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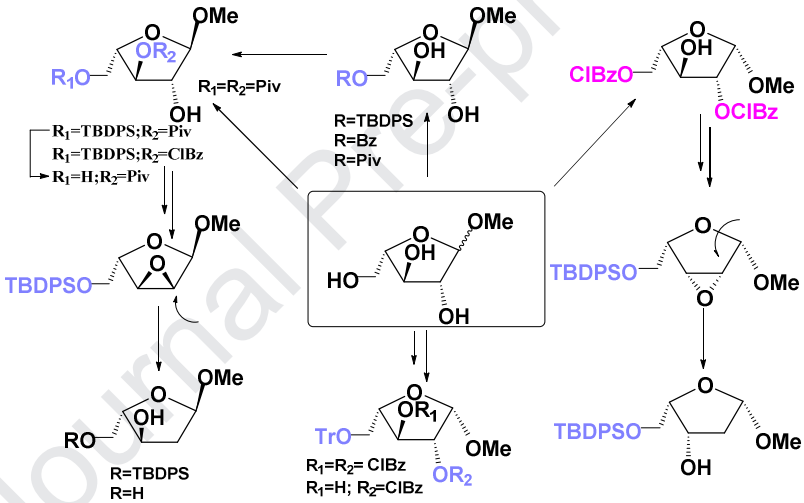

Regioselective and stereocontrolled syntheses of protected L-glycosides from L -arabinofuranosides

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Abstract: Synthesis of novel mono- and di-*O*-protected L-arabinofuranoside derivatives was described via regioselective base-catalyzed acylations of methyl α- and β-L-arabinofuranosides with acyl chlorides. A new method for selective 3(2)-*O*-acylation of 5-*O*-silyl (trityl) L-arabinofuranosides was investigated based upon generation of organoboron compounds using L-Selectride and subsequent reaction of salt carbohydrate species with pivaloyl or 4-chlorobenzoyl chloride as the electrophile. Syntheses of methyl 2,3-anhydro-L-furanosides were accomplished from selectively protected methyl L-arabinofuranosides. 2(3)-Deoxy-L-pentofuranosides, including 2-deoxy-L-ribofuranoside, and their 5-*O*-blocked derivatives were prepared by stereoselective reductions of 2,3-anhydro-L-furanosides with L-Selectride.

Keywords: L-arabinofuranosides / protecting groups / regioselective acylation reactions / anhydro- L-furanosides /stereoselective reduction / L-Selectride

1.Introduction

Carbohydrates are an interesting class of biomolecules which play essential roles in various biological processes and exploit as scaffolds for the generation of different bioactive compounds. As the most abundant natural resource, they have found widespread application in constructing pharmaceuticals, polymers, oligosaccharides and glycoconjugates. Selective modifications of D-monosaccaharides are widely studied and include regioselective functionalization on hydroxyl groups, using different methods [1-4] based upon organotin catalysis [5], metal- and organo-catalysis [6], organoboron reagents [7] and enzyme-mediated selective protection of unprotected glycosides [8] or deprotection of fully acylated glycoside [9]. Selectively protected D- and L-monosaccharide derivatives can be used as both intermediates and building blocks for further use in glycosylation reactions [10,11]. A set of modified L-pentose derivatives have been prepared by different chemical methods and utilized in the development of L-nucleosides as antiviral agents [12]. Identification of several modified nucleosides derived from L-sugars as potent antiviral agents with lower toxicity compared to the D-nucleosides and medicinal application of some L-enantiomers of natural nucleosides have emerged important outcome of broad investigations in the past decades [13].

Fig.1.

Fig.1. L-Pentofuranoside derivatives as versatile intermediates in synthesis of modified L-sugars and oligosaccharides deriving from L-arabinose

The most active L-nucleoside analogues, L-3′-thiacytidine (lamivudine, L-TC), 1-(2-deoxy-β-L-ribofuranosyl)thymine (β-L-thymidine, telbivudine), and L-5-fluoro-3-thiacytidine (L-FTC) with potent and selective antiviral activities approved for use in therapy of acute and chronic hepatitis B infections, and HIV. Various approaches have been reported for preparation of unnatural L-monosaccharides, especially L-ribose and L-deoxyribose derivatives, which are valuable precursors for the synthesis of L-pentofuranonucleosides [12,14]. It should be emphasized that naturally occurring L-deoxy sugars belonging to different classes of deoxygenated hexose derivatives were found to be constituents of oligosaccharide moieties in glycoconjugates or antibiotics with antibacterial or antitumor activity [15].

Furthermore, it has been shown that 2-deoxy-L-ribose and its analogues displayed antitumor activities [16] Noteworthy also is another important aspect of synthetic use of L-monosaccharides in development of antibacterial agents. So selectively protected α-D-arabinofuranoside derivatives, as well as their L-enantiomers, have been used as building blocks in the synthesis of a series of arabinofuranosyl-containing oligosaccharides [10,11,17-20] that are key structural motif in mycobacterial arabinogalactan and lipoarabinomannan [21] found in the wall cell of

mycobacteria. Synthetic routes to 2,3-anhydrofuranose derivatives have been studied from D-xylose, -arabinose or L-glytamic acid [22-25], and 2,3-anhydro-D-sugar thioglycosides have found implementation as intermediates in the synthesis of C-2 functionalized oligosaccharides [26, 27] and 2-deoxy-glycosides. To the best our knowledge, there have been no reports on syntheses of various isomeric 2,3-anhydro-L-furanosides. Thus, the study of synthetic approaches to diverse protected L-pentofuranoside derivatives (Fig.1) useful for glycosylation reactions and building modified L-sugars, L-nucleosides and L-furanose-containing oligosaccharides is of considerable interest from available L-arabinose.

The present paper describes synthetic base-catalyzed routes to different selectively protected α- and β-L-arabinofuranosides, syntheses of isomeric 2,3-anhydro-L-furanosides and novel deoxy-L-pentofuranoside derivatives using regio- and stereoselective transformations of methyl L-arabinofuranosides readily available from L-arabinose. Special attention in this research was directed to regioselective protection of hydroxyl groups of L-arabinofuranosides with various protecting groups and elaboration of new synthetic methods for preparation of methyl 2(3)-deoxy-α-L-pentofuranoside derivatives via epoxide ring opening of 2,3-anhydro-L-furanosides by a complex hydride.

2. Results and discussion

2.1.Regioselective transformations of methyl α-L-arabinofuranoside (1a)

2.1.1. Regioselective acylations of α-L-arabinofuranosides with acyl chlorides

In continuation of our previous investigations into regioselective syntheses of various L-pentose derivatives, [28] selective acylations of individual unprotected methyl α- and β-L-arabinofuranosides **1a** and **1b** prepared by methanolysis of L-arabinose were studied under different reaction conditions with acyl chlorides. It is interesting to note that a number of reports have been described regioselective acylations of mainly D-hexopyranoside derivatives with application of the different acylating agents to prepare selectively protected (benzoylated, pivaloylated and acetylated) carbohydrates using organocatalytic processes [1, 29-33]. However, preparation of mono- and di-*O*-acylated L-arabinofuranosides was little explored [11, 17, 18, 28, 34]. As reported earlier, selective acylation of α-L-arabinofuranoside **1a** with pivaloyl chloride in a mixture of solvents in the presence of pyridine as a catalyst resulted in the 3,5-di-*O*-pivloyl derivative **2** as the main product [28]. The regioselectivity of this reaction was established after separation of a mixture of *O*-acylated L-arabinosides by column chromatography on silica gel (Scheme 1, conditions a_1, table 1, entry 1). The formation of the 3,5-di-*O*-pivalate **2** together with 2,5-di- (**3**), 2,3,5-tri- (**4**) and 5-*O*-pivaloyl (**5**) derivatives was observed in a ratio of 6:2:2.2:1 in combined 78% overall yield as a result of the acylation reaction with 2 equiv of pivaloyl chloride. Additionally, selective acylation of **1a** with 2.1 equiv of pivaloyl chloride in pyridine at 0 ^{0}C gave the 5-*O*-pivaloyl-α-L-arabinofuranoside (**5**) in 64% yield as the main product along with the di-*O*-pivaloyl derivatives **2** and **3** (17%) in a ratio of 2:1 (table 1, entry 2). In contrast to unsuccessful, selective 6-*O*-pivaloylation of a number of methyl hexopyranosides [35], regioselective acylation of **1a** with pivaloyl chloride in pyridine proceeds selectively on the primary 5-OH group over secondary hydroxyl groups in α-L-arabinofuranoside. Regioselective acylation of **1a** with the bulky electrophile in pyridine may be explained by a higher reactivity of the primary 5-OH group compared to secondary hydroxyl groups. It has previously shown [28] that a simple two-step acylation of triol **1a** using an overall twofold excess of 4-chlorobenzoyl chloride as acylating agent in the presence of pyridine resulted in the target 3,5- and 2,5-di-*O*-chlorobenzoylated α-L-arabinofuanosides after chromatography on silica gel of regioisomeric products. Alternatively, direct regioselective acylation of methyl α-L-arabinofuranoside (**1a**) with 1 equiv of 4-chlorobenzoyl chloride in a mixture of anhydrous methylene chloride and pyridine at room temperature followed by the same

acylation at 0 °C→rt furnished a mixture of acylated glycosides with 67% overall yield (a ratio of the di-*O*-acylated L-glycosides - 2.5:1) and more lower regioselectivity than in the previous experiment (table 1, entries 4 and 3).

Scheme 1

Scheme 1. Reagents and conditions. a_1) ref. 28 i) **1a**, 1 equiv PivCl, CH_2Cl_2 1.5 equiv Py, 0 °C→rt, ii) 1 equiv PivCl, CH_2Cl_2 1 equiv Py, 0 °C→rt; a_2) 2.1 equiv PivCl, Py 0 °C, 6 h and 2h, rt; b_1**)** ref. 28, **1a**, 4ClBzCl, CH_2Cl_2, Py, 0 °C→rt; b_2) i) 1 equiv 4ClBzCl, CH_2Cl_2 1equiv Py, rt, ii) 1 equiv 4ClBzCl, CH_2Cl_2 1 equiv Py, 0 °C→rt; c_1) i) **1a**, 1.9 equiv BzCl, THF/Py, 1 equiv DIPEA, rt, 5 h; ii) 1 equiv Et_3N, 48 h rt; c_2) i) **1a**, 2.7 equiv BzCl, THF/Py, 1 equiv DIPEA, rt, 18 h; ii) 1 equiv Et_3N, 18 h, rt; and then 3 h at 35-37 °C; d) i) **9**, 1.5 equiv 4ClBzCl, CH_2Cl_2, 2.1 equiv Py, 0 °C→rt, 1 h and then 20 h, rt; ii) 1 equiv 4ClBzCl, CH_2Cl_2, rt, 3 h.

The acylation reaction of **1a** with 1.9 equiv of benzoyl chloride in a mixture of tetrahydrofuran/pyridine in the presence of iPr_2NEt and Et_3N gave a mixture of 3,5- and 2,5-di-*O*-benzoylated L-arabinofuanosides **10** and **11** in a ratio of 1:1 and 5-*O*-benzoyl derivative **9** (37%) after chromatography on silica gel (conditions c_1, entry 5). The use of 2.7 equiv of benzoyl chloride in the reaction under consideration in the presence of two amines gave rise to the 5-*O*-benzoyl derivative **9** as the main product (64%) and a mixture of the regioisomeric dibenzoyl derivatives **10** and **11** (25%) (table 1, entry 6, conditions c_2). Further, selective acylation of 5-*O*-benzoyalated α-L-arabinofuranoside **9** with 2.5 equiv of 4-chlorobenzoyl chloride (entry 7, conditions d) in anhydrous methylene chloride and pyridine afforded a mixture of regioisomeric di-*O*-benzoates **12** and **13** in 60% overall yield, and the tri-*O*-benzoate **14** (6%) after chromatography on silica gel. It should be noted that the formation of mixtures of acylated L-glycoside derivatives was observed under pyridine-catalysed acylations of **1a** (Table 1) in all cases. The target 3,5 and 2,5-di-*O*-acyl arabinofuranoside derivatives **2**-**3** and **6**-**7** were prepared as individual compounds after acylation of the starting glycoside with pivaloyl or 4-chlorobenzoyl chloride in a mixture of solvents followed by chromatographic separation of acylated products. We have found that synthesized isomeric the 3,5- and 2,5-di-*O*-benzoylated arabinofuranoside derivatives **10** and **11**, **12** and **13** in contrast to the di-*O*-pivalates (**2** and **3**) and the di-*O*-chlorobenozoates (**6** and **7**) were inseparable by chromatography on silica gel in different tested conditions.

Table 1. Selective acylations of α-L-arabinofuranoside **1a** and its 5-*O*-benzoyl derivative **9**

Entry	L-arabinoside (conditions[a])	Acyl chloride	Products (isolated yields, %)			
			3,5-di-	2,5-di-	2,3,5-tri-	5-*O*-acyl
1	**1a** (a_1)	PivCl	**2**(42)	**3** (13)	**4** (16)	**5** (7)
2	**1a** (a_2)	PivCl	**2/3** (17, ratio 2:1)[b]		-	**5** (64)
3	**1a** (b_1)[c]	ClBzCl	**6** (40)	**7** (12)	**8** (24)	-
4	**1a** (b_2)	ClBzCl	**6** (38)	**7** (15)	**8** (14)	-
5	**1a** (c_1)	BzCl	**10/11** (25, ratio 1:1)[b]		-	**9** (37)
6	**1a** (c_2)	BzCl	**10/11** (28, ratio 1:1.4)[b]		-	**9** (62)
7	**9** (d)	ClBzCl	**12/13** (60, ratio 1.7:1)[b]		**14** (6)	-

[a] Conditions according to Scheme 1.
[b] Selectivity ratios were determined by ^1H NMR data in $CDCl_3$.
[c] Yields from ref.28.

2.1.2. Syntheses of selectively protected α-L-arabinofuranosides, 2,3-anhydro-α-L-furanosides and 2(3)-deoxy-α-L-pentofuranosides

Next, investigation on selective protection of hydroxyl groups in **1a** was undertaken to prepare 3,5-di-*O*-protected derivatives with different type of protecting groups. Treatment of L-glycoside **1a** with *tert*-butylchlorodiphenylsilane in pyridine gave 5-*O*-silyl derivative **15** in 82% yield. Regioselective acylation of the protected α-L-arabinoside in the presence of L-Selectride was studied with acyl chlorides (Scheme 2). It can be assumed that reactivity difference of the secondary hydroxyl groups in the glycoside **15** with a complex hydride due to steric hindarance or stereoelectonic effects may be utilized for selective generation of *O*-activated carbohydrate

derivatives on the first step followed by the acylation reaction with the electrophile. Thus, acylation of 5-*O*-protected α-L-arabinofuranoside **15** in the presence of 1.1 equiv of 1 M $Li(i\text{-}Bu)_3BH$ (L-Selectride) in THF and a excess of pivaloyl chloride (Scheme 2, conditions b_1) resulted in only the 3-*O*-pivalate **17** (43%) and the 2,3-di-*O*-pivalate **18** (57%) after column chromatography on silica gel. The formation of acylated L-arabinofuranosides **17** and **18** proceeds via generation of intermediate organoboron compound **16** on the first step as result of reaction of 5-*O*-protected arabinoside **15** with L-Selectride in THF. The use of 4-chlobenzoyl chloride instead of pivaloyl chloride in this reaction gave the 3-*O*-benzoate **19** (40%) and the 2,3-di-*O*-benzoate **20** (50%) (conditions b_2). The removal of silyl group in **17** with ammonium fluoride in methanol furnished new 3-*O*-pivaloyl-α-arabinofuranoside (**21**) in 88% yield (Scheme 2, conditions c).

5-*O*-Protected methyl 2,3-anhydro-α-L-ribofuranoside **26** was prepared from the mesylate **22** in 80% yield using sodium methoxide in methanol. The same reaction of mesyl derivative **23** gave also rise to compound **26** (97%) after chromatography on silica gel (Scheme 2, conditions f). Methyl 2,3-anhydro-α-L-ribofuranoside (**25**) was prepared in 73% yield using two-step process involved mesylation of the 3,5-di-*O*-pivalate **2** followed by basic treatment of the intermediate 2-OMs derivative. Reduction of unprotected 2,3-anhydrosugar **25** with an excess of L-Selectride gave methyl 2-deoxy-α-L-ribofuranoside (**28**) in 93% yield after column chromatography on silica gel. The stereoselective reaction of unprotected 2,3-epoxide **25** likely to proceed via generation of intermediate organoboron compound **27** as a result of interaction of a complex hydride with 5-OH group followed by reduction of the 2,3-anhydrocycle with L-Selectride in THF. Stereospecific reduction of 5-*O*-silyl derivative of epoxysugar **29** by a complex hydride in THF afforded 5-*O*-protected methyl 2-deoxy-α-L-ribofuranoside **29** in 99% yield after a simple treatment of the reaction mixture. Removal of the 2-*O*-chlorobenzoyl protecting group in protected arabinoside **23** with methanolic ammonia followed by reduction of intermediate 2-OMs-L-arabinoside derivative **24** gave L-2-deoxyriboside derivative **28** in 73% overall yield (conditions i) from **24**.

Scheme 2

Scheme 2. Reagents and conditions. a) **1a**, TBDPSCl, Py 82%; b_1) i) **15**, 1.08 equiv 1M $Li(iBu)_3BH$ in THF, 0 $^oC\rightarrow$rt, 30 min, 2 equiv PivCl, 0 ^oC; 5 h, rt; ii) 1.4 equiv. PivCl, 0 ^oC; 18 h, rt, 57% to **18** and 43% to **17** taking account 28% recovery of **15**; b_2) (i) **15**, 1 equiv 1M $Li(i\text{-}Bu)_3BH$ in THF, 0 $^oC\rightarrow$rt, 30 min, (ii) 2.1 equiv 4ClBzCl in THF, 0 $^oC\rightarrow$rt, 4 h, 50% to **20** and 40% to **19** taking account 19% recovery of **15**; c) **17**, NH_4F, MeOH, 29-30 ^oC, 88%; d) **17**, MsCl/Py, DMAP, 0 $^oC\rightarrow$rt, 2 h, 92% to **22**; **19**, MsCl/Py, DMAP, 0 $^oC\rightarrow$rt, 18 h, 97% to **23**; e) MeONa, MeOH, rt, 80% to **26** from **22**; 97% to **26** from **23**; f) i) **2**, MsCl/Py, ref.28; ii) MeONa, MeOH, rt, 73 % to **25**; g) TBDPSCl, Py 85%; h_1) $Li(iBu)_3BH$ in THF, -78 $^oC\rightarrow$rt, 1h, 93% to **28** from **25**; h_2) $Li(iBu)_3BH$ in THF, -78 $^oC\rightarrow$rt, 15 min, 99% to **29** from **26**; i) i) **23**, NH_3/MeOH, rt, 4 h; ii) **24**, $Li(iBu)_3BH$ in THF/DME, -78 $^oC\rightarrow$rt, 18 h, 77% to **29**.

Synthesis of methyl 5-*O*-trityl-2,3-anhydro-α-L-lyxofuranoside (**31**) was carried out in 94% yield via the Mitsunobu reaction with triphenylphospine (Ph_3P) and diisopropylazodicarboxylate (DIAD) starting from 5-*O*-trityl L-arabinoside derivative **30** (Scheme 3) prepared by tritylation of **1a** according the literature protocol described for D-enantiomer [36]. The reduction of the 2,3-epoxy ring in **31** with an excess of L-Selectride gave only 5-*O*-protected 3-deoxy-α-L-*threo*-pentofuranoside **32** which was prepared in 91% yield after column chromatography on silica gel.

Scheme 3

Scheme 3. Reagents and conditions. a) ref. 36; b) Ph_3P, DIAD, THF, rt, reflux,1h, 94%; c) $Li(iBu)_3BH$ in THF, -78 $^oC\rightarrow$rt, 175 min, 91%; d) aq. CH_3COOH, 55 ^0C, 30 min, 82%; e) ref.22; f) $Li(iBu)_3BH$ in THF, -78 $^oC\rightarrow$rt, 50 min, 92%.

Mild removal of the trityl protecting group in the latter with aqueous acetic acid afforded 3-deoxy-α-L-arabinoside **33** in 82% yield. Alternative two-step approach to **33** was studied from arabinoside **1a**. 2,3-Anhydro-α-L-lyxofuranoside **34** was synthesized via epoxidation of **1a** with Ph_3P/DIAD under the Mitsunobu conditions [22]. Selectride reduction of epoxide **34**, which proceeds via formation of intermediate 5-*O*-activated derivative **35** (Scheme 3) under treatment of 2,3-anhydro-α-L-lyxofuranoside with an excess of L-Selectride, gave methyl 3-deoxy-α-L-arabinofuranoside (**33**) in 92% yield after chromatography on silica gel.

The structure of 3-deoxy L-glycoside **33** was confirmed by NMR spectral data. The anomeric proton having the small value of H-1,2 coupling constant (< 1.0 Hz), characteristic of *trans*-relationship H1 and H2, displayed as a singlet at δ 4.8 ppm and signals of protons at C-3 were observed as ddd at δ 2.34 (J = 5.9, J = 9.9, J = 13.4 Hz) and δ 1.66 ppm (J = 1.8, J = 4.8, J = 13.4 Hz), respectively, in the ^{1}H NMR spectrum (CD_3OD). The ^{13}C NMR spectrum of **33** showed C-1 and C-3 at δ 111.12 and δ 35.16 ppm, respectively. The resonances for the anomeric hydrogen of isomeric 2-deoxy L-sugar **28** appeared as a double doublet at δ 5.09 ppm ($J_{1,2'}$ < 1.0, $J_{1,2}$ = 4.6 Hz) and while did protons at C-2 as ddd and a doublet at δ 2.11 and 2.0 ppm, respectively, in the ^{1}H NMR spectrum ($CDCl_3$, experimental part). NMR spectral data of 2-deoxy-L-glycoside **29** are very close to those of D-enantiomer described earlier [37].

The results of the selectride reductions of 5-*O*-protected epoxides **26** and **31** with bulky blocking groups, and unprotected 2,3-anhydro-α-L-ribo- and lyxo-furanosides **25** and **34** indicate that stereoselective cleavages of the 2,3-epoxy rings by a complex hydride at C-2 or C-3 are governed by steric factors and polar effects of the substituents at C-1 and C-4 (5-silyl(trityl)hydroxymethyl/5-hydroxymethyl and α-methoxy groups) as in the case of the reactivity of epoxide ring in 2,3-anhydro-D-pentofuranosides with various nucleophilic agents [38]. For α-lyxo-epoxide **34** and its trityl derivative **31** reductive reactions occurs exclusively at C-3 due to the stereochemistry of the substituent at anomeric center with formation of 3-deoxy-L-furanosides. Stereoselective ring-opening reactions of 2,3-anhydro-α-L-ribofuranoside **25**, its silyl derivative **26** with a bulky reducing agent like L-Selectride as well as the 2-deoxygenation procedure for 2-OMs α-L-arabinofuranoside [28] studied earlier in the similar reaction conditions proceed in high yields to give 2-deoxy-α-L-ribofuranoside derivative. Preferential attack of the reagent at C-2 can be explained by steric hindrances of the substituents at C-4 and minimal polar effects of α-methoxy group. It should be noted that application of the sterically bulky selectride at low reaction temperature in the hydride reductions also favored 2-reduction in α-L-ribo epoxides.

2.2. Regioselective transformations of methyl β-L-arabinofuranoside (1b)

2.2.1. Syntheses of selectively protected β-L-arabinofuranosides, 2,3-anhydro-β-L-lyxofuranosides and 2(3)-deoxy-L-*threo*-pentofuranosides

Next, regioselective acylation of methyl β-L-arabinofuranoside (**1b**) was conducted with 2.0 equiv of 4-chlorobenzoyl chloride in the presence of pyridine under conditions used for α-L-arabinofuranoside **1a** to give rise to three acylated products (Scheme 4, conditions a). Unlike the α-anomer **1a**, predominant formation of 2,5-di-*O*-chlorobenzoyl derivative **36** (38% isolated yield) was achieved in this case. Besides, 2,3,5-tri- (**37**) and 2,3-di-*O*-benzoyl (**38**) β-L-arabinofuranoside derivatives were also isolated by column chromatography in 8% and 3% yields, accordingly. It is interesting that the direct pyridine-catalyzed acylation of isomeric L-glycosides **1a** and **1b** resulted in essential differences in regioselectivity (Table 2, entries 1 and 2) which was lower for α-L-arabinofuranoside. The both L-arabinofuranosides were predominantly benzoylated to give regioisomeric the di-*O*-chlorobenzoyl protected derivatives without generation of monoacylated L-glycosides in the acylation reaction. Benzoylation of unprotected L-glycosides **1a** and **1b** proceeded in moderate overall yields probably because of low solubility of the starting sugars in a mixture of solvents. Regioselective acylation of 5-*O*-trityl β-L-arabinofuranoside **39**, prepared by tritylation of methyl L-glycoside **1b** according to the literature protocol described for D-enantiomer [36], was exploited via generation of organoboron carbohydrate derivatives in the presence of L-Selectride, and subsequent treatment of intermediate salt species with 2 equiv of 4-chlobenzoyl chloride (Scheme 4, conditions c) similarly to synthesis of the 3,5-di-*O*-protected α-L-arabinofuranoside **19**.

Scheme 4

Scheme 4. Reagents and conditions. a) i) 1 equiv. 4ClBzCl, CH_2Cl_2 1.0 equiv Py, rt, 20 h ii) 1 equiv. 4ClBzCl, CH_2Cl_2 1 equiv Py, 0 ^{0}C→rt, 22 h; b) ref. 36; c) (i) 1 equiv 1M $Li(iBu)_3BH$ in THF, 0 ^{o}C→rt, 30 min, (ii), 2.0 equiv 4ClBzCl in THF, 0 ^{o}C→rt; d) MsCl/Py, DMAP, 0 ^{o}C→rt, 18 h, 88%; e) MeONa, MeOH, rt, 91%; f) TBDPDSCl, Py, rt, 80%; g) $Li(iBu)_3BH$ in THF, -78 ^{o}C→rt, 99%; h) i) $Li(iBu)_3BH$ in THF, -78 ^{o}C→rt, 90 min, ii) 10% aq. NaOH, 30% aq.H_2O_2, 51%.

2-*O*-Benzoate **43** (64%) as the major reaction product and 2,3-di-*O*-benzoate **44** (30%) were isolated after the acylation and column chromatography on silica gel. The main direction of the selective acylation reaction at the 2-OH in β-L-arabinofuranoside **39** is unexpected fact since this hydroxyl group is more sterically hindered than 3-OH. Results of regioselective acylations of 5-*O*-protected α-and β-L-arabinofuranoside derivatives with acyl chlorides summarized in Table 2 can be explained by reactivity differences of 2-OH and 3-OH in L-sugars **15** and **39** (entries 3,4 and 5).

Table 2. Regioselective acylations of methyl α-and β-L-arabinofuranosides and their 5-*O*-protected derivatives

Entry	L-arabinoside, (conditions[a], acyl chloride)	Products (isolated yields, %)				
		2,5-di-	2,3,5-tri-	2,3-di-	(3,5-di- or 3-)	2-*O*-acyl
1	**1a** (b_2, ClBzCl)	**7** (15)	**8** (14)		**6** (38)	
2	**1b** (a, ClBzCl)	**36** (36)	**37** (8)	**38** (2)		
3	**15** (b_1, PivCl)	-	-	**17** (57)	**18** (43)	-
4	**15** (b_2, ClBzCl)	-	-	**19** (50)	**20** (40)	*
5	**39** (c, ClBzCl)			**44** (30)	-	**43** (64)

[a] Conditions according to Schemes 1-2,4.
*The formation of 2-*O*-chlorobenzoyl derivative was detected as a minor product (a ratio of 3-/2-substituted -10:1) according to ^{1}H NMR data

A higher reactivity of the 2-OH group in 5-*O*-trityl-β-L-arabinofuranoside **39** relative to that of 3-OH is due to a higher acidity of 2-OH which could be attributed to the intramolecular hydrogen bond network in nonpolar solvent. The anomeric β-methoxy group of **39** and an oxygen atom of the furanose ring probably participates in the formation of hydrogen bonds with 2-hydroxy group to result in the 2-*O*-acylated glycoside as predominant product (entry 5). In the case of 5-*O*-silyl-α-L-arabinofuranoside derivative **15**, the steric factor of the 5-*O*-protecting group along with the internal hydrogen bonding between α-methoxy and 3-OH groups may influence on the regioselectivity of the acylation reactions (entries 3 and 4). The reversal of selectivity for monobenzoylation of 5-*O*-protected L-glycosides **15** and **39** was observed under the similar reaction conditions. Different acidities of 2-OH and 3-OH in L-sugars **15** and **39** should be considered as the important factor determining the regioselectivity of the studied acylation reactions in the presence of basic organoboron reagent. Treatment of diol **39** with 1 equiv of L-Selectride resulted in preferential formation of the 2-*O*-activated organoboron compound **40** which, in turns, may converts to 2-*O*-anions **41** and **42** via producing intermediate alkylborane complexes with 2-hydroxyl group [39**]** or β-methoxy group. Reaction of salt species **40-42** with acyl chloride on the next step gave rise to the 2-*O*-benzoylated derivative **43**. The formation of the di-*O*-benzoate **44** proceeds via generation of intermediate 2,3-di-*O*-Li carbohydrate species from intermediate **40** or **41** followed by acylation reaction with chlorobenzoyl chloride. This study demonstrates that L-Selectride as well as other known organoboron reagents [31,40] described earlier for regioselective acylation of *cis*-1,2-diol groups in carbohydrates (D-hexopyranoside derivatives) can be used for differentiation of secondary hydroxyl groups of 5-*O*-protected L -arabinofuranosides by acyl chlorides.

The mesylation of individual selectively protected β-L-glycoside **36** with methanesulfonyl chloride in pyridine in the presence of DMAP yielded 3-*O*-mesyl-β-L-arabinoside **45** in 88% yield (Scheme 4). Methyl 2,3-anhydro-β-L-lyxofuranoside (**46**) was prepared by treatment of the intermediate 3-OMs derivative with sodium methoxide in methanol in 91% yield. NMR spectral data of **46** is close to that of the D-enantiomer [22] described

earlier. Formation of methyl 2,3-anhydro-β-L-lyxofuranoside from the mesylate **45** confirms the structure of the 2,5-di-*O*-benzoyl β-L-glycoside prepared by selective acylation of **1b**. Silylation of 2,3-ahhydro-L-lyxofuranoside **46** with *tert*-butylchlorodiphenylsilane in pyridine gave 5-*O*-silyl derivative **47** in 80% yield. Methyl 5-*O*-*tert*-butyldiphenylsilyl-2-deoxy-β-L-*threo*-pentofuranoside (**48**) was synthesized using regioselective reduction of the epoxide ring in 5-*O*-silyl 2,3-anhydrosugar derivative **47** with L-Selectride in THF (Scheme 4, conditions g) in 99% yield. Reduction of unprotected methyl 2,3-anhydro-β-L-lyxofuranoside (**43**) with an excess a complex hydride in similar reaction conditions for 2,3-anhydro-α-L-lyxofuranoside **34** followed by oxidative workup of the reaction mixture and chromatography on silica gel gave rise to a mixture of two isomeric products such as 2-deoxy-β-L-*threo*-pentofuranoside **50** and 3-deoxy-β-L-*threo*-pentofuranoside **51** in overall 51% yield (a ratio of 2-deoxy and 3-deoxy-furanosides - 1:1.1 according to $^{1}H/^{13}C$ NMR data) (conditions h). The assignment of the proton signals for **50** in NMR spectrum of prepared mixture was made using ^{1}H NMR spectral data [41] for methyl 2-deoxy-α/β-L-xylofuranoside synthesized from D-sorbitol. It is interesting to note essential differences in selectivity for reductive epoxide opening of protected and unprotected 2,3-anhydro-β-L-sugars **47** and **46** by L-Selectride. These findings cannot be explained by steric and polar factors of the substituents adjacent to the epoxy ring in anhydrosugars and important role likely to play ability of the reducing agent to form intermediate complex organoboron derivatives via adduct **49** during the reductive process of epoxide **46**.

The structures of synthesized L-sugars were supported by ^{1}H NMR, ^{13}C NMR, HRMS and IR spectroscopic data. In all cases, the *trans*-arrangement of H-1 and H-2 protones in α-L-arabinofuranoside derivatives was indicated by characteristic coupling constants ($J_{1,2}$< 1.0 Hz) and appearance of the H-1 signal as a singlet in the ^{1}H NMR spectra. The structural assignments of the anomeric configurations of β-L-arabinofuranosides were made on basis of the $^{3}J_{H\text{-}1,H\text{-}2}$ magnitudes (4.5-4.7 Hz), which are significantly different from those of the α-L-arabinofuranosides. Furthermore, in the ^{13}C NMR spectra C-1 signals of α-L-glycosides resonated between 106 and 109 ppm while did the anomeric carbons of the β-isomers at 101 ppm.

3. Conclusion

In summary, a series of new 5-*O*, 3,5 and 2,5-di-*O*-protected L-arabinofuranoside derivatives were synthesized via regioselective base-catalyzed acylations of methyl α- and β-L-arabinofuranosides with pivaloyl, benzoyl and 4-chlorobenzoyl chlorides. A new method for selective 3(2)-*O*-acylation of 5-*O*-*tert*-butyldiphenylsilyl (trityl) L-arabinofuranosides was investigated through the tandem acylation reaction including generation of intermediate organoboron compounds by L-Selectride/acylation by acyl chloride. Significant differences in regioselectivity of the acylation reactions were found for methyl α-and β-L-arabinofuranosides and their 5-*O*-protected derivatives under the similar reaction conditions. 3-*O*-Pivaloyl α-L-arabinofuranoside derivative was obtained using the protection-deprotection strategy. Syntheses of methyl 2,3-anhydro-L-furanosides were accomplished from selectively 3,5-, 2,5- and 5-*O*-protected methyl L-arabinofuranosides derived from L-arabinose. A simple and efficient procedure for the preparation of 2(3)-deoxy-L-pentofuranosides was developed via selectride reduction of the epoxy ring in 2,3-anhydro-L-furanosides and their 5-*O*-blocked derivatives. It was shown that different methyl L-glycosides can be synthesized via regio- and stereoselective transformations of L-arabinofuranosides. L-Deoxypentofuranoside derivatives and L-2,3-anhydrofuranosides can serve as useful intermediates for the synthesis of modified L-monosaccharides and -nucleoside analogues. Selectively protected L-arabinofuranosides may be used as building blocks (glycosyl acceptors) in the regioselective glycosylation reactions [44,45,11,18] for preparation of L-arabinofuranosyl-containing di-, trisaccharides.

4.Experimental

4.1.General methods. Column chromatography was performed on silica gel 60 H (70-230 mesh; Merck, Darmstadt, Germany), and thin-layer chromatography (TLC) on silica gel plates (Silufol, Czechoslovakia) and Merck silica gel aluminum 60 F_{254} precoated plates with visualization of the spots of L-sugars by heating. All commercially available reagents were used without further purification. The anhydrous solvents were distilled over CaH_2, P_2O_5 or magnesium prior to the use. L-Arabinofuranoside derivatives were coevaporated twice with anhydrous toluene before acylation reactions. ^{1}H and ^{13}C ^{1}NMR spectra were recorded in $CDCl_3$, CD_3OD and DMSO-d_6 with a Bruker Avance-500-DRX spectrometer at 500.13, and 126.76 MHz, respectively. ^{1}H and ^{13}C NMR chemical shifts (δ, ppm) are relative to internal chloroform peak (7.26 ppm for ^{1}H and 77.0 for ^{13}C NMR). Chemical shifts are also reported downfield from internal $SiMe_4$ (^{1}H). Melting points were determined on a Boetius apparatus and were uncorrected. Optical rotations were measured with Autopol III automatic polarimeter. IR spectra were measured on Perkin-Elmer Spectrum 100FT-IR spectrometer. High resolution mass spectra (HRMS) were recorded on an Agilent Q-TOF 6550 Instrument (USA) using ESI (electrospray ionization).

4.2. Regioselective transformations of methyl α-L-arabinofuranoside (1a)

4.2.1. Regioselective acylations of α-L-arabinofuranosides with acyl chlorides

a_1. Acylation with pivaloyl chloride. Pivaloyl chloride (0.22 ml, 1.79 mmol) in anhydrous CH_2Cl_2 (3 ml) was added dropwise to a solution of methyl α-L-arabinoside **1a** (295 mg, 1.79 mmol) in anhydrous CH_2Cl_2 (3 ml) and pyridine (0.29 ml, 3.71 mmol) at 0 ^{o}C (ice and sodium chloride). The reaction mixture was stirred for 1 h under cooling and then 18 h at room temperature. Pyridine (0.14 ml, 1.79 mmol) and pivaloyl chloride (0.22 ml, 1.79 mmol) in anhydrous CH_2Cl_2 (3 ml) were consequently added at 0 ^{o}C. After stirring for 2 h under cooling, the reaction mixture was stirred for 21 h at room temperature. The solution was diluted with CH_2Cl_2 (30 ml), water (10 ml), the aqueous phase was extracted with CH_2Cl_2 (3x30 ml). The combined organic extracts were washed 1 M HCl (3x10 ml), dried over anh. Na_2SO_4 and evaporated to dryness. The residue was chromatographed on silica gel, using mixtures of petroleum ether - EtOAc to afford (121 mg, 16%) of 2,3,5-tri-*O*-pivaloyl-α-L-arabinofuranoside (**4**) as a syrup. IR (film, $CHCl_3$): ν 2977, 2937, 1738, 1285, 1146 cm^{-1}. $[\alpha]_D^{20}$ –45.8 (c 1.0, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 4.99 (d, 1H, H-2), 4.96 (m, 1H, H-3), 4.84 (s, 1H, H-1), 4.32 (dt, 1H, H-4), 4.19-4.23 (m, 2H, H-5 and H-5′), 3.37 (s, 3H, OCH_3), 1.22, 1.20 and 1.96 [3s, 27H, 3x($COC(CH_3)_3$]. ^{13}C NMR (125 MHz, $CDCl_3$) δ: 178.17, 177.7 and 177.4 [(C=O, 3x$COC(CH_3)_3$], 106.86 (C-1), 81.5 and 80.0 (C-2, C-3), 76.89 (C-4), 63.19 (C-5), 54.8 (OCH_3), 38.9, 38.73 and 38.71 [3x($COC(CH_3)_3$], 27.3, 27.2, and 27.15 [3x($COC(CH_3)_3$]. HRMS (ESI$^+$): m/z calcd for $[C_{21}H_{36}O_8+Na]^+$: 439.2308, found 439.2314.

(80 mg, 13%) of 2,5-di-*O*-pivaloyl derivative **3** as a syrup. IR (film, $CHCl_3$): ν 3492, 2975, 1734, 1285, 1159 cm^{-1}. $[\alpha]_D^{20}$ –47.1 (c 1.0, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 4.95 (br. s, 1H, H-1), 4.77 (d, 1H, *J* = 2.5 Hz, H-2), 4.2-4.32 (m, 3H, H-5, H-5′ and H-4), 3.84-3.87 (m, 1H, H-3), 3.39 (s, 3H, OCH_3), 3.19 (d, 1H, 3-OH), 1.21 and 1.20 (2s, 18H, 2x$COC(CH_3)_3$]. ^{13}C NMR (125 MHz, $CDCl_3$) δ: 179.1 and 178.3 [(C=O, 2x$COC(CH_3)_3$], 106.37 (C-1), 85.44, 81.58, 77.55 (C-2, C-4, C-3), 63.25 (C-5), 55.04 (OCH_3), 38.95 and 38.81 [2x($COC(CH_3)_3$], 27.26 and 27.14 [2x($COC(\mathbf{C}H_3)_3$]. HRMS (ESI$^+$): m/z calcd for $[C_{16}H_{28}O_7+Na]^+$: 355.1733, found 355.1728.

(251 mg, 42%) of 3,5-di-*O*-pivaloyl derivative **2** as a syrup. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 4.91 (s, 1H, H-1), 4.58 (dd, 1H, *J* = 6.4, *J* = 2.8 Hz, H-3), 4.35 (dm, 1H, H-5), 4.24-4.24 (m, 2H, H-4, H-5′), 4.04 (d, 1H, H-2), 3.39 (s, 3H, OCH_3), 1.23 and 1.22 (2s, 18H, $COC(CH_3)_3$]. ^{13}C NMR (125 MHz, $CDCl_3$) δ: 179.69, 178.11 [(C=O, 2x$CO\mathit{C}(CH_3)_3$], 108.66 (C-1), 81.52, 81.4, 78.6 (C-4, C-3, C-2), 63.1 (C-5), 54.97 (OCH_3), 38.84, 38.86 [2x($CO\mathit{C}(CH_3)_3$], 27.15, 27.96 [2x($COC(\mathit{C}H_3)_3$].

Further elution with a mixture of methylene chloride/methanol (5:1) gave (27 mg, 6%) of 5-*O*-pivaloyl derivative (**5**) as a syrup. IR (film, $CHCl_3$): ν 3441, 2970, 2934, 1725, 1169, 1109, 1040 cm^{-1}. $[\alpha]_D^{20}$ –16.6 (c 0.6, $CHCl_3$). ^{1}H

NMR (500 MHz, $CDCl_3$) δ: 4.87 (s, 1H, H-1), 4.28 (dd, 1H, H-5), 4.25 (dd, 1H, H-5′), 4.14 (m, 1H, H-4), 4.14 (m, 1H, H-2), 3.27 (dd, 1H, H-3), 3.39 (s, 3H, OCH_3), 1.21 [s, 9H, $COC(CH_3)_3$]. ^{13}C NMR (125 MHz, $CDCl_3$) δ: 178.8 [(C=O, $COC(CH_3)_3$], 108.71 (C-1), 82.9 (C-4), 80.5, 78.1 (C-2, C-3), 64.1 (C-5), 55.17 (OCH_3), 39.0 [($COC(CH_3)_3$], 27.26 [($COC(CH_3)_3$]. HRMS (ESI^+): m/z calcd for $C_{11}H_{20}O_6$ $[M+Na]^+$: 271.1158, found 271.1162; $C_{10}H_{17}O_5$ $[M-OCH_3]^+$: 217.1076, found 217.1084

a_2. Pivaloyl chloride (0.18 ml, 1.46 mmol) in anhydrous pyridine (0.8 ml) was added dropwise to a stirred solution of methyl α-L-arabinoside (**1a**) (114 mg, 0.69 mmol) in anhydrous pyridine (2.0 ml) at 0 ^oC in three portion. The reaction mixture was stirred for 6 h under cooling and then 2 h at rt, diluted with water, extracted with chloroform. The combined organic extracts were washed with 1 N HCl, 5%-aqueous $NaHCO_3$, dried over anhydrous Na_2SO_4 and evaporated to dryness. The residue was chromatographed on silica gel, using a mixture of 3:1 petroleum ether-EtOAc to afford a mixture of the dipivaloyl L-arabinofuranoside derivatives (40 mg, 17%, 2:1) (**2** and **3**) as a syrup. Further elution with a mixture of methylene chloride-methanol (5:1) gave (110 mg, 64%) of 5-*O*-pivaloyl derivative (**5**) as a syrup.

b_2. Acylation with 4-chlorobenzoyl chloride. A solution of methyl α-L-arabinoside **1a** (365 mg, 2.22 mmol) in anhydrous CH_2Cl_2 (4.7 ml) and pyridine (0.17 ml, 2.2 mmol) was stirred for 20 min at rt, then 0.28 ml (2.18 mmol) 4-chlorobenzoyl chloride in 2.9 ml anhydrous CH_2Cl_2 was added dropwise. The reaction mixture was stirred for 18 h at room temperature. Anhydrous pyridine (0.17 ml, 2.2 mmol) and solution of 4-chlorobenzoyl chloride (0.28 ml, 2.18 mmol) in anhydrous CH_2Cl_2 (2.9 ml) were consequently added to a prepared solution at 0 ^0C. After stirring during 45 min under cooling, the reaction mixture was stirred for 20 h at room temperature. The solution was diluted CH_2Cl_2 (40 ml), water (10 ml), the aqueous phase was extracted with CH_2Cl_2 (3x30 ml). The combined organic extracts was washed 1 N HCl (10 ml), 5% aq $NaHCO_3$, dried over anhydrous Na_2SO_4 and evaporated to dryness. The residue was chromatographed on silica gel using a mixture of 6:1, 4:1 and 2.5:1 hexane - EtOAc to afford (175 mg, 14%) of methyl 2,3,5-tri-*O*-4-chlorobenzoyl-α-L-arabinofuranoside (**8**), (370 mg, 38%) of methyl 3,5-di-*O*-4-chlorobenzoyl-α-L-arabinofuranoside (**6**) and (150 mg, 15%) of methyl 2,5-di-*O*-4-chlorobenzoyl derivative (**7**).

c_1. Acylation with benzoyl chloride. To a solution of methyl α-L-arabinoside **1a** (151 mg, 0.92 mmol) in anhydrous THF (7.0 ml) and pyridine (0.22 ml), N,N-diisopropylethylamine (1.4 ml, 0.9 mmol) was added and a mixture was stirred for 30 min at rt, then benzoyl chloride (0.16 ml, 1.38 mmol) was added dropwise to prepared solution. The reaction mixture was stirred for 5 h at rt and then 0.13 ml (0.93 mmol) triethylamine was added dropwise. The reaction mixture was stirred for 48 h at room temperature. The precipitate was filtered off and washed THF (5 ml), the filtrate was diluted with CH_2Cl_2 (40 ml), water (10 ml), the aqueous phase was extracted with CH_2Cl_2 (2x30 ml) and the combined organic extracts were dried over anh. Na_2SO_4 and evaporated to dryness. The residue was chromatographed on a silica gel, using a mixture of 5:1, 3:1 and 1:1 hexane - EtOAc to afford (85 mg, 25%) (a ratio of 1:1 according to ^1H NMR data) of a mixture of methyl 3,5-di-*O*-benzoyl-α-L-arabinofuranoside (**10**) and methyl 2,5-di-*O*-benzoyl derivative **11**. ^1H NMR (500 MHz, $CDCl_3$) δ: 7.37-8.13 (m, 20H, Bz), 5.23 (s, 1H, H-1, 2,5-di-*O*-Bz), 5.19 (br.d, 1H, *J* = 2.3 Hz, H-2), 5.10 (dd, 1H, *J* = 2.7 Hz, H-3, 3,5-di-*O*-Bz), 5.08 (s, 1H, H-1, 3,5-di-*O*-Bz), 4.74-4.78 (m, 1H, H-4), 4.70 (dd, 1H, H-5), 4.46-4.69 (m, 2H, 2H-5), 4.57 (dd, 1H, H-5´), 4.47-4.50 (m, 1H, H-4), 4.38 (br.d, 1H, H-2), 4.30 (dd, 1H, H-3), 3.52 (s, 3H, OCH_3), 3.48 (s, 3H, OCH_3). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 167.30, 166.63, 166.44, 165.40 (4C=O, COC_6H_5), 133.71, 133.23, 133.17, 129.91, 129.88, 129.76, 128.62, 128.55, 128.46, 128.38 (COC_6H_5) 109.03 (C-1, 3,5-di-*O*-*B*z), 106.57 (C-1, 2,5-di-*O*-Bz), 85.46, 81.98, 77.23 (C-4, C-2, C-3, 2,5-di-*O*-Bz), 82.16, 81.33, 79.02 (C-4, C-2, C-3, 3,5-di-*O*-Bz), 63.88 (C-5), 64.01 (C-5), 55.17 (OCH_3). HRMS (ESI^+): m/z calcd for $[C_{20}H_{20}O_7+Na]^+$: 395.1098, found 395.1127.

Further elution with EtOAc-methanol (6:1) gave (89 mg, 36%) of 5-*O*-benzoyl derivative **9** as a syrup. IR (film, $CHCl_3$): ν 3434, 2937, 1719, 1278, 1106, 950 cm^{-1}. $[\alpha]_D^{20}$ –50 (c 1.0, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.45-8.09 (3m, 5H, Bz), 4.97 (s, 1H, H-1), 4.60 (dd, 1H, H-5), 4.56 (dd, 1H, H-5′), 4.34 (m, 1H, H-4), 4.20 (br.d, 1H, H-2), 4.08 (dd, 1H, H-3), 3.73 (br.s, 2H, 2-OH and 3-OH), 3.45 (s, 3H, OCH_3). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 165.77 (C=O, COC_6H_5), 133.34, 130.08, 129.77, 128.52 ($CO\underline{C_6H_5}$), 108.78 (C-1), 82.96 (C-4), 80.76, 78.07 (C-3 and C-2), 64.55 (C-5), 55.23 (OCH_3). HRMS (ESI^+): m/z calcd for $[C_{13}H_{16}O_6+Na]^+$: 291.0845, found 291.0845.

c$_2$. To a solution of methyl α-L-arabinoside (**1a**) (147 mg, 0.89 mmol) in anhydrous THF (5.5 ml) and pyridine (0.17 ml, 2.2 mmol) was added a solution previously prepared by adding benzoyl chloride (0.22 ml, 2.43 mmol) to N,N-diisopropylethylamine (0.14 ml, 0.9 mmol) in abhydrous THF (0,7 ml). The reaction mixture was stirred for 5 h at rt and then triethylamine (0.12 ml, 0.86 mmol) was added dropwise to prepared solution. The reaction mixture was stirred for 18 h at room temperature and then 3 h at 35-37 ^{0}C. After cooling the precipitate was filtered off and washed THF (5 ml), the filtrate was diluted with CH_2Cl_2 (40 ml), water (10 ml), the aqueous phase was extracted with CH_2Cl_2 (2x30 ml), and the combined organic extracts were dried over anh. Na_2SO_4 and evaporated to dryness. The residue was chromatographed on a silica gel, using a mixture of 5:1, 3:1 and 1:1 hexane-EtOAc to afford (93 mg, 28%, a ratio of 1:1.4 according to ^{1}H NMR data) of a mixture of methyl 3,5-di-*O*-benzoyl-α-L-arabinofuranoside (**10**) and 2,5-di-*O*-benzoyl derivative **11**.

Further elution with EtOAc-methanol (6:1) gave (150 mg, 62%) of 5-*O*-benzoyl derivative **9** as a syrup.

4.2.2. Selective acylation of methyl 5-*O*-benzoyl-α-L-arabinofuranoside (9) with 4-chlorobenzoyl chloride.

4-Chlorobenzoyl chloride (0.022 ml, 0.171 mmol) in anhydrous CH_2Cl_2 (0.22 ml) was added dropwise to a solution of methyl 5-*O*-benzoyl-α-L-arabinofuranoside (**9**) (46 mg, 0.171 mmol) in anhydrous CH_2Cl_2 (2 ml) and pyridine (0.03 ml, 0.38 mmol) at 0 ^{o}C (ice and sodium chloride). The reaction mixture was stirred for 1 h under cooling and then for 20 h at room temperature. A solution of 4-chlorobenzoyl chloride (0.022 ml, 1.79 mmol) in anhydrous CH_2Cl_2 (0.8 ml) was added to a prepared solution at rt. After stirring for 2 h the reaction mixture was diluted with CH_2Cl_2 (30 ml), water (10 ml), and the aqueous phase was extracted with CH_2Cl_2 (3x30 ml). The combined organic extracts were washed with 5% aq. $NaHCO_3$, dried over anhydrous Na_2SO_4 and evaporated to dryness. The residue was chromatographed on a silica gel, using a mixture of 7:1, 6:1, 4:1 and 2:1 hexane-EtOAc to afford as the first fraction (6 mg, 6%) of methyl 2,3-di-*O*-4-chlorobenzoyl-5-*O*-benzoyl-α-L-arabinofuranoside (**14**) as a syrup. $[\alpha]_D^{20}$ +39 (c 1.0, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 - 8.08 (m, 13H, C_6H_5CO, 2x COC_6H_4Cl), 5.59 (br.d, 1H, H-3), 5.52 (d, 1H, H-2), 5.21 (s, 1H, H-1), 4.90 (dd, 1H, H-5), 4.71 (dd, 1H, H-5′), 4.52-4.65 (m, 1H, H-4), 3.54 (s, 3H, OCH_3). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 165.15, 164.97 and 164.61 [3C=O, COC_6H_5, $\underline{CO}C_6H_4Cl$], 140.13, 140.09, 133.16, 131.33, 131.20, 131.07, 129.73, 128.33, 128.05, 127.48, 127.40 ($CO\underline{C_6H_5}$, $CO\underline{C_6H_4}Cl$), 106.72 (C-1), 82.27, 80.72, 78.06 (C-2, C-3, C-4), 63.51 (C-5), 55.04 (OCH_3). HRMS (ESI^+): m/z calcd for $[C_{27}H_{22}O_8Cl_2+Na]^+$: 567.0584, found 567.0578.

The second fraction was a mixture of methyl 3-*O*-4-chlorobenzoyl-5-*O*-benzoyl derivative **12** and methyl 2-*O*-4-chlorobenzoyl-5-*O*-benzoyl derivative **13** (42 mg, 60%) (a ratio of **12**:**13** = 1.7:1 according to ^{1}H NMR data). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.39-8.10 (m, 13H, C_6H_5CO, COC_6H_4Cl), 5.22 (s, 0.49H, H-1, 2,5-di-*O*-Bz), 5.16 (dd, 0.49H, *J* = 2.4 Hz, H-2), 5.08 (dd, 1H, *J* = 2.5 Hz, H-3, 3,5-di-*O*-Bz), 5.07 (s, 1H, H-1, 3,5-di-*O*-Bz), 4.74 (dd, 1H, H-5), 4.69 (dd, 0.5H, H-5), 4.60-4.67 (m, 2H, H-4 and H-5'), 4.56 (dd, 0.6H, H-5'), 4.45-4.49 (m, 0.5H, H-4), 4.36 (dd, 1H, H-2), 4.28 (dd, 0.5H, H-3), 3.52 (s, 1.6H, OCH_3), 3.48 (s, 3H, OCH_3). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 166.43, 166.40, 166.35, 166.76 [(4 x C=O, COC_6H_5 and COC_6H_4Cl], 140.27, 133.30, 133.23, 131.56, 131.28, 131.23, 129.88, 129.77, 128.99, 128.94, 128.87, 128.74 ($CO\underline{C_6H_5}$), 108.96 (C-1, 3,5-di-*O*-Bz), 106.40 (C-1, 2,5-di-*O*-Bz), 85.53, 82.03, 77.25 (C-4, C-2, C-3, 2,5-di-*O*-Bz), 82.40, 81.38, 78.90 (C-4, C-2, C-3, 3,5-di-*O*-Bz), 63.89

(C-5, 3,5-di-*O*-Bz) 63.77 (C-5, 2,5-di-*O*-Bz), 55.21 (2xOCH_3). HRMS (ESI^+): m/z calcd for $[C_{20}H_{19}O_7Cl+Na]^+$: 429.0717, found 429.0714.

4.2.3. Methyl 5-*O*-*tert*-butyldiphenylsilyl-α-L-arabinofuranoside (15).

To a solution of methyl α-L-arabinoside (**1a**) (260 mg, 1.58 mmol) in pyridine (7.2 ml) was added *tert*-butylchlorodiphenylsilane (0.62 ml, 2.37 mmol) at 0 ^oC and then the reaction mixture was stirred for 48 h and evaporated, diluted with CH_2Cl_2 and poured into 5% aq $NaHCO_3$, aqueous phase was extracted with CH_2Cl_2 (3x50 ml), the combined organic extracts were dried and evaporated. The residue was chromatographed on a silica gel, using for elution a mixture of hexane-ethylacetate 6:1 and 4:1, 1:1 to give (522 mg, 82%) of 5-*O*-silyl α-L-arabinofuranoside derivative **15** as a colorless oil IR (film, $CHCl_3$): ν 3421, 2931, 2861, 1113, 1073, 1003 cm^{-1}. $[\alpha]_D^{20}$ +47.7 (c 1.3, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$) δ: 7.40-7.71 [2m, 10H, $(CH_3)_3CSi(C_6H_5)_2$], 4.99 (s, 1H, H-1), 4.01-4.20 (m, 4H, H-2, H-3, H-4 and OH), 3.84 (dd (1H, $J_{5,4}$ = 2.2 Hz, $J_{5,5'}$ = 11.4 Hz, H-5), 3.75 (dd, 1H, $J_{5',4}$ = 1.2 Hz, H-5′), 3.42 (s, 3H, OCH_3), 2.95 (d, 1H, OH), 1.06 (s, 9H, $(\underline{CH_3})_3C$-). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 135.79, 135.72, 130.33, 130.21, 128.13, 128.07 [$(CH_3)_3CSi(\underline{C_6H_5})_2$], 109.54 (C-1), 87.57 (C-4), 78.57, 78.13 (C-3, C-2), 64.18 (C-5), 55.01 (OCH_3), 26.80 ($(\underline{CH_3})_3C$-, 19.16 $(CH_3)_3\underline{C}$-. HRMS (ESI^+): m/z calcd for $C_{22}H_{30}SiO_5Na$ $[M+Na]^+$: 425.1760, found 425.1765.

4.2.4. Acylation of 5-*O*-silyl derivative α-L-arabinofuranoside 15 with acyl chlorides.

Acylation with pivaloyl chloride. L-Selectride (0.49 ml 1 M solution in THF, 0.49 mmol) was added dropwise to a solution of 5-*O*-silyl derivative of methyl arabinoside **15** (180 mg, 0.45 mmol) in anhydrous THF (2.7 ml) at 0 ^0C (ice and sodium chloride). The solution was stirred at 0 ^0C for 30 min with gradually raising temperature to room and then, it was stirred for 30 min. Pivaloyl chloride (0.11 ml, 0.89 mmol) was added to prepared solution under cooling 0 ^0C. The reaction mixture was stirred for 5 h at room temperature, then cooled to 0 ^0C and pivaloyl chloride (0.08 ml, 0.65 mmol) was added to it. The reaction mixture was stirred for 18 h at room temperature, poured in cooled 5% aq $NaHCO_3$, the aqueous phase was extracted with CH_2Cl_2 (3x30 ml). The combined organic extracts was washed water, dried over anh. Na_2SO_4, and evaporated to dryness. The residue was chromatographed on silica gel, using for elution a mixture of hexane-ethylacetate 8:1, 6:1 and 4:1, and ethylacetate as the eluent to give (106 mg, 57%) of methyl 5-*O*-*tert*-butyldiphenylsilyl-2,3-di-*O*-pivaloyl-α-L-arabinofuranoside (**18**) as a syrup. IR (film, $CHCl_3$): ν 2967, 2938, 2865, 1739, 1285, 1143, 1110, 1073 cm^{-1}. $[\alpha]_D^{20}$ –29 (c 1.0, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$) δ: 7.26-7.71 [2m, 10H, $(CH_3)_3CSi(\underline{C_6H_5})_2$], 5.14 (dd, 1H, $J_{2,3}$ = 1.8 Hz, $J_{3,4}$ = 5.4 Hz, H-3), 4.97 (d, 1H, H-2), 4.85 (br.s, 1H, H-1), 4.17 (m, 1H, H-4), 3.84 (dd, 1H, $J_{5,4}$ = 4.7 Hz, $J_{5,5'}$ = 11.1 Hz, H-5), 3.81 (dd, 1H, $J_{5',4}$ = 5.3 Hz, H-5′), 3.39 (s, 3H, OCH_3), 1.88 and 1.17 (2s, 9H, $(C\underline{H_3})_3C(CO)$-, 1.07 (s, 9H, $(\underline{CH_3})_3C$-). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 177.40 (CO), 177.29 (CO), 135.62, 133.29, 133.21, 129.67, 127.66 [$(CH_3)_3CSi(\underline{C_6H_5})_2$], 106.78 (C-1), 82.38, 81.46, 76.79 (C-2, C-3 , C-4), 63.51 (C-5), 54.66 (OCH_3), 38.54 $(CH_3)_3C(CO)$-, 26.93, 26.77 [$(\underline{CH_3})_3C$-, $(\underline{CH_3})_3C(CO)$-], 19.26 $(CH_3)_3\underline{C}$-). HRMS (ESI^+): m/z calcd for $C_{32}H_{46}SiO_7Na$ $[M+Na]^+$: 593.2911, found 593.2908.
methyl 5-*O*-*tert*-butyldiphenylsilyl-3-*O*-pivaloyl-α-L-arabinofuranoside (**17**) (68 mg, 43%) as a syrup. IR (film, $CHCl_3$): ν 3457, 2964, 2934, 2861, 1729, 1288, 1162, 1056, 1000 cm^{-1}. $[\alpha]_D^{20}$ –44 (c 1.1, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$) δ: 7.38-7.712 [m, 10H, $(CH_3)_3CSi(\underline{C_6H_5})_2$], 4.99 (s, 1H, H-1), 4.92 (dd, 1H, $J_{2,3}$ = 1.0 Hz, $J_{3,4}$ = 3.6 Hz, H-3), 4.08-4.11 (m, 2H, H-2 and H-4), 3.90 (dd, 1H, $J_{5,4}$ = 2.6 Hz, $J_{5,5'}$ = 11.2 Hz, H-5), 3.85 (dd, 1H, $J_{5',4}$ = 2.64 Hz, H-5′), 3.39 (s, 3H, OCH_3), 3.74 (d, 1H, 2-OH), 1.88 and 1.08 [2s, 9H, $(\underline{CH_3})_3C(CO)$-, $\underline{CH_3})_3C$-]. ^{13}C NMR (125 MHz, $CDCl_3$) δ: 178.87 (CO), 135.62, 129.97, 129.89, 127.87, 127.80 $(CH_3)_3CSi(\underline{C_6H_5})_2$, 109.36 (C-1), 83.38, 80.11, 78.97 (C-3, C-4, C-2), 63.96 (C-5), 54.69 (OCH_3), 38.56 $(CH_3)_3C(CO)$-, 26.89, 26.76 [$(CH_3)_3C$-, $(C\underline{H_3})_3C(CO)$-], 19.15 $(CH_3)_3C$-. HRMS ((ESI^+): m/z calcd for $C_{27}H_{38}SiO_6Na$ $[M+Na]^+$: 509.2335, found 509.2331.
and (50 mg, 28%) of the starting L-arabinoside **15**

Acylation with 4-chlorobenzoyl chloride. L-Selectride (0.46 ml 1 M solution in THF, 0.46 mmol) was added dropwise to a solution of 5-*O*-silyl derivative of arabinoside **15** (184 mg, 0.46 mmol) in anhydrous THF (3.0 ml) at 0 ^{0}C. The solution was stirred at 0 ^{0}C (ice and sodium chloride) for 30 min with gradually raising temperature to room and then, it was stirred for 20 min. 4-Chlorobenzoyl chloride (0.12 ml, 0.95 mmol) in anhydrous THF (0.7 ml) was added dropwise to a solution under cooling 0 ^{0}C. The reaction mixture was stirred under cooling for 30 min and then 4 h at room temperature, poured in cooled 5% aq $NaHCO_3$, the aqueous phase was extracted with EtOAc (3x30 ml). The combined organic extracts was washed water, dried over anh. Na_2SO_4, and evaporated to dryness. The residue was chromatographed on silica gel, using for elution a mixture of hexane-ethylacetate 8:1, 6:1 and 4:1, and ethylacetate as the eluent to give (126 mg, 50%) of methyl 5-*O*-*tert*-butyldiphenylsilyl-2,3-di-*O*-4-chlorobenzoyl-α-L-arabinofuranoside (**20**). M.p.40–42 °C. IR (KBr): ν 2957, 2931, 1729, 1596, 1268, 1106 cm^{-1}. $[\alpha]_D^{20}$ –48 (c 1.0, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.33-7.99 [4m, 18H, $(CH_3)_3CSi(\underline{C_6H_5})_2$, ClBz], 5.61 (dd, 1H, $J_{3,2}$ = 1.1 Hz, $J_{3,4}$ = 5.3 Hz, H-3), 4.42 (d, 1H, H-2), 5.11 (s, 1H, H-1), 4.35 (m, 1H, H-4), 4.04 (dd,. 1H, $J_{5,4}$ = 4.6 Hz, $J_{5,5'}$ = 11.3 Hz, H-5), 3.99 (dd, 1H, $J_{5',4}$ = 4.2 Hz, H-5′), 3.47 (s, 3H, OCH_3), 1.06 [s, 9H, $(C\underline{H_3})_3Si(C_6H_5)_2$]. ^{13}C NMR (125 MHz, $CDCl_3$) δ: 164.77 (CO), 164.64 (CO), 139.87, 135.62, 133.26, 133.15, 131.27, 129.70, 128.74, 127.86, 127.67 [$(CH_3)_3CSi(\underline{C_6H_5})_2$, Cl-$\underline{C_6H_4}$CO], 106.75 (C-1), 82.68, 82.58, 77.79 (C-3, C-2, C-4), 63.38 (C-5), 54.83 (OCH_3), 26.76 ($\boldsymbol{C}H_3)_3$C-, 19.31 $(CH_3)_3\boldsymbol{C}$-. HRMS (ESI$^+$): m/z calcd for $C_{36}H_{36}O_7SiCl_2Na$ $[M+Na]^+$: 701.1505, found 701.1502.

methyl 5-*O*-*tert*-butyldiphenylsilyl-3-*O*-4-chlorobenzoyl-α-L-arabinofuranoside (**19**) (80 mg, 40%) as a syrup. IR (film, $CHCl_3$): ν 3447, 2954, 2931, 2861, 1722, 1272, 1112 cm^{-1}. $[\alpha]_D^{20}$ –56 (c 1.0, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.38-7.95 [3m, 14H, $(CH_3)_3CSi(\underline{C_6H_5})_2$, ClBz], 5.30 (dd, 1H, $J_{2,3}$ = 0.9 Hz, $J_{3,4}$ = 3.6 Hz, H-3), 5.04 (s, 1H, H-1), 4.24-4.28 (m, 2H, H-2 and H-4), 3.97 (dd, 1H, $J_{5,4}$ = 2.5 Hz, $J_{5,5'}$ = 12.7 Hz, H-5), 3.91 (dd, 1H, $J_{5',4}$ = 2.7 Hz, H-5′), 3.42 (s, 3H, OCH_3), 3.78 (d, 1H, 2-OH), 1.09 [s, 9H, $(C\underline{H_3})_3Si(C_6H_5)_2$]. ^{13}C NMR (125 MHz, $CDCl_3$) δ: 165.8 (CO), 139.89, 135.63, 132.38, 132.33, 131.2, 130.02, 129.94, 128.79, 127.90, 127.84 [$(CH_3)_3CSi(\underline{C_6H_5})_2$, ClBz], 109.52 (C-1), 83.87, 80.84, 79.02 (C-4, C-3, C-2), 63.9 (C-5), 54.98 (OCH_3), 26.78 ($\boldsymbol{C}H_3)_3$C-, 19.16 $(CH_3)_3\boldsymbol{C}$-. HRMS (ESI$^+$): m/z calcd for $C_{29}H_{33}O_6SiClNa$ $[M+Na]^+$: 563.1633, found 563.1628.

and the starting L-arabinoside **12** (35 mg, 19%).

4.2.5. Methyl 3-*O*-pivaloyl-α-L-arabinofuranoside (21)

To a solution of **17** (38 mg, 0.078 mmol) in anhydrous methanol (1.5 ml) was added NH_4F (14 mg, 0.38 mmol). The solution was stirred at 29-30 ^{0}C for 85 min, and then the reaction mixture was evaporated. The residue was chromatographed on a silica gel, using for elution a mixture of 6:1, 4:1 hexane-EtOAc and $CHCl_3$:MeOH - 5:1 to give (17 mg, 88%) of methyl 3-*O*-pivaloyl-α-L-arabinofuranoside (**21**) as a colorless oil. IR (film, $CHCl_3$): ν 3418, 2974, 2934, 1729, 1292, 1166, 1112, 990 cm^{-1}. $[\alpha]_D^{20}$ –75 (c 0.43, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 4.98 (s, 1H, H-1), 4.80 (dd, 1H, $J_{3,2}$ = 2.0 Hz, $J_{3,4}$ = 5.0 Hz, H-3), 4.19-4.21 (dt, 1H, H-4), 4.13(br.d, 1H, H-2), 3.96 (dd, 1H, H-5, $J_{5,4}$ = 2.6 Hz, $J_{5,5'}$ = 11.9 Hz, H-5), 3.89 (dd, 1H, $J_{5',4}$ = 2.7 Hz, H-5′), 3.43 (s, 3H, OCH_3), 1.25 [s, 9H, $COC(CH_3)_3$]. ^{13}C NMR (125 MHz, $CDCl_3$) δ: 179.33 $COC(CH_3)_3$, 109.26 (C-1), 82.51, 80.23, 79.96 (C-4, C-2, C-3), 61.75 (C-5), 54.84 (OCH_3), 38.63 $COC(CH_3)_3$, 26.93 $COC(CH_3)_3$. HRMS (ESI$^+$): m/z calcd for $C_{11}H_{20}O_6$ $[M+Na]^+$: 271.1158, found 271.1153.

4.2.6. Methyl 2,3-anhydro-α-L-ribofuranoside (25)

To a solution of intermediate 2-*O*-mesylate (238 mg, 0.58 mmol), prepared from the 3,5-di-*O*-pivaloate **2** according to the previous work [28] in anhydrous methanol (2.5 ml) was added 1 M solution of $NaOCH_3$ in methanol (0.43 ml). The reaction mixture was stirred at room temperature for 18 h, and then was neutralized with glacial acetic acid and evaporated to dryness, coevaporated with a mixture of ethanol-toluene (25 ml). The residue was

chromatographed on a silica gel, using for elution chloroform, $CHCl_3$-petroleum ether-methanol (15:7:2) to give (68 mg, 80%) of methyl 2,3-anhydro-α-L-ribofuranoside (**25**) as a colorless oil. $[\alpha]_D^{20}$ –17.7 (c 1.2, H_2O); lit for D-isomer [24]. $[\alpha]_D^{23}$ +19.2 (c 2.3, H_2O). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 5.21 (br.s, 1H, $J_{1,2}$ < 1.0 Hz, H-1), 4.33 (t, 1H, $J_{4,5}$ = 3.8 Hz, $J_{4,5'}$ = 3.9 Hz, H-4), 3.80 (dd, 1H, $J_{1,2}$ = 0.7 Hz, $J_{2,3}$ = 2.8 Hz, H-2), 3.77 (dd, 1H, $J_{5,5'}$ = 11.5 Hz, H-5), 3.70 (d, 1H, $J_{3,2}$ = 2.8 Hz, H-3), 3.66 (dd, 1H, H-5′), 3.50 (s, 3H, OCH_3). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 102.73 (C-1), 78.99 (C-4), 63.18 (C-5), 57.98 (C-3), 56.84 (OCH_3), 56.47 (C-2). HRMS (ESI^+): m/z calcd for $C_6H_{10}O_4Na$ $[M+Na]^+$: 169.0477, found 169.0481.

4.2.7. Methyl 5-*O*-*tert*-butyldiphenylsilyl-2,3-anhydro-α-L-ribofuranoside (26)

d. To a solution of L-arabinoside derivative **17** (55 mg, 0.11 mmol) and 4-dimethylaminopyridine (9 mg, 0.07 mmol) in anhydrous pyridine (2.0 ml) was added methanesulfonyl chloride (0.03 ml, 0.39 mmol) at 0 ^{0}C. The reaction mixture was stirred for 2 h at rt, the prepared solution was diluted CH_2Cl_2 (10 ml), washed water (4 ml), the aqueous phase was extracted with CH_2Cl_2 (20 ml). The combined organic extracts were washed with 1 N HCl (3x30 ml), 5% aq $NaHCO_3$, dried over anhydrous Na_2SO_4, and evaporated to dryness. The residue was purified by chromatography on silica gel, using mixture of 5:1 and 4:1 hexane-EtOAc to afford (59 mg, 92%) of intermediate mesylate **22** as a syrup. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.37-7.70 [3m, 10H, $CH_3)_3CSi(\underline{C_6H_5})_2$], 5.15 (br.d, 1H, $J_{3,2}$ = 4.2 Hz, H-3), 5.11 (s, 1H, H-1), 4.80 (br.s, 1H, H-2), 4.16 (m, 1H, H-4), 3.87 (dd, 1H, $J_{5,4}$ = 4.4 Hz, $J_{5,5'}$ = 11.2 Hz, H-5), 3.83 (dd, 1H, $J_{5',4}$ =4.7 Hz, H-5′), 3.39 (s, 3H, OCH_3), 3.09 (s, 3H, $-SO_2CH_3$), 1.95 [s, 9H, $(C\underline{H_3})_3C(CO)$], 1.07 [s, 9H, $(\underline{CH_3})_3CSi(C_6H_5)_2$]. HRMS ($ESI^+$): m/z calcd for $C_{22}H_{28}O_4SiNa$ $[M+Na]^+$: 407.1655, found 407.1664.

To a solution of intermediate 2-*O*-mesylate **22** (48 mg, 0.098 mmol) in anhydrous methanol (4.5 ml) was added 1 M solution of $NaOCH_3$ in methanol (0.065 ml). The reaction mixture was stirred at room temperature for 18 h, and then neutralized with glacial acetic acid and evaporated to dryness, coevaporated with a mixture of ethanol-toluene (25 ml). The residue was chromatographed on a silica gel, using for elution a mixture of 10:1 and 7:1 hexane-EtOAc to afford (30 mg, 80%) of methyl 5-*O*-*tert*-butyldiphenylsilyl-2,3-anhydro-α-L-ribofuranoside (**26**) as a colorless oil. $[\alpha]_D^{20}$ –46 (c 1.0, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.38-7.68 [m, 10H, $(CH_3)_3CSi(\underline{C_6H_5})_2$], 5.25 (s, 1H, $J_{1,2}$ <1.0 Hz, H-1), 4.32 (t, 1H, J = 4.3 Hz, J = 2.6 Hz, H-4), 3.82 (dd, 1H, $J_{5,5'}$ = 11.2 Hz, H-5), 3.78 (d, 1H, $J_{2,3}$ = 2.7 Hz, H-2), 3.72 (dd, 1H, H-5`), 3.71 (d, 1H, H-3), 3.52 (s, 3H, OCH_3), 1.07 [s, 9H, $(C\underline{H_3})_3Si(C_6H_5)_2$]. ^{13}C NMR (125 MHz, $CDCl_3$) δ: 135.68, 135.61, 132.97, 130.14, 130.02, 128.0, 127.96 $(CH_3)_3CSi(\mathit{C}_6H_5)_2$, 103.15 (C-1), 78.79 (C-4), 64.81 (C-5), 57.11 (OCH_3), 57.07, 56.35 (C-3, C-2), 26.95 $(\mathit{C}H_3)_3C$-, 19.26 $(CH_3)_3\mathit{C}$-.

d. To a solution of L-arabinoside derivative **19** (35 mg, 0.065 mmol) and 4-dimethylaminopyridine (5 mg, 0.04 mmol) in anhydrous pyridine (2.0 ml) was added methanesulfonyl chloride (0.03 ml, 0.39 mmol) at 0 ^{0}C. The reaction mixture was stirred at rt for 18 h, then diluted CH_2Cl_2 (10 ml), washed water (4 ml), the aqueous phase was extracted with CH_2Cl_2 (20 ml). The combined organic extracts were washed 5% aq $NaHCO_3$, dried over anhydrous Na_2SO_4, and evaporated to dryness. The residue was purified by chromatography on silica gel, using a mixture of 10:1 and 7:1 hexane-EtOAc to afford (39 mg, 97%) of intermediate mesylate **23** as a syrup. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.33-7.99 [4m, 14H, $(CH_3)_3CSi(\underline{C_6H_5})_2$, Cl-Bz], 5.43 (dd, 1H, J = 1.2 Hz, J = 5.4 Hz, H-3), 5.18 (s, 1H, H-1), 5.01 (br.s, 1H, H-2), 4.30 (m, 1H, H-4), 3.98 (dd, 1H, $J_{5,4}$ = 4.3 Hz, $J_{5,5'}$ = 11.3 Hz, H-5), 3.92 (dd, 1H, $J_{5',4}$ = 4.4 Hz, H-5′), 3.42(s, 3H, OCH_3), 3.12 (s, 3H, $-SO_2CH_3$), 1.05 [s, 9H, $(C\underline{H_3})_3Si(C_6H_5)_2$].

To a solution of intermediate 2-*O*-mesylate **23** (37 mg, 0.059 mmol) in anhydrous methanol (2.0 ml) was added 1 M solution of $NaOCH_3$ in methanol (0.039 ml). The reaction mixture was stirred at room temperature for 18 h, and then was diluted with CH_2Cl_2 (5 ml) and neutralized with glacial acetic acid and evaporated to dryness, coevaporated with a mixture of ethanol-toluene (25 ml). The residue was chromatographed on a silica gel, using for

elution a mixture of hexane- EtOAc 8:1 and 6:1 to give (16 mg, 73%) of methyl 5-*O*-*tert*-butyldiphenylsilyl-2,3-anhydro-α-L-ribofuranoside (**26**) as a colorless oil.

g. *tert*-Butyldiphenylchlorosilane (0.12 ml, 0.469 mmol) was added to a solution of epoxide **25** (49 mg, 0.33 mmol) in anhydrous pyridine (1.2 ml). The solution was stirred at room temperature for 48 h, and then the reaction mixture was evaporated, coevaporated with toluene, the residue was dissolved in CH_2Cl_2 and washed with 5% aq $NaHCO_3$, dried over anhydrous Na_2SO_4 and evaporated. The residue was chromatographed on a silica gel, using for elution a mixture of hexane- EtOAc 10:1 and 7:1 to give (110 mg, 85%) of methyl 5-*O*-*tert*-butyldiphenylsilyl-2,3-anhydro-α-L-ribofuranoside (**26**) as a colorless oil.

4.2.8. Methyl 2-deoxy-α-L-*erythro*-pentofuranoside (28)

L-Selectride (1.0 ml 1 M solution in THF, 1.0 mmol) was added dropwise under argon to a solution of epoxide **25** (43 mg, 0.29 mmol) in anhydrous THF (0.18 ml) at -78 ^{0}C. The solution was stirred with gradually warmed to room temperature and then, it was stirred for 1 h. Ethanol (2.5 ml) was added to the prepared solution under cooling, and evaporated to dryness. The residue was chromatographed on a silica gel, using for elution chloroform, $CHCl_3$-petroleum ether-methanol (15:7:2) to give (40 mg, 93%) of methyl 2-deoxy-α-L-*erythro*-pentofuranoside (**28**) as oil. $[\alpha]_D^{20}$ –125 (c 1.0, MeOH). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 5.09 (d, 1H, $J_{1,2'} < 1.0$ Hz, $J_{1,2} = 4.6$ Hz, H-1), 4.11-4.14 (m, 2H, H-3 and H-4), 3.71 (dd, 1H, $J_{4,5} = 3.7$ Hz, $J_{5,5'} = 11.8$ Hz, H-5), 3.61(dd, 1H, $J_{4,5'} = 4.6$ Hz, H-5′), 3.48 (d, 1H, OH), 3.38 (s, 3H, OCH_3), 2.11 (ddd, 1H, $J_{2,3} = 6.3$ Hz, H-2′), 2.0 (d, 1H, $J_{2,2'} = 13.9$ Hz, H-2). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 105.45 (C-1), 87.32 (C-4), 72.73 (C-3), 63.03 (C-5), 54.85 (OCH_3), 41.50 (C-2). HRMS (ESI^+): m/z calcd for $[C_{16}H_{12}O_4+Na]^+$: 171.0628, found 171.0725.

4.2.9. Methyl 5-O-*tert*-butyldiphenylsilyl-2-deoxy-α-L-*erythro*-pentofuranoside (29)

h$_2$. L-Selectride (1.6 ml 1 M solution in THF, 1.6 mmol) was added dropwise under argon to epoxide **26** (200 mg, 0.52 mmol) in 3.0 ml anhydrous THF at -78 ^{0}C. The solution was stirred with gradually warmed to room temperature and then, it was stirred for 1 h. Water (4 ml) was added to the prepared solution, the mixture was extracted with $CHCl_3$ (3x30 ml), combined extracts washed with 5% aq. $NaHCO_3$, water, dried and evaporated to dryness. The residue was dissolved in CCl_4 and then filtered off, filtrate was evaporated. 2-Deoxy-α-L-*erythro*-pentofuranoside (**29**) (200 mg, 99%) was prepared as a colorless oil. IR (film, $CHCl_3$): ν 3457, 2958, 2934, 2857, 1432, 1112, 1079, 1039, 999, 702 cm^{-1}. $[\alpha]_D^{20}$ –58.7 (c 1.0, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.37-7.67 [m, 10H, $(CH_3)_3CSi(\underline{C_6H_5})_2$], 5.11 (d, 1H, $J_{1,2} = 4.6$ Hz, H-1), 4.30 (dd, 1H, H-3), 4.14-4.18 (m, 1H, $J_{4,5} = 3.5$ Hz, $J_{4,5'} = 4.6$ Hz, H-4), 3.75 (dd, 1H, $J_{5,5'} = 10.9$ Hz, H-5), 3.60 (dd, 1H, H-5′), 2.85 (d, 1H, 2-OH), 3.38 (s, 3H, OCH_3), 2.19 (m, 1H, $J = 4.6$, $J = 5.7$, $J = 13.0$ Hz, H-2′), 2.02 (d, 1H, $J_{2,2'} = 13.0$ Hz, H-2), 1.05 [s, 9H, $(\underline{CH_3})_3CSi(C_6H_5)_2$]. ^{13}C NMR (125 MHz, $CDCl_3$) δ: 135.6, 133.55, 133.18, 129.78, 129.72, 127.74, 127.71 $(CH_3)_3CSi(\underline{C_6H_5})_2$), 105.63 (C-1), 87.85 (C-4), 73.25 (C-3), 64.38 (C-5), 54.79 (OCH_3), 41.11 (C-2), 26.79 ($CH_3)_3C$-, 19.22 $(CH_3)_3C$-. HRMS (ESI^+): m/z calcd for $C_{22}H_{30}O_4SiNa$ $[M+Na]^+$: 409.1811, found 409.1811.

i. Methanol (3 ml) saturated at 0 ^{o}C with ammonia was added to a solution of the mesylate **23** (50 mg, 0.081 mmol) in anhydrous methanol (4 ml). The reaction mixture was stirred at room temperature for 5 h, and then was evaporated under diminished pressure. Intermediate 2-*O*-mesylate **24** was prepared as oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.38-7.68 [m, 10H, $(CH_3)_3CSi(\underline{C_6H_5})_2$], 5.04 (br.d, 1H, H-1), 4.84 (dd, 1H, $J_{2,1} = 1.5$ Hz, $J_{2,3} = 3.5$ Hz, H-2), 4.35 (m, 1H, H-3), 4.07 (m, 1H, $J_{4,5} = 4.4$ Hz, $J_{4,5'} = 4.8$ Hz, H-4), 3.88 (dd, 1H, $J_{5,5'} = 11.2$ Hz, H-5), 3.84 (dd, 1H, H-5`), 3.41 (s, 3H, OCH_3), 3.03 (s, 3H, $SO_2\underline{CH_3}$), 2.64 (d, 1H, 3-OH), 1.08 [s, 9H, $(\underline{CH_3})_3Si(C_6H_5)_2$]. ^{13}C NMR (125 MHz, $CDCl_3$) δ: 135.61, 135.57, 129.82, 129.80, 127.76, 127.73 $(CH_3)_3CSi(C_6H_5)_2$, 105.73 (C-1), 88.51, 83.1, 76.21 (C-4, C-2, C-3), 63.17 (C-5), 55.15 (OCH_3), 38.07 (SO_2CH_3), 26.70 ($CH_3)_3C$-, 19.27 $(CH_3)_3C$-. L-Selectride (0.27 ml 1 M solution in THF, 0.27 mmol) was added under argon to intermediate mesylate **24** in anhydrous THF

(0.3 ml) at -78 ^{0}C. The solution was stirred with gradually warmed to room temperature and then, it was stirred for 19 h at room temperature. Water (2 ml) was added to the prepared solution, the mixture was extracted with $CHCl_3$ (2x10ml), combined extracts were washed with 5% aq $NaHCO_3$, dried and evaporated. The residue was chromatographed on a silica gel, using for elution a mixture of hexane- EtOAc 10:1 and 7:1, 5:1 to afford (24 mg, 77%) of 2-deoxy L-glycoside **29** as a colorless oil.

4.2.10. Methyl 5-*O*-trityl-2,3-anhydro-α-L-lyxofuranoside (31)

DIAD (0.4 ml, 2.06 mmol) were added to a solution of methyl 5-*O*-trityl-α-L-arabinofuranoside (**30**) (400 mg, 0.98 mmol) prepared according to the method described for D-isomer [36] and Ph_3P (540 mg, 2.06 mmol) in anhydrous THF (17 ml) at 0 ^{0}C and then a solution was stirred with gradually raising temperature to room and then the reaction mixture was refluxed for 1 h, cooled down to rt and evaporated to dryness. The residue was chromatographed on a silica gel, using for elution a mixture of hexane- EtOAc 10:1, 8:1, and 4:1 to give (364 mg, 94%) of trityl derivative of methyl 2,3-anhydro-α-L-lyxofuranoside **31** as a colorless oil. $[\alpha]_D^{20}$ +46 (c 1.0, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.25-7.52 (2m, 15H, Ar), 4.95 (s, 1H, H-1), 4.24 (dd, 1H, H-4), 3.94 (d, 1H, H-2), 3.71 (d, 1H, H-3), 3.45 (s, 3H, OCH_3), 3.4 (dd, 1H, H-5), 3.3 (dd, 1H, H-5′). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 143.8, 128.7, 127.9, 127. 1 ($C(\mathit{C}_6H_5)_3$, 102.19 (C-1), 86.97 [$\mathit{C}(C_6H_5)_3$], 75.31 (C-4), 62.16 (C-5), 56.51, 55.54, 54.62 (C-2, C-3, OCH_3). HRMS (ESI^+): m/z calcd for $C_{25}H_{24}O_4Na$ $[M+Na]^+$: 411.1567, found 411.1570.

4.2.11. Methyl 5-*O*-trityl-3-deoxy-*α*-L-*threo*-pentofuranoside (32)

L-Selectride (3.3 ml 1 M solution in THF, 3.3 mmol) was added under argon to 2,3-anhydrofuranose derivative **31**, (300 mg, 0.77 mmol) in 7 ml anhydrous THF at -78 ^{0}C. The solution was stirred with gradually warmed to room temperature and then it was stirred for 175 min. Reaction mixture was quenched with cooled 4% aqueous sodium hydroxide, the aqueous phase was extracted with EtOAc (2x50 ml), combined organic extracts washed with water (2x15 ml), dried over sodium hydride and evaporated to dryness. The residue was dissolved in CCl_4 and then filtered off, filtrate was evaporated. The product was chromatographed on a silica gel, using for elution a mixture of hexane-EtOAc 5:1, 3:1, and 1:1 to give (272 mg, 91%) of L-3-deoxy sugar **32** as a colorless oil. $[\alpha]_D^{20}$ –77 (c 1.0, $CHCl_3$). ^{1}H NMR (500 MHz, DMSO-d_6) δ: 7.24-7.41 (m,15H, Ar), 5.00 (d, 1H, 2-OH), 4.70 (s, 1H, H-1), 4.14-4.19 (m, 1H, H-4), 3.97 (m, 1H, H-2), 3.23 (s, 3H, OCH_3), 3.14 (dd, 1H, $J_{5,4}$ = 6.5 Hz, $J_{5',5}$ = 9.5 Hz, H-5), 2.97 (dd, 1H, $J_{5',4}$ = 4.8 Hz, H-5′), 2.16 (ddd, 1H, J = 6.4 Hz, J = 8.0 Hz, $J_{3,3'}$ = 13.2 Hz, H-3), 1.44 (ddd, 1H, J = 2.6 Hz, J = 5.7 Hz, H-3'). ^{13}C NMR (125 MHz, DMSO-d_6) δ: 143.77, 128.22, 127.84 126.9 C($\mathit{C}_6H_5)_3$, 109.57 (C-1), 85.82 [$\mathit{C}(C_6H_5)_3$], 76.85 (C-4), 74.03 (C-2), 66.61 (C-5), 53.87 (OCH_3), 35.21 (C-3). HRMS (ESI^+): m/z calcd for $C_{25}H_{26}O_4Na$ $[M+Na]^+$: 413.1723, found 413.1728

4.2.12. Methyl 3-deoxy-α-L-*threo*-pentofuranoside (33)

d. A solution of trityl derivative **32** (210 mg, 0.55 mmol) in 63%-aqueous CH_3COOH (7 ml) was stirred at 55 ^{0}C for 30 min, and then toluene was added, the reaction mixture was evaporated. The residue was chromatographed on a silica gel, using for elution chloroform and a mixture of $CHCl_3$:acetone - 1:1 to give (63 mg, 82%) of methyl 3-deoxy-α-L-*threo*-pentofuranoside (**33**) as a colorless oil. $[\alpha]_D^{20}$ –43 (c 1.0, $CHCl_3$). ^{1}H NMR 500 MHz, CD_3OD) δ: 4.8 (s, 1H, H-1), 4.21-4.26 (m, 1H, H-4), 4.70 (dd, 1H, $J_{2,3}$ = 1.8 Hz, $J_{2,3'}$ = 5.9 Hz, H-2), 3.68 (dd, 1H, H-5, $J_{5,4}$ = 3.2 Hz, $J_{5,5'}$ = 11.5 Hz, H-5), 3.59 (dd, 1H, $J_{5',4}$ = 4.7 Hz, H-5′), 3.34 (s, 3H, OCH_3), 2.34 (ddd,1H, J = 5.9 Hz, J = 8.7 Hz, $J_{3,3'}$ = 13.4 Hz, H-3'), 1.66 (ddd, 1H, J = 1.8 Hz, J = 4.8 Hz, H-3). ^{13}C NMR (125 MHz, CD_3OD) δ: 111.12 (C-1), 80.16 (C-4), 75.73 (C-2), 61.15 (C-5), 54.77 (OCH_3), 35.16 (C-3). HRMS (ESI^+): m/z calcd for $C_6H_{12}O_4$ $[M+Na]^+$: 171.0628, found 171.0625.

e. L-Selectride (1.74 ml 1 M solution in THF) was added under argon to methyl 2,3-anhydro-α- L-lyxofuranoside (**34**) (75 mg, 0.457 mmol) prepared according to the known procedure from methyl α-L-arabinoside **1a** [22] in 0.6 ml

anhydrous THF at -78^{0}C. The reaction mixture was stirred with gradually warmed to room temperature and then it was stirred for 50 min. To the prepared solution was added ethanol (5 ml) under cooling and it was evaporated. The residue was chromatographed on a silica gel, using for elution chloroform and a mixture of $CHCl_3$:acetone - 1:1 to give (70 mg, 92%) of methyl 3-deoxy-α-L-*threo*-pentofuranoside (**33**) as a colorless oil.

4.3. Synthesis of selectively protected β-L-arabinofuranosides, 2,3-anhydro-β-L-lyxofuranoside and 2-deoxy-L-*threo*-pentofuranoside derivatives

4.3.1. Acylation of β-L-arabinofuranoside 1b with 4-chlorobenzoyl chloride

To methyl β-L-arabinoside (**1b**, 400 mg, 2.4 mmol) was added anhydrous CH_2Cl_2 (10 ml) and pyridine (0.2 ml, 2.4 mmol) and a solution was stirred for 30 min at room temperature, then 4-chlorobenzoyl chloride (0.32 ml, 2.5 mmol) in anhydrous CH_2Cl_2 (3.5 ml) was added dropwise to prepared solution. The reaction mixture was stirred for 20 h at room temperature. Anhydrous pyridine (0.2 ml, 2.4 mmol) and solution of 4-chlorobenzoyl chloride (0.32 ml, 2.5 mmol) in anhydrous CH_2Cl_2 (3.5 ml) were consequently added to the prepared solution at 0 ^{0}C. The reaction mixture was stirred for 22 h at room temperature, and then was diluted CH_2Cl_2 (80 ml), water (15 ml), the aqueous phase was extracted with CH_2Cl_2 (3x60 ml). The combined organic extracts was washed 0.5 N HCl (5 ml), 5% aq $NaHCO_3$, dried over anhydrous Na_2SO_4 and evaporated to dryness. The residue was chromatographed on a silica gel, using for elution a mixture of 6:1, 4:1 and 2.5:1 hexane-EtOAc to afford (110 mg, 8%) of methyl 2,3,5-tri-*O*-4-chlorobenzoyl-β-L-arabinofuranoside (**37**) as a syrup. IR (film, $CHCl_3$): ν 2950, 2931, 1732, 1599, 1404, 1268, 1093, 1020 cm^{-1}. $[\alpha]_D^{20}$ +102 (c 1.0, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.36-8.02 (4m, 12H, 3 x COC_6H_4Cl), 5.91 (dd, 1H, $J_{3,2}$ = 7.0 Hz, $J_{3,4}$ = 5.4 Hz, H-3), 5.45 (dd, 1H, H-2), 5.32 (d, 1H, $J_{1,2}$ = 4.6 Hz, H-1), 4.73 (dd, 1H, $J_{5,4}$ = 4.6 Hz, $J_{5,5'}$ = 11.6 Hz, H-5), 4.60 (dd, 1H, $J_{5',4}$ = 6.6 Hz, H-5′), 4.45 (m, 1H, H-4), 3.37 (s, 3H, OCH_3). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 165.32, 165.05 (C=O, 3xCOC_6H_4Cl), 140.24, 140.11, 139.63, 131.36, 131.20, 131.14, 128.92, 128.87, 128.71, 127.47, 127.37 (3xCOC_6H_4Cl), 101.35 (C-1), 78.58 (C-4), 77.63, 76.64 (C-2, C-3), 65.85 (C-5), 55.61 (OCH_3). HRMS (ESI$^+$): m/z calcd for $C_{27}H_{21}O_8Cl_3Na$ [M+Na]$^+$: 601.0200, found 601.0201.

methyl 2,5-di-*O*-4-chlorobenzoyl-β-L-arabinofuranoside (**36**) (388 mg, 36%) as white solid. M.p.114–115 °C. IR (KBr): ν 3426, 2953, 1722, 1594, 1285, 1266, 1095 cm^{-1}. $[\alpha]_D^{20}$ +28.7 (c 1.0, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.00 and 7.42 (2m, 8H, 2 x ClBz), 5.17 (d, 1H, $J_{1,2}$ = 4.48 Hz, H-1), 5.09 (dd, 1H, $J_{3,2}$ = 7.37 Hz, $J_{1,2}$ = 4.5 Hz, H-2), 4.62 (t, 1H, H-3), 4.55 (dd, 1H, $J_{5,4}$ = 4.5 Hz, $J_{5,5'}$ = 11.8 Hz, H-5), 4.47 (dd, 1H, $J_{5',4}$ = 5.7 Hz, H-5′), 4.28 (m, 1H, H-4), 3.35 (s, 3H, OCH_3). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 166.17 and 165.65 (C=O, 2xCOC_6H_4Cl), 140.15, 139.70, 131.32, 131.13, 128.85, 128.77, 128.17, 127.49 (2xCOC_6H_4Cl), 101.35 (C-1), 80.71, 79.95, 74.44 (C-4, C-2, C-3), 65.58 (C-5), 55.42 (OCH_3). HRMS (ESI$^+$): m/z calcd for $C_{20}H_{18}O_7Cl_2Na$ [M+Na]$^+$: 463.0327, found 463.0321.

methyl 2,3-di-*O*-4-chlorobenzoyl-β-L-arabinofuranoside (**38**) (20 mg, 2%) was isolated as a syrup after additional separation of a mixture of dibenzoates **36** and **38** by column chromatography on a silica gel, using for elution hexane-EtOAc 3:1. IR (film, $CHCl_3$): ν 3471, 2938, 1725, 1592, 1404, 1275, 1096, 1016 cm^{-1}. $[\alpha]_D^{20}$ +181 (c 0.37, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.99, 7.96, 7.42 and 7.40 (4d, 8H, 2 x COC_6H_4Cl), 5.60 (dd, 1H, $J_{2,3}$ = 6.41 Hz, $J_{2,1}$ = 4.71 Hz, H-2), 5.46 (dd, 1H, H-3), 5.30 (d, 1H, $J_{1,2}$ = 4.71 Hz, H-1), 4.24 (m, 1H, H-4), 3.92 (dd, 1H, $J_{5,4}$ = 4.0 Hz, $J_{5,5'}$ = 12.0 Hz, H-5), 3.87 (dd, 1H, $J_{5',4}$ = 4.7 Hz, H-5′), 3.43 (s, 3H, OCH_3). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 166.17 and 165.65 (C=O, 2xCOC_6H_4Cl), 140.19, 140.05, 131.31, 131.18, 128.87, 128.82, 128.68, 128.24 (2x$CO\underline{C_6H_4}Cl$), 101.14 (C-1), 82.48, 78.03, 76.85 (C-4, C-2, C-3), 64.02 (C-5), 55.04 (OCH_3). HRMS (ESI$^+$): m/z calcd for $C_{20}H_{18}O_7Cl_2$ [M+Na]$^+$: 463.0327, found 463.0322.

4.3.2. Acylation of 5-*O*-trityl β-L-arabinofuranoside 36 with 4-chlorobenzoyl chloride

L-Selectride (0.6 ml 1 M solution in THF, 0.6 mmol) was added dropwise to a solution of 5-*O*-trityl β-L-arabinoside **39** [36] (255 mg, 0.627 mmol) in anhydrous THF (3.8 ml) at 0 ^{0}C (ice and sodium chloride). The solution was stirred at 0 ^{0}C for 30 min and then for 20 min at room temperature. 4-Chlorobenzoyl chloride (0.16 ml, 1.26 mmol) was added dropwise to prepared solution at 0 ^{0}C (ice and sodium chloride). The reaction mixture was stirred under cooling for 35 min and then 210 min at room temperature, poured in cooled 5% aq $NaHCO_3$, the aqueous phase was extracted with EtOAc (3x30 ml). The combined organic extracts were washed with water, dried over anh. Na_2SO_4, and evaporated to dryness. The residue was chromatographed on a silica gel, using for elution a mixture of hexane-EtOAc 8:1, 6:1 and 4:1, and EtOAc as the eluent to give (130 mg, 30%) of methyl 5-*O*-trityl-2,3-di-*O*-4-chlorobenzoyl-β-L-arabinofuranoside (**44**) as white solid. M.p.62–64 °C. IR (KBr): ν 3063, 3033, 1728, 1596, 1444, 1275, 1096, 758, 702 cm^{-1}. $[\alpha]_D^{20}$ +47 (c 1.0, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.23-7.98 [m, 23H, $(C_6H_5)_3C$, 2xClBz], 5.91 (dd, 1H, $J_{2,3}$ = 6.8 Hz, $J_{3,4}$ = 5.7 Hz, H-3), 5.33 (dd, 1H, $J_{2,1}$ = 4.5 Hz, H-2), 5.25 (d, 1H, H-1), 4.22 (m, 1H, H-4), 3.48 (dd, 1H, $J_{5,4}$ = 5.5 Hz, $J_{5,5'}$ = 9.9 Hz, H-5), 3.44 (dd, 1H, $J_{5',4}$ = 6.5 Hz, H-5′), 3.27 (s, 3H, OCH_3). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 165.09, 164.59 (C=O, 2xCOC_6H_4Cl), 143.75, 139.88, 131.36, 131.19, 128.67, 127.91, 127.7, 127.23 [$(C_6H_5)_3C$, Cl-Bz], 101.2 (C-1), 86.81 $(C_6H_5)_3C$, 79.34, 77.91, 76.64 (C-4, C-2, C-3), 65.44 (C-5), 55.34 (OCH_3). HRMS (ESI$^+$): m/z calcd for $C_{39}H_{32}O_7Cl_2Na$ $[M+Na]^+$: 705.1423, found 705.1419.

methyl 5-*O*-trityl-2-*O*-4-chlorobenzoyl-β-L-arabinofuranoside (**43**) (220 mg, 64%) as oil. $[\alpha]_D^{20}$ +56 (c 1.0, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.23-7.99 [m, 19H, $(C_6H_5)_3C$, Cl-Bz], 5.15 (d, 1H, $J_{1,2}$ = 4.5 Hz, H-1), 5.04 (dd, 1H, $J_{2,3}$ = 7.67 Hz, H-2), 4.99 (t, 1H, H-3), 4.10 (m, 1H, H-4), 3.38 (dd, 1H, $J_{5,4}$ = 5.7 Hz, $J_{5,5'}$ = 9.8 Hz, H-5), 3.30 (dd, 1H, $J_{5',4}$ = 5.27 Hz, H-5′), 3.28 (s, 3H, OCH_3). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 165.97 (C=O, COC_6H_4Cl), 143.81, 139.84, 131.31, 128.78, 128.67, 127.86, 127.1 [$(C_6H_5)_3C$, Cl-Bz], 101.1 (C-1), 86.75 $(C_6H_5)_3C$, 80.79 , 80.36, 74.85 (C-4, C-2, C-3), 65.44 (C-5), 55.34 (OCH_3). HRMS (ESI$^+$): m/z calcd for $C_{32}H_{29}O_6ClNa$ $[M+Na]^+$: 567.1550, found 567.1559.

4.3.3. Methyl 3-*O*-methanesulfonyl-2,5-di-*O*-4-chlorobenzoyl-β-L-arabinofuranoside (45)

To a solution of 2,5-di-*O*-acyl-β-L-arabinofuranoside **36** (360 mg, 0.82 mmol) in anhydrous pyridine (14 ml) and 4-dimethylaminopyridine (50 mg, 0.4 mmol) was added methanesulfonyl chloride (0.3 ml, 3.8 mmol) at 0 ^{0}C. The reaction mixture was stirred at rt for 3 h, then diluted CH_2Cl_2 (50 ml), washed with water (10 ml), the aqueous phase was extracted with CH_2Cl_2 (50 ml). The combined organic extracts were washed with 1 N HCl (3x30 ml), 5% aq $NaHCO_3$, dried over anhydrous Na_2SO_4, and evaporated to dryness. The residue was purified by chromatography on silica gel, using a mixture of 5:1 and 4:1 hexane -EtOAc to afford (370 mg, 88%) of mesylate **45** as a syrup. $[\alpha]_D^{20}$ +55.4 (c 1, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ: ^{1} H NMR ($CDCl_3$): 8.04, 8.02, 7.45 and 7.42 (4m, 8H, 2 x ClBz), 5.56 (dd, 1H, $J_{3,2}$ = 7.2 Hz, $J_{3,4}$ = 5.7 Hz, H-3), 5.31 (dd 1H, H-2), 5.26 (d, 1H, $J_{1,2}$ = 4.5 Hz, H-1), 4.64 (dd, 1H, $J_{5,4}$ = 4.7 Hz, $J_{5,5'}$ = 11.7 Hz, H-5), 4.53 (dd, 1H, $J_{5',4}$ = 5.7 Hz, H-5′), 4.48 (m, 1H, H-4), 3.33 (s, 3H, OCH_3), 3.08 (s, 3H, SO_2CH_3). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 165.31, 164.78 (C=O, 2xCOC_6H_4Cl), 140.34, 139.79, 131.34, 131.23, 129.01, 128.80, 127.18, (2x$CO\underline{C_6H_4}Cl$), 100.79 (C-1), 80.37 (C-3), 77.31 (C-4), 77.26 (C-2), 64.48 (C-5), 55.66 (OCH_3), 38.66 (SO_2CH_3). HRMS (ESI$^+$): m/z calcd for $C_{29}H_{20}O_9SCl_2$ $[M+Na]^+$: 541.0103, found 541.0108.

4.3.4. Methyl 2,3-anhydro-β-L-lyxofuranoside (46)

1 M solution of $NaOCH_3$ in methanol (1.2 ml) was added to a solution of mesylate (**45**, 360 mg, 0.69 mmol) in anhydrous methanol (10 ml). The prepared solution was stirred at room temperature for 18 h, and then the reaction mixture was neutralized with glacial acetic acid and evaporated to dryness, coevaporated with a mixture of ethanol-toluene (40 ml). The residue was chromatographed on a silica gel, using for elution chloroform, $CHCl_3$-petroleum ether-methanol (16:8:2) to give (93 mg, 91%) of methyl 2,3-anhydro-β-L-lyxofuranoside (**46**) as a colorless oil.

$[\alpha]_D^{20}$ +88 (c 1.1, $CHCl_3$). Lit. for D-isomer [42]. $[\alpha]_D^{25}$ –106.8 (c 1.0, H_2O). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 5.02 (s, 1H, $J_{1,2}$ <1.0 Hz, H-1), 4.01 (t, 1H, $J_{4,3}$ <1.0 Hz, $J_{4,5}$ = 5.7 Hz, $J_{4,5'}$ = 5.4 Hz, H-4), 3.88 (dd, 1H, $J_{5,5'}$ = 11.4 Hz, H-5), 3.85 (dd, 1H, H-5), 3.71 (br.d, 1H, H-3), 3.69 (br.d, 1H, $J_{2,3}$ = 2.9 Hz, H-2), 3.51 (s, 3H, OCH_3). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 102.35 (C-1), 76.68 (C-4), 61.81 (C-5), 56.88 (OCH_3), 55.31 (C-2), 54.82 (C-3). HRMS (ESI^+): m/z calcd for $C_6H_{10}O_4Na$ $[M+Na]^+$: 169.0477, found 169.0482.

4.3.5. Methyl 5-*O*-*tert*-butyldiphenylsilyl-2,3-anhydro-β-L-lyxofuranoside (47)

To a solution of epoxide **46** (31 mg, 0.21 mmol) in anhydrous pyridine (0.9 ml) was added *tert*-butyldiphenylchlorosilane (0.08 ml, 0.31 mmol). The solution was stirred at room temperature for 48 h, and then the reaction mixture was evaporated, coevaporated with toluene, then residue was dissolved in CH_2Cl_2 and washed with 5% aq $NaHCO_3$, dried and evaporated to dryness. The residue was chromatographed on a silica gel, using for elution a mixture of hexane-ethylacetate 10:1 and 7:1 to give (65 mg, 80%) of silyl derivative of methyl 2,3-anhydro-β-L-lyxofuranoside **47** as a colorless oil. IR (film, $CHCl_3$): ν 2956, 2934, 2894, 2861, 1115, 1063, 1055 cm^{-1}. $[\alpha]_D^{20}$ +53.6 (c 0.5, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.37-7.71 [m, 10H, $(CH_3)_3CSi(\underline{C_6H_5})_2$], 5.00 (d, 1H, $J_{1,2}$ = 0.5 Hz, H-1), 4.04 (ddd, 1H, $J_{4,5}$ = 5.3 Hz, $J_{4,5'}$ = 8.4 Hz, $J_{4,3}$ = 0.8 Hz, H-4), 3.91 (dd, 1H, $J_{5,5'}$ = 9.7 Hz, H-5), 3.85 (dd, 1H, $J_{2,3}$ =3.0 Hz, H-3), 3.84 (dd, 1H, H-5′), 3.72 (d, 1H, H-2), 3.46 (s, 3H, OCH_3), 1.08 (s, 9H, $(\underline{CH_3})_3CSi(C_6H_5)_2$. ^{13}C NMR (125 MHz, $CDCl_3$) δ: 135.49, 133.35, 133.21, 129.71, 127.72, 127.69 $(CH_3)_3CSi(\underline{C_6H_5})_2$, 102.32 (C-1), 76.75 (C-4), 62.07 (C-5), 56.67(OCH_3), 55.92, 55.27 (C-3, C-2), 26.80 (CH_3)$_3$C-, 19.22 $(CH_3)_3C$-. HRMS (ESI^+): m/z calcd for $C_{22}H_{28}O_4SiNa$ $[M+Na]^+$: 407.1655, found 407.1651.

4.3.6. Methyl 5-*O*-*tert*-butyldiphenylsilyl-2-deoxy-β-L-*threo*-pentofuranoside (48)

L-Selectride (0.45 ml 1 M solution in THF, 0.45 mmol) was added under argon to epoxide **47** (60 mg, 0.156 mmol) in anhydrous THF (0.5 ml) at -78 ^{0}C. The solution was stirred with gradually warmed to room temperature and then, it was stirred for 1 h. Water (3 ml) was added to the prepared solution, the reaction mixture was extracted with $CHCl_3$ (2x20 ml), combined extracts washed with 5% aq $NaHCO_3$, water, dried and evaporated to dryness. The residue was dissolved in CCl_4 and then filtered off, filtrate was evaporated. 2-Deoxy L-sugar **48** (60 mg, 99%) was prepared as a colorless oil. IR (film, $CHCl_3$): ν 3450, 2956, 2934, 2862, 1107, 1049, 1015, 805, 409 cm^{-1}. $[\alpha]_D^{20}$ +36 (c 0.67, $CHCl_3$). Lit. for D-isomer [43]. $[\alpha]_D^{20}$ –54 (c 0.31, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.37-7.73 [m, 10H, $(CH_3)_3CSi(\underline{C_6H_5})_2$], 5.04 (dd, 1H, $J_{1,2'}$ = 1.6 Hz, $J_{1,2}$ = 3.7 Hz, H-1), 4.33 (m, 1H, H-4), 4.10 (m, 1H, H-3), 4.05 (dd, 1H, $J_{4,5}$ = 5.7 Hz, $J_{5,5'}$ = 10.6 Hz, H-5), 3.87 (dd 1H, $J_{4,5'}$ = 5.8 Hz, H-5′), 3.29 (s, 3H, OCH_3), 2.94 (d, J = 9.7 Hz, 3-OH), 2.10-2.14 (m, 2H, H-2 and H-2′), 1.07 [s, 9H, $(C\underline{H_3})_3CSi(C_6H_5)_2$]. ^{13}C NMR (125 MHz, $CDCl_3$) δ: 135.60, 133.39, 133.39, 129.65, 127.66 $(CH_3)_3CSi(\underline{C_6H_5})_2$, 105.04 (C-1), 84.57 (C-4), 71.47 (C-3), 63.67 (C-5), 54.92 (OCH_3), 41.39 (C-2), 26.80 (CH_3)$_3$C-, 19.17 $(CH_3)_3C$-. HRMS (ESI^+): m/z calcd for $C_{22}H_{30}O_4SiNa$ $[M+Na]^+$: 409.1811, found 409.1807.

4.3.7. Methyl 2-deoxy-β-L-*threo*-pentofuranoside (50) and methyl 3-deoxy-β-L-*threo*-pentofuranoside (51)

L-Selectride (2.0 ml 1 M solution in THF) was added under argon to methyl 2,3-anhydro-β-L-lyxofuranoside (**46**) (90 mg, 0.61 mmol) in 0.7 ml anhydrous THF at -78^{0}C. The reaction mixture was stirred with gradually warmed to room temperature and then it was stirred for 90 min. Reaction mixture was treated with 10% NaOH (3 ml) and 30% H_2O_2 (2.1 ml) under 0 ^{0}C ice-cooling and then was stirred for 10 min at rt and evaporated under high vacuum and mild heating. The residue was chromatographed on a silica gel, using for elution chloroform and a mixture of $CHCl_3$:acetone - 1:1 to give a mixture (47 mg, a ratio of 2-deoxy and 3-deoxy-isomers - 1:1.1, 51%) of methyl 2-deoxy-β-L-*threo*-pentofuranoside (**50**) and methyl 3-deoxy-β-L-*threo*-pentofuranoside (**51**) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 5.04 (d, 1H, $J_{1,2}$ = 4.7 Hz, H-1, 2-deoxy-derivative), 4.75 (d, 1.1 H, $J_{1,2}$ = 4.5 Hz, H-1, 3-deoxy-derivative), 4.37 (t, 1H, H-4), 4.19-4.26 (m, 2.2H, H-4 and H-3), 4.11 (t, 1H, H-3), 3.87 (d, 2H, 2H-5), 3.70

(dd, 1H, $J_{4,5}$ = 2.9 Hz, $J_{5,5'}$ = 11.8 Hz, H-5), 3.48-3.51 (dd, 1H, H-5′), 3.49 (s, 3.3H, OCH_3), 3.40 (s, 3H, OCH_3), 2.23-2.29 (ddd, 1H, H-3′), 2.16-2.21 (ddd, 1H, H-2′), 2.10 (dd, 1H, H-2), 1.74 (dt, 1H, H-3). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 104.99 (C-1, 2-deoxy), 102.48 (C-1, 3-deoxy), 83.34 (C-4), 78.5 (C-4), 72.69, 71.97 (C-2 and C-3), 65.23 (C-5, 3-deoxy), 62.58 (C-5, 2-deoxy), 54.78 (OCH_3, 3-deoxy), 55.08 (OCH_3, 2-deoxy), 41.83 (C-2, 2-deoxy), 32.20 (C-3, 3-deoxy). HRMS (ESI^+): m/z calcd for $C_6H_{12}O_4$ $[M+Na]^+$: 171.0628, found 171.0631.

Supplementary data

Supplementary data associated with this article can be found, in the online version.

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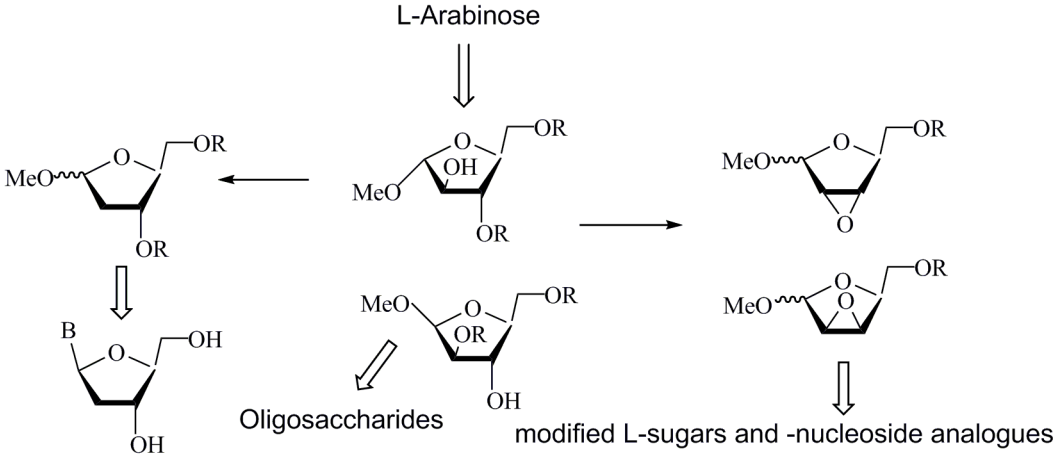

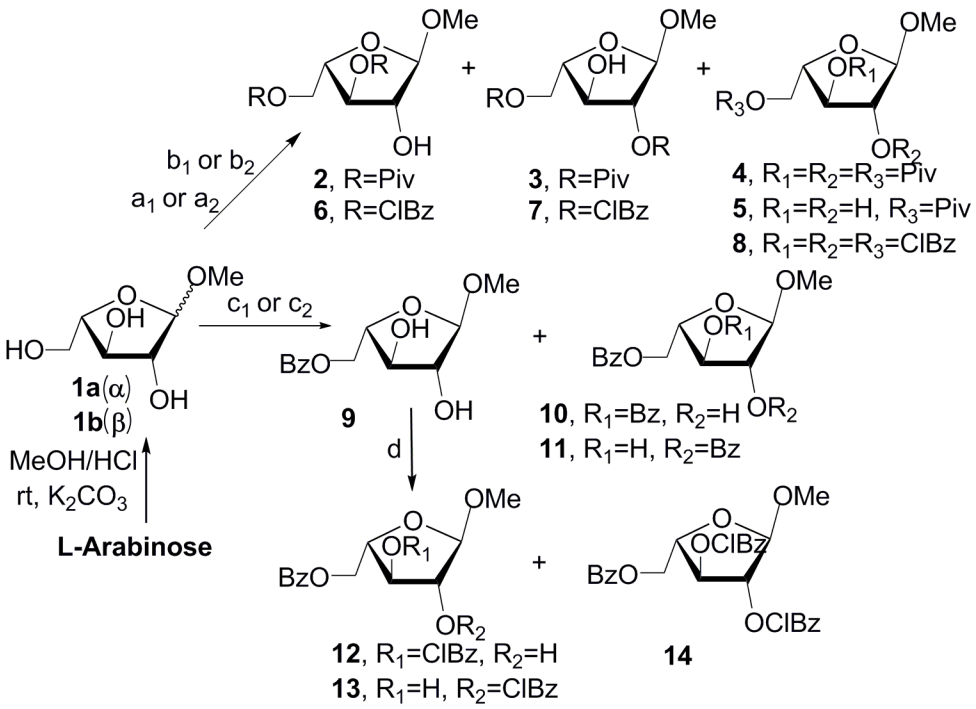
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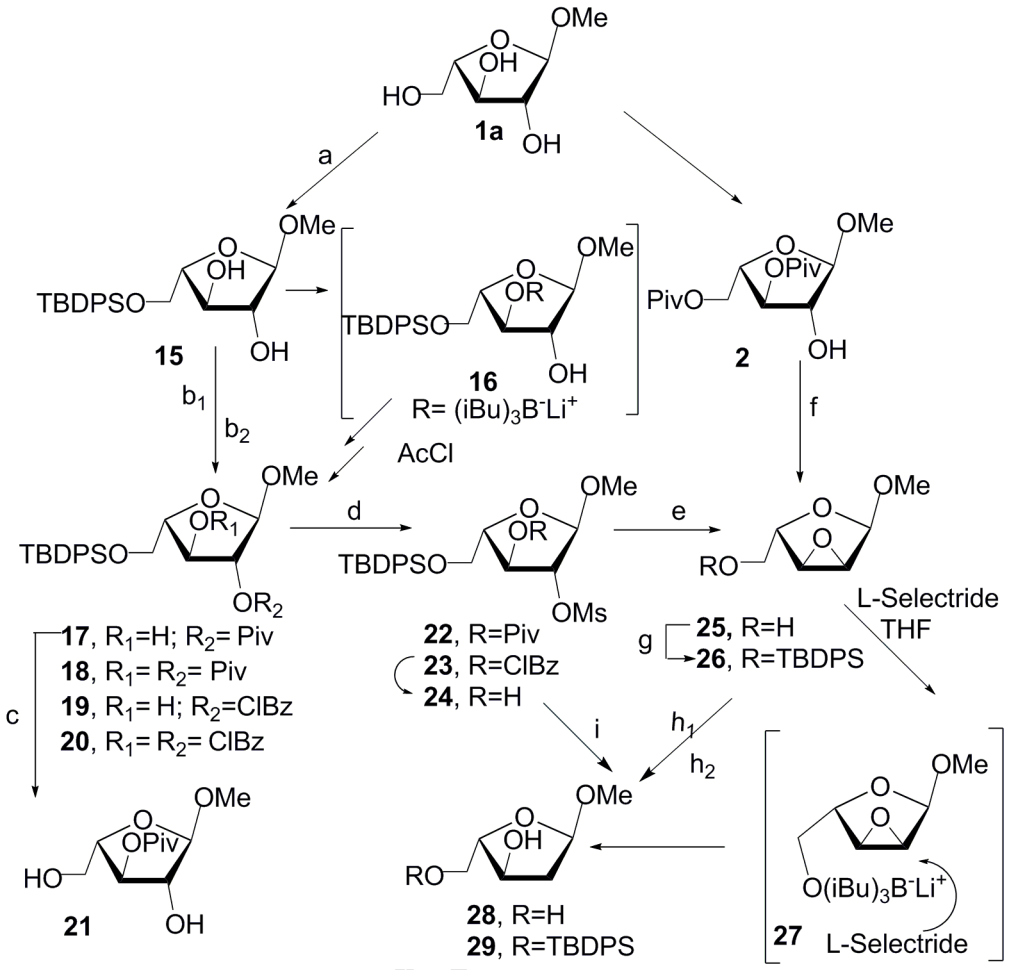
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18, R1= R2= Piv
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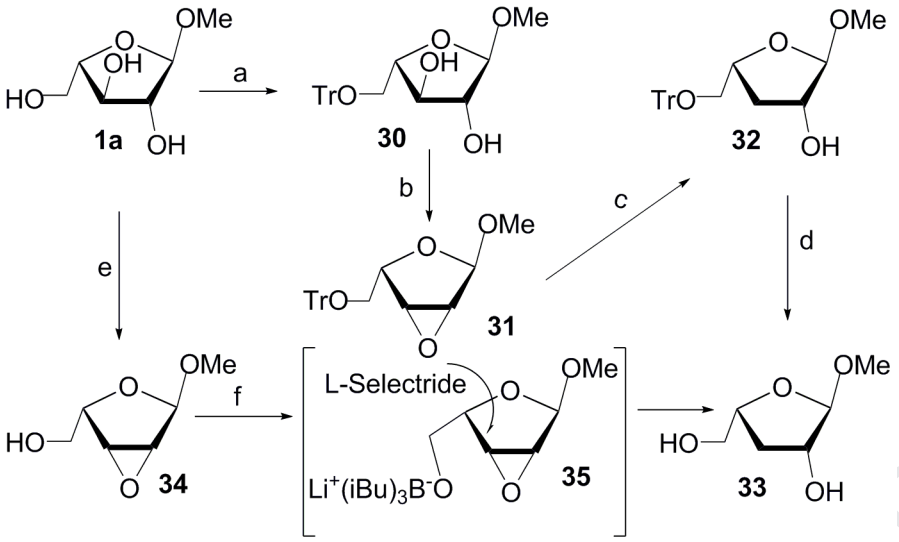
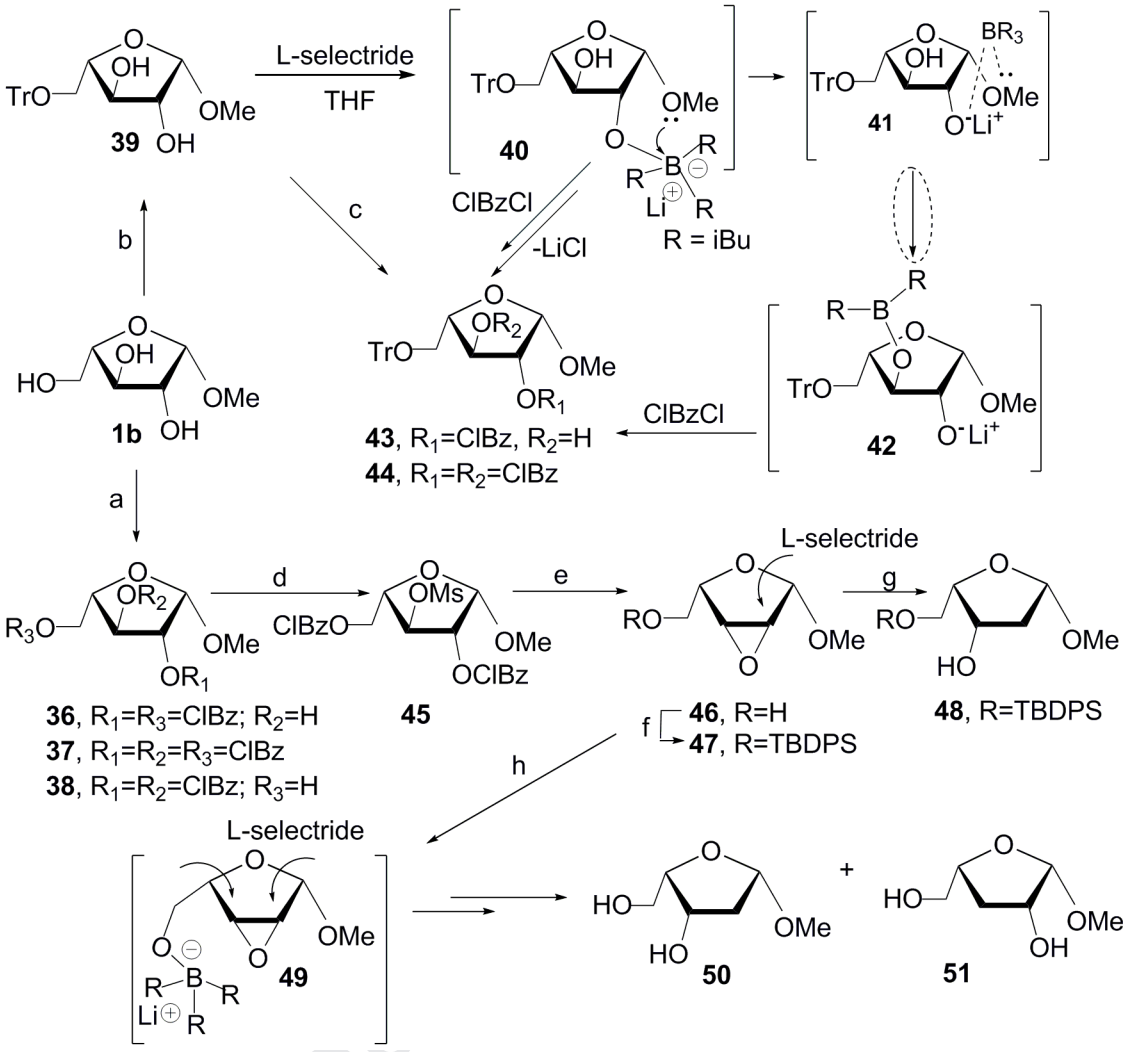
L-Selectride




L-selectride
THF
39
40
41
R = iBu
ClBzCl
-LiCl
c
b
a
1b
43, R1=ClBz, R2=H
44, R1=R2=ClBz
42
ClBzCl
d
e
g
36, R1=R3=ClBz; R2=H
37, R1=R2=R3=ClBz
38, R1=R2=ClBz; R3=H
45
46, R=H
47, R=TBDPS
48, R=TBDPS
f
h
L-selectride
49
50
51

- Novel mono- and di-O-protected L-arabinofuranoside derivatives were synthesized.
- A method of selective acylation of 5-O-protected L-arabinosides was investigated.
- Acylation reactions of α- and β-L-arabinofuranosides differ in regioselectivity.
- 2(3)-L-deoxyglycosides were prepared via stereoselective L-Selectride reductions.

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Declarations of interests: none