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Synthesis of aryl-2-deoxy-D-*lyxo*/*arabino*-hexopyranosides from 2-deoxy-1-thioglycosides

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Abstract—The synthesis of either anomers of aryl 2-deoxy-D-glycopyranosides from 2-deoxy-1-thioglycosides is reported. The α-anomers form as the major product when thioglycosides react with differently substituted phenols and naphthols, in the presence of *N*-iodosuccinimide/triflic acid. On the other hand, reaction of the thioglycosides with bromine initially, followed by reaction with aryloxy anions lead to aryl 2-deoxy-β-D-glycosides with high specificities.
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Keywords: Aryl glycosides; Deoxysugars; Glycosylations; Thioglycosides

1. Introduction

Many naturally-occurring antibiotic and antitumor drugs contain 2-deoxy glycosides as important structural components.[1] The synthesis of these biologically important 2-deoxy glycosides encounters difficulties due to the absence of stereoelectronic influences at C-2 carbon of 2-deoxy glycosyl derivatives.[2] Various methodologies have been developed to synthesize 2-deoxy glycosides. Prominent among them are the radical-mediated or reductive cleavage of a halo-[3] or a sulfur[4] or an oxygen[5] or a nitrogen[6] or a selenium[7] functionality at C-2 of the glycosides. Direct methods of activating 2-deoxy sugars with phosphates,[8] phosphoroamidites,[9] phosphites,[10] phosphorodithioates,[11] phenylthioglycosides,[12] and (2′-carboxyl)benzyl glycosides[13] are also known.

We have developed previously an efficient method to synthesize activated 2-deoxy-1-thio sugar derivatives that result from the reaction of glycals with a thiol reagent in the presence of catalytic amount of ceric ammonium nitrate.[14] The 2-deoxy-1-thioglycosides being an activated glycosyl donor, could be subjected to glycosylation reactions directly. Glycosylation of few aglycosyl and glycosyl acceptors with the 2-deoxy-1-thioglycosides, in the presence of thiophilic activators, provided the α-anomeric glycosylated products. In continuing the efforts to involve the newly formed 2-deoxy-1-thioglycosides in glycosylations, the preparation of aryl 2-deoxy-D-glycosides was undertaken. β-Anomeric configuration is seen commonly in the aryl 2-deoxy-glycosides present in naturally occurring compounds. Known synthetic methods to prepare the aryl 2-deoxy-glycosides are (i) acid catalyzed reaction of a glycal with phenol;[15] (ii) [4+2] cycloaddition of a glycal with *ortho*-thioquinones, followed by a desulfurization;[16] (iii) an S_N2-like displacement of 2-deoxy-glycopyranosyl iodide sugar derivatives with aryloxy anion;[17] (iv) Lewis acid catalyzed reaction of anomeric fluorides and acetates of 2-deoxy sugar donor with phenols;[18] (v) 2-deoxygenations of an arylglycoside;[19] and (vi) a Mitsunobu glycosylation protocol.[20] We herein present the synthesis of aryl 2-deoxy-D-glycosides, initiated from a 2-deoxy-1-thioglycoside as the sugar donor.

2. Results and discussion

2.1. Synthesis of aryl 2-deoxy-α-D-glycosides

Direct glycosylation of phenols with 2-deoxy-1-thio glycosides was targeted initially, by employing commonly

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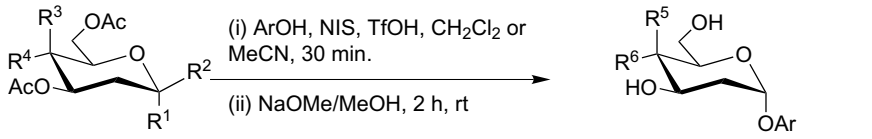


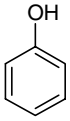
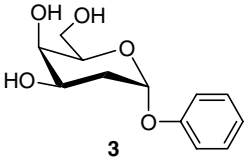
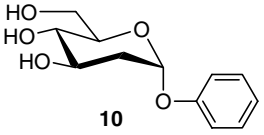
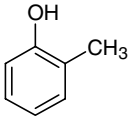
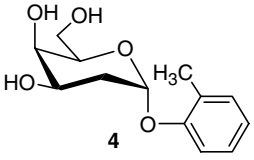
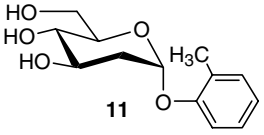
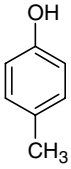
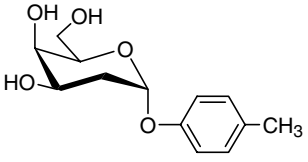
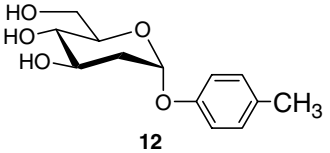
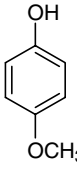
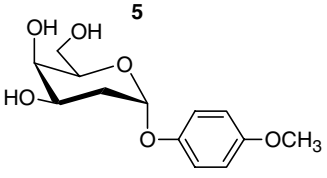
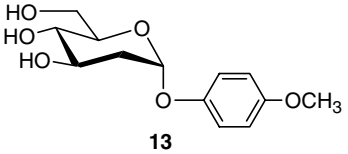
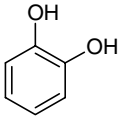
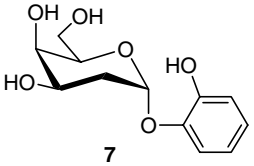
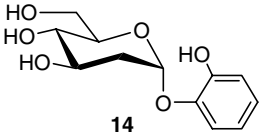
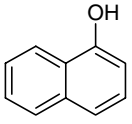
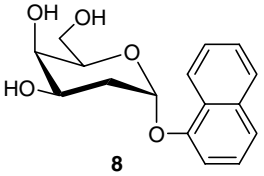
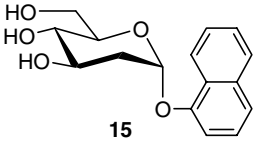
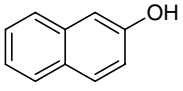
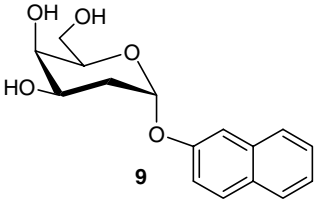
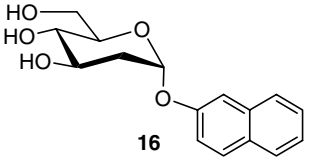
1: R^1 = SEt (or H), R^2 = H (or SEt), R^3 = OAc, R^4 = H
2: R^1 = H, R^2 = SEt, R^3 = H, R^4 = OAc

3-9: R^5 = OH, R^6 = H (from **1**)
10-16: R^5 = H, R^6 = OH (from **2**)

Scheme 1. Synthesis of aryl-2-deoxy-α-D-*lyxo*/*arabino*-hexopyranosides **3**–**16**.

used thiophilic activator *N*-iodosuccinimide/triflic acid (NIS/TfOH). Reaction of various substituted phenols and naphthols with thioglycosides **1** and **2** afforded the glycosylated product in a nearly quantitative yield.

Table 1. Synthesis of different aryl-2-deoxy-α-D-*lyxo*/*arabino*-hexopyranoside **3**–**16**[a]

Entry	Glycosyl donor	Acceptor	Product from **1**	Product from **2**
1	**1**, **2**		 **3**	 **10**
2	**1**, **2**		 **4**	 **11**
3	**1**, **2**		 **5**	 **12**
4	**1**, **2**		 **6**	 **13**
5	**1**, **2**		 **7**	 **14**
6	**1**, **2**		 **8**	 **15**
7	**1**, **2**		 **9**	 **16**

[a] Isolated yields after two steps were between 85% and 90%.

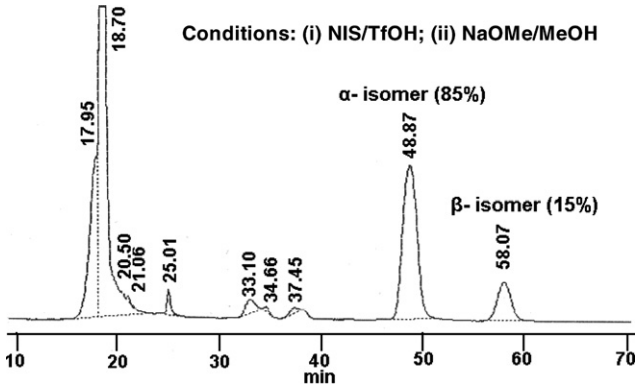


Figure 1. The HPLC trace for the reaction leading to the formation of *o*-tolyl 2-deoxy-D-*lyxo*-hexopyranoside.

Analysis of the reaction mixtures by HPLC technique showed that α-anomers formed as the major product (Scheme 1, Table 1). A HPLC trace of the reaction mixture resulting from glycosylation of **1** with *o*-cresol is presented in Figure 1.

The α-anomeric configuration of the glycosides was ascertained by ^{1}H and ^{13}C NMR spectroscopies. The anomeric proton appeared as an apparent doublet in the range of 5.5–5.9 ppm, with coupling constant approximately 3.0 ppm. The H-2 protons resonated between 2.15 and 1.85 ppm, with the exception of mono-O-glycosyated catechol **7**, which showed the H-2 protons at 2.90 and 2.65 ppm. The ^{1}H and ^{13}C NMR chemical shift values of all the products are presented in Tables 2–5.

2.2. Synthesis of aryl 2-deoxy-β-D-glycosides

In the absence of formation of the β-anomeric product in significant amounts in glycosylation involving 2-deoxy-1-thioglycosides, formation of aryloxy anion intermediates as glycosyl acceptors and the reaction of such intermediates with the glycosyl component to provide the β-anomer was conducted. Preparation of aryl glycosides using aryloxy anions is known previously.[21] Lam and Gervey-Hague have reported the reaction of 2-deoxy-glycopyranosyl iodide with aryl anions,[17] to obtain aryl

Table 2. ^{1}H NMR chemical shifts (in ppm), multiplicities and coupling constants of **3**–**9** in acetone-d_6/D_2O[a]

	3	**4**	**5**	**6**	**7**	**8**	**9**
H-1	5.66 (d) (3.0)	5.69 (d) (2.7)	5.55 (d) (2.7)	5.59 (d) (3.0)	5.60 (d) (2.9)	5.89 (d) (2.7)	5.89 (d) (3.0)
H-2_a	2.11 (ddd) (3.1, 11.7, 12.5)	2.15 (ddd) (2.9, 8.1, 12.0)	2.07 (ddd) (3.0, 11.7, 12.0)	2.16 (ddd) (3.0, 11.5, 12.5)	2.90–2.65[f] (m)	2.24 (ddd) (2.7, 11.9, 12.5)	2.25 (ddd) (3.6, 12.0, 12.5)
H-2_e	1.95 (app.dd) (5.1, 12.5)	2.03 (app.dd) (5.1, 12.1)	1.89 (app.dd) (5.1, 12.3)	2.02 (app.dd) (5.1, 12.5)		2.15 (app.dd) (5.5, 12.5)	2.08 (app.dd) (4.9, 12.5)
H-3	4.15 (ddd) (3.1, 5.1, 11.9)	4.23 (ddd) (3.0, 5.1, 8.1)	4.10–4.04[c] (band)	4.19 (ddd) (3.0, 5.1, 11.7)	4.23 (ddd) (3.1, 5.4, 10.0)	4.38 (ddd) (2.7, 5.4, 11.9)	4.08–4.03[h] (band)
H-4	3.94 (app.s)	3.99 (app.s)	3.89 (app.s)	3.98–3.94[d]	3.94–3.61[g]	3.99 (app.s)	
H-5	3.84–3.63[b] (m)	3.87 (app.t) (6.4)	3.80 (app.t) (6.0)	(band)	(band)	3.88 (app.t) (5.9)	3.95 (app.t) (6.3)
H-6a		3.74 (dd) (6.3, 11.1)	3.65 (dd) (6.0, 10.5)	3.74–3.63[e] (m)		3.81–3.61[e] (m)	3.77 (dd) (6.2, 11.2)
H-6b		3.63 (dd) (6.0, 11.0)	3.54 (dd) (6.3, 10.8)				3.66 (dd) (6.1, 11.2)
Ph-H	7.33–6.94 (m)	7.19–6.86 (m)	7.01 (d), 6.92 (d)	7.09 (dd), 6.90 (dd)	7.27–7.20 (m)	8.26–7.26 (m)	7.89–7.29 (m)
Other signals		2.21 (s)	2.17 (s)	3.78 (br s)			

[a] ^{1}H NMR recorded in 300 MHz instrument.
Signals for [b]H-4, H-5, H-6a,b; [c]H-3 with residual H_2O peak; [d]H-4, H-5; [e]H-6a, H-6b; [f]H-2_a, H-2_e; [g]H-4, H-5, H-6a,b; [h]H-3, H-4 overlap.

Table 3. ^{13}C NMR chemical shift assignments of **3**–**9** in acetone-d_6/D_2O[a]

Compound	C-1	C-2	C-3[b]	C-4[b]	C-5	C-6	Other signals
3	97.5	33.8	69.1	65.9	72.6	62.7	156.0, 130.1, 122.5, 117.6,
4	96.9	33.1	68.2	65.8	72.4	61.7	155.6, 131.2, 127.7, 127.4, 122.1, 115.4, 16.1
5	97.4	32.9	68.1	65.6	72.1	61.6	155.4, 131.6, 130.3, 117.5, 117.4, 20.3
6	96.4	34.9	70.3	67.8	74.4	61.6	157.5, 153.7, 121.5, 117.4, 58.1
7	98.8	33.6	69.1	65.7	72.8	62.7	148.2, 145.9, 123.3, 120.4, 117.6, 116.5
8	97.5	33.9	69.1	66.1	73.0	62.7	135.6, 128.4, 127.0, 126.9, 126.1, 122.6, 121.8, 109.5
9	97.5	33.1	68.4	65.8	72.7	61.9	155.5, 130.4, 130.1, 128.4, 127.9, 127.2, 124.9, 120.0

[a] ^{13}C NMR recorded in 75 MHz instrument.
[b] Assignments interchangeable.

Table 4. ^{1}H NMR chemical shifts, multiplicities, and coupling constants of **10–16** in acetone-d_6/D_2O[a]

	10	11	12	13	14	15	16
H-1	5.60 (d) (2.7)	5.56 (d) (2.1)	5.54 (d) (2.1)	5.47 (d) (3.0)	5.52 (d) (2.7)	5.81 (d) (1.8)	5.74 (d) (2.7)
H-2_a	2.19 (app.ddd) (2.8, 11.7, 12.0)	2.20 (app.ddd) (2.1, 11.4, 12.0)	2.19 (app.ddd) (2.1, 11.7, 11.7)	2.17 (app.ddd) (2.7, 11.7, 12.3)	2.29 (app.ddd) (2.7, 11.7, 12.0)	2.37 (app.ddd) (2.0, 11.7, 12.3)	2.26 (app.ddd) (2.7, 11.7, 11.7)
H-2_e	1.72 (app.dd) (4.8, 11.7)	1.78–1.66 (band)	1.69 (app.dd) (4.8, 11.4, 11.7)	1.69 (app.dd) (5.4, 12.3)	1.73 (app.dd) (3.6, 11.7)	1.86 (app.dd) (5.1, 11.7)	1.82 (app.dd) (5.1, 11.7)
H-3	3.96 (ddd) (5.1, 9.0, 11.7)	3.99 (ddd) (5.1, 8.4, 11.4)	3.94 (ddd) (4.8, 9.1, 11.4)	3.93 (ddd) (5.4, 9.0, 11.7)	4.05 (ddd) (5.1, 9.0, 11.7)	4.19 (ddd) (5.1, 9.3, 12.0)	4.06 (ddd) (5.1, 9.3, 11.7)
H-4	3.41 (t) (9.0)	3.40– 3.21[c] (band)	3.34 (t) (9.1)	3.35 (t) (9.3)	3.38 (t) (9.3)	3.45 (t) (9.0)	3.46 (t) (9.3)
H-5	3.26–3.09[b] (m)		3.26–3.12[b] (band)	3.26–3.11[b] (band)	3.73–3.54[b] (band)	3.69–3.52[b] (band)	3.72–3.55[b] (band)
H-6a							
H-6b							
Ph-H	7.22–6.77 (m)	6.99–6.76 (band)	6.93 (d), 6.82 (d)	6.77 (d), 6.94 (d)	7.08–6.67 (band)	7.43–7.07 (band), 8.10–7.70 (band)	7.41–7.10 (band), 7.69–7.63 (band)
Other signals		2.20 (s)	2.12 (br s)	3.63 (br s)			

[a] ^{1}H NMR recorded in 300 MHz instrument.
Signals for [b] H-5, H-6a,b; [c] H-4, H-5, H-6a,b overlap.

2-deoxy-β-D-glycopyranoside. The 2-deoxy-1-thioglycosides were converted first to 2-deoxy glycopyranosyl halides. The in situ formed 2-deoxy glycopyranosyl halide was reacted with aryloxy acceptors using LHMDS as the base. Analysis of the product formed, following the deprotection, had shown the formation of the β-anomeric product **17–30**, in excellent yields (Scheme 2 and Table 6). Figure 2 presents the HPLC trace of the reaction mixture corresponding to the reaction of **1** with *o*-cresol under the above reaction conditions.

The β-anomers of the aryl 2-deoxy-D-glycosides were characterized by ^{1}H and ^{13}C NMR spectroscopies and mass spectrometry. Consistent up-field chemical shifts with detectable double-doublet splitting pattern in the ^{1}H NMR spectra and down-field chemical shifts in the ^{13}C NMR spectra of the anomeric proton and carbon nuclei, respectively, were observed for all the β-anomers, in comparison to that for the α-anomer.

^{1}H and ^{13}C NMR chemical shifts for various aryl 2-deoxy-β-D-glycosides are presented in Tables 7–10. The coupling constants $J_{1,2a}$ of 9.8 Hz and $J_{1,2e}$ of 2.0 Hz indicate the β-configuration of the substituent at C-1. The chemical shift of the anomeric carbon in the β-anomer resonated at ~98–101 ppm. The ^{13}C resonances corresponding to C-2 appeared in the range of 34–39 ppm for the β-anomers. High resolution mass spectrometry further confirmed the constitutions of the glycosides. A single crystal X-ray structure of the aryl glycoside **18** is presented in Figure 3.[22]

The fact that NIS/TfOH mediated glycosylation, using thioglycoside donor, led to formation of α-glycosylated product as the major product and β-glycosylated product as the minor product, indicate that an oxocarbenium ion forms as the intermediate. The α-anomer product formation may be compared analogous to such α-anomer formation in non-neighboring group participating glycosylations. Further, when the glycosylation reaction was performed in the coordinating solvent MeCN, the α:β ratio was observed to change significantly. In studying the glycosylation of *o*-cresol with ethyl 2-deoxy-3,4,6-tri-*O*-acetyl-1-thio-*arabino*-hexopyranoside, in NIS/TfOH, in MeCN solution, the HPLC analysis of the reaction mixture had shown an α:β ratio of 60:40, as opposed to the ratio of 90:10 for the same reaction performed in CH_2Cl_2 solution. The increase in the β-anomer in this reaction is likely to be due to the effect of MeCN coordinating the α-face of the intermediate oxocarbenium ion.

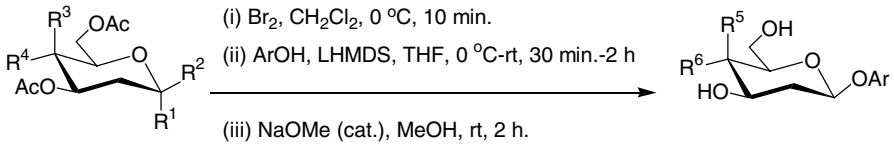
The glycosylation via the bromide route, involving a phenoxide as the glycosyl acceptor, led to the β-glycosylated product in more than 90% specificity, presumably due to an S_N2 type of mechanism.

In conclusion, the methodology presented herein allows a facile preparation of each of the anomers of aryl 2-deoxy-D-glycosides from a common precursor, namely, 2-deoxy-1-thioglycoside.

Table 5. ^{13}C NMR chemical shift assignments of **10**–**16** in acetone-d_6/D_2O

Compound	C-1	C-2	C-3[c]	C-4[c]	C-5	C-6	Other signals
10[a]	97.7	37.2	73.4	70.8	76.7	61.3	138.7, 130.0, 123.2, 116.8
11[b]	96.0	37.5	73.5	70.9	76.8	61.5	155.4, 131.1, 127.7, 127.3, 122.7, 115.0, 15.9
12[a]	97.7	38.6	73.4	70.8	76.6	60.9	153.4, 130.4, 123.2, 116.9, 14.7
13[a]	97.6	37.4	73.4	70.9	76.7	61.7	157.8, 154.1, 119.0, 115.2, 55.9
14[b]	97.5	37.3	71.1	71.0	73.4	60.8	146.6, 144.6, 123.6, 120.8, 117.8, 116.5
15[a]	96.4	37.0	72.0	69.6	75.0	59.7	133.0, 126.1, 125.0, 124.6, 120.5, 120.5, 120.1, 107.7, 107.5
16[a]	96.1	37.1	71.8	69.6	75.1	59.8	152.8, 132.9, 127.9, 126.0, 125.6, 122.9, 117.2, 109.4

^{13}C NMR recorded in [a]100 MHz, [b]75 MHz instrument.
[c] Assignments interchangeable.



1: R^1 = SEt (or H), R^2 = H (or SEt), R^3 = OAc, R^4 = H
2: R^1 = H, R^2 = SEt, R^3 = H, R^4 = OAc

17-23: R^5 = OH, R^6 = H (from **1**)
24-30: R^5 = H, R^6 = OH (from **2**)

Scheme 2. Synthesis of aryl-2-deoxy-β-D-*lyxo*/*arabino*-hexopyranosides **17**–**30**.

3. Experimental

3.1. General methods

Chemicals were purchased from commercial sources and were used without further purification. Solvents were dried and distilled according literature procedures. Analytical TLC was performed on commercial Merck plates coated with silica gel GF_{254} (0.25 mm). Silica gel (100–200 mesh) was used for column chromatography. Optical rotations were recorded on a Jasco Model P-1020 polarimeter at the sodium D line at 24 °C. Microanalyses were performed on an automated C, H, N analyzer. High-resolution mass spectra were obtained from Q-TOF instrument by electron spray ionization (ESI) technique. ^1H and ^{13}C NMR spectral analysis were performed on a 300/400 MHz and 75/100 MHz spectrometer, respectively, with residual solvent signal acting as the internal standard. The following abbreviations were used to explain the multiplicities: s, singlet; d, doublet; t, triplet; m, multiplet; band, several overlapping signals; br, broad.

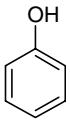
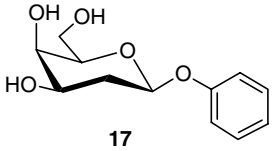
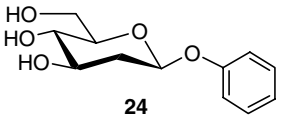
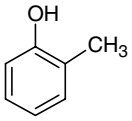
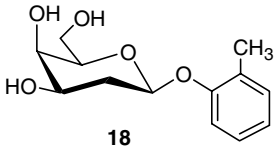
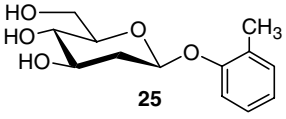
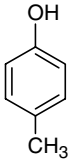
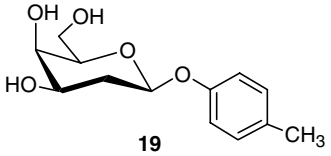
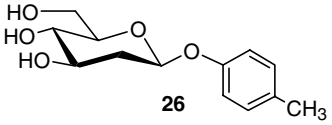
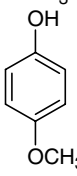
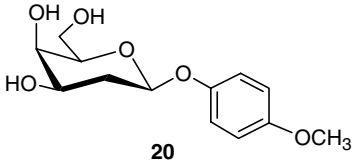
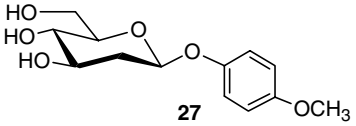
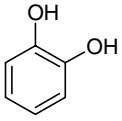
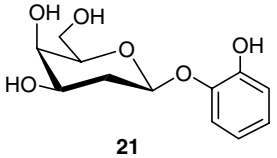
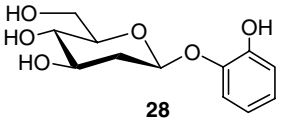
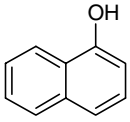
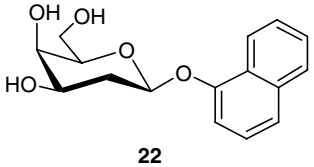
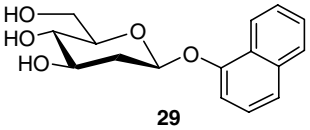
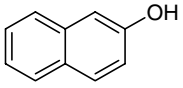
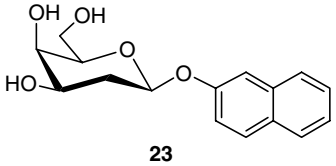
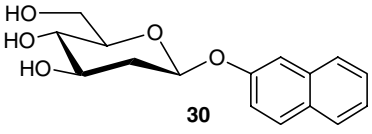
3.2. General procedure for synthesis of aryl-2-deoxy-α-D-*lyxo*/*arabino*-hexopyranoside (3–16)

Ethyl 2-deoxy-3,4,6-tri-*O*-acetyl-1-thio-*lyxo*/*arabino*-hexopyranoside (**1**, **2**)[14] (1 mmol), molecular sieves 4 Å (~0.7 g), NIS (1.2 mmol), and acceptor phenol (1.2–2 mmol) was dissolved in CH_2Cl_2 or MeCN (3 mL) and stirred for 1 h at rt. A solution of TfOH (0.1 mmol) in CH_2Cl_2 or MeCN (1 mL) was added and stirred at 0 °C for 15–30 min. The reaction mixture was diluted with CH_2Cl_2 (50 mL), washed with aqueous $Na_2S_2O_3$ (50 mL), brine (50 mL), dried (Na_2SO_4) and concentrated. De-O-acetylation was performed by dissolving the crude reaction mixture in MeOH, addition of NaOMe (1 M in MeOH) and stirring for 2 h at room temperature. The reaction mixture was then neutralized (AcOH–MeOH 1:9 v/v), concentrated, and purified (SiO_2, $CHCl_3$–MeOH eluant mixture), to afford the desired product.

3.3. General procedure for synthesis of aryl-2-deoxy-β-D-*lyxo*/*arabino*-hexopyranoside (17–30)

Bromine (1.2 mmol) was added at 0 °C to a solution of ethyl 2-deoxy-3,4,6-tri-*O*-acetyl-1-thio-*lyxo*/*arabino*-hexopyranoside (**1**, **2**)[14] (1 mmol) in CH_2Cl_2 (3 mL). After 10 min, reaction mixture was concentrated and co-evaporated twice with PhMe to afford bromide, which was used in the next step without purification. A solution of the acceptor phenol (1.2 mmol) in THF (2 mL) was admixed with LHMDS in THF (1 M) (1.2 mmol) at 0 °C and stirred for 30 min. A solution of the bromide in THF (2 mL) was added to the reaction mixture dropwise at 0 °C and stirred for 2.5 h. The reaction mixture was diluted with EtOAc, washed with aq $Na_2S_2O_3$ solution, followed by brine and concentrated in vacuo. De-O-acetylation and product isolation were performed, as detailed in the previous paragraph.

Table 6. Synthesis of different aryl-2-deoxy-β-D-hexopyranosides **17**–**30**[a]

Entry	Glycosyl donor	Acceptor	Product from **1**	Product from **2**
1	**1**, **2**		 **17**	 **24**
2	**1**, **2**		 **18**	 **25**
3	**1**, **2**		 **19**	 **26**
4	**1**, **2**		 **20**	 **27**
5	**1**, **2**		 **21**	 **28**
6	**1**, **2**		 **22**	 **29**
7	**1**, **2**		 **23**	 **30**

[a] Isolated yields after two steps were above 90%.

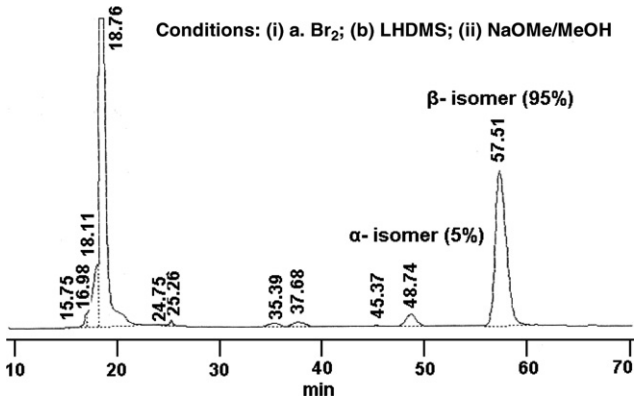


Figure 2. The HPLC trace for the reaction leading to the formation of *o*-tolyl 2-deoxy-D-*lyxo*-hexopyranoside.

3.4. Phenyl 2-deoxy-α-D-*lyxo*-hexopyranoside (3)

Mp 127–129 °C, lit.[23] mp 126–127 °C, lit.[24] mp 125 °C; $[\alpha]_D^{24}$ +159.0 (*c* 1.0, MeOH), lit.[23] $[\alpha]_D^{20}$ +154 (H_2O), lit.[24] $[\alpha]_D^{24}$ +150 (*c* 2.02, H_2O). ESIMS *m*/*z* calcd for $C_{12}H_{16}O_5$: 263.0895 $[M+Na]^+$. Found: 263.0889. Anal. Calcd: C, 60.00; H, 6.71. Found: C, 59.75; H, 7.03.

3.5. *o*-Tolyl 2-deoxy-α-D-*lyxo*-hexopyranoside (4)

Mp 128–129 °C; $[\alpha]_D^{24}$ +154.3 (*c* 1.0, MeOH). ESIMS *m*/*z* calcd for $C_{13}H_{18}O_5$: 277.1052 $[M+Na]^+$. Found: 277.1060. Anal. Calcd: C, 61.40; H, 7.14. Found: C, 61.12; H, 7.48.

Table 7. ^{1}H NMR chemical shifts, multiplicities, and coupling constants of **17**–**23** in acetone-d_6/D_2O[a]

	17	**18**	**19**	**20**	**21**	**22**	**23**
H-1	5.25 (dd) (1.9, 9.7)	5.17 (dd) (2.1, 7.0)	5.17 (dd) (1.8, 7.2)	5.03 (dd) (3.1, 8.8)	5.93 (dd) (3.1, 9.0)	5.32 (dd) (3.9, 7.8)	5.25 (dd) (2.4, 9.3)
H-2_a	1.94 (ddd) (9.8, 11.7, 12.5)	2.14–2.07[c] (band)	2.14–2.00[c] (m)	2.05–1.94[c] (m)	2.21–2.02[c] (m)	2.14 (ddd) (8.0, 11.4, 12.5)	2.05–1.90[c] (band)
H-2_e	2.11 (ddd) (2.1, 3.0, 12.5)					2.03 (ddd) (3.3, 3.9, 12.5)	
H-3	3.93 (ddd) (3.3, 4.5, 11.9)	3.96–3.88[d] (band)	3.92 (ddd) (2.4, 3.3, 11.7)	3.85–3.79[d] (band)	4.59–4.50[d] (band)	3.93–3.84[d] (band)	3.86 (ddd) (3.0, 5.0, 11.4)
H-4	3.83–3.65[b] (band)		3.88 (app.s)				3.80 (app.s)
H-5		3.66 (app.t) (6.3)	3.48 (app.t) (6.1)	3.71–3.67[f] (band)	4.39 (app.t) (5.7)	3.73–3.66[g] (band)	3.70–3.62[g] (band)
H-6a		3.84–3.73[e]	3.79–3.74[e] (band)		4.59–4.50[e]		
H-6b		(band)			(band)		
Ph-H	7.33–7.03 (m)	7.14–6.88 (m)	7.10 (d), 6.97 (d)	6.95 (d), 6.79 (d)	7.95–7.53 (m)	8.13–7.14 (m)	7.15–7.12 (m)
Other signals		2.20 (s)	2.17 (s)	3.71–3.67[f] (band)			

[a] ^{1}H NMR recorded in 300 MHz instrument.
Signals for [b]H-4, H-5, H-6a,b; [c]H-2_a, H-2_e with residual H_2O peak; [d]H-3, H-4, [e]H-6a, H-6b; [f]H-5, H-6a,b, and benzylic proton; [g]H-5, H-6a,b overlap.

Table 8. ^{13}C NMR chemical shift assignment of **17**–**23** in acetone-d_6/D_2O[a]

Compound	C-1	C-2	C-3[b]	C-4[b]	C-5	C-6	Other signals
17	101.3	36.9	71.3	70.1	79.0	64.5	159.9, 133.3, 126.3, 119.9
18	98.9	34.9	68.7	67.3	76.1	61.6	156.1, 131.0, 127.5, 122.4, 114.5, 114.5, 16.1
19	98.7	34.8	68.7	67.3	76.1	61.6	155.8, 131.7, 130.3, 117.0, 116.9, 20.3
20	99.4	34.8	68.7	67.3	76.1	61.6	155.3, 131.9, 118.4, 115.0, 55.7
21	103.2	35.0	71.4	70.2	79.1	64.4	151.1, 148.4, 126.8, 123.0, 121.4, 119.5
22	98.8	34.5	68.5	67.2	76.1	61.5	153.1, 134.9, 128.0, 126.9, 126.0, 122.0, 109.4
23	98.8	34.6	68.7	67.5	76.4	61.8	155.5, 135.1, 130.4, 128.4, 128.0, 127.5, 125.2, 119.5

[a] ^{13}C NMR recorded in 75 MHz instrument.
[b] Assignments interchangeable.

Table 9. ^{1}H NMR chemical shifts, multiplicities, and coupling constants of **24**–**30** in acetone-d_6/D_2O[a]

	24	**25**	**26**	**27**	**28**	**29**	**30**
H-1	5.21 (dd) (2.1, 9.6)	5.10 (dd) (1.9, 9.7)	5.15 (dd) (1.8, 9.9)	5.09 (dd) (1.9, 9.9)	5.23 (dd) (1.9, 9.7)	5.30 (dd) (2.3, 8.7)	5.39 (dd) (1.9, 9.4)
H-2_a	1.69 (app.ddd) (9.6, 11.1, 12.3)	1.68 (app.ddd) (9.7, 11.1, 12.3)	1.65 (app.ddd) (9.9, 11.7, 12.3)	1.65 (app.ddd) (9.9, 12.0, 12.3)	1.97 (app.ddd) (9.7, 11.8, 12.3)	2.03 (app.ddd) (8.7, 11.1, 12.0)	1.78 (app.ddd) (9.4, 11.8, 12.2)
H-2_e	2.26 (ddd) (2.1, 5.1, 12.3)	2.25 (ddd) (2.1, 5.2, 11.1)	2.24 (ddd) (1.8, 4.8, 12.3)	2.24 (ddd) (1.9, 5.4, 12.3)	2.11 (ddd) (2.0, 4.9, 12.3)	2.14 (ddd) (2.1, 5.1, 12.0)	2.33 (ddd) (2.1, 5.4, 12.2)
H-3	3.41–3.26[b] (band)	3.37–3.29 (m)	3.39–3.32 (m)	3.39–3.23[b] (band)	3.90 (ddd) (4.9, 9.0, 11.8)	3.73–3.66[b] (band)	3.60–3.55 (m)
H-4		3.23 (t) (9.1)	3.26 (t) (8.7)		3.81–3.58[e] (band)		3.23 (t) (9.1)
H-5							
H-6a	3.84–3.62[c] (band)	3.77–3.58[c] (band)	3.80–3.58[c] (band)	3.81–3.59[d] (band)		3.93–3.84[c] (band)	3.88–3.66[c] (band)
H-6b							
Ph-H	7.25–6.90 (band)	7.01–6.78 (band)	6.99 (d), 6.84 (d)	6.94 (d), 6.78 (d)	7.33–7.00 (m)	7.90–7.45 (band)	7.78–7.16 (band)
Other signals		2.04 (br s)	2.13 (br s)	3.81–3.59[d] (band)			

[a] ^{1}H NMR recorded in 300 MHz instrument.
Signal for [b]H-3, H-4; [c]H-5, H-6a,b; [d]H-5, H-6a, H-6b and benzylic proton; [e]H-4, H-5, H-6a,b overlap.

3.6. *p*-Tolyl 2-deoxy-α-D-*lyxo*-hexopyranoside (5)

Mp 123–125 °C; $[\alpha]_D^{24}$ +178.5 (*c* 1.0, MeOH). ESIMS *m*/*z* calcd for $C_{13}H_{18}O_5$: 277.1052 $[M+Na]^+$. Found: 277.1042. Anal. Calcd: C, 61.40; H, 7.14. Found: C, 61.50; H, 7.21.

3.7. 4-Methoxylphenyl 2-deoxy-α-D-*lyxo*-hexopyranoside (6)

Mp 127–130 °C; $[\alpha]_D^{24}$ +167.0 (*c* 1.0, MeOH). ESIMS *m*/*z* calcd for $C_{13}H_{18}O_6$: 293.1001 $[M+Na]^+$. Found:

Table 10. ^{13}C NMR chemical shift assignments of **24**–**30** in acetone-d_6/D_2O[a]

Compound	C-1	C-2	C-3[b]	C-4[b]	C-5	C-6	Other signals
25	98.1	39.7	72.3	71.6	77.6	62.2	130.3, 122.9, 117.2
26	98.2	39.1	71.5	70.9	76.9	61.6	155.6, 131.0, 127.5, 127.4, 122.7, 115.4, 15.9
27	98.3	39.4	71.9	71.3	77.3	61.9	132.7, 130.8, 117.8, 117.2, 20.6
28	98.7	39.3	71.7	71.1	77.0	61.8	155.3, 151.6, 118.8, 114.9, 101.0, 55.7
29	101.3	37.0	71.3	70.0	79.1	64.4	160.0, 130.2, 122.4, 117.0
30	98.8	39.0	71.5	70.2	79.0	64.0	155.2, 130.4, 130.0, 128.4, 127.3, 124.8, 120.1
31	97.9	39.3	71.9	71.2	77.2	61.9	155.4, 135.0, 130.1, 129.9, 128.0, 127.7, 126.9, 124.7, 119.2, 111.1

[a] ^{13}C NMR recorded in 75 MHz instrument.
[b] Assignments interchangeable.

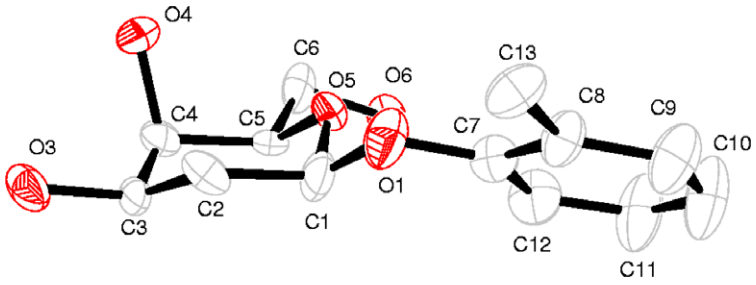


Figure 3. Single crystal X-ray structure of *o*-tolyl 2-deoxy-β-D-*lyxo*-hexopyranoside (**18**).

293.1017. Anal. Calcd: C, 57.77; H, 6.71. Found: C, 57.23; H, 6.69.

3.8. 2-Hydroxy-phenyl 2-deoxy-α-D-*lyxo*-hexopyranoside (7)

Mp 130–131 °C; $[\alpha]_D^{24}$ +164.6 (*c* 0.9, MeOH). ESIMS *m*/*z* calcd for $C_{12}H_{16}O_6$: 279.0845 $[M+Na]^+$. Found: 279.0833. Anal. Calcd: C, 56.24; H, 6.29. Found: C, 56.23; H, 6.26.

3.9. 1-Naphthyl 2-deoxy-α-D-*lyxo*-hexopyranoside (8)

Mp 192–194 °C; $[\alpha]_D^{24}$ +76.0 (*c* 1.1, MeOH). ESIMS *m*/*z* calcd for $C_{16}H_{18}O_5$: 313.1052 $[M+Na]^+$. Found: 313.1064. Anal. Calcd: C, 66.19; H, 6.25. Found: C, 66.43; H, 6.16.

3.10. 2-Naphthyl 2-deoxy-α-D-*lyxo*-hexopyranoside (9)

Mp 198–201 °C; $[\alpha]_D^{24}$ +164.8 (*c* 2.1, MeOH). ESIMS *m*/*z* calcd for $C_{16}H_{18}O_5$: 313.1052 $[M+Na]^+$. Found: 313.1056. Anal. Calcd: C, 66.19; H, 6.25. Found: C, 66.55; H, 6.28.

3.11. Phenyl 2-deoxy-α-D-*arabino*-hexopyranoside (10)

Mp 159–161 °C, lit.[25] mp 162–163 °C, lit.[26] mp 163.5 °C; $[\alpha]_D^{24}$ +162.2 (*c* 1.1, MeOH) , lit.[25] $[\alpha]_D$ +159 (H_2O), lit.[26] $[\alpha]_D^{20}$ +161 (*c* 0.5, MeOH). ESIMS *m*/*z* calcd for $C_{12}H_{16}O_5$: 263.0895 $[M+Na]^+$. Found: 263.0899. Anal. Calcd: C, 60.00; H, 6.71. Found: C, 59.90; H, 7.29.

3.12. *o*-Tolyl 2-deoxy-α-D-*arabino*-hexopyranoside (11)

Mp 117–119 °C; $[\alpha]_D^{24}$ +113.8 (*c* 1.1, MeOH). ESIMS *m*/*z* calcd for $C_{13}H_{18}O_5$: 277.1052 $[M+Na]^+$. Found: 277.1049. Anal. Calcd: C, 61.40; H, 7.14. Found: C, 61.74; H, 7.39.

3.13. *p*-Tolyl 2-deoxy-α-D-*arabino*-hexopyranoside (12)

Mp 168–170 °C, lit.[26] mp 170 °C; $[\alpha]_D^{24}$ +165.1 (*c* 1.0, MeOH), lit.[26] $[\alpha]_D$ +166 (MeOH). ESIMS *m*/*z* calcd for $C_{13}H_{18}O_5$: 277.1052 $[M+Na]^+$. Found: 277.1039. Anal. Calcd: C, 61.40; H, 7.14. Found: C, 61.70; H, 6.93.

3.14. 4-Methoxylphenyl 2-deoxy-α-D-*arabino*-hexopyranoside (13)

Mp 157–160 °C; $[\alpha]_D^{24}$ +135.9 (*c* 0.3, MeOH). ESIMS *m*/*z* calcd for $C_{13}H_{18}O_6$: 293.1001 $[M+Na]^+$. Found: 293.1006. Anal. Calcd: C, 57.77; H, 6.71. Found: C, 57.54; H, 6.81.

3.15. 2-Hydroxy-phenyl 2-deoxy-α-D-*arabino*-hexopyranoside (14)

Mp 150–152 °C; $[\alpha]_D^{24}$ +161.5 (*c* 1.0, MeOH). ESIMS *m*/*z* calcd for $C_{12}H_{16}O_6$: 279.0845 $[M+Na]^+$. Found:

279.0847. Anal. Calcd: C, 56.24; H, 6.29. Found: C, 55.75; H, 6.03.

3.16. 1-Naphthyl 2-deoxy-α-D-*arabino*-hexopyranoside (15)

Mp 154–156 °C, lit.[26] mp 157 °C; $[\alpha]_D^{24}$ +57.6 (*c* 1.0, MeOH), lit.[26] $[\alpha]_D$ +53.6 (MeOH). ESIMS *m*/*z* calcd for $C_{16}H_{18}O_5$: 313.1052 $[M+Na]^+$. Found: 313.1060. Anal. Calcd: C, 66.19; H, 6.25. Found: C, 66.65; H, 6.44.

3.17. 2-Naphthyl 2-deoxy-α-D-*arabino*-hexopyranoside (16)

Mp 163–165 °C; $[\alpha]_D^{24}$ +160.6 (*c* 1.0, MeOH). ESIMS *m*/*z* calcd for $C_{16}H_{18}O_5$: 313.1052 $[M+Na]^+$. Found: 313.1051. Anal. Calcd: C, 66.19; H, 6.25. Found: C, 66.54; H, 6.39.

3.18. Phenyl 2-deoxy-β-D-*lyxo*-hexopyranoside (17)

Mp 147–149 °C; $[\alpha]_D^{24}$ −31.0 (*c* 0.9, MeOH). ESIMS *m*/*z* calcd for $C_{12}H_{16}O_5$: 263.0895 $[M+Na]^+$. Found: 263.0893. Anal. Calcd: C, 60.00; H, 6.71. Found: C, 59.63; H, 6.29.

3.19. *o*-Tolyl 2-deoxy-β-D-*lyxo*-hexopyranoside (18)

Mp 161–163 °C; $[\alpha]_D^{24}$ −35.0 (*c* 1.0, MeOH). ESIMS *m*/*z* calcd for $C_{13}H_{18}O_5$: 277.1052 $[M+Na]^+$. Found: 277.1037. Anal. Calcd: C, 61.40; H, 7.14. Found: C, 61.15; H, 7.19.

3.20. *p*-Tolyl 2-deoxy-β-D-*lyxo*-hexopyranoside (19)

Mp 161–162 °C; $[\alpha]_D^{24}$ −38.1 (*c* 0.9, MeOH). ESIMS *m*/*z* calcd for $C_{13}H_{18}O_5$: 277.1052 $[M+Na]^+$. Found: 277.1061. Anal. Calcd: C, 61.40; H, 7.14. Found: C, 61.68; H, 6.78.

3.21. 4-Methoxyphenyl 2-deoxy-β-D-*lyxo*-hexopyranoside (20)

Mp 169–172 °C; $[\alpha]_D^{24}$ −40.0 (*c* 1.1, MeOH). ESIMS *m*/*z* calcd for $C_{13}H_{18}O_6$: 293.1001 $[M+Na]^+$. Found: 293.1001. Anal. Calcd: C, 57.77; H, 6.71. Found: C, 57.68; H, 6.96.

3.22. 2-Hydroxy-phenyl 2-deoxy-β-D-*lyxo*-hexopyranoside (21)

Mp 157–160 °C; $[\alpha]_D^{24}$ −26.4 (*c* 0.9, MeOH). ESIMS *m*/*z* calcd for $C_{12}H_{16}O_6$: 279.0845 $[M+Na]^+$. Found: 279.0848. Anal. Calcd: C, 56.24; H, 6.29. Found: C, 55.77; H, 6.31.

3.23. 1-Naphthyl 2-deoxy-β-D-*lyxo*-hexopyranoside (22)

Mp 227–228 °C; $[\alpha]_D^{24}$ −36.1 (*c* 0.9, MeOH). ESIMS *m*/*z* calcd for $C_{16}H_{18}O_5$: 313.1052 $[M+Na]^+$. Found: 313.1051. Anal. Calcd: C, 66.19; H, 6.25. Found: C, 66.48; H, 6.65.

3.24. 2-Naphthyl 2-deoxy-β-D-*lyxo*-hexopyranoside (23)

Mp 224–226 °C; $[\alpha]_D^{24}$ −43.3 (*c* 2.1, MeOH). ESIMS *m*/*z* calcd for $C_{16}H_{18}O_5$: 313.1052 $[M+Na]^+$. Found: 313.1040. Anal. Calcd: C, 66.19; H, 6.25. Found: C, 66.25; H, 5.96.

3.25. Phenyl 2-deoxy-β-D-*arabino*-hexopyranoside (24)

Mp 179–181 °C, lit.[27] mp 143–146 °C; $[\alpha]_D^{24}$ −65.0 (*c* 1.0, MeOH), lit.[27] $[\alpha]_D^{20}$ −75.0 (*c* 0.5, H_2O). ESIMS *m*/*z* calcd for $C_{12}H_{16}O_5$: 263.0895 $[M+Na]^+$. Found: 263.0893. Anal. Calcd: C, 60.00; H, 6.71. Found: C, 59.78; H, 7.32.

3.26. *o*-Tolyl 2-deoxy-β-D-*arabino*-hexopyranoside (25)

Mp 137–139 °C; $[\alpha]_D^{24}$ −47.6 (*c* 1.1, MeOH). ESIMS *m*/*z* calcd for $C_{13}H_{18}O_5$: 277.1052 $[M+Na]^+$. Found: 277.1062. Anal. Calcd: C, 61.40; H, 7.14. Found: C, 61.26; H, 7.20.

3.27. *p*-Tolyl 2-deoxy-β-D-*arabino*-hexopyranoside (26)

Mp 182–184 °C; $[\alpha]_D^{24}$ −65.0 (*c* 0.7, MeOH). ESIMS *m*/*z* calcd for $C_{13}H_{18}O_5$: 277.1052 $[M+Na]^+$. Found: 277.1065. Anal. Calcd: C, 61.40; H, 7.14. Found: C, 61.11; H, 7.56.

3.28. 4-Methoxyphenyl 2-deoxy-β-D-*arabino*-hexopyranoside (27)

Mp 185–187 °C; $[\alpha]_D^{24}$ −55.3 (*c* 1.2, MeOH). ESIMS *m*/*z* calcd for $C_{13}H_{18}O_6$: 293.1001 $[M+Na]^+$. Found: 293.1018. Anal. Calcd: C, 57.77; H, 6.71. Found: C, 57.44; H, 7.03.

3.29. 2-Hydroxy-phenyl 2-deoxy-β-D-*arabino*-hexopyranoside (28)

Mp 186–188 °C; $[\alpha]_D^{24}$ −33.7 (*c* 0.4, MeOH). ESIMS *m*/*z* calcd for $C_{12}H_{16}O_6$: 279.0845 $[M+Na]^+$. Found: 279.0855. Anal. Calcd: C, 56.24; H, 6.29. Found: C, 56.02; H, 6.21.

3.30. 1-Naphthyl 2-deoxy-β-D-*arabino*-hexopyranoside (29)

Mp 193–195 °C; $[\alpha]_D^{24}$ −29.0 (*c* 1.0, MeOH). ESIMS *m*/*z* calcd for $C_{16}H_{18}O_5$: 313.1052 $[M+Na]^+$. Found: 313.1061. Anal. Calcd: C, 66.19; H, 6.25. Found: C, 65.93; H, 6.37.

3.31. 2-Naphthyl 2-deoxy-β-D-*arabino*-hexopyranoside (30)

Mp 191–193 °C; $[\alpha]_D^{24}$ −76.2 (*c* 1.2, MeOH). ESIMS *m*/*z* calcd for $C_{16}H_{18}O_5$: 313.1052 $[M+Na]^+$. Found: 313.1044. Anal. Calcd: C, 66.19; H, 6.25. Found: C, 66.07; H, 6.45.

3.32. HPLC analysis

HPLC analysis of reaction mixtures was carried out on a Phenogel (5 μ silica gel, 100 Å) semi preparative column attached to a Shimadzu HPLC system and eluted with 3% MeOH/ EtOAc (flow rate: 0.8 mL/min) and detected with a UV detector ($\lambda = 272$ nm).

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22. See Supplementary data for crystallographic data. This has been deposited with the Cambridge Crystallographic Data center as supplementary publication number CCDC 630599. Copies of the data can be obtained free of charge, on application to CCDC, 2 Union Road, Cambridge CB2 1EZ, UK [fax: +44(0) 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk].
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