 3.60 (dd, 1H, H-2′, $J_{2',3'} = 9.7$ Hz), 3.93, 4.32 ($2 \times$ d, 2×1 H, H-5′a, H-5′b, $J_{5'a,5'b} = 12.2$ Hz), 4.51, 4.65 ($2 \times$ d, $2 \times$ 1H, OCH_2), 4.66 (d, 1H, H-1′, $J_{1',2'} = 3.1$ Hz), 4.68, 4.74 ($2 \times$ d, $2 \times$ 1H, H-2, H-4, $J_{2,3} = 4.1$ Hz), 4.69, 4.87 ($2 \times$ d, $2 \times$ 1H, OCH_2), 5.01, 5.03 ($2 \times$ br s, $2 \times$ 1H, =CH_2), 5.09 (dd, 1H, H-3, $J_{3,4} = 4.1$ Hz), 5.29 (s, 1H, H-1, $J_{1,2} = 0$ Hz), 5.88 (d, 1H, H-3′), 7.26–7.38 (m, 10H, aryl); ^{13}C NMR (100 MHz, $CDCl_3$): δ 25.34, 26.38 (2C, $2 \times$ Me), 55.93 (1C, OMe), 63.67, 69.79, 73.83 (3C, C-5′, $2 \times$ benzyl–OCH_2) 74.24, 78.84, 84.80, 81.04, 84.75 (5C, C-2, C-3, C-4, C-2′, C-3′), 99.95 (1C, C-1′), 106.30 (1C, C-1), 110.67 (1C, =CH_2), 113.81 (1C, *i*Prdn), 128.20–138.78 (12C, aryl), 139.87 (1C, C-4′), 166.81 (1C, C-5).

3.17. Methyl [benzyl 2,3-*O*-isopropylidene-4-*C*-(methyl 2-*O*-benzyl-3,4-dideoxy-α-L-*glycero*-pent-3-enopyranoside-4-yl)-methyl α-D-lyxofuranoside]-uronate 13a and methyl [benzyl 2,3-*O*-isopropylidene-4-*C*-(methyl 2-*O*-benzyl-3,4-dideoxy-α-L-*glycero*-pent-3-enopyranoside-4-yl)-methyl β-L-ribofuranoside]-uronate 13b

A solution of compound **12** (145 mg, 0.275 mmol) in anhydrous THF (1.5 mL) and HMPA (0.375 mL) was cooled under argon to −100 °C and treated with chlorotrimethylsilane (130 μL, 1.0 mmol). A freshly prepared and −78 °C precooled solution of lithium diisopropylamide obtained from diisopropylamine (84 μL, 0.64 mmol) in THF (0.5 mL) and *n*-butyllithium in hexane (1.6 M, 0.36 mL) was dropwise added such that the temperature could be maintained at −100 °C. After addition, the mixture was warmed to room temperature within 40 min and kept under stirring for 5 h. A solution of tetrabutylammonium fluoride in THF (1 M, 1.5 mL) was then added and stirring continued for 30 min. For work-up the mixture was diluted with diethyl ether and extracted with 1 M sodium hydroxide solution. The alkaline extracts were acidified with concd HCl and extracted with dichloromethane. After evaporation, the residue was dissolved in benzene (3 mL) and methanol (1 mL). Then a solution of trimethylsilyldiazomethane in hexane (2 M, 0.15 mL) was added and stirred

for 40 min. The reaction mixture was evaporated to dryness, purified and separated by column chromatography (petroleum ether/ethyl acetate 10:1).

Compound **13a**: 12 mg, 8%; yellowish syrup; $[\alpha]_D^{20} = -12.2$ (*c* 1.0, $CHCl_3$); $C_{30}H_{36}O_9$ (540.6); ^1H NMR (400 MHz, $CDCl_3$): δ 1.21, 1.34 (2 × s, 2 × 3H, 2 × Me), 2.49, 2.70 (2 × d, 2 × 1H, CH_2), 3.35, 3.68 (2 × s, 2 × 3H, 2 × OMe), 3.98 (br s, 1H, H-2′), 3.90, 4.10 (2 × d, 2 × 1H, H-5′a, H-5′b, $J_{5'a,5'b}$ = 16.1 Hz), 4.49 (d, 1H, OCH_2), 4.56 (s, 2H, OCH_2), 4.61 (s, 1H, H-1′), 4.63, 4.69 (2 × d, 2 × 1H, H-2, H-3, $J_{2,3}$ = 5.4 Hz), 4.74 (d, 1H, OCH_2), 5.31 (s, 1H, H-1, $J_{1,2}$ = 0 Hz), 5.53 (br s, 1H, H-3′), 7.14–7.29 (m, 10H, aryl); ^{13}C NMR (100 MHz, $CDCl_3$): δ 23.94, 24.96 (2C, 2 × Me), 40.01 (1C, CH_2), 51.24, 54.86 (2C, 2 × OMe), 61.79, 69.69, 70.13 (3C, C-5′, 2 × benzyl–OCH_2) 70.16, 84.15, 85.34 (3C, C-2, C-3, C-2′), 91.59 (1C, C-4), 95.91 (1C, C-1′), 107.68 (1C, C-1), 112.38 (1C, *i*Prdn), 121.11 (1C, C-3′), 126.67–137.38 (13C, C-4′, aryl), 168.57 (1C, C-5).

Compound **13b**: 11 mg, 7%; yellowish syrup; $[\alpha]_D^{20} = +25.7$ (*c* 1.0, $CHCl_3$); $C_{30}H_{36}O_9$ (540.6); H NMR (400 MHz, $CDCl_3$): δ 1.26, 1.39 (2 × s, 2 × 3H, 2 × Me), 2.49, 2.58 (2 × d, 2 × 1H, CH_2), 3.42, 3.45 (2 × s, 2 × 3H, 2 × OMe), 3.94 (s, 1H, H-2′), 3.96, 4.10 (2 × d, 2 × 1H, H-5′a, H-5′b, $J_{5'a,5'b}$ = 16.0 Hz), 4.41 (d, 1H, OCH_2), 4.57 (d, 1H, H-1′, $J_{1',2'}$ = 2.0 Hz), 4.59 (d, 1H, H-2, $J_{2,3}$ = 5.9 Hz), 4.63, 4.65 (2 × d, 3H, OCH_2), 4.98 (s, 1H, H-1, $J_{1,2}$ = 0 Hz), 5.19 (d, 1H, H-3), 5.42 (s, 1H, H-3′), 7.19–7.29 (m, 10H, aryl); ^{13}C NMR (100 MHz, $CDCl_3$): δ 23.83, 23.05 (2C, 2 × Me), 35.84 (1C, CH_2), 51.15, 54.81 (2C, 2 × OMe), 61.99, 68.17, 70.05 (3C, C-5′, 2 × benzyl–OCH_2) 70.17, 80.39, 84.24 (3 C, C-2, C-3, C-2′), 88.22 (1C, C-4), 96.16 (1C, C-1′), 104.77 (1C, C-1), 111.55 (1C, *i*Prdn), 121.89 (1C, C-3′), 126.64–137.45 (13C, C-4′, aryl), 171.14 (1C, C-5).

3.18. Methyl [benzyl 2,3-*O*-isopropylidene-4-*C*-(methyl 2-*O*-benzyl-3,4-dideoxy-α-D-*glycero*-pent-3-enopyranoside-4-yl)-methyl α-D-lyxofuranoside]-uronate 19a and methyl [benzyl 2,3-*O*-isopropylidene-4-*C*-(methyl 2-*O*-benzyl-3,4-dideoxy-α-D-*glycero*-pent-3-enopyranoside-4-yl)-methyl β-L-ribofuranoside]-uronate 19b

The synthesis and work-up is analogous to that for **13a** and **13b**. Employed are compound **18** (84 mg, 0.16 mmol); (a) THF (1 mL), HMPA (0.25 mL), chlorotrimethylsilane (90 μL, 0.71 mmol) diisopropylamine (56 μL, 0.43 mmol), in THF (0.5 mL), *n*-butyllithium in hexane (1.6 M, 0.25 mL); (b) tetrabutylammoniumfluoride in THF (1 M, 1 mL); (c) benzene (3 mL), methanol (1 mL), trimethylsilyldiazomethane in hexane (2 M, 0.1 mL); column chromatography (petroleum ether/ethyl acetate 5:1).

Compound **19a**: 19 mg, 22% yellowish syrup; $[\alpha]_D^{20} = +18.1$ (*c* 1.0, $CHCl_3$); $C_{30}H_{36}O_9$ (540.6); ^1H NMR (400 MHz, $CDCl_3$): δ 1.22, 1.34 (2 × s, 2 × 3H, 2 × Me), 2.53, 2.71 (2 × d, 2 × 1H, CH_2), 3.39, 3.73 (2 × s, 2 × 3H, 2 × OMe), 3.80 (d, 1H, H-5′a, $J_{5'a,5'b}$ = 16.1 Hz), 3.94 (br s, 1H, H-2′), 4.03 (d, 1H, H-5′b), 4.45 (d, 2H, OCH_2), 4.50 (d, 1H, H-2/H-3), 4.61 (d, 1H, H-1′, $J_{1',2'}$ = 2.0 Hz), 4.62 (d, 1H, OCH_2), 4.71 (d, 1H, H-2/H-3, $J_{2,3}$ = 6.1 Hz), 4.73 (d, 1H, OCH_2), 5.32 (s, 1H, H-1, $J_{1,2}$ = 0 Hz), 5.59 (s, 1H, H-3′), 7.17–7.29 (m, 10H, aryl); ^{13}C NMR (100 MHz, $CDCl_3$): δ 23.88, 24.88 (2C, 2 × Me), 39.86 (1C, CH_2), 51.43, 54.88 (2C, 2 × OMe), 61.67, 69.46, 69.88 (3C, C-5′, 2 × benzyl–OCH_2) 69.95, 84.12, 85.55 (3C, C-2, C-3, C-2′), 90.77 (1C, C-4), 96.25 (1C, C-1′), 107.32 (1C, C-1), 112.38 (1C, *i*Prdn), 121.12 (1C, C-3′), 126.55–137.45 (13C, C-4′, aryl), 169.00 (1C, C-5).

Compound **19b**: 15 mg, 17% yellowish syrup; $[\alpha]_D^{20} = +64.5$ (*c* 1.0, $CHCl_3$); $C_{30}H_{36}O_9$ (540.6); ^1H NMR (400 MHz, $CDCl_3$): δ 1.25, 1.39 (2 × s, 2 × 3H, 2 × Me), 2.41, 2.56 (2 × d, 2 × 1H, CH_2), 3.42, 3.46 (2 × s, 2 × 3H, 2 × OMe), 2.95 (br s, 1H, H-2′), 4.00, 4.16 (2 × d, 2 × 1H, H-5′a, H-5′b, $J_{5'a,5'b}$ = 16.3 Hz), 4.40 (d, 1H, OCH_2), 4.56 (d, 1H, H-2, $J_{2,3}$ = 5.9 Hz), 4.57 (s, 2H, OCH_2), 4.64 (d, 1H, H-1′, $J_{1',2'}$ = 3.1 Hz), 4.69 (d, 1H, OCH_2), 5.02 (s, 2H, H-1, $J_{1,2}$ = 0 Hz), 5.16 (d, 1, H-3), 5.44 (s, 1H, H-3′), 7.14–7.29 (m, 10H, aryl); ^{13}C NMR (100 MHz, $CDCl_3$): δ 23.79, 24.99 (2C, 2 × Me), 36.64 (1C, CH_2), 51.11, 54.82 (2C, 2 × OMe), 61.84, 68.20, 70.08 (3C, C-5′, 2 × benzyl–OCH_2) 70.11, 81.21, 83.87 (3C, C-2, C-3, C-2′), 88.59 (1C, C-4), 95.94 (1C, C-1′), 104.96 (1C, C-1), 111.57 (1C, *i*Prdn), 121.47 (1C, C-3′), 126.63–137.42 (13C, C-4′, aryl), 171.09 (1C, C-5).

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