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Note

Alkylalanes and methyl furanosides: regioselective O-debenzylation or acetal cleavage

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Abstract—Perbenzylated methyl pentofuranosides were submitted to the action of three alkylalanes and regioselective debenzylation at O-2 of the four pentoses was observed when choosing the right match between anomeric configuration and aluminium reagent. Diisobutylalane (DIBAL-H) allowed an easy access to reduced open-chain compounds, whereas trimethylalane (TMAL) stereoselectively produced methylated open chain derivatives.

Keywords: Furanose; Aluminium; Acetal cleavage; Regioselective deprotection

The regioselective access to a specific hydroxyl function is an important target in carbohydrate chemistry, usually achieved through protecting group manipulation. Among them, the benzyl group is particularly appreciated due to both its stability and to the mildness of its cleavage. Various strategies have thus been developed to regioselectively introduce it, but the selective debenzylation of easily obtainable polybenzylated compounds is an interesting alternative option.[1] In this context, we have shown that isobutylalanes could be very efficient agents of regioselective stripping of perbenzylated pyranosidic mono-, di- and even cyclic oligosaccharides.[2,3] We now report on the action of three alkylalanes on the four possible anomeric pairs of perbenzylated methyl D-pentofuranosides.

When submitted to the action of triisobutylalane (TIBAL), all methyl pentofuranosides[†] gave a complex mixture of compounds except for perbenzylated methyl β-D-lyxofuranoside **17** and β-D-arabinofuranoside **22** that both gave the products of selective O-debenzylation at O-2, **18** and **23**, respectively, in similar yields (48%). Upon reaction with diisobutylalane (DIBAL-H), almost all furanosidic compounds (**1**, **7**, **9**, **12**, **14**, **20** and **22**) gave the endocyclic reductive cleavage of the acetal functionality to afford the corresponding acyclic products (**2**, **2**, **10**, **10**, **15**, **21**, **24**, respectively). The only exception was the β-D-lyxofuranoside derivative **17** which gave a 1.1:1 mixture of 2-O and 3-O debenzylated products **18** and **19** in 75% yield. In the course of our studies on aluminium-promoted rearrangements, we also showed that trimethylalane (TMAL) was able to achieve an O-debenzylation reaction.[4] We therefore submitted the four pairs of D-pentofuranoside anomers, to the action of TMAL and two types of reactions occurred: (i) selective debenzylation at O-2 of β-ribofuranoside (**7**), α-xylofuranoside (**9**), β-lyxofuranoside (**17**) derivatives, or; (ii) stereoselective reductive cleavage of β-*xylo* (**12**) and α-*lyxo* (**14**) compounds resulting in methylated alditols.[5] In the three other cases, a mixture was obtained (Table 1).

Two reactions are therefore possible upon reaction between pentofuranosides and alkylalanes: regioselective O-monodebenzylation and acetal cleavage.

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† All methyl pentofuranosides were prepared by Fisher methanol glycosylation followed by perbenzylation. The structures were assigned by NMR spectroscopy according to Ref. 5.

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Table 1. Reactions of perbenzylated methyl pentofuranosides with TIBAL, DIBAL-H and TMAL

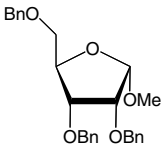
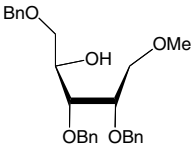
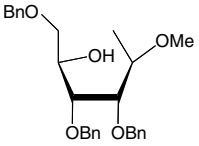
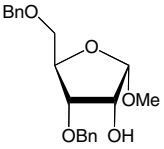
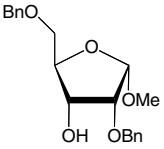
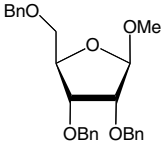
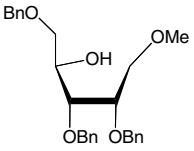
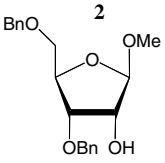
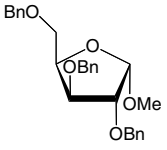
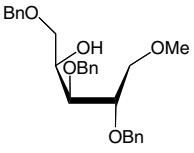
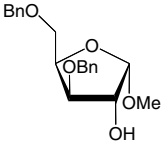
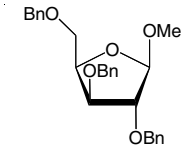
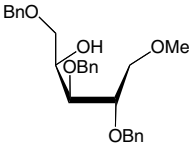
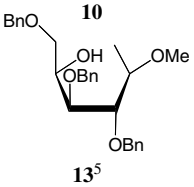
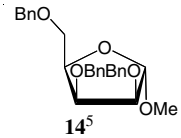
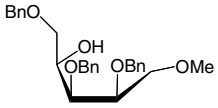
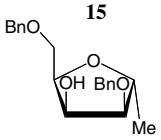
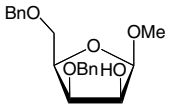
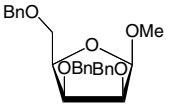
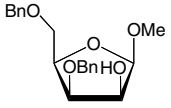
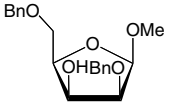
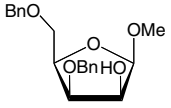
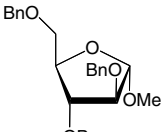
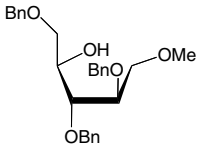
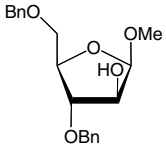
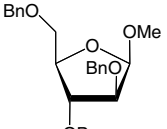
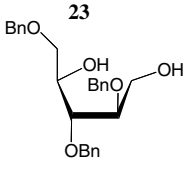
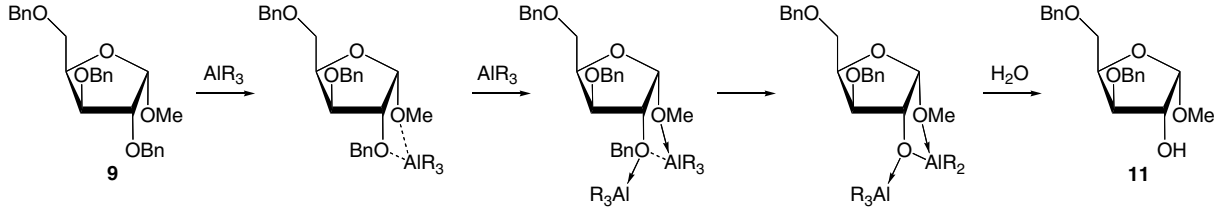
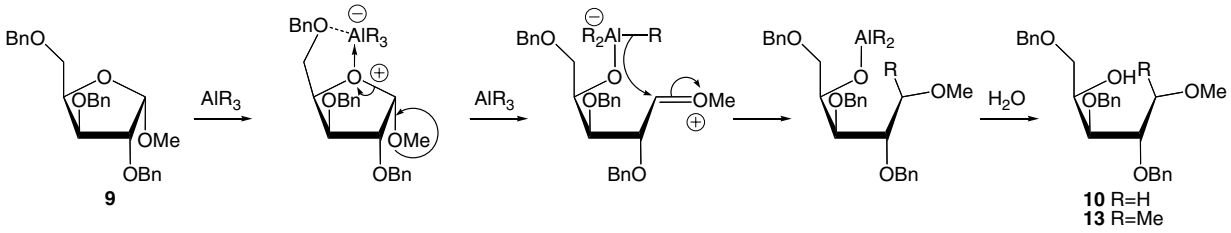
Substrates	Reagents and conditions	Results	Entry
 **1**[5]	TIBAL (5 equiv), 60 °C, toluene, 20 h	Mixture	1
	DIBAL-H (5 equiv), 60 °C, toluene, 1 h, 65%	 **2**	2
	TMAL (15 equiv), 50 °C, toluene, 20 h 43% **3/4** (1/3.8) 39% **5/6** (3.3/1)	 **3,4**[5]  **5**[6]  **6**	3
 **7**[5]	TIBAL (5 equiv), 60 °C, toluene, 80 h	Mixture	4
	DIBAL-H (6 equiv), 60 °C, toluene, 0.5 h, 60%	 **2**	5
	TMAL (15 equiv), 50 °C, toluene, 48 h, 38%	 **8**[7]	6
 **9**[5]	TIBAL (15 equiv), 60 °C, toluene, 2 h	Mixture	7
	DIBAL-H (5 equiv), 60 °C, toluene, 0.5 h, 72%	 **10**	8
	TMAL (15 equiv), 50 °C, toluene, 45 h, 40%	 **11**[5]	9
 **12**[5]	TIBAL (5 equiv), 60 °C, toluene, 42 h	Mixture	10
	DIBAL-H (5 equiv), 60 °C, toluene, 1 h, 75%	 **10**	11
	TMAL (15 equiv), 50 °C, toluene, 48 h, 50%	 **13**[5]	12

Table 1 (*continued*)

Substrates	Reagents and conditions	Results	Entry
	TIBAL (10 equiv), 60 °C, toluene, 12 h	Mixture	13
 **14**[5]	DIBAL-H (5 equiv), 60 °C, toluene, 15 min, 64%	 **15**	14
	TMAL (15 equiv), 50 °C, toluene, 96 h, 50%	 **16**	15
	TIBAL (5 equiv), 60 °C, toluene, 22 h, 48%	 **18**	16
 **17**[5]	DIBAL-H (5 equiv), 60 °C, toluene, 4 h 75%, **18/19** (1.1/1)	 **18**  **19**	17
	TMAL (15 equiv), 50 °C, toluene, 96 h, 74%	 **18**	18
	TIBAL (5 equiv), 60 °C, toluene, 18 h	Mixture	19
 **20**[5]	DIBAL-H (10 equiv), 60 °C, toluene, 15 h, 36%	 **21**	20
	TMAL (15 equiv), 50 °C, toluene, 42 h	Mixture	21
	TIBAL (15 equiv), 60 °C, toluene, 22 h, 48%	 **23**	22
 **22**[5]	DIBAL-H (5 equiv), 60 °C, toluene, 1 h, 31%	 **24**	23
	TMAL (15 equiv), 50 °C, toluene, 60 h	Mixture	24



Scheme 1. Proposed mechanism for aluminium induced deprotection.



Scheme 2. Proposed mechanism for endocleavage.

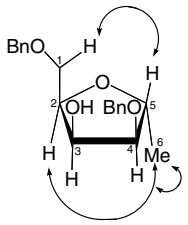


Figure 1. NOESY correlations for compound **16**.

Regioselective deprotection of benzyl groups, or their derivatives, has been reported on furanosides but often in particular cases.[8] Alkylalanes allow the access at O-2 of *ribo*, *xylo*, *lyxo* and *arabino* derivatives (entries 6, 9, 16–18 and 22). As previously proposed a vicinal-cis di-oxygenated pattern seems to be necessary for the debenzylation to occur, although the regioselectivity appears to be more difficult to explain in the case of furanosides compared to pyranosides. As recently proposed by us,[2] this O-dealkylation would start with the formation of a penta-coordinated complex between the aluminium reagent and the 1,2-cis oxygen pattern of the sugar. A second aluminium atom would then select the less hindered oxygen atom and direct the O-dealkylation. In the case of TIBAL and DIBAL-H, a molecule of toluene is probably formed, whereas the reaction with TMAL might lead to ethylbenzene (Scheme 1).

The deprotection reaction is in competition with Lewis acid induced endocyclic cleavage of furanosides.[9] When DIBAL-H is used, a reduced compound is obtained through complexation of the endocyclic oxygen and hydride transfer. The same mechanism applies to TMAL with stereoselective methyl addition, the configuration of the formed stereogenic centres has not been assigned (Scheme 2).

A noticeable difference in reactivity was observed with the *lyxo* derivative **14**. Upon reaction with TMAL the *C*-glycosyl derivative **16** was formed, probably via exo-cleavage and nucleophilic methylation of the transient carbenium. Absolute configuration at C-5 of **16** was assigned from NOESY experiment (Fig. 1).

Finally, it should be stressed that compound **22**, when reacted with DIBAL-H, results in the open chain compound **24** with loss of a methyl group. It is likely that this compound is formed via O-demethylation followed by reduction, because no further deacetalation product is observed in all other ring opening cases.

This systematic study of the reactivity of perbenzylated methyl pentofuranosides with three alkylalanes shows that it is possible to regioselectively O-debenzylate the four pentoses at O-2 when choosing the right match between anomeric configuration and aluminium reagent. DIBAL-H allows an easy access to open-chain compounds and TMAL can stereoselectively produce methylated open chain derivatives.

1. Experimental

1.1. General

Optical rotations were measured at 20 ± 2 °C with a Perkin–Elmer Model 241 digital polarimeter, using a 10 cm, 1 mL cell. Mass spectra (CI (ammonia) and FAB) were obtained with a JMS-700 spectrometer. ^{1}H NMR spectra were recorded with a Bruker DRX 400 for solns in $CDCl_3$ at ambient temperature. Assignments were confirmed by COSY experiments. ^{13}C NMR spectra were recorded at 100.6 MHz with a Bruker DRX 400 spectrometer for solns in $CDCl_3$ adopting 77.00 ppm for

the central line of $CDCl_3$. Assignments were confirmed by *J*-mode technique and HMQC. Reactions were monitored by thin-layer chromatography (TLC) on a precoated plate of Silica Gel 60 F_{254} (layer thickness 0.2 mm; E. Merck, Darmstadt, Germany) and detection by charring with H_2SO_4. Flash column chromatography was performed on Silica Gel 60 (230–400 mesh, E. Merck). DIBAL-H, TIBAL and TMAL were purchased from Aldrich as 1.5, 1 and 2 M solns in toluene, respectively.

1.2. Reaction of methyl 2,3,5-tri-*O*-benzyl-α-D-ribofuranoside (1) with DIBAL-H

To a soln of the perbenzylated furanoside derivative **1** (0.23 g, 0.53 mmol) in dry toluene (0.9 mL), a soln of DIBAL-H in toluene (1.8 mL, 2.7 mmol, 1.5 M) was added at room temperature under argon. The reaction mixture was heated at 60 °C for 1 h. When TLC indicated the presence of a major product, the reaction was carefully quenched with toluene saturated with water and then aq NaOH (10%) was added at 0 °C. The products were extracted with DCM and the organic layers were combined, dried and concentrated. The resulting residue was submitted to flash column chromatography (4:1, cyclohexane–EtOAc) to afford **2** (0.15 g, 0.34 mmol, 65%).

1.2.1. 2,3,5-Tri-*O*-benzyl-1-*O*-methyl-D-ribitol (2). $[\alpha]_D^{20}$ +10 (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 7.39–7.29 (m, 15H, H-arom.), 4.78 (d, 1H, *J* 11.8 Hz, CHPh), 4.75 (d, 1H, *J* 11.3 Hz, CHPh), 4.66 (d, 1H, *J* 11.8 Hz, CHPh), 4.62 (d, 1H, *J* 11.3 Hz, CHPh), 4.59 (d, 1H, *J* 12.0 Hz, CHPh), 4.55 (d, 1H, *J* 12.0 Hz, CHPh), 4.04 (m, 1H, H-2), 3.95 (q, 1H, *J* 4.4 Hz, H-4), 3.81 (dd, 1H, $J_{3,4}$ 4.2, $J_{3,2}$ 6.9 Hz, H-3), 3.77 (dd, 1H, $J_{5,4}$ 4.2, $J_{5,5}$ 10.3 Hz, H-5), 3.68–3.61 (m, 3H, H-5, 2H-1), 3.41 (s, 3H, OCH_3), 2.92 (d, 1H, *J* 4.4 Hz, 4-OH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.33, 138.31, 138.0 (3C-quat. arom.), 128.4–127.6 (15C-arom.), 79.0 (C-3), 78.7 (C-4), 73.8 (CH_2Ph), 73.4 (CH_2Ph), 72.4 (CH_2Ph), 71.8 (C-5), 71.2 (C-1), 70.9 (C-2), 59.1 (OMe); HRCIMS: Calcd for $C_{27}H_{36}O_5N$ $[M+NH_4]^+$: 454.2594. Found: *m*/*z* 454.2601.

1.3. Reaction of methyl 2,3,4-tri-*O*-benzyl-α-D-ribofuranoside (1) with TMAL

To a soln of the perbenzylated furanoside **1** (54 mg, 0.12 mmol) in dry toluene (0.8 mL), a soln of TMAL in toluene (0.96 mL, 1.92 mmol, 2 M) was added at room temperature under argon. The reaction mixture was heated at 60 °C for 20 h. When TLC indicated the presence of major products, the reaction was carefully quenched with toluene saturated with water and then aq NaOH (10%) was added at 0 °C. The products were extracted with DCM and the organic layers were combined, dried and concentrated. The resulting residue was submitted to a flash column chromatography (8:1–5:1, cyclohexane–EtOAc) to afford the acyclic compound **3** (5 mg, 0.011 mmol, 9%), its isomer **4** (19 mg, 0.042 mmol, 34%), alcohol **5** (13 mg, 0.038 mmol, 30%) and its regioisomer **6** (4 mg, 0.012 mmol, 9%).

1.3.1. 3,4,6-Tri-*O*-benzyl-1-deoxy-2-*O*-methyl-D-allitol or altritol (3). $[\alpha]_D^{20}$ +20 (*c* 0.4, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 7.38–7.30 (m, 15H, H-arom.), 4.74 (d, 1H, *J* 11.5 Hz, CHPh), 4.70 (d, 1H, *J* 11.5 Hz, CHPh), 4.69 (d, 1H, *J* 11.4 Hz, CHPh), 4.61 (d, 1H, *J* 11.4 Hz, CHPh), 4.59 (d, 1H, *J* 12.0 Hz, CHPh), 4.55 (d, 1H, *J* 12.0 Hz, CHPh), 4.12–4.07 (m, 1H, H-5), 3.77–3.72 (m, 2H, H-4, H-3), 3.71–3.62 (m, 3H, 2H-6, H-2), 3.23 (d, 1H, $J_{OH,5}$ 3.6 Hz, 5-OH), 1.25 (d, 3H, $J_{1,2}$ 6.0 Hz, 3H-1); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.3, 138.26, 138.1 (3C-quat. arom.), 128.4–127.6 (15C-arom.), 81.5 (C-3), 78.9 (C-4), 77.2 (C-2), 73.5 (CH_2Ph), 73.4 (CH_2Ph), 73.3 (CH_2Ph), 71.3 (C-6), 71.2 (C-5), 56.6 (OCH_3), 15.1 (C-1); HRCIMS: Calcd for $C_{28}H_{35}O_5$ $(M+H)^+$: 451.2484. Found: *m*/*z* 451.2480.

1.3.2. 3,4,6-Tri-*O*-benzyl-1-deoxy-2-*O*-methyl-D-allitol or altritol (4). $[\alpha]_D^{20}$ +17 (*c* 0.9, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 7.38–7.30 (m, 15H, H-arom.), 4.77 (d, 1H, *J* 11.5 Hz, CHPh), 4.72 (d, 1H, *J* 11.5 Hz, CHPh), 4.66 (d, 1H, *J* 11.3 Hz, CHPh), 4.62 (d, 1H, *J* 11.3 Hz, CHPh), 4.59 (d, 1H, *J* 11.7 Hz, CHPh), 4.55 (d, 1H, *J* 11.7 Hz, CHPh), 4.19 (m, 1H, H-2), 3.82 (d, 1H, $J_{3,5}$ 6.3, $J_{3,4}$ 4.1 Hz, H-4), 3.74 (dd, 1H, $J_{6,5}$ 3.0, $J_{6,6'}$ 9.8 Hz, H-6), 3.70 (dd, 1H, $J_{6',5}$ 6.2, $J_{6',6}$ 9.8 Hz, H-6′), 3.68–3.64 (m, 2H, H-3, H-2), 3.40 (s, 3H, OCH_3), 3.17 (d, 1H, $J_{OH,5}$ 3.5 Hz, 5-OH), 1.25 (d, 3H, $J_{1,2}$ 6.2 Hz, 3H-1); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.34, 138.28, 138.2 (3C-quat. arom.), 128.4–127.6 (15C-arom.), 82.6 (C-3), 80.0 (C-4), 77.4 (C-2), 74.4 (CH_2Ph), 73.4 (CH_2Ph), 73.3 (CH_2Ph), 71.4 (C-6), 71.0 (C-5), 56.9 (OCH_3), 15.8 (C-1); HRCIMS: Calcd for $C_{28}H_{35}O_5$ $(M+H)^+$: 451.2484. Found: *m*/*z* 451.2483.

1.3.3. Methyl 3,5-di-*O*-benzyl-α-D-ribofuranoside (5). $[\alpha]_D^{20}$ +72 (*c* 0.8, $CHCl_3$), lit.[6] $[\alpha]_D^{20}$ +67 (*c* 1, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 7.38–7.29 (m, 10H, H-arom.), 4.93 (d, 1H, $J_{1,2}$ 4.7 Hz, H-1), 4.77 (d, 1H, *J* 12.4 Hz, CHPh), 4.62 (d, 1H, *J* 12.4 Hz, CHPh), 4.55 (d, 1H, *J* 12.1 Hz, CHPh), 4.49 (d, 1H, *J* 12.1 Hz, CHPh), 4.20 (q, 1H, $J_{4,3}$ 3.2, $J_{4,5}$ 4.0 Hz, H-4), 4.16 (ddd, 1H, $J_{2,OH}$ 11.2, $J_{2,1}$ 4.8, $J_{2,3}$ 7.2 Hz, H-2), 3.83 (dd, 1H, $J_{3,2}$ 7.2, $J_{3,4}$ 3.2 Hz, H-3), 3.52 (s, 3H, OCH_3), 3.48 (dd, 1H, $J_{5,4}$ 4.0, $J_{5,5'}$ 10.3 Hz, H-5), 3.40 (dd, 1H, $J_{5',4}$ 4.0, $J_{5',5}$ 10.3 Hz, H-5′), 2.99 (d, 1H, $J_{OH,2}$ 11.2 Hz, 2-OH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.85, 137.8 (2C-quat. arom.), 128.6–127.6 (10C-arom.), 103.0 (C-1), 82.0 (C-4), 76.3 (C-3), 73.5

(CH_2Ph), 73.0 (CH_2Ph), 71.8 (C-2), 70.0 (C-5), 55.7 (OCH_3); HRCIMS: Calcd for $C_{20}H_{28}O_5N$ $(M+NH_4)^+$: 362.1968. Found: *m*/*z* 362.1973.

1.3.4. Methyl 2,5-di-*O*-benzyl-α-D-ribofuranoside (6). $[\alpha]_D^{20}$ +30 (*c* 0.4, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 7.39–7.30 (m, 10H, H-arom.), 4.95 (d, 1H, $J_{1,2}$ 4.1 Hz, H-1), 4.79 (d, 1H, *J* 11.9 Hz, CHPh), 4.65 (d, 1H, *J* 11.9 Hz, CHPh), 4.59 (d, 1H, *J* 12.2 Hz, CHPh), 4.52 (d, 1H, *J* 12.2 Hz, CHPh), 4.30 (dt, 1H, $J_{3,4}$ 1.9, $J_{4,5}$ 3.6 Hz, H-4), 4.10 (ddd, 1H, $J_{3,4}$ 1.9, $J_{3,2}$ 6.0, $J_{3,OH}$ 8.9 Hz, H-3), 3.95 (dd, 1H, $J_{2,1}$ 4.1, $J_{2,3}$ 6.0 Hz, H-2), 3.60 (d, 2H, $J_{5,4}$ 3.7 Hz, 2H-5), 3.47 (s, 3H, OCH_3), 3.06 (d, 1H, $J_{OH,3}$ 8.9 Hz, 3-OH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.9, 137.2 (2C-quat. arom.), 128.5–127.5 (10C-arom.), 102.6 (C-1), 85.5 (C-4), 77.1 (C-2), 73.5 (CH_2Ph), 72.3 (CH_2Ph), 70.2 (C-5), 70.0 (C-3), 55.1 (OCH_3); HRCIMS: Calcd for $C_{20}H_{28}O_5N$ $[M+NH_4]^+$: 362.1968. Found: *m*/*z* 362.1973.

1.4. Reaction of methyl 2,3,5-tri-*O*-benzyl-β-D-ribofuranoside (7) with DIBAL-H

To a soln of the perbenzylated furanoside derivative **7** (0.3 g, 0.69 mmol) in dry toluene (3 mL), a soln of DIBAL-H in toluene (2.7 mL, 4.1 mmol, 1.5 M) was added at room temperature under argon. The reaction mixture was heated at 60 °C for 0.5 h. When TLC indicated the presence of a major product, the reaction was carefully quenched with aq NaOH (10%) at 0 °C. The products were extracted with DCM and the organic layers were combined, dried and concentrated. The resultant residue was submitted to a flash column chromatography (4:1, cyclohexane–EtOAc) to afford **2** (0.18 g, 0.41 mmol, 60%).

1.5. Reaction of methyl 2,3,5-tri-*O*-benzyl-β-D-ribofuranoside (7) with TMAL

To a soln of the perbenzylated furanoside derivative **7** (143 mg, 0.33 mmol) in dry toluene (7 mL), a soln of TMAL in toluene (3.5 mL, 7.0 mmol, 2 M) was added at room temperature under argon. The reaction mixture was heated at 60 °C for 48 h. When TLC indicated the presence of a major product, the reaction was carefully quenched with toluene saturated with water and then aq NaOH (10%) was added at 0 °C. The products were extracted with DCM and the organic layers were combined, dried and concentrated. The resultant residue was submitted to a flash column chromatography (4:1, cyclohexane–EtOAc) to afford **8** (43 mg, 0.13 mmol, 38%).

1.5.1. Methyl 3,5-di-*O*-benzyl-β-D-ribofuranoside (8). $[\alpha]_D^{20}$ −20 (*c* 1.0, $CHCl_3$), lit.[7] $[\alpha]_D^{20}$ −23 (*c* 0.5, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 7.39–7.30 (m, 10H, H-arom.), 4.91 (s, 1H, H-1), 4.62 (s, 4H, $2CH_2Ph$), 4.28 (q, 1H, $J_{4,3} = J_{4,5} = J_{4,5'}$ 5.6 Hz, H-4), 4.12 (dd, 1H, $J_{3,2}$ 4.9, $J_{3,4}$ 6.2 Hz, H-3), 4.08–4.06 (m, 1H, H-2), 3.588 (d, 1H, $J_{5,4}$ 5.1 Hz, H-5), 3.587 (d, 1H, $J_{5',4}$ 5.8 Hz, H-5′), 3.36 (s, 3H, OCH_3), 2.76 (d, 1H, $J_{OH,2}$ 3.2 Hz, 2-OH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.1, 137.0 (2C-quat. arom.), 128.4–127.6 (10C-arom.), 108.5 (C-1), 80.5 (C-4), 79.5 (C-3), 73.3 (C-2), 73.2 (CH_2Ph), 72.7 (CH_2Ph), 71.6 (C-5), 55.0 (OCH_3). FABMS: calcd 344.2 for $C_{20}H_{24}O_5$. Found: *m*/*z* 367.2 $(M+Na)^+$.

1.6. Reaction of methyl 2,3,5-tri-*O*-benzyl-α-D-xylofuranoside (9) with DIBAL-H

To a soln of the perbenzylated furanoside derivative **9** (0.10 g, 0.24 mmol) in dry toluene (1 mL), a soln of DIBAL-H in toluene (0.79 mL, 1.2 mmol, 1.5 M) was added at room temperature under argon. The reaction mixture was heated at 60 °C for 0.5 h. When TLC indicated the presence of a major product, the reaction was carefully quenched with aq NaOH (10%) at 0 °C. The products were extracted with DCM and the organic layers were combined, dried and concentrated. The resultant residue was submitted to a flash column chromatography (5:1, cyclohexane–EtOAc) to afford product **10** (75 mg, 0.17 mmol, 72%).

1.6.1. 2,3,5-Tri-*O*-benzyl-1-*O*-methyl-D-xylitol (10). $[\alpha]_D^{20}$ −6 (*c* 0.9, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 7.40–7.30 (m, 15H, H-arom.), 4.78 (d, 1H, *J* 11.4 Hz, CHPh), 4.76 (d, 1H, *J* 11.8 Hz, CHPh), 4.65 (d, 1H, *J* 11.8 Hz, CHPh), 4.60 (d, 1H, *J* 11.4 Hz, CHPh), 4.56 (d, 1H, *J* 11.9 Hz, CHPh), 4.50 (d, 1H, *J* 11.9 Hz, CHPh), 4.05 (td, 1H, $J_{2,3}$ 2.5, $J_{2,1} = J_{2,1}$ 6.1 Hz, H-2), 3.85 (dt, 1H, $J_{4,3}$ 5.9, $J_{4,5} = J_{4,5'}$ 4.4 Hz, H-4), 3.78 (dd, 1H, $J_{3,4}$ 5.9, $J_{3,2}$ 2.5 Hz, H-3), 3.68 (dd, 1H, $J_{5,4}$ 4.4, $J_{5,5'}$ 10.6 Hz, H-5), 3.65 (dd, 1H, $J_{5',4}$ 4.4, $J_{5',5}$ 10.6 Hz, H-5′), 3.55 (dd, 1H, $J_{1,2}$ 6.3, $J_{1,1}$ 9.4 Hz, H-1), 3.49 (dd, 1H, $J_{1,2}$ 6.0, $J_{1,1}$ 9.4 Hz, H-1), 3.41 (s, 3H, OCH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.3, 138.1, 138.0 (3C-quat. arom.), 128.3–127.6 (15C-arom.), 78.6 (C-4), 78.0 (C-3), 74.5 (CH_2Ph), 73.2 (CH_2Ph), 72.8 (CH_2Ph), 71.9 (C-5), 71.2 (C-1), 69.4 (C-2), 59.2 (OMe); HRCIMS: Calcd for $C_{27}H_{36}O_5N$ $[M+NH_4]^+$: 454.2594. Found: *m*/*z* 454.2586.

1.7. Reaction of methyl 2,3,5-tri-*O*-benzyl-α-D-xylofuranoside (9) with TMAL

To a soln of the perbenzylated furanoside derivative **9** (110 mg, 0.25 mmol) in dry toluene (1.5 mL), a soln of TMAL in toluene (0.70 mL, 1.4 mmol, 2 M) was added at room temperature under argon. The reaction mixture was heated at 60 °C for 45 h. When TLC indicated the presence of a major product, the reaction was carefully

quenched with toluene saturated with water and then aq NaOH (10%) was added at 0 °C. The products were extracted with DCM and the organic layers were combined, dried and concentrated. The resultant residue was submitted to a flash column chromatography (5:1, cyclohexane–EtOAc) to afford **11** (34 mg, 0.10 mmol, 40%).

1.7.1. Methyl 3,5-di-*O*-benzyl-α-D-xylofuranoside (11). $[\alpha]_D^{20}$ +65 (*c* 0.6, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 7.39–7.30 (m, 10H, H-arom.), 5.04 (d, 1H, $J_{1,2}$ 4.7 Hz, H-1), 4.78 (d, 1H, *J* 12.0 Hz, CHPh), 4.68 (d, 1H, *J* 12.1 Hz, CHPh), 4.60 (d, 1H, *J* 12.0 Hz, CHPh), 4.58 (d, 1H, *J* 12.1 Hz, CHPh), 4.44 (dt, 1H, $J_{4,3}$ 6.3, $J_{4,5}$ 4.2, $J_{4,5'}$ 6.4 Hz, H-4), 4.31 (dt, 1H, $J_{2,OH}$ 7.4, $J_{2,1} = J_{2,3}$ 4.4 Hz, H-2), 4.05 (dd, 1H, $J_{3,2}$ 4.1, $J_{3,4}$ 6.0 Hz, H-3), 3.78 (dd, 1H, $J_{5,4}$ 4.2, $J_{5,5'}$ 10.6 Hz, H-5), 3.70 (dd, 1H, $J_{5',4}$ 6.7, $J_{5',5}$ 10.6 Hz, H-5′), 3.54 (s, 3H, OCH_3), 2.65 (d, 1H, $J_{2,OH}$ 7.4 Hz, 2-OH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.2, 137.9 (2C-quat. arom.), 128.3–127.5 (10C-arom.), 101.7 (C-1), 83.5 (C-3), 77.3 (C-4), 76.9 (C-2), 73.4 (CH_2Ph), 71.8 (CH_2Ph), 69.0 (C-5), 55.7 (OCH_3); HRCIMS: Calcd for $C_{20}H_{25}O_5$ $[M+H]^+$: 345.1702. Found: *m*/*z* 345.1701.

1.8. Reaction of methyl 2,3,5-tri-*O*-benzyl-β-D-xylofuranoside (12) with DIBAL-H

To a soln of the perbenzylated furanoside derivative **12** (0.23 g, 0.52 mmol) in dry toluene (1 mL), a soln of DIBAL-H in toluene (1.8 mL, 2.7 mmol, 1.5 M) was added at room temperature under argon. The reaction mixture was heated at 60 °C for 1 h. When TLC indicated the presence of a major product, the reaction was carefully quenched with aq NaOH (10%) at 0 °C. The products were extracted with DCM and the organic layers were combined, dried and concentrated. The resultant residue was submitted to a flash column chromatography (5:1, cyclohexane–EtOAc) to afford **10** (0.17 g, 0.39 mmol, 75%).

1.9. Reaction of methyl 2,3,5-tri-*O*-benzyl-β-D-xyloside (12) with TMAL

To a soln of the perbenzylated furanoside derivative **12** (53 mg, 0.12 mmol) in dry toluene (0.8 mL), a soln of TMAL in toluene (0.92 mL, 1.84 mmol, 2 M) was added at room temperature under argon. The reaction mixture was heated at 60 °C for 48 h. When TLC indicated the presence of a major product, the reaction was carefully quenched with toluene saturated with H_2O and then aqueous NaOH soln (10%) at 0 °C. The products were extracted with DCM and the organic layers were combined, dried and concentrated. The resultant residue was submitted to a flash column chromatography (7:1, cyclohexane–EtOAc) to afford **13** (27 mg, 0.06 mmol, 50%).

1.9.1. 3,4,6-Tri-*O*-benzyl-1-deoxy-2-*O*-methyl-D-gulitol or iditol (13). $[\alpha]_D^{20}$ −17 (*c* 0.6, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 7.38–7.28 (m, 15H, H-arom.), 4.81 (d, 1H, *J* 11.3 Hz, CHPh), 4.78 (d, 1H, *J* 11.3 Hz, CHPh), 4.70 (d, 1H, *J* 11.3 Hz, CHPh), 4.57 (d, 1H, *J* 11.3 Hz, CHPh), 4.54 (d, 1H, *J* 11.3 Hz, CHPh), 4.49 (d, 1H, *J* 11.3 Hz, CHPh), 3.95 (dq, 1H, $J_{5,4}$ 2.5, $J_{5,6} = J_{5,6'} = J_{5,OH}$ 6.3 Hz, H-5), 3.81 (dd, 1H, $J_{4,3}$ 6.4, $J_{3,2}$ 4.3 Hz, H-3), 3.71 (dd, 1H, $J_{4,5}$ 2.5, $J_{3,4}$ 6.4 Hz, H-4), 3.59 (dq, 1H, $J_{2,3}$ 4.3, $J_{2,1}$ 6.4 Hz, H-2), 3.55 (dd, 1H, $J_{6,5}$ 6.2, $J_{6,6'}$ 9.3 Hz, H-6), 3.49 (dd, 1H, $J_{6',5}$ 6.3, $J_{6',6}$ 9.3 Hz, H-6′), 3.38 (s, 3H, OCH_3), 2.79 (d, 1H, $J_{OH,5}$ 6.3 Hz, 5-OH), 1.31 (d, 3H, $J_{1,2}$ 6.3 Hz, 3H-1); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.6, 138.3, 138.0 (3C-quat. arom.), 128.4–127.5 (15C-arom.), 81.5 (C-3), 79.0 (C-4), 77.9 (C-2), 74.9 (CH_2Ph), 74.3 (CH_2Ph), 73.3 (CH_2Ph), 71.2 (C-6), 70.0 (C-5), 56.4 (OCH_3), 14.9 (C-1); HRCIMS: Calcd for $C_{28}H_{35}O_5$ $[M+H]^+$: 451.2484. Found: *m*/*z* 451.2480.

1.10. Reaction of methyl 2,3,5-tri-*O*-benzyl-α-D-lyxofuranoside (14) with DIBAL-H

To a soln of the perbenzylated furanoside derivative **14** (138 mg, 0.32 mmol) in dry toluene (0.6 mL), a soln of DIBAL-H in toluene (1.23 mL, 1.8 mmol, 1.5 M) was added at room temperature under argon. The reaction mixture was heated at 60 °C for 15 min. When TLC indicated the presence of a major product, the reaction was carefully quenched with aq NaOH (10%) at 0 °C. The products were extracted with DCM and the organic layers were combined, dried and concentrated. The resultant residue was submitted to a flash column chromatography (5:1–3:1, cyclohexane–EtOAc) to afford **15** (0.07 g, 0.16 mmol, 51%).

1.10.1. 1,3,4-Tri-*O*-benzyl-5-*O*-methyl-D-arabinitol (15). $[\alpha]_D^{20}$ −16 (*c* 0.9, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 7.38–7.30 (m, 15H, H-arom.), 4.86 (d, 1H, *J* 11.7 Hz, CHPh), 4.71 (d, 1H, *J* 11.3 Hz, CHPh), 4.68 (d, 1H, *J* 11.7 Hz, CHPh), 4.56 (d, 1H, *J* 12.0 Hz, CHPh), 4.56 (d, 1H, *J* 11.3 Hz, CHPh), 4.51 (d, 1H, *J* 12.0 Hz, CHPh), 4.09 (td, 1H, $J_{4,3}$ 2.2, $J_{4,5} = J_{4,5'}$ 6.0 Hz, H-4), 3.84 (dt, 1H, $J_{2,3}$ 6.3, $J_{2,1} = J_{2,1'}$ 3.6 Hz, H-2), 3.81 (dd, 1H, $J_{3,4}$ 2.4, $J_{3,2}$ 6.3 Hz, H-3), 3.69 (dd, 1H, $J_{1,2}$ 3.4, $J_{1,1'}$ 10.3 Hz, H-1), 3.63 (dd, 1H, $J_{1',2}$ 4.2, $J_{1,1'}$ 10.3 Hz, H-1′), 3.58 (dd, 1H, $J_{5,4}$ 6.1, $J_{5,5'}$ 9.6 Hz, H-5), 3.53 (dd, 1H, $J_{5',4}$ 5.9, $J_{5',5}$ 9.6 Hz, H-5′), 3.40 (s, 3H, OCH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.0 (3C-quat. arom.), 128.4–127.6 (15C-arom.), 78.3 (C-2), 77.3 (C-3), 73.9 (CH_2Ph), 73.3 (CH_2Ph), 72.6 (CH_2Ph), 71.4 (C-1), 71.3 (C-5), 69.7 (C-4), 59.1 (OMe); HRCIMS: Calcd for $C_{27}H_{32}O_5N$ $[M+NH_4]^+$: 454.2594. Found: *m*/*z* 454.2599.

1.11. Reaction of methyl 2,3,5-tri-*O*-benzyl-α-D-lyxofuranoside (14) with TMAL

To a soln of the perbenzylated furanoside derivative **14** (96 mg, 0.22 mmol) in dry toluene (1.3 mL), a soln of TMAL in toluene (1.65 mL, 3.3 mmol, 2 M) was added at room temperature under argon. The reaction mixture was heated at 60 °C for 96 h. When TLC indicated the presence of major products, the reaction was carefully quenched with toluene saturated with water and then aq NaOH (10%) was added at 0 °C. The products were extracted with DCM and the organic layers were combined, dried and concentrated. The resultant residue was submitted to a flash column chromatography (6:1, cyclohexane–EtOAc) to afford **16** (36 mg, 0.10 mmol, 50%).

1.11.1. 2,5-Anhydro-1,4-di-*O*-benzyl-6-deoxy-D-altritol (16). $[\alpha]_D^{20}$ +41 (*c* 0.5, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 7.42–7.30 (m, 10H, H-arom.), 4.71 (d, 1H, *J* 11.7 Hz, CHPh), 4.67 (d, 1H, *J* 12.2 Hz, CHPh), 4.61 (d, 1H, *J* 11.7 Hz, CHPh), 4.60 (d, 1H, *J* 12.2 Hz, CHPh), 4.30 (q, 1H, *J* 3.9 Hz, H-3), 4.23 (dt, 1H, $J_{2,1'}$ 6.6, $J_{2,3} = J_{2,1}$ 4.3 Hz, H-2), 4.12 (dq, 1H, $J_{5,4}$ 7.5, $J_{5,6}$ 6.3 Hz, H-5), 3.83 (dd, 1H, $J_{1,2}$ 4.8, $J_{1,1'}$ 10.0 Hz, H-1), 3.73 (dd, 1H, $J_{1',2}$ 6.5, $J_{1',1}$ 10.0 Hz, H-1′), 3.66 (dd, 1H, $J_{4,3}$ 4.5, $J_{4,5}$ 7.5 Hz, H-4), 2.68 (d, 1H, $J_{OH,3}$ 3.3 Hz, 3-OH), 1.32 (d, 3H, $J_{6,5}$ 6.3 Hz, 3H-6); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.1, 137.2 (2C-quat. arom.), 128.6–127.6 (10C-arom.), 85.1 (C-4), 79.2 (C-2), 75.4 (C-5), 73.5 (CH_2Ph), 72.6 (CH_2Ph), 70.2 (C-3), 69.1 (C-1), 19.0 (C-6); HRCIMS: Calcd for $C_{20}H_{28}O_4N$ $[M+NH_4]^+$: 346.2018. Found: *m*/*z* 346.2025.

1.12. Reaction of methyl 2,3,5-tri-*O*-benzyl-β-D-lyxofuranoside (17) with TIBAL

A soln of TIBAL in toluene (2.4 mL, 2.4 mmol, 1 M) was added to the perbenzylated furanoside derivative **17** (197 mg, 0.45 mmol) at room temperature under argon. The reaction mixture was heated at 60 °C for 22 h. When TLC indicated the presence of a major product, the reaction was carefully quenched with ice-cold water. The products were extracted with DCM and the organic layers were combined, dried and concentrated. The resultant residue was submitted to a flash column chromatography (4:1, cyclohexane–EtOAc,) to afford **18** (75 mg, 0.22 mmol, 48%).

1.12.1. Methyl 3,5-di-*O*-benzyl-β-D-lyxofuranoside (18). $[\alpha]_D^{20}$ +47 (*c* 0.7, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 7.41–7.36 (m, 10H, H-arom.), 4.78 (d, 1H, *J* 11.6 Hz, CHPh), 4.76 (d, 1H, *J* 10.3 Hz, CHPh), 4.74 (d, 1H, *J* 10.3 Hz, CHPh), 4.70 (d, 1H, $J_{1,2}$ 3.2 Hz, H-1), 4.68 (d, 1H, *J* 11.6 Hz, CHPh), 4.00 (q, 1H, $J_{2,1} = J_{2,3} = J_{2,OH}$ 2.6 Hz, H-2), 3.86–3.85 (m, 2H, H-3, H-4), 3.79 (dd, 1H, $J_{5,4}$ 4.7, $J_{5,5'}$ 10.5 Hz, H-5), 3.60 (dd, 1H, $J_{5',4}$ 8.5, $J_{5',5}$ 10.5 Hz, H-5′), 3.43 (s, 3H, OCH_3), 2.59 (d, 1H, $J_{2,OH}$ 2.3 Hz, 2-OH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.3, 138.0 (2C-quat. arom.), 128.4–127.7 (10C-arom.), 100.5 (C-1), 78.6, 74.0 (C-3, C-4), 72.9, 72.5 ($2CH_2Ph$), 68.7 (C-2), 60.7 (C-5), 55.1 (OCH_3); HRCIMS: Calcd for $C_{20}H_{28}O_5N$ $[M+NH_4]^+$: 362.1968. Found: *m*/*z* 362.1970.

1.13. Reaction of methyl 2,3,5-tri-*O*-benzyl-β-D-lyxofuranoside (17) with DIBAL-H

To a soln of the perbenzylated furanoside derivative **17** (0.2 g, 0.46 mmol) in dry toluene (1.6 mL), a soln of DIBAL-H in toluene (1.6 mL, 2.4 mmol, 1.5 M) was added at room temperature under argon. The reaction mixture was heated at 60 °C for 4 h. When TLC indicated the presence of major products, the reaction was carefully quenched with aq NaOH (10%) at 0 °C. The products were extracted with DCM and the organic layers were combined, dried and concentrated. The resultant residue was submitted to a flash column chromatography (5:1–3:1, cyclohexane–EtOAc) to afford products **19** (32 mg, 0.073 mmol, 35%) and **18** (36 mg, 0.083 mmol, 40%).

1.13.1. Methyl 2,5-di-*O*-benzyl-β-D-lyxofuranoside (19). $[\alpha]_D^{20}$ +5 (*c* 0.9, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 7.41–7.30 (m, 10H, H-arom.), 4.79 (d, 1H, *J* 11.8 Hz, CHPh), 4.74 (d, 1H, *J* 11.9 Hz, CHPh), 4.69 (d, 1H, *J* 11.9 Hz, CHPh), 4.68 (d, 1H, $J_{1,2}$ 3.3 Hz, H-1), 4.67 (d, 1H, *J* 11.8 Hz, CHPh), 3.99 (ddd, 1H, $J_{3,2}$ 3.5, $J_{3,OH}$ 6.3, $J_{3,4}$ 7.8 Hz, H-3), 3.81–3.71 (m, 3H, H-2, H-4, H-5), 3.58 (dd, 1H, $J_{5,4}$ 8.0, $J_{5,5}$ 10.8 Hz, H-5), 3.41 (s, 3H, OCH_3), 2.46 (d, 1H, $J_{OH,3}$ 6.3 Hz, 3-OH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.3, 137.9 (2C-quat. arom.), 128.6–127.7 (10C-arom.), 99.2 (C-1), 77.6, 75.8 (C-2, C-4), 73.3 (CH_2Ph), 72.6 (CH_2Ph), 70.6 (C-3), 60.8 (C-5), 55.3 (OMe); HRCIMS: Calcd for $C_{20}H_{28}O_5N$ $[M+NH_4]^+$: 362.1968. Found: *m*/*z* 362.1957.

1.14. Reaction of methyl 2,3,5-tri-*O*-benzyl-β-D-lyxofuranoside (17) with TMAL

To a soln of the perbenzylated furanoside derivative **17** (82 mg, 0.19 mmol) in dry toluene (1.2 mL), a soln of TMAL in toluene (1.41 mL, 2.82 mmol, 2 M) was added at room temperature under argon. The reaction mixture was heated at 60 °C for 96 h. When TLC indicated the presence of a major product, the reaction was carefully quenched with toluene saturated with water and then aq NaOH (10%) was added at 0 °C. The products were extracted with DCM and the organic layers were combined, dried and concentrated. The resultant residue was submitted to a flash column chromatography (4:1,

cyclohexane–EtOAc) to afford **18** (48 mg, 0.14 mmol, 74%).

1.15. Reaction of methyl 2,3,5-tri-*O*-benzyl-α-D-arabinofuranoside (20) with DIBAL-H

To a soln of the perbenzylated furanoside derivative **20** (0.16 g, 0.37 mmol) in dry toluene (1.8 mL), a soln of DIBAL-H in toluene (2.5 mL, 3.8 mmol, 1.5 M) was added at room temperature under argon. The reaction mixture was heated at 60 °C for 15 h. When TLC indicated the presence of a major product, the reaction was carefully quenched with aq NaOH (10%) at 0 °C. The products were extracted with DCM and the organic layers were combined, dried and concentrated. The resultant residue was submitted to a flash column chromatography (5:1, cyclohexane–EtOAc) to afford **21** (57 mg, 0.13 mmol, 35%).

1.15.1. 2,3,5-Tri-*O*-benzyl-1-*O*-methyl-D-arabinitol (21). $[\alpha]_D^{20}$ +6 (*c* 1.3, $CHCl_3$); ^1H NMR (250 MHz, $CDCl_3$): δ 7.30–7.16 (m, 15H, H-arom.), 4.63 (d, 1H, *J* 11.6 Hz, CHPh), 4.54 (d, 1H, *J* 11.6 Hz, CHPh), 4.47 (s, 2H, CH_2Ph), 4.44 (s, 2H, CH_2Ph), 3.90 (m, 1H, H-2), 3.80 (m, 1H, H-4), 3.60 (dd, 1H, *J* 3.3, 7.5 Hz, H-3), 3.52 (m, 4H, 2 H-5, 2 H-1), 3.23 (s, 3H, OCH_3), 2.85 (d, 1H, *J* 5.3 Hz, 4-OH); ^{13}C NMR (62.5 MHz, $CDCl_3$): δ 138.2, 138.2, 138.1 (3C-quat. arom.), 128.6–127.0 (15C-arom.), 77.9, 77.7 (C-4, C-3), 73.8 (CH_2Ph), 73.4 (CH_2Ph), 73.2 (CH_2Ph), 72.1 (C-5), 71.2 (C-1), 70.4 (C-2), 59.0 (OMe); HRCIMS: Calcd for $C_{27}H_{36}O_5N$ $[M+NH_4]^+$: 454.2594. Found: *m*/*z* 454.2599.

1.16. Reaction of methyl 2,3,5-tri-*O*-benzyl-β-D-arabinofuranoside (22) with TIBAL

A soln of TIBAL in toluene (3.8 mL, 3.8 mmol, 1 M) was added to the perbenzylated furanoside derivative **22** (0.11 g, 0.25 mmol) at room temperature under argon. The reaction mixture was heated at 60 °C for 22 h. When TLC indicated the presence of a major product, the reaction was carefully quenched with ice-cold water. The products were extracted with DCM and the organic layers were combined, dried and concentrated. The resultant residue was submitted to a flash column chromatography (5:1, cyclohexane–EtOAc) to afford product **23** (42 mg, 0.12 mmol, 48%).

1.16.1. Methyl 3,5-di-*O*-benzyl-β-D-arabinofuranoside (23). $[\alpha]_D^{20}$ −16 (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 7.40–7.30 (m, 10H, H-arom.), 4.91 (d, 1H, $J_{1,2}$ 4.7 Hz, H-1), 4.80 (d, 1H, *J* 11.9 Hz, CHPh), 4.67 (d, 1H, *J* 11.9 Hz, CHPh), 4.64 (d, 1H, *J* 12.2 Hz, CHPh), 4.60 (d, 1H, *J* 12.2 Hz, CHPh), 4.31 (ddd, 1H, $J_{2,1}$ 4.7, $J_{2,3}$ 5.9, $J_{2,OH}$ 9.5 Hz, H-2), 4.19 (q, 1H, $J_{4,3} = J_{4,5}$ 5.6 Hz, H-4), 3.90 (t, 1H, $J_{3,2} = J_{3,4}$ 5.8 Hz, H-3), 3.58 (d, 2H $J_{4,5}$ 5.7 Hz, 2H-5), 3.46 (s, 3H, OCH_3), 2.65 (d, 1H, $J_{OH,2}$ 9.5 Hz, 2-OH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.0, 137.9 (2C-quat. arom.), 128.3–127.6 (10C-arom.), 102.6 (C-1), 84.5 (C-3), 80.7 (C-4), 77.9 (C-2), 73.2 (CH_2Ph), 72.0 (C-5), 71.8 (CH_2Ph), 55.3 (OCH_3); HRCIMS: Calcd for $C_{20}H_{28}O_5N$ $[M+NH_4]^+$: 362.1968. Found: *m*/*z* 362.1971.

1.17. Reaction of methyl 2,3,5-tri-*O*-benzyl-β-D-arabinofuranoside (22) with DIBAL-H

To a soln of the perbenzylated furanoside derivative **22** (116 mg, 0.25 mmol) in dry toluene (1 mL), a soln of DIBAL-H in toluene (0.84 mL, 1.3 mmol, 1.5 M) was added at room temperature under argon. The reaction mixture was heated at 60 °C for 1 h. When TLC indicated the presence of a major product, the reaction was carefully quenched with aq NaOH (10%) at 0 °C. The products were extracted with DCM and the organic layers were combined, dried and concentrated. The resultant residue was submitted to a flash column chromatography (3:1, cyclohexane–EtOAc) to afford **24** (35 mg, 0.083 mmol, 31%).

1.17.1. 2,3,5-Tri-*O*-benzyl-D-arabinitol (24). $[\alpha]_D^{20}$ +2 (*c* 1.7, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 7.41–7.30 (m, 15H, H-arom.), 4.70 (d, 1H, *J* 11.6 Hz, CHPh), 4.67 (d, 1H, *J* 11.6 Hz, CHPh), 4.66 (d, 1H, *J* 11.4 Hz, CHPh), 4.62 (d, 1H, *J* 11.4 Hz, CHPh), 4.60 (d, 1H, *J* 11.9 Hz, CHPh), 4.57 (d, 1H, *J* 11.9 Hz, CHPh), 4.10–4.05 (m, 1H, H-4), 3.88–3.75 (m, 4H, 2H-1, H-2, H-3), 3.71 (dd, 1H, $J_{5,4}$ 4.0, $J_{5,5'}$ 9.8 Hz, H-5), 3.69 (dd, 1H, $J_{5',4}$ 5.0, $J_{5,5'}$ 9.8 Hz, H-5′), 3.08 (d, 1H, $J_{OH,4}$ 5.2 Hz, 4-OH), 2.38 (br t, 1H, 1-OH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.82, 137.80, 137.7 (3C-quat. arom.), 128.5–127.7 (15C-arom.), 79.3, 78.3 (C-2, C-3), 73.7 (CH_2Ph), 73.4 (CH_2Ph), 72.7 (CH_2Ph), 70.9 (C-5), 70.4 (C-4), 61.4 (C-1); HRCIMS: Calcd for $C_{26}H_{34}O_5N$ $[M+NH_4]^+$: 440.2437. Found: *m*/*z* 440.2442.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.carres.2006.05.002.

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