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Effect of acyl chain length on selective biocatalytic deacylation on *O*-aryl glycosides and separation of anomers

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ABSTRACT

It has been demonstrated that Lipozyme® TL IM (*Thermomyces lanuginosus* lipase immobilised on silica) can selectively deacylate the ester function involving the C-5′ hydroxyl group of α-anomers over the other acyl functions of anomeric mixture of peracylated *O*-aryl α,β-D-ribofuranoside. The analysis of results of biocatalytic deacylation reaction revealed that the reaction time decreases with the increase in the acyl chain length from C_1 to C_4. The unique selectivity of Lipozyme® TL IM has been harnessed for the separation of anomeric mixture of peracylated *O*-aryl α,β-D-ribofuranosides, The lipase mediated selective deacylation methodology has been used for the synthesis of *O*-aryl α-D-ribofuranosides and *O*-aryl β-D-ribofuranosides in pure forms, which can be used as chromogenic substrate for the detection of pathogenic microbial parasites containing glycosidases.

1. Introduction

O-Aryl ribofuranosides are used as chromogenic substrates, which on reaction with nucleoside hydrolases or nucleoside phosphorylases release phenolic chromophore that can be detected spectrophotometrically and thus provide an easy diagnostic method for the detection of glycosidase enzymes and microbial parasites containing them, which may have adverse effect on human health and animal population [1]. Park and Shin [2] have recently reported a simple and rapid method to characterize glycosidase activities that relies on the use of a mixture of coumarin-linked glycosides. In addition, aromatic analogues of DNA nucleobases have become a valuable tool to study DNA–DNA and DNA–protein interactions [3].

Many a time synthesis of *O*-aryl glycosides becomes difficult due to the electron-withdrawing property of aromatic rings [4]. Additionally, the facile rearrangement of *O*-aryl glycosides often leads to their corresponding *C*-aryl glycosides [5]. The other problem associated with the synthesis of *O*-aryl glycosides is the formation of mixtures of α,β-anomers, which is difficult to separate using conventional chromatographic techniques [2,4]. The potential of enzymes in carbohydrate/nucleoside chemistry is well recognized for selective acylation/deacylation of different functional groups of similar reactivity [6,7]. Lipases have been used for the separation of isomeric nucleosides [8], resolution of β-D/L-2′-deoxynucleosides [9] and for the separation of N-7 and N-9 guanine nucleosides [10]. Chien and Chern [11] have used native CRL to catalyse the selective hydrolysis of one of the ester functions in α-anomer of 1,2,3,5-tetra-*O*-acetylribofuranose to afford the corresponding 5-hydroxyl derivative. Inigo et al. [12] have studied *Candida antarctica* lipase B catalysed deacetylation of 1-*O*-methyl-2,3,5-tri-*O*-acetyl-α-D-ribofuranoside and 1-*O*-methyl-2,3,5-tri-*O*-acetyl-β-D-ribofuranoside and observed regioselective deacetylation in the former compound to afford 1-*O*-methyl-2,3-di-*O*-acetyl-α-D-ribofuranoside in good yield; selectivity was not observed in β-diastereoisomer. Recently, we have reported the separation of anomeric mixture of 2,3,5-tri-*O*-acetyl-1-*O*-aryl-α,β-D-ribofuranosides *via* Lipozyme® TL IM catalyzed enzymatic deacylation reaction [13]. Though deacetylation reaction was selective and high yielding, the reaction time was as high as 48 h. Herein we present the results of study of effect of acyl chain length on lipase-mediated selective deacylation on anomeric mixtures of peracylated *O*-aryl-α,β-D-ribofuranosides.

2. Results and discussion

The tetra-*O*-acylated α,β-D-ribofuranosides **10**–**13** were chemoenzymatically synthesized in two steps following literature procedure [14], *i.e.* by CAL-B mediated selective acylation of lone

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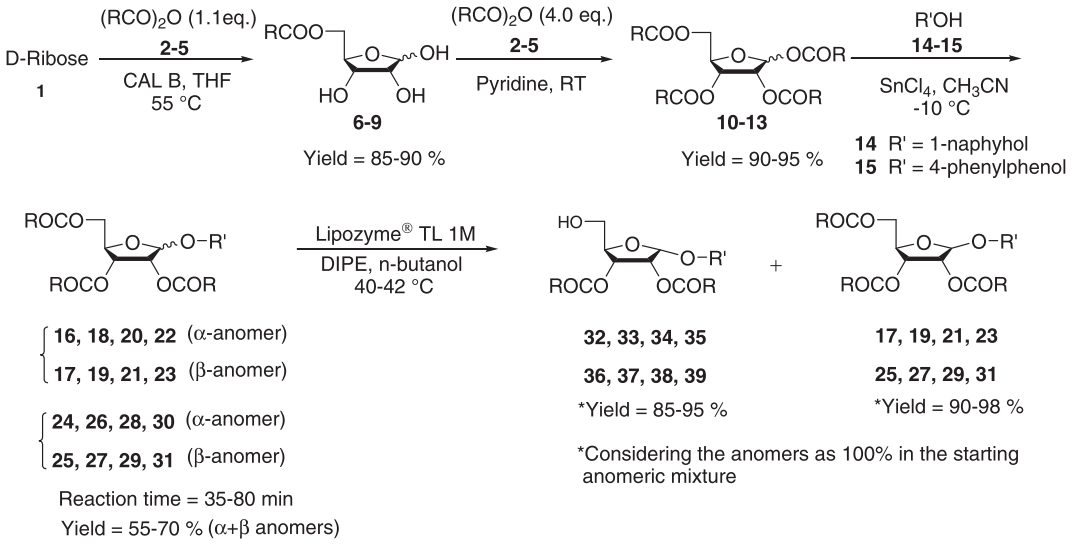
primary hydroxyl group of D-ribose with acetic-, propanoic-, butanoic- and pentanoic anhydrides in THF at 55 °C followed by classical peracylation of the other three secondary hydroxyl groups with corresponding acylating agents in pyridine in high yields, respectively (Scheme 1). The coupling of 1,2,3,5-tetra-*O*-acyl-α,β-D-ribofuranoside **10**–**13** with each of the two phenols, *i.e.* 1-naphthol (**14**) and 4-phenylphenol (**15**) in presence of tin (IV) chloride (1 M solution in DCM) in dry acetonitrile gave anomeric mixtures of 2,3,5-tri-*O*-acetyl-, 2,3,5-tri-*O*-propanoyl-, 2,3,5-tri-*O*-butanoyl- and 2,3,5-tri-*O*-pentanoyl-, -*O*-(1-naphthyl)-α,β-D-ribofuranosides (**16**–**17**, **18**–**19**, **20**–**21** and **22**–**23**, respectively), and 2,3,5-tri-*O*-acetyl-, 2,3,5-tri-*O*-propanoyl-, 2,3,5-tri-*O*-butanoyl- and 2,3,5-tri-*O*-pentanoyl-, -*O*-(4-phenylphenyl)-α,β-D-ribofuranosides (**24**–**25**, **26**–**27**, **28**–**29** and **30**–**31**, respectively) in moderate to good yield. The ratio of the α- and β-anomers in eight anomeric mixtures were determined on the basis of comparison of intensities of anomeric protons of α- and β-anomers in the ^{1}H NMR spectrum of the mixtures. The anomeric proton of β-anomer appeared as a singlet, whereas the anomeric proton of α-anomer appeared as a doublet or as a broad singlet at higher δ value with respect to the corresponding proton of the β-anomer [15]. Our attempts to separate α- and β-anomers from the anomeric mixture of triacylated *O*-aryl-α,β-D-ribofuranosides **16**–**31** by silica gel coloumn chromatography or by crystallization failed in most of the cases. This prompted us to develop efficient enzymatic methodology for the separation of α- and β-anomers of the synthesized *O*-aryl ribofuranosides and study the effect of acyl chain length on selectivity and turnover number of the enzymatic deacylation reaction.

Four different lipases, *i.e. Candida rugosa* lipase (CRL), *Candida antarctica* lipase B immobilized on accurel [CAL-L(A)], *Candida antarctica* lipase B immobilized on polyacrylate (lewatit, CAL-B) and *Thermomyces lanuginosus* lipase immobilised on silica (Lipozyme® TL IM) were screened for regioselective deacylation of acyloxy function(s) of one anomer over the other in different organic solvents, *i.e.* tetrahydrofuran (THF), dioxane, acetonitrile, toluene, ethanol and diisopropyl ether (DIPE) at different temperature (35–60 °C). Although CAL-B, initially showed selectivity for the deacylation of C-5′-acyloxy group of α-anomer, it started deacylation of acyloxy functions of the β-anomer as well with time and led to a mixture of compounds. CRL and CAL-L(A) did not show any appreciable selectivity in the deacylation studies on anomeric mixtures. It was observed that Lipozyme® TL in DIPE at 40–42 °C selectively and most efficiently deacylates the acyloxy function involving C-5′-hydroxyl group of the α-anomers over the other acyloxy functions present in anomeric mixture of peracylated 1-*O*-aryl-α,β-D-ribofuranosides [13].

To explore enzyme selectivity and reaction rate for different acyl groups, anomeric mixtures of tri-*O*-propanoyl-*O*-aryl-α,β-D-ribofuranosides (**18**–**19** and **26**–**27**), tri-*O*-butanoyl-*O*-aryl-α,β-D-ribofuranosides (**20**–**21** and **28**–**29**) and tri-*O*-pentanoyl-*O*-aryl-α,β-D-ribofuranosides (**22**–**23** and **30**–**31**) were incubated with Lipozyme® TL IM in DIPE at 40–42 °C. It was observed that in all



Compounds 2-39	R	R'
2, 6, 10	CH_3-	-
3, 7, 11	CH_3CH_2-	-
4, 8, 12	$CH_3CH_2CH_2$-	-
5, 9, 13	$CH_3CH_2CH_2CH_2$-	-
16, 17, 32	CH_3-	1-naphthyl
18, 19, 33	CH_3CH_2-	1-naphthyl
20, 21, 34	$CH_3CH_2CH_2$-	1-naphthyl
22, 23, 35	$CH_3CH_2CH_2CH_2$-	1-naphthyl
24, 25, 36	CH_3-	4-phenylphenyl
26, 27, 37	CH_3CH_2-	4-phenylphenyl
28, 29, 38	$CH_3CH_2CH_2$-	4-phenylphenyl
30, 31, 39	$CH_3CH_2CH_2CH_2$-	4-phenylphenyl

Scheme 1. Lipase catalyzed deacylation reaction: separation of anomeric mixtures.

the cases, Lipozyme® TL IM selectively catalyzed the deacylation of acyloxy functions involving C-5′-hydroxyl group of α-anomer over the other acyloxy function of the α- and β-anomers in the mixture, leading to the formation of monohydroxy *O*-aryl ribofuranosides **33** and **37**, **34** and **38** and **35** and **39** in high yields. However, the rate of deacylation of acyloxy function involving C-5′-hydroxyl of α-anomers in case of 2,3,5-tri-*O*-acyl-1-*O*-(1-naphthyl)-α,β-D-ribofuranosides (**16**–**17**, **18**–**19**, **20**–**21** and **22**–**23**) was different. The Lipozyme® TL IM catalyzed the depentanoylation of α-anomer **22** to form the monohydroxy *O*-aryl ribofuranosides **35** six times faster than the deacetylation of the α-anomer **16**, while debutanoylation and depropanoylation of the α-anomers **20** and **18** was three and two times faster, respectively. Similar trend was observed in case of deacylation of 2,3,5-tri-*O*-acyl-1-*O*-(4-phenylphenyl)-α,β-D-ribofuranosides (**24**–**25**, **26**–**27**, **28**–**29** and **30**–**31**) as shown in Table 1. Thus, the reaction time for deacylation reaction decreases with increase in carbon chain length of the acyl moiety in case of tri-*O*-acylateD-1-*O*-aryl-α,β-D-ribofuranosides (**16**–**31**). This may be due to the increase in lipophilicity of the peracylates and its better compatibility in the active site of the enzyme that make them better substrates for the enzyme.

The monohydroxy *O*-aryl-α-D-ribofuranosides **32**, **33**, **34**, **35**, **36**, **37**, **38** and **39** obtained on lipase catalysed deacylation reactions on **16**–**17**, **18**–**19**, **20**–**21**, **22**–**23**, **24**–**25**, **26**–**27**, **28**–**29** and **30**–**31** were acylated chemically using acetic-, propanoic-, butanoic- and pentanoic anhydrides **2**–**5** to give pure tri-*O*-acylated *O*-aryl ribofuranosides **16**, **18**, **20**, **22**, **24**, **26**, **28** and **30** in 91–95% yields (Scheme 2). Thus, both peracylated α- and β-*O*-aryl ribofuranoside could be prepared in pure forms. Moreover, Lipozyme® TL IM regioseletively deacetylates only the C-5′ acetoxy group of α-anomer from the anomeric mixture of peracetylated 1-*O*-(1-naphthyl)-α,β-D-ribofuranosides **16**–**17** is proved from ^{1}H NMR spectrum of 5-*O*-acetylated compound **16** that showed a downfield shift for the C-5′ protons from δ 3.83–3.85 ppm to δ 4.21–4.38 ppm.

Further, complete deacylation of both, α- and β-anomers of tri-*O*-acylated *O*-aryl-D-ribofuranosides using saturated methanolic ammonia afforded *O*-aryl-α-D-ribofuranosides and *O*-aryl-β-D-ribo furanosides, respectively. 2,3,5-Tri-*O*-acyl-1-*O*-(1-naphthyl)-α-D-ribofuranosides **16**, **18**, **20**, **22** and 2,3,5-Tri-*O*-acyl-1-*O*-(4-phenyl phenyl)-α-D-ribofuranosides **24**, **26**, **28**, **30** gave 1-*O*-(1-naph thyl)-α-D-ribofuranoside (**40**) and 1-*O*-(4-phenylphenyl)-α-D-ribo furanoside (**42**), respectively (Scheme 2). Similarly, 2,3,5-Tri-*O*-acyl-1-*O*-(1-naphthyl)-β-D-ribofuranosides **17**, **19**, **21**, **23** and 2,3,5-tri-*O*-acyl-1-*O*-(4-phenylphenyl)-β-D-ribofuranosides **25**, **27**, **29**, **31** gave 1-*O*-(1-naphthyl)-β-D-ribofuranoside (**41**) and 1-*O*-(4-phenylphenyl)-β-D-ribofuranoside (**43**), respectively in quantitative yields (Scheme 3). The structures of synthesized compounds **6**–**13** and **16**–**43** were unambiguously established by analysis of their spectral data (^{1}H NMR, ^{13}C NMR, IR, HRMS spectra). The structures of known compounds **6** [16], **7** [14], **8** [16], **9** [16], **10** [17], **11** [17], **12** [17], **13** [17], **17** [13], **25** [13], **32** [13], **36** [13], **40** [13], **41** [13], **42** [13] and **43** [13] were further confirmed by comparison of their spectral data with those reported in the literature.

Selective deacylation of the ester function involving the C-5′ hydroxyl group of α-anomers **16**, **18**, **20**, **22**, **24**, **26**, **28** and **30** over the other ester functions in the anomeric mixtures **16**–**17**, **18**–**19**, **20**–**21**, **22**–**23**, **24**–**25**, **26**–**27**, **28**–**29** and **30**–**31** results in the sufficient difference in the polarity of the monohydroxy α-D-ribofuranosides and their corresponding triacylated β-anomers. This selective lipase mediated deacylation methodology enabled us to achieve the separation of α- and β-anomers of *O*-aryl ribosides, which is otherwise almost impossible to achieve by simple chromatographic methods. Both, α- and β-*O*-aryl ribofuranosides can be obtained in pure forms using the biocatalytic methodology [13]. All these enzymatic reactions did not yield any product when performed in the absence of Lipozyme® TL IM. The yields reported for partially deacylated α-anomers **32**, **33**, **34**, **35**, **36**, **37**, **38** and **39** and unreacted peracylated β-anomers **17**, **19**, **21**, **23**, **25**, **27**, **29** and **31** are calculated by taking the amounts of α- and β-anomers in the starting mixtures as 100%.

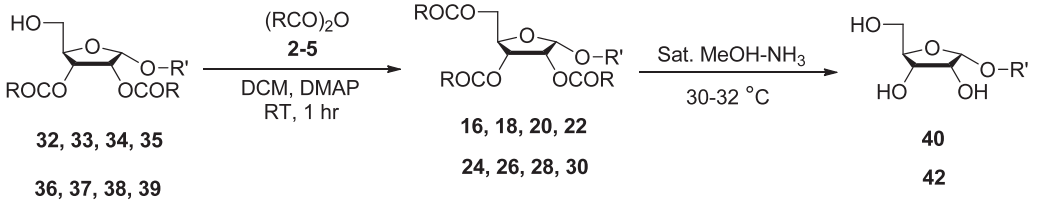
3. Conclusion

We have successfully demonstrate the selectivity and specificity of Lipozyme® TL IM for the regio- and stereoselective deacylation of acyl moiety from the C-5′ acyloxy group of α-anomer *versus* the corresponding C-5′ acyloxy function of the β-anomer and the two acyloxy moieties present at the C-2′ and C-3′ position of each of the α- and β-anomers of 2,3,5-tri-*O*-acyl-1-*O*-aryl-D-ribofuranosides. The rate of deacylation reaction of C-5′ acyloxy function of the α-anomer decreases with the increase in the acyl chain length in peracylated *O*-aryl-α,β-D-ribofuranosides. This methodology enabled us to separate the anomeric mixtures of *O*-

Table 1
Lipozyme® TL IM-catalyzed regio- and chemoselective deacylation studies on mixture of α,β-anomers of peracylated 1-*O*-aryl-D-ribofuranosides in DIPE at 40–42 °C.

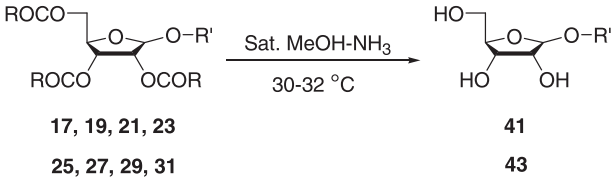
Anomeric mixtures[a]	Ratio of α:β anomers	Reaction time (hrs)	Deacylated and unreacted ribofuranosides[a]	% Yield[b] (isolated)
16 and **17** [13]	1.0:0.9	12.5	**32**	95
			17	98
18 and **19**	1.0:1.3	6.5	**33**	86
			19	90
20 and **21**	1.0:1.6	4.0	**34**	88
			21	92
22 and **23**	1.0:3.6	2.0	**35**	87
			23	90
24 and **25** [13]	1.0:3.3	11.5	**36**	95
			25	97
26 and **27**	1.0:2.7	8.0	**37**	91
			27	93
28 and **29**	1.0:2.4	6.5	**38**	85
			29	90
30 and **31**	1.0:2.4	3.0	**39**	85
			31	91

[a] All these reactions did not yield any product when performed in the absence of Lipozyme® TL IM.
[b] The yields reported are calculated by taking α- and β-anomers in the mixture as 100%.



Compounds	R	R'
2	CH_3-	-
3	CH_3CH_2-	-
4	$CH_3CH_2CH_2$-	-
5	$CH_3CH_2CH_2CH_2$-	-
16, 32	CH_3-	1-naphthyl
18, 33	CH_3CH_2-	1-naphthyl
20, 34	$CH_3CH_2CH_2$-	1-naphthyl
22, 35	$CH_3CH_2CH_2CH_2$-	1-naphthyl
24, 36	CH_3-	4-phenylphenyl
26, 37	CH_3CH_2-	4-phenylphenyl
28, 38	$CH_3CH_2CH_2$-	4-phenylphenyl
30, 39	$CH_3CH_2CH_2CH_2$-	4-phenylphenyl
40	-	1-naphthyl
42	-	4-phenylphenyl

Scheme 2. Synthesis of pure peracylated *O*-aryl-α-D-ribofuranosides and finally *O*-aryl-α-D-ribofuranosides.



Compounds	R	R'
17	CH_3-	1-naphthyl
19	CH_3CH_2-	1-naphthyl
21	$CH_3CH_2CH_2$-	1-naphthyl
23	$CH_3CH_2CH_2CH_2$-	1-naphthyl
25	CH_3-	4-phenylphenyl
27	CH_3CH_2-	4-phenylphenyl
29	$CH_3CH_2CH_2$-	4-phenylphenyl
31	$CH_3CH_2CH_2CH_2$-	4-phenylphenyl
41	-	1-naphthyl
43	-	4-phenylphenyl

Scheme 3. Synthesis of *O*-aryl-β-D-ribofuranosides.

aryl ribofuranosides, which were impossible to separate by normal chromatographic techniques. In this process, simultaneous synthesis of both the anomers, *i.e.* natural β- and unnatural α-anomers of *O*-aryl-D-ribofuranosides was achieved. The enzymatic methodology developed herein may find wide applications in the separation of anomeric mixtures of *O*-aryl/alkyl glycosides and nucleosides.

4. Experimental

Melting points were determined on Buchi M-560 instrument and are uncorrected. The IR spectra were recorded on a Perkin–Elmer model 2000 FT-IR spectrometer by making KBr disc for solid samples and thin film for oils. The ^1H and ^{13}C NMR spectra were recorded on a Bruker Avance spectrometer at 300 and 75.5 MHz or at Jeol alpha-400 spectrometer at 400 and 100.5 MHz, respectively using TMS as internal standard. The chemical shift values are on δ scale and the coupling constants (*J*) are in Hz. Signals from OH groups in ^1H NMR spectra recorded in $CDCl_3$ were verified by D_2O exchange. HR–ESI–TOF–MS analyses were carried out on a microTOF-Q instrument from Bruker Daltonics, Bremen. The optical rotations were measured with Rudolph autopol II automatic polarimeter using light of 546 nm wavelength. *Thermomyces lanuginosus* lipase immobilized on silica (Lipozyme® TL IM), *Candida antarctica* lipase B immobilized on accurel [CAL-L(A)] and *Candida antarctica* lipase B immobilized on polyacrylate (lewatite, CAL-B or Novozyme-435) were provided by Novozymes Inc. (Copenhagen, Denmark), whereas *Candida rugosa* lipase (CRL) was purchased from Sigma Chemical Co. (USA). All enzymes were used after storing *in vacuum* over P_2O_5 for more than 24 h. Acetonitrile and diisopropyl ether were distilled and kept over molecular sieves (4 Å) prior to use. Analytical TLCs were performed on precoated Merck silica-gel $60F_{254}$ plates; the spots were detected either under UV

light or by charring with 4% alcoholic H_2SO_4. Silica gel (100–200 mesh) was used for column chromatography.

*4.1. General procedure for the synthesis of peracylated 1-O-aryl α,β-D-ribofuranosides **16–17**, **18–19**, **20–21**, **22–23**, **24–25**, **26–27**, **28–29** and **30–31***

Anomeric mixture of 1,2,3,5-tetra-*O*-acyl-D-ribofuranose **10–13** were chemoenzymatically synthesized following literature procedure from D-ribose (**1**) in two steps in quantitative yields [14]. Compound **10–13** (2.0 mmol) and the corresponding phenol (**14–15**, 2.0 mmol) were mixed in dry acetonitrile (10 mL) and stirred under nitrogen atomosphere at −10 °C. After 10 min., tin (IV) chloride (1 M solution in DCM, 2.0 mmol) was added dropwise to the above solution under stirring and the progress of the reaction was monitored by TLC. On completion, the reaction was stopped by pouring the reaction mixture into bicarbonate solution. The reaction mixture was passed through Celite pad and was thoroughly washed with chloroform (3 × 50 mL). The chloroform solution was then washed with water, dried and concentrated to afford the crude products as viscous oils, which were purified by column chromatography to obtain anomeric mixtures of the peracylated 1-*O*-aryl α,β-D-ribofuranosides (**16–17**, **18–19**, **20–21**, **22–23**, **24–25**, **26–27**, **28–29** and **30–31**) in 55–70% yields by using ethyl acetate and petroleum ether as eluent (Scheme 1). The anomeric mixtures of 1-*O*-aryl-α,β-D-ribofuranosides were unambiguously identified on the basis of their spectral data analysis and by comparison of chemical shift values of anomeric protons of α- and β-anomers in the mixture with those reported for pure 1-*O*-phenyl-α-D-ribofuranoside and 1-*O*-phenyl-β-D-ribofuranoside [15]. The ratio of anomers in the mixtures **16–17**, **18–19**, **20–21**, **22–23**, **24–25**, **26–27**, **28–29** and **30–31** were calculated based on the integration of corresponding anomeric proton in the ^{1}H NMR spectrum of the mixture (Table 1).

*4.2. General procedure for the Lipozyme® TL IM-catalyzed deacylation of peracylated 1-O-aryl-α,β-D-ribofuranosides (**16–17**, **18–19**, **20–21**, **22–23**, **24–25**, **26–27**, **28–29** and **30–31**): Synthesis of monodeacylated O-aryl ribofuranosides **32**, **33**, **34**, **35**, **36**, **37**, **38** and **39** and recovery of pure unreacted peracylated O-aryl ribofuranosides **17**, **19**, **21**, **23**, **25**, **27**, **29** and **31***

The anomeric mixture of peracylated 1-*O*-aryl-α,β-D-ribofuranoside **16–17**, **18–19**, **20–21**, **22–23**, **24–25**, **26–27**, **28–29** and **30–31** was dissolved in diisopropyl ether (25 mL) and incubated with Lipozyme® TL IM (substrate-enzyme ratio, approximately 1:0.5, w/w) and *n*-butanol (0.05 mL) at 40–42 °C (Scheme 1). The progress of the reaction was monitored by TLC in ethyl acetate–petroleum ether as solvent system. Absence of one anomer and appearance of a slow moving product on TLC observed on multiple run indicated completion of the reaction. On completion, the reaction was stopped by filtering off the enzyme and solvent evaporated to dryness under reduced pressure to obtain the crude product. The crude product thus obtained was purified by column chromatography to afford the unreacted β-anomers **17**, **19**, **21**, **23**, **25**, **27**, **29** and **31** and the 5′-*O*-deacylated compounds **32**, **33**, **34**, **35**, **36**, **37**, **38** and **39** in high yields. All the unreacted peracylated 1-*O*-aryl-β-D-ribofuranosides **17**, **19**, **21**, **23**, **25**, **27**, **29** and **31** and enzymatically deacylated 2,3-di-*O*-acetyl-1-*O*-aryl-α-D-ribofuranoside **32**, **33**, **34**, **35**, **36**, **37**, **38** and **39** were unambiguously identified on the basis of their spectral data analysis; the structure of the known compound **17**, **25**, **32** and **36** was further confirmed on the basis of comparison of its spectral data with these reported in the literature [13].

*4.2.1. Selectively monodeacylated O-aryl glycosides **33**, **34**, **35**, **37**, **38** and **39***

*4.2.1.1. 2,3,-Di-O-propanoyl-1-O-(1-naphthyl)-α-D-ribofuranoside (**33**).* It was obtained as colorless oil in 86% yield. R_f = 0.33 (15% ethyl acetate in petroleum ether, v/v); $[\alpha]_D^{22} = +110.06^\circ$ (*c* 0.10, MeOH); IR (KBr) ν_{max}: 3498 (OH), 2983, 1746, 1487, 1355, 1176, 1048 and 769 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.14 (t, *J* = 7.3 Hz, 3H, –$COCH_2CH_3$), 1.25 (t, *J* = 7.3 Hz, 3H, –$COCH_2CH_3$), 2.40–2.54 (m, 4H, 2 × –$COCH_2CH_3$), 3.83–3.87 (m, 2H, C–$5H_{\alpha+\beta}$), 4.38 (d, *J* = 3.0 Hz, 1H, C–4H), 5.23 (dd, *J* = 6.6 and 4.4 Hz, 1H, C–2H), 5.49 (dd, *J* = 7.3 and 2.2 Hz, 1H, C–3H), 6.14 (d, *J* = 4.4 Hz, 1H, C–1H), 7.14, 7.38, 7.44–7.52, 7.81 and 8.27 (7H; d, *J* = 8.1 Hz, 1H; t, *J* = 8.8 Hz, 1H; m, 3H; d, *J* = 8.1 Hz, 1H and d, *J* = 8.8 Hz, 1H; all aromatic protons); ^{13}C NMR (100.5, $CDCl_3$): δ 8.90 and 9.12 (2 × –$COCH_2CH_3$), 27.24 and 27.61 (2 × –$COCH_2CH_3$), 62.26 (C-5), 70.26 (C-3), 71.57 (C-2), 83.83 (C-4), 99.02 (C-1), 108.78, 121.78, 121.95, 125.27, 125.82, 126.26, 126.33, 127.57, 134.54 and 152.29 (all aromatic carbons), 173.29 and 174.05 (2 × *C*O); HR–ESI–TOF–MS: *m/z* 411.1403 ([M+Na]$^+$), calcd. for [$C_{21}H_{24}O_7$+Na]$^+$ 411.1414.

*4.2.1.2. 2,3-Di-O-butanoyl-1-O-(1-naphthyl)-α-D-ribofuranoside (**34**).* It was obtained as colorless oil in 88% yield. R_f = 0.18 (5% ethyl acetate in petroleum ether, v/v); $[\alpha]_D^{25} = +16.80^\circ$ (*c* 0.05, MeOH); IR (KBr) ν_{max}: 3476 (OH), 2965, 2934, 1743, 1464, 1399, 1265, 1176, 1046 and 773 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.92 (t, *J* = 7.3 Hz, 3H, –$COCH_2CH_2CH_3$), 1.03 (t, *J* = 7.3 Hz, 3H, –$COCH_2CH_2CH_3$), 1.63–1.80 (m, 4H, 2 × –$COCH_2CH_2CH_3$), 2.36–2.49 (m, 4H, 2 × –$COCH_2CH_2CH_3$), 3.84–3.92 (m, 2H, C–$5H_{\alpha+\beta}$), 4.37 (d, *J* = 3.0 Hz, 1H, C–4H), 5.22 (dd, *J* = 6.6 and 4.4 Hz, 1H, C–2H), 5.49 (dd, *J* = 7.3 and 2.9 Hz, 1H, C–3H), 6.15 (d, *J* = 4.4 Hz, 1H, C–1H), 7.14, 7.39, 7.44–7.53, 7.82 and 8.27 (7H; d, *J* = 8.1 Hz, 1H; t, *J* = 8.1 Hz, 1H; m, 3H; d, *J* = 8.1 Hz, 1H and d, *J* = 8.8 Hz, 1H; all aromatic protons); ^{13}C NMR (100.5, $CDCl_3$): δ 13.61 and 13.75 (2 × –$COCH_2CH_2CH_3$), 18.22 and 18.47 (2 × –$COCH_2CH_2CH_3$), 35.72 and 36.20 (2 × –$COCH_2CH_2CH_3$), 62.32 (C-5), 70.22 (C-3), 71.56 (C-2), 83.94 (C-4), 98.98 (C-1), 108.76, 121.91, 121.97, 125.22, 125.83, 126.27, 126.36, 127.57, 134.57 and 152.28 (all aromatic carbons), 172.57 and 173.26 (2 × *C*O); HR–ESI–TOF–MS: *m/z* 439.1716 ([M+Na]$^+$), calcd. for [$C_{23}H_{28}O_7$+Na]$^+$ 439.1727.

*4.2.1.3. 2,3-Di-O-pentanoyl-1-O-(1-naphthyl)-α-D-ribofuranoside (**35**).* It was obtained as colorless oil in 87% yield. R_f = 0.25 (15% ethyl acetate in petroleum ether, v/v); $[\alpha]_D^{27} = +73.85^\circ$ (*c* 0.05, MeOH); IR (KBr) ν_{max}: 3447 (OH), 2960, 2932, 2874, 1740, 1581, 1464, 1239, 1174, 1050 and 773 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.86 (t, *J* = 7.3 Hz, 3H, –$COCH_2CH_2CH_2CH_3$), 0.95 (t, *J* = 7.3 Hz, 3H, –$COCH_2CH_2CH_2CH_3$), 1.29–1.35 (m, 2H, –$COCH_2CH_2CH_2CH_3$), 1.41–1.46 (m, 2H, –$COCH_2CH_2CH_2CH_3$), 1.57–1.65 (m, 2H, –$COCH_2CH_2$-CH_2CH_3), 1.62–1.79 (m, 2H, 2 × –$COCH_2CH_2CH_2CH_3$), 1.69–1.77 (m, 2H, –$COCH_2CH_2CH_2CH_3$), 2.40 (t, *J* = 7.3 Hz, 2H, –$COCH_2CH_2$-CH_2CH_3), 2.46–2.51 (m, 2H, –$COCH_2CH_2CH_2CH_3$), 3.84–3.91 (m, 1H, C–$5H_\alpha$), 4.37 (q, *J* = 2.9 Hz, 1H, C–$5H_\beta$), 5.21 (dd, *J* = 7.3 and 4.4 Hz, 1H, C–2H), 5.48 (dd, *J* = 6.6 and 2.9 Hz, 1H, C–3H), 6.15 (d, *J* = 4.4 Hz, 1H, C–1H), 7.14, 7.39, 7.43–7.53, 7.82 and 8.28 (7H; d, *J* = 8.0 Hz, 1H; t, *J* = 8.0 Hz, 1H; m, 3H; d, *J* = 7.4 Hz, 1H and d, *J* = 8.0 Hz, 1H; all aromatic protons); ^{13}C NMR (100.5, $CDCl_3$): δ 13.63 and 13.72 (2 × –$COCH_2CH_2CH_2CH_3$), 22.18 and 22.31 (2 × –$COCH_2CH_2CH_2CH_3$), 26.83 and 27.09 (2 × –$COCH_2CH_2CH_2CH_3$), 33.64 and 34.08 (2 × –$COCH_2CH_2CH_2CH_3$), 62.32 (C-5), 70.23 (C-3), 71.57 (C-2), 83.95 (C-4), 98.96 (C-1), 108.70, 121.92, 121.97, 125.23, 125.82, 126.24, 126.36, 127.57, 134.56 and 152.28 (all aromatic carbons), 172.75 and 173.43 (2 × *C*O); HR–ESI–TOF–MS: *m/z* 467.2033 ([M+Na]$^+$), calcd. for [$C_{25}H_{32}O_7$+Na]$^+$ 467.2030.

*4.2.1.4. 2,3-Di-O-propanoyl-1-O-(4-phenylphenyl)-α-D-ribofuranoside (**37**).* It was obtained as colorless oil in 91% yield. R_f = 0.38 (15% ethyl acetate in petroleum ether, v/v); $[\alpha]_D^{24} = +76.53^\circ$ (*c* 0.05, MeOH); IR (KBr) ν_{max}: 3489 (OH), 2943, 1745, 1579, 1464, 1357, 1266, 1176, 1050 and 774 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 1.14–1.26 (m, 6H, 2 × –$COCH_2CH_3$), 2.40–2.49 (m, 4H, 2 × –$COCH_2CH_3$), 3.81–3.91 (m, 1H, C–5$H_{\alpha+\beta}$), 4.34 (q, *J* = 2.9 Hz, 1H, C–4H), 5.16 (dd, *J* = 7.3 and 4.4 Hz, 1H, C–2H), 5.38–5.43 (m, 1H, C–3H), 5.96 (d, *J* = 4.4 Hz, 1H, C–1H), 7.11, 7.32, 7.42 and 7.53 (9H; d, *J* = 8.1 Hz, 2H; t, *J* = 7.3 Hz, 1H; t, *J* = 7.3 Hz, 2H and t, *J* = 7.3 Hz, 4H; all aromatic protons); ^{13}C NMR (100.5, $CDCl_3$): δ 9.03 and 9.13 (2 × –$COCH_2CH_3$), 27.25 and 27.57 (2 × –$COCH_2CH_3$), 62.15 (C-5), 69.97 (C-3), 71.19 (C-2), 83.13 (C-4), 99.22 (C-1), 117.46, 126.84, 126.90, 128.19, 128.73, 135.72, 140.62 and 155.21 (all aromatic carbons), 173.34 and 174.06 (3 × *C*O); HR–ESI–TOF–MS: *m/z* 437.1566 ([M+Na]$^+$), calcd. for $[C_{23}H_{26}O_7+Na]^+$ 437.1571.

*4.2.1.5. 2,3-Di-O-butanoyl-1-O-(4-phenylphenyl)-α-D-ribofuranoside (**38**).* It was obtained as colorless oil in 85% yield. R_f = 0.38 (15% ethyl acetate in petroleum ether, v/v); $[\alpha]_D^{26} = +43.66^\circ$ (*c* 0.05, MeOH); IR (KBr) ν_{max}: 3474 (OH), 2966, 1740, 1609, 1519, 1487, 1237, 1046 and 764 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 0.98 (t, *J* = 7.3 Hz, 3H, –$COCH_2CH_2CH_3$), 1.03 (t, *J* = 7.3 Hz, 3H, –$COCH_2CH_2CH_3$), 1.66–1.76 (m, 4H, 2 × –$COCH_2CH_2CH_3$), 2.04 (brs, 1H, –O*H*), 2.36–2.44 (m, 4H, 2 × –$COCH_2CH_2CH_3$), 3.81–3.91 (m, 2H, C–5$H_{\alpha+\beta}$), 4.33 (q, *J* = 2.9 Hz, 1H, C–4H), 5.14 (dd, *J* = 7.3 and 4.4 Hz, 1H, C–2H), 5.40 (dd, *J* = 7.3 and 3.6 Hz, 1H, C–3H), 5.97 (d, *J* = 4.4 Hz, 1H, C–1H), 7.11, 7.32, 7.42 and 7.53 (9H; d, *J* = 8.8 Hz, 2H; t, *J* = 7.3 Hz, 1H; t, *J* = 7.3 Hz, 2H and t, *J* = 7.3 Hz, 4H; all aromatic protons); ^{13}C NMR (100.5, $CDCl_3$): δ 13.62 and 13.68 (2 × –$COCH_2CH_2CH_3$), 18.32 and 18.41 (2 × –$COCH_2CH_2CH_3$), 35.74 and 36.09 (2 × –$COCH_2CH_2CH_3$), 62.16 (C-5), 69.95 (C-3), 71.21 (C-2), 83.20 (C-4), 99.16 (C-1), 117.41, 126.84, 126.88, 128.19, 128.72, 135.69, 140.63 and 156.19 (all aromatic carbons), 172.57 and 173.26 (2 × *C*O); HR–ESI–TOF–MS: *m/z* 465.1877 ([M+Na]$^+$), calcd. for $[C_{25}H_{30}O_7+Na]^+$ 465.1884.

*4.2.1.6. 2,3-Di-O-pentanoyl-1-O-(4-phenylphenyl)-α-D-ribofuranoside (**39**).* It was obtained as colorless oil in 85% yield. R_f = 0.25 (10% ethyl acetate in petroleum ether, v/v); $[\alpha]_D^{27} = +41.06^\circ$ (*c* 0.05, MeOH); IR (KBr) ν_{max}: 3457 (OH), 2960, 2929, 2874, 1736, 1581, 1464, 1236, 1174, 1046 and 763 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 0.90–0.97 (m, 6H, 2 × –$COCH_2CH_2CH_2CH_3$), 1.33–1.45 (m, 4H, 2 × –$COCH_2CH_2CH_2CH_3$), 1.62–1.73 (m, 4H, 2 × –$COCH_2CH_2CH_2CH_3$), 2.02 (brs, 1H, –O*H*), 2.38–2.46 (m, 4H, 2 × –$COCH_2CH_2CH_2CH_3$), 3.81–3.91 (m, 2H, C–5$H_{\alpha+\beta}$), 4.33 (q, *J* = 2.9 Hz, 1H, C–4H), 5.14 (dd, *J* = 7.3 and 4.4 Hz, 1H, C–2H), 5.38 (dd, *J* = 7.3 and 3.6 Hz, 1H, C–3H), 5.97 (d, *J* = 4.4 Hz, 1H, C–1H), 7.11, 7.32, 7.42 and 7.53 (9H; d, *J* = 8.0 Hz, 2H; t, *J* = 7.3 Hz, 1H; t, *J* = 7.3 Hz, 2H and t, *J* = 8.8 Hz, 4H; all aromatic protons); ^{13}C NMR (100.5, $CDCl_3$): δ 13.68 and 13.76 (2 × –$COCH_2CH_2CH_2CH_3$), 22.16 and 22.21 (2 × –$COCH_2CH_2CH_2CH_3$), 26.90 and 27.02 (2 × –$COCH_2CH_2CH_2CH_3$), 33.61 and 33.94 (2 × –$COCH_2CH_2CH_2CH_3$), 62.18 (C-5), 69.97 (C-3), 71.22 (C-2), 83.22 (C-4), 99.17 (C-1), 117.41, 126.85, 126.90, 128.19, 128.73, 135.69, 140.55 and 156.12 (all aromatic carbons), 172.75 and 173.43 (2 × *C*O); HR–ESI–TOF–MS: *m/z* 493.2184 ([M+Na]$^+$), calcd. for $[C_{27}H_{34}O_7+Na]^+$ 493.2197.

*4.2.2. Pure unreacted peracylated O-aryl ribofuranosides **19**, **21**, **23**, **27**, **29** and **31***

*4.2.2.1. 2,3,5-Tri-O-propanoyl-1-O-(1-naphthyl)-β-D-ribofuranoside (**19**).* It was obtained as colorless oil in 90% yield. R_f = 0.60 (15% ethyl acetate in petroleum ether, v/v); $[\alpha]_D^{21} = -33.28^\circ$ (*c* 0.10, MeOH); IR (KBr) ν_{max}: 2983, 1748, 1579, 1463, 1353, 1266, 1176, 1063 and 774 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 0.86 (t, *J* = 7.7 Hz, 3H, –$COCH_2CH_3$), 1.13–1.21 (m, 6H, 2 × –$COCH_2CH_3$), 1.97–2.14 (m, 2H, –$COCH_2CH_3$), 2.35–2.47 (m, 4H, 2 × –$COCH_2CH_3$), 4.06–4.11 (m, 1H, C–5H_α), 4.45–4.49 (m, 2H, C–4H and C–5H_β), 5.67–5.74 (m, 2H, C–2H and C–3H), 5.83 (s, 1H, C–1H), 7.10, 7.36, 7.48–7.52, 7.79–7.81 and 8.17–8.19 (7H; d, *J* = 7.3 Hz, 1H; t, *J* = 8.0 Hz, 1H; m, 3H; m, 1H and m, 1H; all aromatic protons); ^{13}C NMR (100.5, $CDCl_3$): δ 8.64, 8.91 and 9.08 (3 × –$COCH_2CH_3$), 27.09, 27.24 and 27.31 (3 × –$COCH_2CH_3$), 63.11 (C-5), 71.00 (C-3), 74.94 (C-2), 79.41 (C-4), 103.47 (C-1), 108.45, 121.74, 122.13, 125.51, 125.61, 125.66, 126.47, 127.50, 134.46 and 151.78 (all aromatic carbons), 173.09, 173.24 and 174.05 (3 × *C*O); HR–ESI–TOF–MS: *m/z* 467.1666 ([M+Na]$^+$), calcd. for $[C_{24}H_{28}O_8+Na]^+$ 467.1676.

*4.2.2.2. 2,3,5-Tri-O-butanoyl-1-O-(1-naphthyl)-β-D-ribofuranoside (**21**).* It was obtained as colorless oil in 92% yield. R_f = 0.50 (5% ethyl acetate in petroleum ether, v/v); $[\alpha]_D^{24} = -15.52^\circ$ (*c* 0.10, MeOH); IR (KBr) ν_{max}: 2964, 1748, 1579, 1464, 1385, 1241, 1174 and 773 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 0.65 (t, *J* = 7.3 Hz, 3H, –$COCH_2CH_2CH_3$), 0.92–1.01 (m, 6H, 2 × –$COCH_2CH_2CH_3$), 1.29–1.40 (m, 2H, –$COCH_2CH_2CH_3$), 1.64–1.75 (m, 4H, 2 × –$COCH_2CH_2CH_3$), 1.87–2.06 (m, 2H, –$COCH_2CH_2CH_3$), 2.32–2.41 (m, 4H, 2 × –$COCH_2CH_2CH_3$), 4.06–4.11 (m, 1H, C–5H_α), 4.43–4.48 (m, 2H, C–4H and C–5H_β), 5.67–5.74 (m, 2H, C–2H and C–3H), 5.82 (s, 1H, C–1H), 7.09, 7.35, 7.47–7.51, 7.78–7.81 and 8.17–8.20 (7H; d, *J* = 8.1 Hz, 1H; t, *J* = 8.1 Hz, 1H; m, 3H; m, 1H and m, 1H; all aromatic protons); ^{13}C NMR (100.5, $CDCl_3$): δ 13.32 and 13.60 (3 × –$COCH_2CH_2CH_3$), 17.97, 18.21 and 18.38 (3 × –$COCH_2CH_2CH_3$), 35.63, 35.71 and 35.84 (3 × –$COCH_2CH_2CH_3$), 62.87 (C-5), 70.89 (C-3), 74.87 (C-2), 79.38 (C-4), 103.39 (C-1), 108.37, 121.77, 122.06, 125.52, 125.59, 125.66, 126.45, 127.50, 134.47 and 151.79 (all aromatic carbons), 172.20, 173.40 and 173.21 (3 × *C*O); HR–ESI–TOF–MS: *m/z* 509.2128 ([M+Na]$^+$), calcd. for $[C_{27}H_{34}O_8+Na]^+$ 509.2146.

*4.2.2.3. 2,3,5-Tri-O-pentanoyl-1-O-(1-naphthyl)-β-D-ribofuranoside (**23**).* It was obtained as colorless oil in 90% yield. R_f = 0.32 (3% ethyl acetate in petroleum ether, v/v); $[\alpha]_D^{26} = -23.46^\circ$ (*c* 0.10, MeOH); IR (KBr) ν_{max}: 2960, 2934, 2874, 1748, 1580, 1465, 1385, 1239, 1170, 1091, 969 and 772 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 0.71 (t, *J* = 7.3 Hz, 3H, –$COCH_2CH_2CH_2CH_3$), 0.92–0.96 (m, 6H, 2 × –$COCH_2CH_2CH_2CH_3$), 0.99–1.06 (m, 2H, –$COCH_2CH_2CH_2CH_3$), 1.21–1.29 (m, 2H, –$COCH_2CH_2CH_2CH_3$), 1.34–1.42 (m, 4H, 2 × –$COCH_2CH_2CH_2CH_3$), 1.62–1.79 (m, 4H, 2 × –$COCH_2CH_2CH_2CH_3$), 1.88–2.08 (m, 2H, –$COCH_2CH_2CH_2CH_3$), 2.34–2.43 (m, 4H, 2 × –$COCH_2CH_2CH_2CH_3$), 4.05–4.09 (m, 1H, C–5H_α), 4.44–4.48 (m, 2H, C–4H and C–5H_β), 5.66–5.69 (m, 1H, C–2H), 5.73 (d, *J* = 4.4 Hz, 1H, C–3H), 5.82 (s, 1H, C–1H), 7.09, 7.36, 7.46–7.52, 7.79–7.81 and 8.17–8.20 (7H; d, *J* = 7.3 Hz, 1H; t, *J* = 8.0 Hz, 1H; m, 3H; m, 1H and m, 1H; all aromatic protons); ^{13}C NMR (100.5, $CDCl_3$): δ 13.49 and 13.67 (3 × –$COCH_2CH_2CH_2CH_3$), 21.95 and 22.19 (3 × –$COCH_2CH_2CH_2CH_3$), 26.53, 26.78 and 26.96 (3 × –$COCH_2CH_2CH_2CH_3$), 33.51, 33.60 and 33.72 (3 × –$COCH_2CH_2CH_2CH_3$), 62.90 (C-5), 70.92 (C-3), 74.90 (C-2), 79.40 (C-4), 103.43 (C-1), 108.40, 121.78, 122.09, 125.53, 125.62, 125.66, 126.47, 127.50, 134.48 and 151.82 (all aromatic carbons), 172.41, 172.60 and 173.45 (3 × *C*O); HR–ESI–TOF–MS: *m/z* 551.2597 ([M+Na]$^+$), calcd. for $[C_{30}H_{40}O_8+Na]^+$ 551.2615.

*4.2.2.4. 2,3,5-Tri-O-propanoyl-1-O-(4-phenylphenyl)-β-D-ribofuranoside (**27**).* It was obtained as white solid in 93% yield. Mp = 71–72 °C. R_f = 0.50 (5% ethyl acetate in petroleum ether, v/v); $[\alpha]_D^{23} = -44.24^\circ$ (*c* 0.10, MeOH); IR (KBr) ν_{max}: 2989, 1751, 1603, 1350, 1240, 1191, 1052 and 760 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 1.03 (t, *J* = 7.3 Hz, 3H, –$COCH_2CH_3$), 1.15–1.20 (m, 6H, 2 × –$COCH_2CH_3$), 2.21–2.45 (m, 6H, 3 × –$COCH_2CH_3$), 4.07–4.11 (m,

1H, C–5H$_\alpha$), 4.40–4.47 (m, 2H, C–5H$_\beta$ and C–4H), 5.54–5.58 (m, 2H, C–2H and C–3H), 5.68 (s, 1H, C–1H), 7.07, 7.31, 7.41 and 7.49–7.55 (9H; d, J = 8.8 Hz, 2H; t, J = 7.3 Hz, 1H; t, J = 7.3 Hz, 2H and m, 4H; all aromatic protons); ^{13}C NMR (100.5, $CDCl_3$): δ 8.79, 8.89 and 9.04 (3 × –$COCH_2CH_3$), 27.21, 27.25 and 27.28 (3 × –$COCH_2CH_3$), 63.30 (C-5), 71.03 (C-3), 74.85 (C-2), 79.36 (C-4), 103.37 (C-1), 116.64, 126.78, 126.86, 128.15, 128.69, 135.53, 140.54 and 155.69 (all aromatic carbons), 172.98, 173.08 and 173.95 (3 × CO)); HR–ESI–TOF–MS: m/z 493.1824 ([M+Na]$^+$), calcd. for [$C_{26}H_{30}O_8$+Na]$^+$ 493.1833.

*4.2.2.5. 2,3,5-Tri-O-butanoyl-1-O-(4-phenylphenyl)-β-D-ribofuranoside (**29**).* It was obtained as white solid in 90% yield. Mp = 74–76 °C. R_f = 0.50 (5% ethyl acetate in petroleum ether, v/v); $[\alpha]_D^{26} = -30.16°$ (c 0.05, MeOH); IR (KBr) ν_{max}: 2966, 1742, 1606, 1490, 1383, 1239, 1173 and 760 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.85 (t, J = 7.3 Hz, 3H, –$COCH_2CH_2CH_3$), 0.98 (q, J = 7.3 Hz, 6H, 2 × –$COCH_2CH_2CH_3$), 1.49–1.56 (m, 2H, –$COCH_2CH_2CH_3$), 1.64–1.72 (m, 4H, 2 × –$COCH_2CH_2CH_3$), 2.13–2.24 (m, 2H, –$COCH_2CH_2CH_3$), 2.30–2.40 (m, 4H, 2 × –$COCH_2CH_2CH_3$), 4.07–4.12 (m, 1H, C–5H$_\alpha$), 4.42–4.45 (m, 2H, C–5H$_\beta$ and C–4H), 5.55–5.57 (m, 2H, C–2H and C–3H), 5.67 (s, 1H, C–1H), 7.07, 7.31, 7.42 and 7.50–7.55 (9H; d, J = 8.8 Hz, 2H; t, J = 7.3 Hz, 1H; t, J = 7.3 Hz, 2H and m, 4H; all aromatic protons); ^{13}C NMR (100.5, $CDCl_3$): δ 13.55 and 13.59 (3 × –$COCH_2CH_2CH_3$), 18.13, 18.21 and 18.36 (3 × –$COCH_2CH_2CH_3$), 35.71 and 35.81 (3 × –$COCH_2CH_2CH_3$), 63.24 (C-5), 70.97 (C-3), 74.76 (C-2), 79.32 (C-4), 103.34 (C-1), 116.63, 126.79, 126.86, 128.16, 128.70, 135.52, 140.56 and 155.71 (all aromatic carbons), 172.17, 172.33 and 173.20 (3 × CO); HR–ESI–TOF–MS: m/z 535.2289 ([M+Na]$^+$), calcd. for [$C_{29}H_{36}O_8$+Na]$^+$ 535.2202.

*4.2.2.6. 2,3,5-Tri-O-pentanoyl-1-O-(4-phenylphenyl)-β-D-ribofuranoside (**31**).* It was obtained as white solid in 91% yield. Mp = 49–50 °C. R_f = 0.53 (2.5% ethyl acetate in petroleum ether, v/v); $[\alpha]_D^{27} = -49.61°$ (c 0.10, MeOH); IR (KBr) ν_{max}: 2960, 2934, 2874, 1748, 1609, 1490, 1518, 1487, 1381, 1233, 1170, 1053 and 764 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.84 (t, J = 7.3 Hz, 3H, –$COCH_2CH_2CH_2CH_3$), 0.91–0.95 (m, 6H, 2 × –$COCH_2CH_2CH_2CH_3$), 1.24–1.28 (m, 2H, –$COCH_2CH_2CH_2CH_3$), 1.34–1.41 (m, 4H, 2 × –$COCH_2CH_2CH_2CH_3$), 1.45–1.53 (m, 2H, –$COCH_2CH_2CH_2CH_3$), 1.59–1.64 (m, 4H, 2 × –$COCH_2CH_2CH_2CH_3$), 2.14–2.25 (m, 2H, –$COCH_2CH_2CH_2CH_3$), 2.32–2.42 (m, 4H, 2 × –$COCH_2CH_2CH_2CH_3$), 4.07–4.11 (m, 1H, C–5H$_\alpha$), 4.41–4.45 (m, 2H, C–5H$_\beta$ and C–4H), 5.54 (s, 2H, C–2H and C–3H), 5.66 (s, 1H, C–1H), 7.07, 7.31, 7.42 and 7.50–7.55 (9H; d, J = 8.0 Hz, 2H; t, J = 7.3 Hz, 1H; t, J = 7.3 Hz, 2H and m, 4H; all aromatic protons); ^{13}C NMR (100.5, $CDCl_3$): δ 13.62 and 13.67 (3 × –$COCH_2CH_2CH_2CH_3$), 22.15 and 22.19 (3 × –$COCH_2CH_2CH_2CH_3$), 26.70, 26.78 and 26.93 (3 × –$COCH_2CH_2CH_2CH_3$), 33.61 and 33.69 (3 × –$COCH_2CH_2CH_2CH_3$), 63.27 (C-5), 70.99 (C-3), 74.79 (C-2), 79.34 (C-4), 103.40 (C-1), 116.66, 126.81, 126.88, 128.17, 128.71, 135.55, 140.57 and 155.74 (all aromatic carbons), 172.36, 172.51 and 173.42 (3 × CO); HR–ESI–TOF–MS: m/z 577.2771 ([M+Na]$^+$), calcd. for [$C_{32}H_{42}O_8$+Na]$^+$ 577.2772.

*4.3. General procedure for the acylation of 2,3-di-O-acyl-1-O-aryl-α-D-ribofuranosides: Synthesis of peracylated O-aryl glycosides **16**, **18**, **20**, **22**, **24**, **26**, **28** and **30***

To a stirred solution of partially deacylated 2,3-di-*O*-acyl-1-*O*-aryl-α-D-ribofuranosides (**32**, **33**, **34**, **35**, **36**, **37**, **38** and **39**; 0.1 mmol) in DCM (5 mL), added catalytic amount of DMAP and acetic anhydride, propionic anhydride, butanoic anhydride and pentanoic anhydride (0.12 mmol). On completion of reaction, the solvent was removed under reduced pressure and the residue was subjected to column chromatography over silica gel with ethyl acetate in petroleum ether as eluent to afford the 2,3,5-tri-*O*-acyl-1-*O*-aryl-α-D-ribofuranoside (**16**, **18**, **20**, **22**, **24**, **26**, **28** and **30**) in 90–95% yield (Scheme 2).

*4.3.1. 2,3,5-Tri-O-acetyl-1-O-(1-naphthyl)-α-D-ribofuranoside (**16**)*

It was obtained as semisolid in 95% yield. R_f = 0.25 (10% ethyl acetate in petroleum ether, v/v); $[\alpha]_D^{27} = +54.01°$ (c 0.05, MeOH); IR (Nujol) ν_{max}: 1748, 1580, 1369, 1233, 1043, 953 and 774 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.05, 2.08 and 2.17 (3s, 3H each, 9H, 3 × $COCH_3$), 3.83–3.85 (dd, J = 12.4 and 3.6 Hz, 1H, C–5H$_\alpha$), 4.21–4.38 (dd, J = 12.4 and 2.9 Hz, 1H, C–5H$_\beta$), 4.44 (q, J = 2.9 Hz, 1H, C–4H), 5.15–5.18 (m, 1H, C–2H), 5.34–5.37 (m, 1H, C–3H), 6.04 (d, J = 4.4 Hz, 1H, C–1H), 7.05, 7.32, 7.39–7.47, 7.74–7.76 and 8.16–8.18 (7H; d, J = 8.0 Hz, 1H; t, J = 8.0 Hz, 1H; m, 3H; m, 1H and m, 1H; all aromatic protons); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 20.46, 20.78 and 21.80 (3 × $COCH_3$), 63.47 (C-5), 70.20 (C-3), 71.20 (C-2), 80.82 (C-4), 98.82 (C-1), 108.87, 121.69, 122.11, 125.38, 125.83, 126.24, 126.36, 127.63, 134.56 and 152.15 (all aromatic carbons), 169.91, 170.42 and 170.52 (3 × CO); HR–ESI–TOF–MS: m/z 425.1200 ([M+Na]$^+$), calcd. for [$C_{21}H_{22}O_8$+Na]$^+$ 425.1207.

*4.3.2. 2,3,5-Tri-O-propanoyl-1-O-(1-naphthyl)-α-D-ribofuranoside (**18**)*

It was obtained as white solid in 95% yield. Mp = 70–71 °C. R_f = 0.55 (15% ethyl acetate in petroleum ether, v/v); $[\alpha]_D^{22} = +50.97°$ (c 0.10, MeOH); IR (KBr) ν_{max}: 2986, 1752, 1596, 1352, 1271, 1176, 1037 and 796 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.13–1.20 (m, 6H, 2 × –$COCH_2CH_3$), 1.26 (t, J = 7.3 Hz, 3H, –$COCH_2CH_3$), 2.39–2.55 (m, 6H, 3 × –$COCH_2CH_3$), 4.30 (dd, J = 11.7 and 3.6 Hz, 1H, C–5H$_\alpha$), 4.40 (dd, J = 12.4 and 2.9 Hz, 1H, C–5H$_\beta$), 4.52 (q, J = 2.9 Hz, 1H, C–4H), 5.25 (dd, J = 7.3 and 4.4 Hz, 1H, C–2H), 5.46 (dd, J = 7.3 and 2.2 Hz, 1H, C–3H), 6.1 (d, J = 4.4 Hz, 1H, C–1H), 7.15, 7.38, 7.46–7.53, 7.81 and 8.25 (7H; d, J = 8.1 Hz, 1H; t, J = 8.0 Hz, 1H; m, 3H; d, J = 7.3 Hz, 1H; d, J = 7.3 Hz, 1H; all aromatic protons). ^{13}C NMR (100.5, $CDCl_3$): δ 8.88, 9.90 and 9.15 (3 × –$COCH_2CH_3$), 27.22, 27.40 and 27.57 (3 × –$COCH_2CH_3$), 63.38 (C-5), 70.09 (C-3), 71.18 (C-2), 80.99 (C-4), 98.92 (C-1), 108.80, 121.74, 122.00, 125.28, 125.84, 126.21, 126.33, 127.60, 134.55 and 152.27 (all aromatic carbons), 173.22, 173.78 and 173.91 (3 × CO); HR–ESI–TOF–MS: m/z 467.1659 ([M+Na]$^+$), calcd. for [$C_{24}H_{28}O_8$+Na]$^+$ 467.1676.

*4.3.3. 2,3,5-Tri-O-butanoyl-1-O-(1-naphthyl)-α-D-ribofuranoside (**20**)*

It was obtained as semisolid in 95% yield. R_f = 0.40 (5% ethyl acetate in petroleum ether, v/v); $[\alpha]_D^{25} = +16.99°$ (c 0.05, MeOH); IR (KBr) ν_{max}: 2927, 1742, 1464, 1216, 1175, 1045 and 758 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.90–1.05 (m, 9H, 3 × –$COCH_2CH_2CH_3$), 1.63–1.79 (m, 6H, 3 × –$COCH_2CH_2CH_3$), 2.35–2.49 (m, 9H, 3 × –$COCH_2CH_2CH_3$), 4.31 (dd, J = 12.4 and 3.6 Hz, 1H, C–5H$_\alpha$), 4.40 (dd, J = 12.4 and 3.6 Hz, 1H, C–5H$_\beta$), 4.51 (q, J = 2.9 Hz, 1H, C–4H), 5.23–5.25 (m, 1H, C–2H), 5.45 (dd, J = 7.3 and 2.2 Hz, 1H, C–3H), 6.12 (d, J = 4.4 Hz, 1H, C–1H), 7.14, 7.39, 7.44–7.53, 7.81 and 8.26 (7H; d, J = 7.2 Hz, 1H; t, J = 8.0 Hz, 1H; m, 3H; d, J = 7.4 Hz, 1H and d, J = 7.3 Hz, 1H; all aromatic protons). ^{13}C NMR (100.5, $CDCl_3$): δ 13.60 and 13.75 (3 × –$COCH_2CH_2CH_3$), 18.18, 18.32 and 18.48 (3 × –$COCH_2CH_2CH_3$), 35.70, 35.94 and 36.13 (3 × –$COCH_2CH_2CH_3$), 63.28 (C-5), 70.04 (C-3), 71.18 (C-2), 81.09 (C-4), 98.86 (C-1), 108.77, 121.85, 121.98, 125.21, 125.84, 126.21, 126.34, 127.58, 134.54 and 152.23 (all aromatic carbons), 172.52, 172.99 and 173.14 (3 × CO); HR–ESI–TOF–MS: m/z 509.2141 ([M+Na]$^+$), calcd. for [$C_{27}H_{34}O_8$+Na]$^+$ 509.2146.

*4.3.4. 2,3,5-Tri-O-pentanoyl-1-O-(1-naphthyl)-α-D-ribofuranoside (**22**)*

It was obtained as colorless oil in 93% yield. R_f = 0.25 (3% ethyl acetate in petroleum ether, v/v); $[\alpha]_D^{27} = +18.52°$ (c 0.10, MeOH);

IR (KBr) ν_{max}: 2960, 2933, 2874, 1748, 1580, 1465, 1381, 1239, 1169, 1090 and 773 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 0.85–0.97 (m, 9H, 3 × $-COCH_2CH_2CH_2CH_3$), 1.29–1.36 (m, 4H, 2 × $-COCH_2CH_2CH_2CH_3$), 1.40–1.47 (m, 2H, $-COCH_2CH_2CH_2CH_3$), 1.59–1.66 (m, 4H, 2 × $-COCH_2CH_2CH_2CH_3$), 1.70–1.76 (m, 2H, $-COCH_2CH_2CH_2CH_3$), 2.37–2.42 (m, 4H, 2 × $-COCH_2CH_2CH_2CH_3$), 2.46–2.51 (m, 2H, $-COCH_2CH_2CH_2CH_3$), 4.28 (2d, J = 3.7 and 2.9 Hz, 1H, C–$5H_\alpha$), 4.39 (2d, J = 3.7 and 2.9 Hz, 1H, C–$5H_\beta$), 4.50 (q, J = 2.9 Hz, 1H, C–4H), 5.22–5.24 (m, 1H, C–2H), 5.45 (dd, J = 7.3 and 2.9 Hz, 1H, C–3H), 6.12 (d, J = 4.4 Hz, 1H, C–1H), 7.14, 7.39, 7.44–7.53, 7.81 and 8.27 (7H; d, J = 7.3 Hz, 1H; t, J = 8.0 Hz, 1H; m, 3H; d, J = 8.1 Hz, 1H and d, J = 8.1 Hz, 1H; all aromatic protons); ^{13}C NMR (100.5, $CDCl_3$): δ 13.64, 13.69 and 13.73 (3 × $-COCH_2CH_2CH_2CH_3$), 22.20 and 22.33 (3 × $-COCH_2CH_2CH_2CH_3$), 26.80, 26.90 and 27.11 (3 × $-COCH_2CH_2CH_2CH_3$), 33.62, 33.82 and 34.04 (3 × $-COCH_2CH_2CH_2CH_3$), 63.33 (C-5), 70.06 (C-3), 71.21 (C-2), 81.09 (C-4), 98.85 (C-1), 108.72, 121.87, 121.98, 125.23, 125.85, 126.19, 126.36, 127.59, 134.56 and 152.26 (all aromatic carbons), 172.67, 173.18 and 173.35 (3 × CO); HR–ESI–TOF–MS: m/z 551.2599 ($[M+Na]^+$), calcd. for $[C_{30}H_{40}O_8+Na]^+$ 551.2615.

4.3.5. 2,3,5-Tri-O-acetyl-1-O-(4-phenylphenyl)-α-D-ribofuranoside (**24**)

It was obtained as colorless oil in 93% yield. R_f = 0.25 (10% ethyl acetate in petroleum ether, v/v); $[\alpha]_D^{24} = +32.2^\circ$ (c 0.1, MeOH); IR (Nujol) ν_{max}: 1748, 1519, 1487, 1370, 1230, 1045 and 765 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 2.12, 2.17 and 2.19 (3s, 3H each, 9H, 3 × $-COCH_3$), 4.24–4.28 (m, 1H, C–$5H_\alpha$), 4.36–4.40 (m, 1H, C–$5H_\beta$), 4.48 (q, J = 3.6 Hz, 1H, C–4H), 5.15–5.19 (m, 1H, C–2H), 5.31–5.34 (m, 1H, C–3H), 5.93 (d, J = 4.4 Hz, 1H, C–1H), 7.13, 7.32, 7.42 and 7.52–7.56 (9H; d, J = 8.8 Hz, 2H; t, J = 7.3 Hz, 1H; t, J = 7.3 Hz, 2H and m, 4H; all aromatic protons); ^{13}C NMR (100.5 MHz, $CDCl_3$): δ 20.51, 20.77 and 20.81 (3 × $-COCH_3$), 63.35 (C-5), 69.97 (C-3), 70.81 (C-2), 80.22 (C-4), 99.16 (C-1), 117.58, 126.85, 126.93, 128.19, 128.73, 135.88, 140.58 and 156.10 (all aromatic carbons), 169.92, 170.48 and 170.54 (3 × CO); HR–ESI–TOF–MS: m/z 451.1348 ($[M+Na]^+$), calcd. for $[C_{23}H_{24}O_8+Na]^+$ 451.1363.

4.3.6. 2,3,5-Tri-O-propanoyl-1-O-(4-phenylphenyl)-α-D-ribofuranoside (**26**)

It was obtained as colorless oil in 93% yield. R_f = 0.40 (5% ethyl acetate in petroleum ether, v/v); $[\alpha]_D^{23} = +43.84^\circ$ (c 0.05, MeOH); IR (KBr) ν_{max}: 2984, 1748, 1519, 1352, 1273, 1176, 1077 and 766 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 1.14–1.25 (m, 9H, $-COCH_2CH_3$), 2.36–2.50 (m, 6H, 3 × $-COCH_2CH_3$), 4.27 (dd, J = 12.4 and 3.6 Hz, 1H, C–$5H_\alpha$), 4.38 (dd, J = 12.4 and 2.9 Hz, 1H, C–$5H_\beta$), 4.49 (q, J = 2.9 Hz, 1H, C–4H), 5.16–5.19 (m, 1H, C–2H), 5.35–5.38 (m, 1H, C–3H), 5.93 (d, J = 4.4 Hz, 1H, C–1H), 7.11, 7.32, 7.42, 7.50–7.55 (9H; d, J = 8.8 Hz, 2H; t, J = 7.3 Hz, 1H; t, J = 7.3 Hz, 2H and m, 4H; all aromatic protons); ^{13}C NMR (100.5, $CDCl_3$): δ 8.98, 9.01 and 9.14 (3 × $-COCH_2CH_3$), 27.23, 27.40 and 27.54 (3 × $-COCH_2CH_3$), 63.28 (C-5), 69.93 (C-3), 70.84 (C-2), 80.34 (C-4), 99.05 (C-1), 117.38, 126.84, 126.90, 128.19, 128.73, 135.69, 140.54 and 156.18 (all aromatic carbons), 173.30, 173.81 and 173.97 (3 × CO); HR–ESI–TOF–MS: m/z 493.1814 ($[M+Na]^+$), calcd. for $[C_{26}H_{30}O_8+Na]^+$ 493.1833.

4.3.7. 2,3,5-Tri-O-butanoyl-1-O-(4-phenylphenyl)-α-D-ribofuranoside (**28**)

It was obtained as colorless oil in 91% yield. R_f = 0.40 (5% ethyl acetate in petroleum ether, v/v); $[\alpha]_D^{26} = +54.95^\circ$ (c 0.05, MeOH); IR (KBr) ν_{max}: 2967, 1747, 1610, 1519, 1487, 1383, 1237, 1175 and 764 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 0.94–1.05 (m, 9H, 3 × $-COCH_2CH_2CH_3$), 1.65–1.77 (m, 6H, 3 × $-COCH_2CH_2CH_3$), 2.31–2.44 (m, 6H, 3 × $-COCH_2CH_2CH_3$), 4.26 (dd, J = 12.4 and 3.7 Hz, 1H, C–$5H_\alpha$), 4.38 (dd, J = 12.4 and 2.9 Hz, 1H, C–$5H_\beta$), 4.47 (q, J = 2.9 Hz, 1H, C–4H), 5.14 (m, 1H, C–2H), 5.34–5.37 (m, 1H, C–3H), 5.94 (d, J = 5.1 Hz, 1H, C–1H), 7.10, 7.32, 7.42, 7.51–7.55 (9H; d, J = 11.7 Hz, 2H; t, J = 7.3 Hz, 1H; t, J = 7.3 Hz, 2H and m, 4H; all aromatic protons); ^{13}C NMR (100.5, $CDCl_3$): δ 13.61 and 13.69 (3 × $-COCH_2CH_2CH_3$), 18.29, 18.32 and 18.41 (3 × $-COCH_2CH_2CH_3$), 35.72, 35.93 and 36.04 (3 × $-COCH_2CH_2CH_3$), 63.17 (C-5), 69.89 (C-3), 70.85 (C-2), 80.38 (C-4), 98.99 (C-1), 117.33, 126.84, 126.89, 128.18, 128.73, 135.69, 140.54 and 156.17 (all aromatic carbons), 172.53, 172.98 and 173.16 (3 × CO); HR–ESI–TOF–MS: m/z 535.2296 ($[M+Na]^+$), calcd. for $[C_{29}H_{36}O_8+Na]^+$ 535.2302.

4.3.8. 2,3,5-Tri-O-pentanoyl-1-O-(4-phenylphenyl)-α-D-ribofuranoside (**30**)

It was obtained as colorless oil in 93% yield. R_f = 0.40 (2.5% ethyl acetate in petroleum ether, v/v); $[\alpha]_D^{27} = +42.28^\circ$ (c 0.05, MeOH); IR (KBr) ν_{max}: 2959, 2928, 2873, 1747, 1610, 1518, 1487, 1235, 1172 and 763 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 0.90–0.98 (m, 9H, 3 × $-COCH_2CH_2CH_2CH_3$), 1.34–1.46 (m, 6H, 3 × $-COCH_2CH_2CH_2CH_3$), 1.59–1.61 (m, 6H, 3 × $-COCH_2CH_2CH_2CH_3$), 2.35–2.45 (m, 6H, 3 × $-COCH_2CH_2CH_2CH_3$), 4.26 (dd, J = 12.4 and 3.7 Hz, 1H, C–$5H_\alpha$), 4.38 (dd, J = 11.7 and 2.9 Hz, 1H, C–$5H_\beta$), 4.47 (q, J = 3.7 Hz, 1H, C–4H), 5.14–5.16 (m, 1H, C–2H), 5.33–5.36 (m, 1H, C–3H), 5.94 (d, J = 4.4 Hz, 1H, C–1H), 7.11, 7.32, 7.42 and 7.53 (9H; d, J = 8.8 Hz, 2H; t, J = 7.3 Hz, 1H; t, J = 7.3 Hz, 2H and t, J = 8.8 Hz 4H; all aromatic protons); ^{13}C NMR (100.5, $CDCl_3$): δ 13.67 and 13.74 (3 × $-COCH_2CH_2CH_2CH_3$), 22.14, 22.18 and 22.20 (3 × $-COCH_2CH_2CH_2CH_3$), 26.85, 26.88 and 27.00 (3 × $-COCH_2CH_2CH_2CH_3$), 33.56, 33.79 and 33.88 (3 × $-COCH_2CH_2CH_2CH_3$), 63.19 (C-5), 69.90 (C-3), 70.85 (C-2), 80.37 (C-4), 98.99 (C-1), 117.31, 126.83, 126.88, 128.16, 128.72, 135.68, 140.61 and 156.17 (all aromatic carbons), 172.67, 173.15 and 173.34 (3 × CO); HR–ESI–TOF–MS: m/z 577.2751 ($[M+Na]^+$), calcd. for $[C_{32}H_{42}O_8+Na]^+$ 577.2772.

4.4. General procedure for the deacylation of peracylated O-aryl-α-D-ribofuranosides **16**, **18**, **20**, **22**, **24**, **26**, **28** and **30** and peracylated O-aryl-β-D-ribofuranosides **17**, **19**, **21**, **23**, **25**, **27**, **29** and **31**: Preparation of 1-O-aryl-α-D-ribofuranosides and 1-O-aryl-β-D-ribofuranosides **40**, **41**, **42** and **43**

The peracylated *O*-aryl-α-D-ribofuronosides **16**, **18**, **20**, **22**, **24**, **26**, **28** and **30** and their β-anomer **17**, **19**, **21**, **23**, **25**, **27**, **29** and **31** (1.0 mmol) were dissolved in methanol (10 mL) and saturated methanolic ammonia solution (10 mL) was added (Schemes 2 and 3). The reaction mixture was stirred for 6–8 h at room temperature to achieve the complete deacetylation as indicated by TLC. The methanol was removed under reduced pressure and the residue was subjected to column chromatography over silica gel with chloroform in methanol as eluent to afford the α- and *O*-aryl-β-D-ribofuranosides **40** and **42** and **41** and **43** in high yields, respectively. Their structures were further confirmed on the basis of comparison of their spectral data with that reported in the literature [13].

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.bioorg.2014.02.004.

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