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An Expeditious Route to the Synthesis of Kelampayosides A and B

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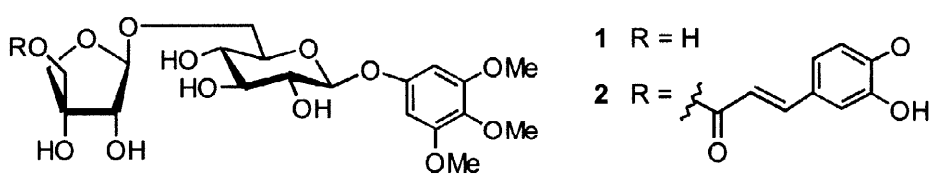
Abstract: Chemoselective NIS/ cat. TfOH-mediated glycosylation of ethyl 2,3,4-tri-*O*-benzoyl-1-thio-β-D-glucopyranoside (**13**) with ethyl 2,3-di-*O*-acetyl-5-*O*-benzyl-1-thio-α/β-D-*erythro*-apiofuranoside (**4a**) gave dimer **14** in an excellent yield. BF_3•Et_2O-catalysed condensation of the α-trichloroacetimidate **31**, accessible in two steps from **14**, with 3,4,5-trimethoxyphenol gave β-linked derivative **32** followed by deprotection gave Kelampayoside A. Protecting group manipulations of **32** and subsequent caffeoylation of resulting **36** followed by deprotection gave Kelampayoside B.

Keywords: Carbohydrates, Chemoselective Glycosidation, Apiose, Fries-rearrangement.

Introduction

More than ten years ago, Shiraga *et al.*[1] showed that 3,4,5-trimethoxyphenyl β-D-*erythro*-apiofuranosyl-(1→6)-β-D-glucopyranoside (**1**, see Figure 1), isolated earlier[2] from the dried stem bark of *Cinnamomum cassia* Blume, exhibits antiulcerogenic activity in rats. Recently, Kitagawa *et al.*[3] isolated the same active compound **1** as well as its 5''-*O*-caffeoyl derivative **2** (so-called kelampayoside A and B, respectively) from the bark of *Anthocephalus chinensis*. Both **1** and **2** are characterized by the presence of the rare apiofuranose sugar, the occurrence of which is restricted[4] to the plant kingdom, and the rather electron-rich 3,4,5-trimethoxyphenyl moiety. Thus far only scarce information[5] on the glycosylating properties of apiofuranosyl donors is available. Moreover, it was anticipated that a Lewis acid catalyzed introduction of the requisite β-linked 3,4,5-trimethoxyphenyl portion could be accompanied by Fries-type rearrangement[6] resulting in the formation of the unwanted *C*-aryl derivative. The aforementioned chemical and, to a lesser extent, pharmacological aspects seemed to us a justifiable objective in preparing[7] kelampayosides A (**1**) and B (**2**).

Figure 1



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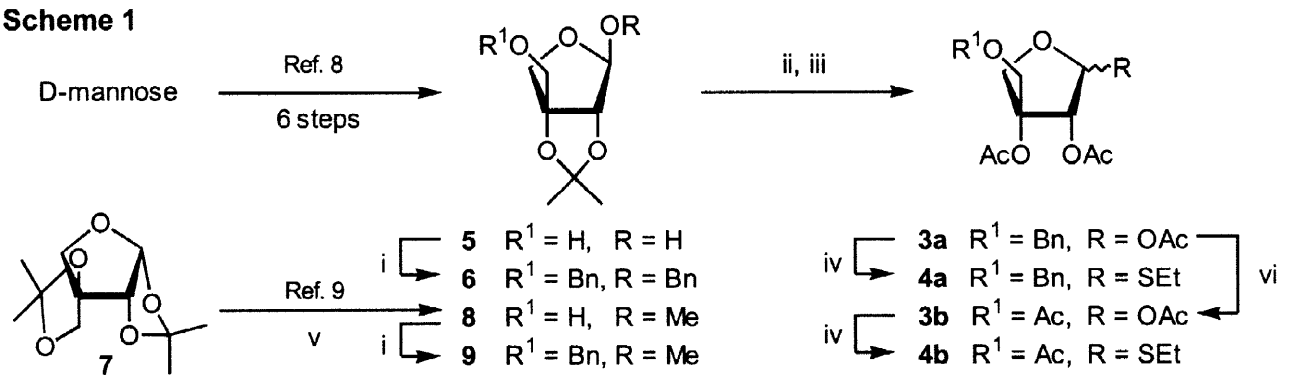
Results and discussion

Prior to the assembly of the target molecules **1** and **2**, attention was focused on the glycosylating properties of apiofuranosyl donors **3a** and **4a-b**. The 1,2,3-tri-*O*-acetyl-5-*O*-benzyl-α/β-D-apiofuranose (**3a**, see Scheme 1) was prepared from 2,3-*O*-isopropylidene-β-D-*erythro*-apiofuranose[8] (**5**) by sequential benzylation (→**6**), acidolysis and acetylation according to the procedure of Tapiéro[5a]. An alternative route to **3a** entails treatment[9] of commercially available, although expensive, 1,2:3,5-di-*O*-isopropylidene-α-D-*threo*-apiofuranose (**7**) with hydrogen chloride in dry methanol to give methyl 2,3-*O*-isopropylidene-β-D-*erythro*-apiofuranoside[9] (**8**), which was converted into **3a** by the same three-step procedure used before for the conversion of **5** into **3a**. Reaction of **3a** with ethanethiol in the presence of a catalytic amount of $SnCl_4$ gave ethyl 2,3-di-*O*-acetyl-5-*O*-benzyl-1-thio-α/β-D-*erythro*-apiofuranoside (**4a**) in 83% yield. In the same way, the fully acetylated ethyl 1-thio-α/β-D-apiofuranoside **4b** was prepared from **3b**[5a], which in turn was readily accessible by hydrogenolysis and acetylation of **3a**.

Scheme 1

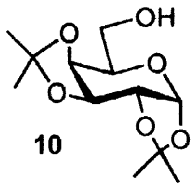


Reagents and Conditions: (i) BnBr, NaH, DMF, **6**: 85%, **9**: 82%; (ii) 80% formic acid, 60°C; (iii) Ac_2O, DMAP, pyridine (79% based on 2 steps; (iv) EtSH, cat. $SnCl_4$, CH_2Cl_2, **4a**: 83%, **4b**: 86%; (v) dry HCl in MeOH, 81%; (vi) a) H_2, 10% Pd/C; b) Ac_2O, pyridine, (92%, 2 steps).

The results of the glycosylations of the primary and secondary acceptors **10**[10], **11**[11] and **12** with apiofuranosyl donors **3a** and **4a-b** are recorded in Table 1. It can be seen that trimethylsilyl triflate (TMSOTf) assisted glycosylation of acceptors **10** and **11** with 1-*O*-acetyl-α/β-D-*erythro*-apiofuranose **3a** proceeded in a moderate yield (entry 1 and 2). Conversely, the condensation of ethyl 1-thio-α/β-D-*erythro*-apiofuranoside **4a** with the individual acceptors **10-12** in the presence of *N*-iodosuccinimide and catalytic triflic acid[12] (NIS / cat. TfOH) proceeded in a highly stereoselective fashion and excellent yield (entry 3, 4 and 5). A similar result was obtained (entry 6) using the fully acetylated ethyl 1-thio-apiosyl donor **4b**.

The latter auspicious results were an incentive to explore (see Scheme 2) the feasibility whether the functionalized dimer **14**, a key intermediate en route to kelampayoside A and B, could be prepared via a chemoselective glycosylation of the partially benzoylated ("disarmed")[13] ethyl 1-thio-glucosyl acceptor **13**[14]

Figure 2 The Acceptors



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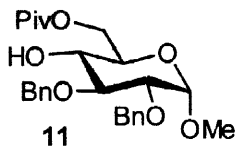

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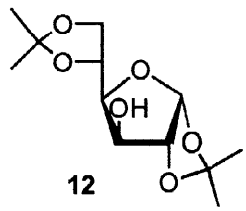

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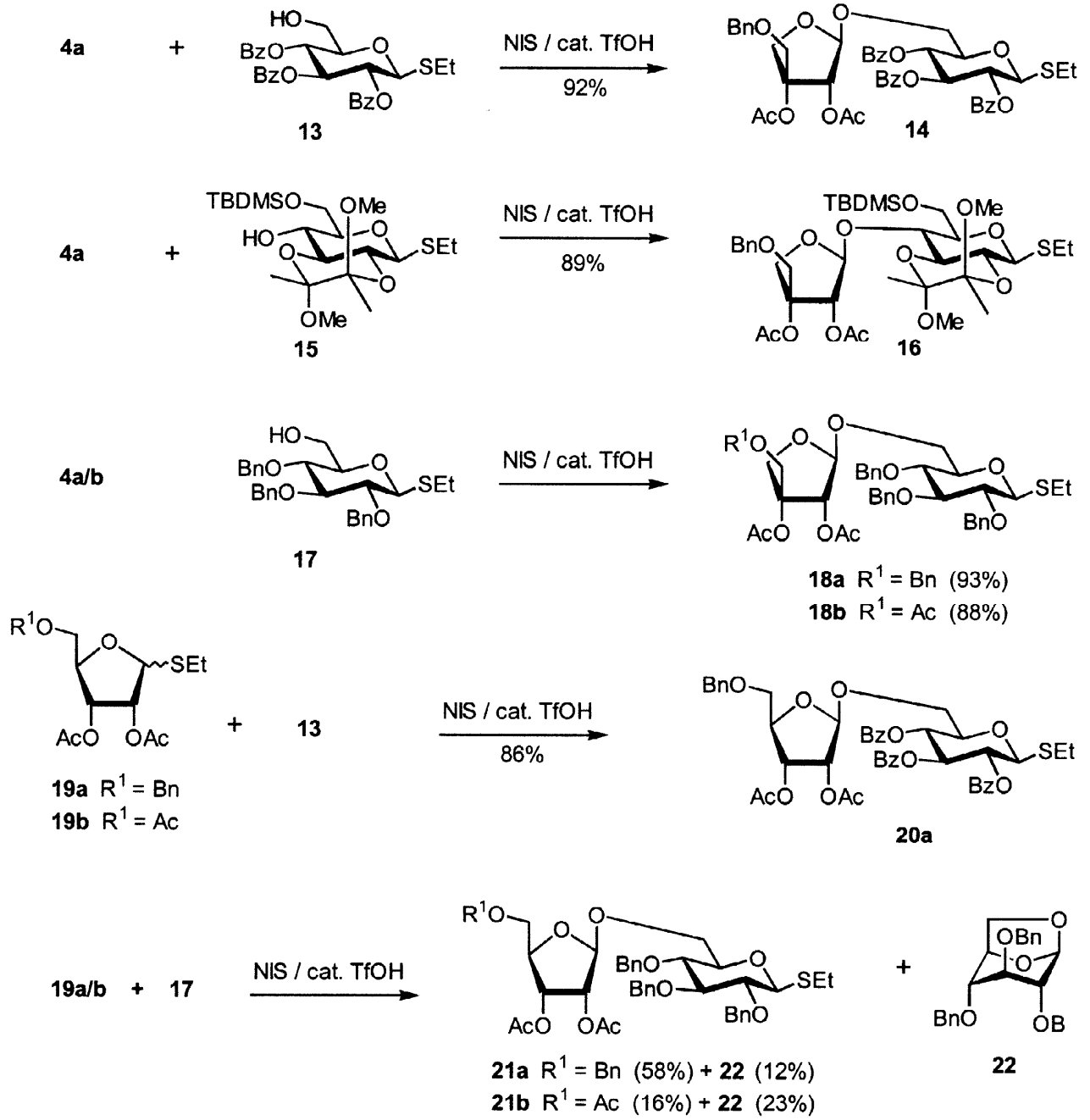
Table 1. Results of glycosylations of acceptors (**10-12**) with apiosyl donors (**3a** and **4a-b**).

Entry	Donor	Acceptor	Promoter	Temperature	Time	Yield[a]
1	**3a**	**10**	cat. TMSOTf	23°C	15 min	73%
2	**3a**	**11**	cat. TMSOTf	23°C	15 min	52%
3	**4a**	**10**	NIS / cat. TfOH	0°C	1 min	98%
4	**4a**	**11**	NIS / cat. TfOH	0°C	1 min	93%
5	**4a**	**12**	NIS / cat. TfOH	0°C	1 min	95%
6	**4b**	**11**	NIS / cat. TfOH	0°C	1 min	91%

[a] In all cases, only the β-isomer was detected by ^{1}H NMR spectroscopy.

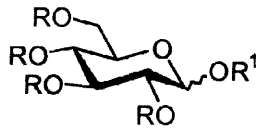
with the also in principle "disarmed" ethyl 1-thio-apiosyl donor **4a**. It was established that NIS / cat. TfOH mediated glycosylation of the glycosyl acceptor **13** with donor **4a** proceeded with a high degree of chemoselectivity to give the β-linked dimer **14** in 92% yield (see Scheme 2). The outcome of this experiment indicates that the deactivating effect of the 2-*O*-acetyl group in donor **4a** is more than fully compensated by the intrinsically higher reactivity of a glycosylating species derived from a furanosyl than a pyranosyl donor. The latter effect may also explain the unexpected high chemoselectivity in the NIS / cat. TfOH-assisted glycosylation of both more hindered "semi disarmed"[15] pyranosyl acceptor **15** (→**16**) and the partially benzylated ("armed")[13] acceptor **17**[16] (→**18a**) with apiosyl donor **4a**. The general nature of the furanosyl effect was also demonstrated (see Scheme 2) in the highly chemoselective glycosylation of "disarmed" acceptor **13** (→**20a**) with "disarmed" ethyl 2,3-di-*O*-acetyl-5-*O*-benzyl-1-thio-α/β-D-ribofuranoside[17] (**19a**). In contrast to the high-yielding condensation of **17** with apiofuranosyl donor **4a**, the glycosylation of **17** with ribofuranosyl donor **19a** proceeds moderately as evidenced by the relatively low yield of **21a** as well as the formation of the 1,6-anhydro derivative **22**. The latter results showed that the apiofuranosyl donor (**4a**) is more reactive than the corresponding ribofuranosyl donor (**19a**). This observation was confirmed by the outcome of the glycosylation of **17** with fully acetylated ethyl 1-thio-apiofuranosyl and ethyl 1-thio-ribofuranosyl donors **4b** and **19b**, respectively. Thus, condensation of **17** with apiosyl donor **4b** resulted in the formation of **18b** in 88% yield, whereas glycosylation of **17** with ribofuranosyl donor **19b** led mainly to the 1,6-anhydro product **22**.

Scheme 2

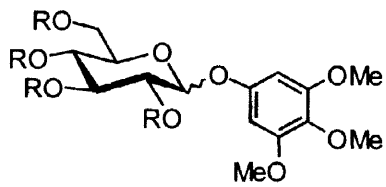


At this stage, attention was focused on the introduction of the requisite β-linked 3,4,5-trimethoxyphenyl moiety in the target compounds **1** and **2**. Initially, the glucopyranose derivatives **23** and **24** (Figure 3) were condensed with commercially available 3,4,5-trimethoxyphenol under Mitsunobu[18] conditions. The results of this study are summarized in Table 2. It can be seen (entry 1) that Mitsunobu glycosylation of 3,4,5-trimethoxyphenol with anomerically pure **23** (α) proceeds as expected[18] with inversion of configuration to give the *O*-β-glycoside **27**. It is also evident (entry 2) that the β-directing effect of the 2-*O*-benzoyl group in the anomerically impure donor **24** is reflected in the predominant formation of the *O*-β-glucoside **28**.

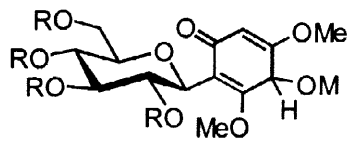
Figure 3



23 R = Bn, R^1 = H (α/β, 1/0)
24 R = Bz, R^1 = H (α/β, 4/1)
25 R = Ac, R^1 = Ac (β)
26 R = Bz, R^1 = C(=NH)CCl_3 (α)



27 R = Bn
28 R = Bz



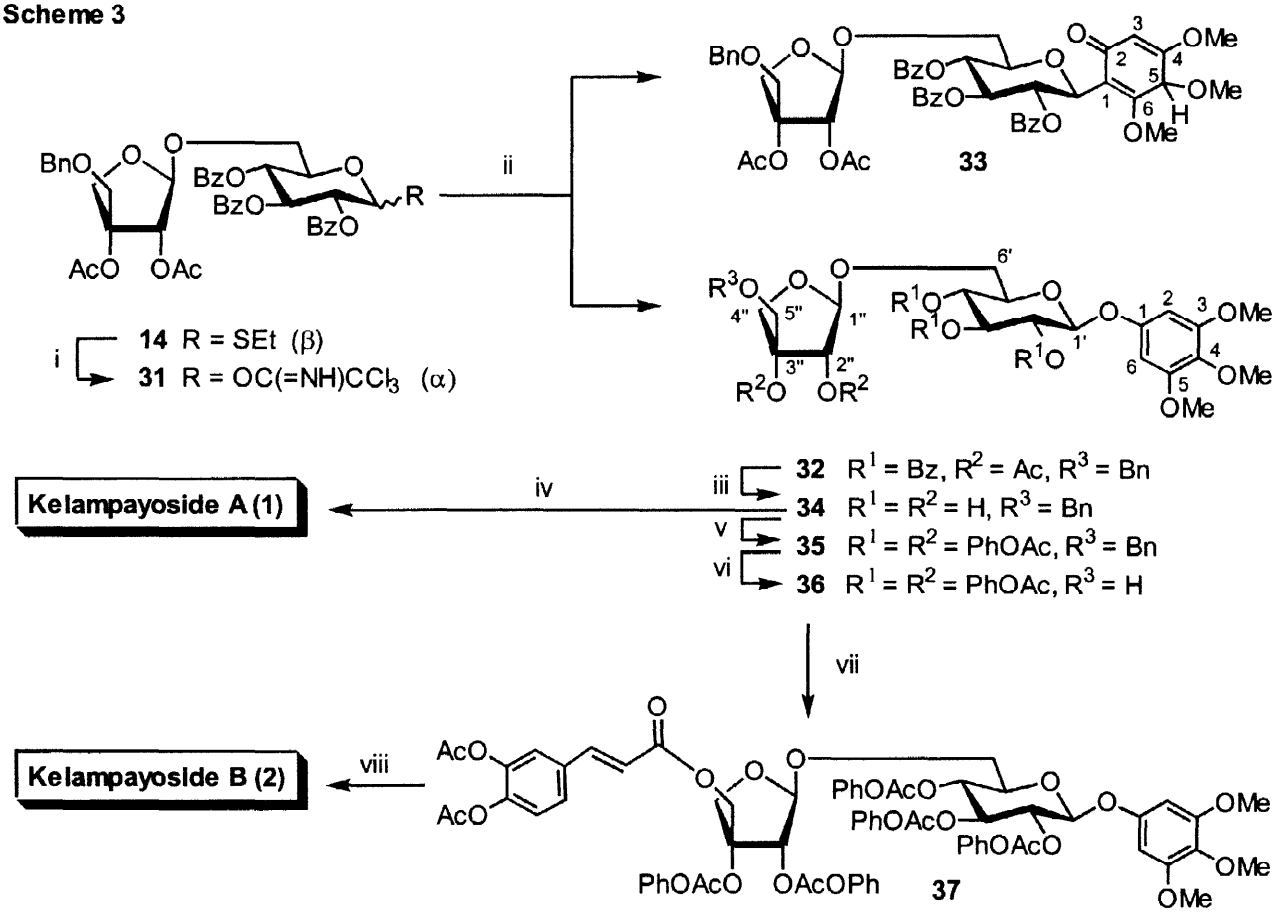
29 R = Ac
30 R = Bz

Table 2. Relevant data on the glycosylation of trimethoxyphenol with the glucopyranosyl donors **23-26**.

Entry	Donor	Activator	Solvent	*O*-aryl	*C*-aryl
1	**23**	DEAD, Ph_3P	THF	62% (**27**: α/β, 0/1)	-
2	**24**	DEAD, Ph_3P	THF	55% (**28**: α/β, 1/7)	-
3	**25**	BF_3• Et_2O (1.0 equiv.)	CH_2Cl_2	-	88% (**29**)
4	**26**	BF_3•Et_2O (0.25 equiv.)	CH_2Cl_2	41% (**28**: α/β, 0/1)	18% (**30**)
5	**26**	BF_3•Et_2O (0.25 equiv.)	CH_2Cl_2/THF, (10/1, v/v)	64% (**28**: α/β, 0/1)	5% (**30**)

Another route to *O*-aryl glycosides comprises Lewis acid mediated glycosylation of free phenolic hydroxyl functions. On the other hand, it is well documented[6] that the initially formed *O*-aryl glycoside may participate in an *O*→*C*-glycoside rearrangement to give a *C*-aryl glycoside (Fries-type rearrangement). Several studies towards the synthesis of *C*-aryl glycosides have shown that reactive glycosyl donors (fully *O*-alkylated or 2-deoxypyranosides) undergo more facile *O*→*C*-migration. In addition, it became clear that the construction of *O*-aryl glycosides can be executed successfully using boron trifluoride diethyl etherate (BF_3•Et_2O) as the promoter. For example, the synthesis of several[19] *O*-aryl β-D-glucopyranosides from penta-*O*-acetyl-β-D-glucopyranose (**25**) and the corresponding aryl acceptors could be accomplished using an equimolar amount of BF_3•Et_2O in CH_2Cl_2. However, condensation of **25** with 3,4,5-trimethoxyphenol under these conditions led to the exclusive formation of *C*-aryl derivative **29** (Table 2, entry 3), indicating that the 3,4,5-trimethoxyphenyl glycoside is more prone to Fries-type rearrangement, due to the electron-donating methoxy substituents in the phenyl moiety. It occurred to us, that the application[20] of the α-trichloroacetimidate donor **26**, which can be activated by a catalytic amount of BF_3•Et_2O, would have a beneficial effect on the outcome of the glycosylation reaction. Nevertheless, condensation of **26** with 3,4,5-trimethoxyphenol under the influence of a small amount of BF_3•Et_2O gave apart from the β-*O*-glucoside **28** an unacceptable quantity of the β-*C*-glucoside **30** (entry 4). It was therefore gratifying to find that **28** was the main product (entry 5) by executing the same glycosidation in CH_2Cl_2 containing a small amount of THF. Moreover, β-*O*-glucoside **28** could be readily separated by silica gel chromatography from the undesired β-*C*-glucoside **30**. In an attempt to completely

Scheme 3



Reagents and conditions: (i) a) NIS / cat. TfOH, CH_2Cl_2/H_2O, (100/1, v/v); b) Cs_2CO_3, CCl_3CN, CH_2Cl_2 (86%, 2 steps); (ii) 3,4,5-trimethoxyphenol, 0.25 equiv. $BF_3{\bullet}Et_2O$, CH_2Cl_2/THF (10/1, v/v), (**32**: 63%, **33**: 4%); (iii) NaOMe, $MeOH/CH_2Cl_2$, (5/1, v/v), 88%; (iv) H_2, 10% Pd/C, *i*-PrOH/H_2O (10/1, v/v), 91%; (v) PhOAcCl, CH_2Cl_2, pyridine, 88%; (vi) H_2, 10% Pd/C, *i*-PrOH/EtOAc/H_2O (12/8/1, v/v/v), 86%; (vii) 3,4-di-*O*-acetylcaffeoyl chloride, CH_2Cl_2, pyridine, 77%; (viii) 0.005 M K_2CO_3, $MeOH/CH_2Cl_2$ (1/2, v/v), 49%.

suppress *O*→*C* migration,the glycosidation was also carried out at lower temperature (–20°C) and in neat THF. However, under these conditions no condensation of trichloroacetimidate donor **26** with 3,4,5-trimethoxyphenol was observed.

On the basis of the latter results, it became apparent that the trichloroacetimidate derivative **31**, which can be readily prepared (see Scheme 3) in two steps form the corresponding ethyl 1-thio-disaccharide **14**, would be an ideal starting compound for the synthesis of kelampayoside A (**1**) and B (**2**). Indeed, condensation (see Scheme 3) of the α-trichloroacetimidate **31** with 3,4,5-trimethoxyphenol in the presence of a catalytic amount of $BF_3{\bullet}Et_2O$ in CH_2Cl_2/THF gave, after purification by silica gel chromatography, the 3,4,5-trimethoxyphenyl β-*O*-glycoside **32** and the corresponding β-*C*-aryl derivative **33** in a yield of 63% and 4%, respectively. Zemplén deacylation of **32** and subsequent hydrogenolysis of **34** gave homogeneous kelampayoside A (**1**), the

physical data of which were in full accord with those reported[3] by Kitagawa *et al.* It was expected that kelampayoside B (**2**) could be prepared by regioselective acylation of kelampayoside A (**1**) with 3,4-di-*O*-acetylcaffeoyl chloride.[21] However, the latter possibility was thwarted by the poor solubility of **1** and impelled us to adopt the following four-step approach. Acylation of **34** with phenoxyacetyl chloride followed by debenzylation of **35** gave **36**. Treatment of the latter compound with excess 3,4-di-*O*-acetylcaffeoyl chloride, and then mild deesterification of the phenoxyacetyl and acetyl groups of **37**, gave kelampayoside B (**2**) in a yield of 29% over four steps. The ^{1}H and ^{13}C NMR data of the target compound **2** were in excellent agreement with those reported[3] for kelampayoside B (**2**).

Conclusion

The expeditious route of synthesis for kelampayosides described in this paper, clearly shows that apiofuranosyl donor **4** is an effective and highly potent glycosylating agent. In addition, $BF_3 \bullet Et_2O$ catalyzed Fries-type rearrangement (*O*→*C*-aryl migration) of an electron-rich aryl group at the anomeric center of sugars can be attenuated by the addition of THF to the reaction mixture. These findings can be implemented in the design and synthesis of other biologically interesting oligosaccharides.

Experimental

General Methods and Materials

^{1}H NMR and ^{13}C NMR spectra were recorded with a Bruker WM-200 (200/50.1 MHz), a Bruker WM-300 (300/75.1 MHz) or a Bruker MDX-600 spectrometer (600/150 MHz). Electrospray mass-spectra were recorded using Perkin-Elmer SCIEX API 165 Single Quadruple LC/MS instrument. Dichloromethane was dried by refluxing over CaH_2 (5 g/L) for 5 h, then distilled and stored over molecular sieves (4Å). Pyridine was dried by refluxing over P_2O_5 (5 g/L) for 5 h, then distilled and stored over molecular sieves (4Å). Diethyl ether was freshly distilled from $LiAlH_4$ and dried over 4Å molecular sieves for 1 hour. Methanol (Rathburn, HPLC-grade) was stored over 3Å molecular sieves. The following chemicals were obtained from Acros Organics Co. and were used as received: triethylamine, trimethylsilyl trifluoromethanesulfonate (TMSOTf), trifluoromethanesulfonic acid (TfOH), *N*-iodosuccinimide (NIS), trichloroacetonitrile, phenoxyacetyl chloride, ethanethiol, stannic chloride, palladium on carbon (10%) and 3,4,5-trimethoxyphenol. Boron trifuoride diethyl etherate, diethyl azodicarboxylate and triphenyl phosphine were purchased from Aldrich. 1,2,3,5-Tetra-*O*-acetyl-β-D-ribofuranose and Dowex 50W X4 were purchased from Fluka. Reactions were followed by TLC-analysis conducted on Schleicher and Schüll DC Fertigfolien (F 1500 LS 254). Compounds were visualized by UV light and by spraying with 20% sulfuric acid in methanol followed by charring at 140 °C. Unsaturated compounds were visualized by spraying with a solution of $KMnO_4$ (2%) and K_2CO_3 (1%) in water. Eluents for column chromatography were of technical grade and distilled before use. All reactions were performed under anhydrous conditions at room temperature unless stated otherwise. Gel-filtration was performed on Sephadex LH-20 (Pharmacia). Column chromatography was performed on silica gel 60 0.063-0.200 mm (Baker).

Ethyl 2,3-di-*O*-acetyl-5-*O*-benzyl-1-thio-α/β-D-*erythro*-apiofuranoside (4a)

To a cooled mixture (0 °C) of compound **3a**[5a] (2.33g, 6.37 mmol) and ethanethiol (7.0 mmol, 517 μL) in CH_2Cl_2 (40 mL) was added a small amount of $SnCl_4$ (0.63 mmol, 73 μL). After stirring for 30 min, the reaction mixture was

diluted with CH_2Cl_2, washed successively with 1 M KF, 1 M $NaHCO_3$ and with water. The organic layer was dried ($MgSO_4$), filtered and concentrated *in vacuo*. The crude product was purified by column chromatography (20 → 40% Et_2O/light petroleum) to furnish the *title compound* **4a** (1.94 g, 83%) as a colourless syrup; [Found: C, 58.8; H, 6.5. $C_{18}H_{24}O_6S$ requires C, 58.68; H, 6.57%]; R_f (50% Et_2O/light petroleum) 0.5; δ_H (200 MHz, $CDCl_3$) 1.26 (m, 3H, CH_3, SEt), 2.06, 2.07, 2.08, 2.11 (4 × s, 6H, CH_3, Ac), 2.64 (m, 2H, CH_2, SEt), 3.83, 4.18 (2 × m, 4H, H-4a, H-4b, H-5a, H-5b), 4.54, 4.56 (2 × s, CH_2, Bn), 5.13 (d, 0.65H, H-2β), 5.31 (d, 0.65H, H-1β, $J_{1,2}$ 4.4 Hz), 5.45 (d, 0.35H, H-2α), 5.53 (d, 0.35H, H-1α, $J_{1,2}$ 5.7 Hz), 7.26-7.34 (m, 5H, Bn); δ_C (200 MHz, $CDCl_3$); 14.4, 14.5 (CH_3, SEt), 19.8, 19.9, 20.6, 20.7 (CH_3, Ac), 24.4, 24.6 (CH_2, SEt), 68.2, 69.9 (C-4α, C-5α), 68.6, 72.3 (C-4β, C-5β), 72.5 (C-2α), 72.8 (CH_2, Bn), 76.0 (C-2β), 82.8 (C-3α), 84.5 (C-3β), 86.4 (C-1β), 86.8 (C-1α), 126.9-127.7 (CH, Bn), 137.0, 137.2 (Cq, Bn), 168.6, 169.0 (C=O, Ac).

Ethyl 2,3,5-tri-*O*-acetyl-1-thio-α/β-D-*erythro*-apiofuranoside (4b)

To a cooled mixture (0 °C) of compound **3b**[5a] (1.86g, 5.87 mmol) and ethanethiol (6.45 mmol, 477 μL) in CH_2Cl_2 (30 mL) was added a small amount of $SnCl_4$ (0.6 mmol, 70 μL). After stirring for 45 min the reaction mixture was diluted with CH_2Cl_2, washed successively with 1 M KF, 1 M $NaHCO_3$ and with water. The organic layer was dried ($MgSO_4$), filtered and concentrated *in vacuo*. The crude product was purified by flash column chromatography (40% Et_2O/light petroleum) to furnish the *title compound* **4b** (1.61 g, 86%) as a light yellow syrup; [Found: C, 48.9; H, 6.3. $C_{13}H_{20}O_7S$ requires C, 48.74; H, 6.29%]; R_f (50% Et_2O/light petroleum) 0.3; δ_H (300 MHz, $CDCl_3$) 1.28 (m, 3H, CH_3, SEt), 2.06, 2.10, 2.12 (6 × s, 9H, CH_3, Ac), 2.67 (m, 2H, CH_2, SEt), 4.13, 4.30, 4.65 (3 × m, 4H, H-4a, H-4b, H-5a, H-5b), 5.14 (d, 0.65H, H-2β), 5.28 (d, 0.65H, H-1β, $J_{1,2}$ 3.9 Hz), 5.51 (d, 0.35H, H-2α), 5.56 (d, 0.35H, H-1α, $J_{1,2}$ 5.8 Hz); δ_C (200 MHz, $CDCl_3$) 14.6, 14.7 (CH_3, SEt), 20.2, 20.4, 21.0 (3 × CH_3, Ac), 25.0 (CH_2, SEt), 62.3, 69.5 (C-4α, C-5α), 62.6, 69.5 (C-4β, C-5β), 72.4 (C-2α), 76.4 (C-2β), 82.4 (C-3α), 83.4 (C-3β), 86.5 (C-1α), 86.7 (C-1β), 168.4, 169.9 (C=O, Ac).

6-*O*-(2,3-Di-*O*-acetyl-5-*O*-benzyl-β-D-*erythro*-apiofuranosyl)-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (Table 1, entry 3)

N-Iodosuccinimide (0.63 mmol, 142 mg) and a catalytic amount of triflic acid (0.06 mmol, 5 μL) was added to a mixture of donor **4a** (0.60 mmol, 185 mg) acceptor **10** (0.50 mmol, 131 mg) and powdered molecular sieves in 1,2-dichloroethane/Et_2O (12 mL, 1/1, v/v) at 0°C under an atmosphere of N_2. After 2 min, the reaction was filtered, diluted with CH_2Cl_2, washed successively with 1 M $Na_2S_2O_3$, 1 M $NaHCO_3$ and H_2O, dried ($MgSO_4$), and concentrated *in vacuo*. Purification of the crude product by flash chromatograpy (35% Et_2O/light petroleum) gave the *title compound* (276 mg, 98%) as a colourless syrup; [Found: C, 59.6; H, 6.7. $C_{28}H_{38}O_{12}$ requires C, 59.36; H, 6.76%]; R_f (50% Et_2O/light petroleum) 0.25; $[\alpha]_D^{20}$ -7.2° (*c* 1.0, $CHCl_3$); *m/z* 567.4 $(M+H)^+$, 589.3 $(M+Na)^+$; δ_H (300 MHz, $CDCl_3$) 1.28, 1.32, 1.42, 1.52 (4 × s, 12H, CH_3, isopr.), 2.06, 2.08 (2 × s, 6H, CH_3, Ac), 3.60 (dd, 1H, H-6a, $J_{5,6a}$ 7.2 Hz, $J_{6a,6b}$ 9.7 Hz), 3.75 (dd, 1H, H-6b, $J_{5,6b}$ 5.8 Hz), 3.93 (m, 1H, H-5), 4.00 (AB, 2H, H-4a', H-4b' or H-5a', H-5b'), 4.02 (dd, 1H, H-4, $J_{3,4}$ 7.9 Hz, $J_{4,5}$ 1.9 Hz), 4.21 (AB, 2H, H-4a', H-4b' or H-5a', H-5b'), 4.29 (dd, 1H, H-2, $J_{2,3}$ 2.4 Hz), 4.53 (m, 3H, H-3, CH_2, Bn), 5.03 (s, 1H, H-2'), 5.36 (s, 1H, H-1'), 5.51 (d, 1H, H-1, $J_{1,2}$ 5.0 Hz), 7.27-7.37 (m, 5H, Bn); δ_C (200 MHz, $CDCl_3$) 20.5, 21.2 (2 × CH_3, Ac), 24.3, 24.8, 25.7, 25.8 (4 × CH_3, isopr.), 66.1 (C-6), 66.5, 70.2, 70.5, 70.8, 76.5 (C-2, C-3, C-4, C-5, C-2'), 69.6, 69.7, 73.2 (CH_2, Bn, C-4', C-5'), 85.4 (C-3'), 96.1 (C-1), 105.8 (C-1'), 108.4, 109.0 (Cq, isopr.), 127.4-128.2 (CH, Bn), 137.8 (Cq, Bn), 169.1, 169.8 (C=O, Ac).

Methyl 4-*O*-(2,3-di-*O*-acetyl-5-*O*-benzyl-β-D-*erythro*-apiofuranosyl)-2,3-di-*O*-benzyl-6-*O*-pivaloyl-α-D-glucopyranoside (Table 1, entry 4)

N-Iodosuccinimide (0.63 mmol, 142 mg) and a catalytic amount of triflic acid (0.06 mmol, 5 μL) was added to a

mixture of donor **4a** (0.60 mmol, 221 mg) acceptor **11** (0.50 mmol, 221 mg) and powdered molecular sieves in 1,2-dichloroethane/Et_2O (12 mL, 1/1, v/v) at 0°C under an atmosphere of N_2. After 2 min, the reaction was filtered, diluted with CH_2Cl_2, washed successively with 1 M $Na_2S_2O_3$, 1 M $NaHCO_3$ and H_2O, dried ($MgSO_4$), and concentrated *in vacuo*. Purification of the crude product by flash chromatograpy (35% Et_2O/light petroleum) followed further purification on a sephadex LH20 column (50% CH_2Cl_2/MeOH) to afford the *title compound* (333 mg, 93%) as a colourless syrup; [Found: C, 66.0; H, 6.8. $C_{42}H_{52}O_{13}$ requires C, 65.95; H, 6.85%]; R_f (33% Et_2O/light petroleum) 0.2; $[\alpha]_D^{20}$ -6.1° (*c* 2, $CHCl_3$); *m/z* 765.5 $(M+H)^+$, 787.4 $(M+Na)^+$; δ_H (300 MHz, $CDCl_3$) 1.18 (s, 9H, Piv), 2.02, 2.04 (2 × s, 6H, Ac), 3.38 (s, 3H, OMe), 3.45 (dd, 1H, H-2, $J_{2,3}$ 9.5 Hz), 3.60 (t, 1H, H-4, $J_{4,5}$ 9.8 Hz), 3.79 (m, 2H, H-3, H-5), 4.00 (AB, 2H, H-4a', H-4b' or H-5a', H-5b'), 4.11 (m, 1H, H-6a), 4.17 (AB, 2H, H-4a', H-4b' or H-5a', H-5b'), 4.42 (m, 1H, H-6b), 4.54 (d, 1H, $J_{1,2}$ 3.7 Hz), 4.61 (AB, CH_2, Bn), 4.70 (AB, CH_2, Bn), 4.75 (AB, CH_2, Bn), 5.10 (d, 1H, H-2'), 5.25 (d, 1H, H-1', $J_{1',2'}$ 1.5 Hz), 7.26-7.38 (m, 20H, Bn); δ_C (200 MHz, $CDCl_3$) 20.4, 21.1 (2 × CH_3, Ac), 27.0 ($(CH_3)_3$, Piv), 38.6 (Cq, Piv), 55.0 (OMe), 62.3, 68.7, 72.6, 73.2, 75.5 (3 × CH_2, Bn, C-4', C-5', C-6), 68.4, 76.8, 77.3, 79.7 (C-2, C-3, C-4, C-5, C-2'), 84.4 (C-3'), 97.7 (C-1), 107.1 (C-1'), 127.5-128.2 (CH, arom.), 137.4, 137.8, 138.4 (Cq, Bn), 169.3, 169.6 (C=O, Ac), 177.6 (C=O, Piv).

3-*O*-(2,3-Di-*O*-acetyl-5-*O*-benzyl-β-D-*erythro*-apiofuranosyl)-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (Table 1, entry 5)

N-Iodosuccinimide (0.63 mmol, 142 mg) and a catalytic amount of triflic acid (0.06 mmol, 5 μL) was added to a mixture of donor **4a** (0.60 mmol, 221 mg) acceptor **12** (0.50 mmol, 130 mg) and powdered molecular sieves in 1,2-dichloroethane/Et_2O (12 mL, 1/1, v/v) at 0°C under an atmosphere of N_2. After 2 min, the reaction was filtered, diluted with CH_2Cl_2, washed successively with 1 M $Na_2S_2O_3$, 1 M $NaHCO_3$ and H_2O, dried ($MgSO_4$), and concentrated *in vacuo*. Purification of the crude product by flash chromatograpy (35% Et_2O/light petroleum) gave the *title compound* (268 mg, 95%) as a colourless syrup; [Found: C, 59.6; H, 6.8. $C_{28}H_{38}O_{12}$ requires C, 59.36; H, 6.76%]; R_f (50% Et_2O/light petroleum) 0.3; $[\alpha]_D^{20}$ -14.8° (*c* 1.1, $CHCl_3$); *m/z* 567.2 $(M+H)^+$, 589.2 $(M+Na)^+$; δ_H (300 MHz, $CDCl_3$) 1.26, 1.29, 1.38, 1.47 (4 × s, 12H, CH_3, isopr.), 2.06, 2.11 (2 × s, 6H, CH_3, Ac), 4.00 (m, 4H, H-4, H-5, H-6a, H-6b), 4.03 (AB, 2H, H-4a', H-4b' or H-5a', H-5b'), 4.25 (AB, 2H, H-4a', H-4b' or H-5a', H-5b'), 4.28 (d, 1H, H-3, $J_{3,4}$ 3.1 Hz), 4.50 (d, 1H, H-2), 4.51 (AB, 2H, CH_2, Bn), 5.10 (s, 1H, H-2'), 5.26 (s, 1H, H-1'), 5.85 (d, 1H, H-1, $J_{1,2}$ 3.7 Hz), 7.27-7.37 (m, 5H, Bn); δ_C (200 MHz, $CDCl_3$) 20.5, 21.1 (2 × CH_3, Ac), 25.1, 26.0, 26.6 (4 × CH_3, isopr.), 67.5, 69.3, 73.2, 73.6 (C-6, CH_2, Bn, C-4', C-5'), 72.0, 76.8, 77.4, 80.7, 81.7 (C-2, C-3, C-4, C-5, C-2'), 103.6 (C-1), 105.0 (C-1'), 108.9, 111.7 (Cq, isopr.), 127.4-128.2 (CH, Bn), 137.5 (Cq, Bn), 169.3, 169.8 (C=O, Ac).

Methyl 4-*O*-(2,3,5-tri-*O*-acetyl-β-D-*erythro*-apiofuranosyl)-2,3-di-*O*-benzyl-6-*O*-pivaloyl-α-D-glucopyranoside (Table 1, entry 6)

N-Iodosuccinimide (0.63 mmol, 142 mg) and a catalytic amount of triflic acid (0.06 mmol, 5 μL) was added to a mixture of donor **4b** (0.60 mmol, 192 mg) acceptor **11** (0.50 mmol, 221 mg) and powdered molecular sieves in 1,2-dichloroethane/Et_2O (12 mL, 1/1, v/v) at 0°C under an atmosphere of N_2. After 2 min, the reaction was filtered, diluted with CH_2Cl_2, washed successively with 1 M $Na_2S_2O_3$, 1 M $NaHCO_3$ and H_2O, dried ($MgSO_4$), and concentrated *in vacuo*. Purification of the crude product by flash chromatograpy (50% Et_2O/light petroleum) gave the *title compound* (236 mg, 91%) as a colourless syrup; [Found: C, 62.2; H, 6.8. $C_{37}H_{48}O_{14}$ requires C, 62.00; H, 6.75%]; R_f (50% Et_2O/light petroleum) 0.2; $[\alpha]_D^{20}$ –8.3° (*c* 2, $CHCl_3$); *m/z* 739.5 $(M+Na)^+$; δ_H (300 MHz, $CDCl_3$) 1.19 (s, 9H, Piv), 2.00, 2.03, 2.06 (3 × s, 9H, Ac), 3.37 (s, 3H, OMe), 3.48 (dd, 1H, H-2, $J_{2,3}$ 9.6 Hz), 3.63 (t, 1H, H-4, $J_{4,5}$ 9.8 Hz), 3.80 (m, 1H, H-5), 3.84 (t, 1H, H-3, $J_{3,4}$ 9.7 Hz), 4.13 (AB, 2H, H-4a', H-4b'), 4.15 (dd, 1H, H-6a), 4.41 (dd, 1H, H-6b), 4.55 (d, 1H, H-1, $J_{1,2}$ 3.6 Hz), 4.60 (AB, 2H, H-5a', H-5b'), 4.60 (AB, CH_2, Bn), 4.68 (AB, CH_2, Bn), 4.88 (AB, CH_2, Bn), 5.12 (s, 1H, H-2'), 5.23 (s, 1H, H-1'), 7.26-7.38 (m, 20H, Bn); δ_C (200 MHz, $CDCl_3$) 20.3, 20.4,

20.8 (3 × CH_3, Ac), 27.0 ($(CH_3)_3$, Piv), 38.6 (Cq, Piv), 55.0 (OMe), 62.2, 62.6, 72.0, 73.1, 75.3 (2 × CH_2, Bn, C-4', C-5', C-6), 68.2, 76.3, 76.8, 79.6 (C-2, C-3, C-4, C-5, C-2'), 82.3 (C-3'), 97.6 (C-1), 106.6 (C-1'), 127.5-128.2 (CH, Bn), 137.7, 138.4 (Cq, Bn), 169.0, 169.3 (C=O, Ac), 177.6 (C=O, Piv).

Ethyl 6-*O*-(2,3-di-*O*-acetyl-5-*O*-benzyl-β-D-*erythro*-apiofuranosyl)-2,3,4-tri-*O*-benzoyl-1-thio-β-D-glucopyranoside (14)

N-Iodosuccinimide (4.75 mmol, 1.08 g) and a catalytic amount of triflic acid (0.43 mmol, 37 μL) was added to a mixture of donor **4a** (4.3 mmol, 1.59 g) acceptor **13** (3.6 mmol, 1.93 g) and powdered molecular sieves in 1,2-dichloroethane/Et_2O (100 mL, 1/1, v/v) at 0°C under an atmosphere of N_2. After 2 min, the reaction was filtered, diluted with CH_2Cl_2, washed successively with 1 M $Na_2S_2O_3$, 1 M $NaHCO_3$ and H_2O, dried ($MgSO_4$), and concentrated *in vacuo*. Purification of the crude product by flash chromatograpy (50 →75% Et_2O/light petroleum) gave the *title compound* **14** (2.79 g, 92%) as a light yellow syrup; [Found: C, 64.2; H, 5.5. $C_{45}H_{46}O_{14}S$ requires C, 64.12; H, 5.50%]; R_f (66% Et_2O/light petroleum) 0.2; $[\alpha]_D^{20}$ –7.2° (*c* 0.5, $CHCl_3$); *m/z* 843.2 $(M+H)^+$, 865.3 $(M+Na)^+$; δ_H (300 MHz, $CDCl_3$) 1.26 (3H, t, CH_3, SEt), 2.04, 2.06 (2 × s, CH_3, Ac), 2.74 (m, 2H, CH_2, SEt), 3.75 (m, 3H, H-6a, H-6b, H-5), 3.95 (AB, 2H, H-4a', H-4b' or H-5a', H-5b'), 4.14 (AB, 2H, H-4a', H-4b' or H-5a', H-5b'), 4.54 (s, 2H, CH_2, Bn), 4.75 (d, 1H, H-1, $J_{1,2}$ 10.0 Hz), 5.03 (d, 1H, H-2'), 5.30 (d, 1H, H-1', $J_{1',2'}$ 0.7 Hz), 5.41 (t, 1H, H-4, $J_{4,5}$ 9.7 Hz), 5.47 (t, 1H, H-2, $J_{2,3}$ 9.5 Hz), 5.87 (t, 1H, H-3, $J_{3,4}$ 9.6 Hz), 7.24-7.55 (m, 14H, Bz, Bn), 7.78-7.96 (m, 6H, Bz); δ_C (200 MHz, $CDCl_3$) 14.8 (CH_3, SEt), 20.4, 21.1 (2 × CH_3, Ac), 24.0 (CH_2, SEt), 66.2 (C-6), 69.3, 73.1, 73.2 (CH_2, Bn, C-4', C-5'), 69.6, 70.6, 74.1, 76.4, 77.6 (C-2, C-3, C-4, C-5, C-2'), 83.4 (C-1), 85.2 (C-3'), 106.4 (C-1'), 127.4-133.3 (CH, arom.), 128.6, 128.7, 129.0 (3 × Cq, Bz), 137.8 (Cq, Bn), 164.6, 165.6 (C=O, Bz), 169.1, 169.8 (C=O, Ac).

Ethyl 4-*O*-(2,3-di-*O*-acetyl-5-*O*-benzyl-β-D-*erythro*-apiofuranosyl)-2,3-*O*-(2,3-dimethoxybutane-2,3-diyl)-6-*O*-*tert*-butyldimethylsilyl-1-thio-β-D-glucopyranoside (16)

N-Iodosuccinimide (0.63 mmol, 142 mg) and a catalytic amount of triflic acid (0.06 mmol, 5 μL) was added to a mixture of donor **4a** (0.60 mmol, 221 mg) acceptor **15** (0.50 mmol, 226 mg) and powdered molecular sieves in 1,2-dichloroethane/Et_2O (12 mL, 1/1, v/v) at 0°C under an atmosphere of N_2. After 2 min, the reaction was filtered, diluted with CH_2Cl_2, washed successively with 1 M $Na_2S_2O_3$, 1 M $NaHCO_3$ and H_2O, dried ($MgSO_4$), and concentrated *in vacuo*. Purification of the crude product by flash chromatograpy (20% Et_2O/light petroleum) gave the *title compound* **16** (337 mg, 89%) as a light yellow syrup; [Found: C, 56.7; H, 7.6. $C_{36}H_{58}O_{13}SSi$ requires C, 56.97; H, 7.70%]; R_f (33% Et_2O/light petroleum) 0.6; $[\alpha]_D^{20}$ –17.4° (*c* 0.9, $CHCl_3$); *m/z* 758.8 $(M+H)^+$; δ_H (300 MHz, $CDCl_3$) 0.05, 00.8 (2 × s, 6H, CH_3, TBDMS), 0.88 (s, 9H, $(CH_3)_3$, TBDMS), 1.22 (t, 3H, CH_3, SEt), 1.31 (s, 6H, CH_3, BDA), 2.06 (s, 6H, CH_3, Ac), 2.61 (m, 2H, CH_2, SEt), 3.18, 3.28 (2 × s, 6H, OMe, BDA), 3.21 (m, 1H, H-6a), 3.48 (d, 1H, H-1, $J_{1,2}$ 7.8 Hz), 3.60 (AB, 2H, H-4a', H-4b' or H-5a', H-5b'), 3.78 (AB, 2H, H-4a', H-4b' or H-5a', H-5b'), 3.88 (m, 3H, H-5, CH_2, Bn), 4.23 (dd, 1H, H-4, $J_{3,4}$ 9.7 Hz, $J_{4,5}$ 9.1 Hz), 4.48 (m, 2H, H-2, H-3), 5.17 (s, 1H, H-2'), 5.24 (s, 1H, H-1'), 7.26-7.38 (m, 5H, Bn); δ_C (200 MHz, $CDCl_3$) -5.0, -6.0 (2 × CH_3, TBDMS), 15.1 (CH_3, SEt), 17.7 (CH_3, BDA), 20.5, 21.3 (2 × CH_3, Ac), 23.7 (CH_2, SEt), 25.7 ($(CH_3)_3$, TBDMS), 47.9, 47.7 (2 × OMe, DBA), 61.4 (C-6), 69.9, 73.3, 73.7 (CH_2, Bn, C-4', C-5'), 69.1, 71.4, 72.5, 76.8, 80.3 (C-2, C-3, C-4, C-5, C-2'), 81.0 (C-1), 85.8 (C-3'), 106.0 (C-1'), 127.4-128.4 (CH, Bn), 137.6 (Cq, Bn), 169.1, 170.1 (C=O, Ac).

Ethyl 6-*O*-(2,3-di-*O*-acetyl-5-*O*-benzyl-β-D-*erythro*-apiofuranosyl)-2,3,4-tri-*O*-benzyl-1-thio-β-D-glucopyranoside (18a)

N-Iodosuccinimide (0.63 mmol, 142 mg) and a catalytic amount of triflic acid (0.06 mmol, 5 μL) was added to a mixture of donor **4a** (0.60 mmol, 221 mg) acceptor **17** (0.50 mmol, 239 mg) and powdered molecular sieves in 1,2-

dichloroethane/Et_2O (12 mL, 1/1, v/v) at 0°C under an atmosphere of N_2. After 2 min, the reaction was filtered, diluted with CH_2Cl_2, washed successively with 1 M $Na_2S_2O_3$, 1 M $NaHCO_3$ and H_2O, dried ($MgSO_4$), and concentrated *in vacuo*. Purification of the crude product by flash chromatograpy (20% Et_2O/light petroleum) gave the *title compound* **18a** (372 mg, 93%) as a coulorless syrup; [Found: C, 67.6; H, 6.6. $C_{45}H_{52}O_{11}S$ requires C, 67.48; H, 6.54%]; R_f 0.3 (50% Et_2O/light petroleum) 0.3; $[\alpha]_D^{20}$ –2.2° (*c* 1, $CHCl_3$); *m/z* 801.5 $(M+H)^+$, 823.4 $(M+Na)^+$; δ_H (300 MHz, $CDCl_3$) 1.26 (t, 3H, CH_3, SEt), 2.05, 2.06 (2 × s, CH_3, Ac), 2.74 (m, 2H, CH_2, SEt), 3.48 (m, 5H, H-2, H-3, H-6a, H-6b, H-5), 3.62 (AB, 2H, H-4a', H-4b' or H-5a', H-5b'), 4.08 (AB, 2H, H-4a', H-4b' or H-5a', H-5b'), 5.41 (t, 1H, H-4, $J_{4,5}$ 9.7 Hz), 5.47 (t, 1H, H-2, $J_{2,3}$ 9.5 Hz), 5.87 (t, 1H, H-3, $J_{3,4}$ 9.6 Hz), 4.46 (d, 1H, H-1, $J_{1,2}$ 10.2 Hz), 4.64 (AB, 2H, CH_2, Bn), 4.80 (AB, 2H, CH_2, Bn), 4.83 (AB, 2H, CH_2, Bn), 5.46 (d, 1H, H-2'), 5.33 (d, 1H, H-1', $J_{1',2'}$ 0.6 Hz), 7.24-7.44 (m, 20H, Bz, Bn); δ_C (200 MHz, $CDCl_3$) 15.2 (CH_3, SEt), 20.6, 21.4 (2 × CH_3, Ac), 24.8 (CH_2, SEt), 66.2 (C-6), 69.8, 73.4, 75.0, 75.4, 75.7 (4 × CH_2, Bn, C-4', C-5'), 76.6, 77.7, 78.3, 81.8, 84.8 (C-2, C-3, C-4, C-5, C-2'), 85.5 (C-3'), 86.5 (C-1), 105.8 (C-1'), 127.5-128.4 (CH, arom.), 137.9, 138.4 (Cq, Bn), 169.1, 170.1 (C=O, Ac).

Ethyl 6-*O*-(2,3,5-tri-*O*-acetyl-β-D-*erythro*-apiofuranosyl)-2,3,4-tri-*O*-benzyl-1-thio-β-D-glucopyranoside (18b)

N-Iodosuccinimide (0.63 mmol, 142 mg) and a catalytic amount of triflic acid (0.06 mmol, 5 μL) was added to a mixture of donor **4b** (0.60 mmol, 192 mg) acceptor **17** (0.50 mmol, 240 mg) and powdered molecular sieves in 1,2-dichloroethane/Et_2O (12 mL, 1/1, v/v) at 0°C under an atmosphere of N_2. After 2 min, the reaction was filtered, diluted with CH_2Cl_2, washed successively with 1 M $Na_2S_2O_3$, 1 M $NaHCO_3$ and H_2O, dried ($MgSO_4$), and concentrated *in vacuo*. Purification of the crude product by flash chromatograpy (50% Et_2O/light petroleum) gave the *title compound* **18b** (331 mg, 88%) as a light yellow syrup; [Found: C, 63.6; H, 6.5. $C_{40}H_{48}O_{12}S$ requires C, 63.81; H, 6.43%]; R_f (33% Et_2O/light petroleum) 0.4; $[\alpha]_D^{20}$ +13.2° (*c* 1.3, $CHCl_3$); *m/z* 753.3 $(M+H)^+$, 775.2 $(M+Na)^+$; δ_H (200 MHz, $CDCl_3$) 4.51 (d, 1H, H-1, $J_{1,2}$ 10.2 Hz), 5.25 (s, 1H, H-1'); δ_C (200 MHz, $CDCl_3$) 15.3 (CH_3, SEt), 20.3, 20.4, 20.8 (3 × CH_3, Ac), 24.7 (CH_2, SEt), 66.2 (C-6), 69.9, 75.4, 75.8, 75.9 (3 × CH_2, Bn, C-4', C-5'), 76.6, 77.7, 78.3, 81.8, 84.8 (C-2, C-3, C-4, C-5, C-2'), 85.8 (C-3'), 86.6 (C-1), 106.1 (C-1'), 127.5-128.4 (CH, arom.), 137.9, 138.4, 138.5 (Cq, Bn), 168.8, 169.1, 170.1 (C=O, Ac).

Ethyl 2,3-di-*O*-acetyl-5-*O*-benzyl-1-thio-α/β-D-ribofuranoside (19a)

To a cooled mixture (0 °C) of 1,2,3-tri-*O*-acetyl-5-*O*-benzyl-β-D-ribofuranose (1.83 g, 5.0 mmol) and ethanethiol (6 mmol, 0.44 mL) in CH_2Cl_2 (25 mL) was added a small amount of $SnCl_4$ (0.5 mmol, 58 μL). After stirring for 60 min the reaction mixture was diluted with CH_2Cl_2, washed successively with 1 M KF, 1 M $NaHCO_3$ and with water. The organic layer was dried ($MgSO_4$), filtered and concentrated *in vacuo*. The crude product was purified by flash column chromatography (35% Et_2O/light petroleum) to furnish the *title compound* **19a** (1.60 g, 87%) as a light yellow syrup; [Found: C, 58,5; H, 6.5. $C_{18}H_{24}O_6S$ requires C, 58.68; H, 6.57%]; R_f (50% Et_2O/light petroleum) 0.4; δ_H (300 MHz, $CDCl_3$) 1.24 (m, 3H, CH_3, SEt), 2.08, 2.10 (2 × s, 6H, CH_3, Ac), 2.68 (m, 2H, CH_2, SEt), 3.63, 3.65 (2 × s, 2H, H-5α, H-5β), 4.20 (dd, 1H, H-3α, $J_{2,3}$ 6.1 Hz, $J_{3,4}$ 3.3 Hz), 3.29 (dd, 1H, H-3β, $J_{2,3}$ 5.1 Hz, $J_{3,4}$ 4.8 Hz), 4.55 (dd, 2H, CH_2, Bn), 5.31 (d, 0.65H, H-1α, $J_{1,2}$ 5.9 Hz), 5.28 (m, 1H, H-2α), 5.39 (m, 1H, H-2β), 3.83, 4.18 (2 × m, 4H, H-4a, H-4b, H-5a, H-5b), 5.13 (d, 0.65H, H-2β), 5.62 (d, 1H, H-1β, $J_{1,2}$ 5.0 Hz), 7.26-7.34 (m, 5H, Bn); δ_C (200 MHz, $CDCl_3$) 14.7 (CH_3, SEt), 20.3 (CH_3, Ac), 25.1, 23.7 (CH_2, SEt), 68.6, 70.0 (C-5α, C-5β), 73.0 (CH_2, Bn), 70.6, 71.4, 72.1, 73.6, 79.0, 81.1 (C-2α, C-2β, C-3α, C-3β, C-4α, C-4β), 84.8, 86.6 (C-1α, C-1β), 127.2, 128.0 (CH, Bn), 137.5 (Cq, Bn), 169.1, 169.4 (C=O, Ac).

Ethyl 2,3,5-tri-*O*-acetyl-1-thio-α/β-D-ribofuranoside (19b)

To a cooled mixture (0 °C) of 1,2,3,5-tetra-*O*-acetyl-β-D-ribofuranose (7.95 g, 25.0 mmol) and ethanethiol (30

mmol, 2.22 mL) in CH_2Cl_2 (75 mL) was added a small amount of $SnCl_4$ (2.5 mmol, 288 μL). After stirring for 60 min the reaction mixture was diluted with CH_2Cl_2, washed successively with 1 M KF, 1 M $NaHCO_3$ and with water. The organic layer was dried ($MgSO_4$), filtered and concentrated *in vacuo*. The crude product was purified by flash column chromatography (35% Et_2O/light petroleum) to furnish the *title compound* **19b** (7.28 g, 91%) as a courless syrup; [Found: C, 48.8; H, 6.3. $C_{13}H_{20}O_7S$ requires C, 48.74; H, 6.29%]; R_f (33% Et_2O/light petroleum) 0.4; δ_H (300 MHz, $CDCl_3$) 1,24 (t, 3H, CH_3, SEt), 2.05-2.08 (6 × s, 9H, CH_3, Ac), 2.65 (m, 2H, CH_2, SEt), 4.11 (dd, 0.7H, H-5"β, $J_{5',5''}$ 11.9 Hz, $J_{5'',4}$ 4.5 Hz), 4.16 (dd, 0.3H, H-5"α, $J_{5',5''}$ 12.0 Hz, $J_{5'',4}$ 4.0 Hz), 4.22 (m, 1H, H-4), 4.30 (dd, 0.3H, H-5'α, $J_{5',4}$ 3.8 Hz), 4.33 (dd, 0.7H, H-5'β, $J_{5',4}$ 3.4 Hz), 5.13 (t, 0.3H, H-3α, $J_{3,4}$ 6.0 Hz), 5.15 (d, 0.7H, H-1β, $J_{1,2}$ 4.4 Hz), 5.21 (t, 0.7H, H-3β, $J_{3,4}$ 5.3 Hz), 5.31 (t, 0.7H, H-2β, $J_{2,3}$ 4.8 Hz), 5.34 (t, 0.7H, H-2α, $J_{2,3}$ 6.0 Hz), 5.59 (d, 0.3H, H-1α, $J_{1,2}$ 5.6 Hz); δ_C (200 MHz, $CDCl_3$) 14.5 (CH_3, SEt), 20.3, 20.4, 20.5 (3 × CH_3, Ac), 24.2, 24.9 (CH_2, SEt), 62.5 (C-5α), 63.2 (C-5β), 70.1, 70.9 (C-3α, C-4α), 71.2, 74.0 (C-3β, C-4β), 76.3 (C-2α), 79.2 (C-2β), 85.1 (C-1β), 86.4 (C-1α), 169.0, 169.9 (C=O, Ac).

Ethyl 6-*O*-(2,3-di-*O*-acetyl-5-*O*-benzyl-β-D-ribofuranosyl)-2,3,4-tri-*O*-benzoyl-1-thio-β-D-glucopyranoside (20a)

N-Iodosuccinimide (0.63 mmol, 142 mg) and a catalytic amount of triflic acid (0.06 mmol, 5 μL) was added to a mixture of donor **19a** (0.60 mmol, 221 mg) acceptor **13** (0.50 mmol, 268 mg) and powdered molecular sieves in 1,2-dichloroethane/Et_2O (12 mL, 1/1, v/v) at 0°C under an atmosphere of N_2. After 2 min, the reaction was filtered, diluted with CH_2Cl_2, washed successively with 1 M $Na_2S_2O_3$, 1 M $NaHCO_3$ and H_2O, dried ($MgSO_4$), and concentrated *in vacuo*. Purification of the crude product by flash chromatograpy (12% EtOAc/toluene) followed by gel-filtration using an LH20 column (50% CH_2Cl_2/MeOH) gave the *title compound* **20a** (362 mg, 86%) as a colouless oil; [Found: C, 64.2; H, 5.6. $C_{45}H_{46}O_{14}S$ requires C, 64.12; H, 5.50%]; R_f (33% Et_2O/light petroleum, v/v) 0.2; $[\alpha]_D^{20}$ –7.1° (*c* 0.5, $CHCl_3$); *m/z* 865.4 $(M+Na)^+$; δ_H (300 MHz, $CDCl_3$) 1.27 (t, 3H, CH_3, SEt), 2.05, 2.07 (2 × s, CH_3, Ac), 2.71 (m, 2H, CH_2, SEt), 3.75 (m, 3H, H-6a, H-6b, H-5), 4.39 (AB, 2H, CH_2, Bn), 4.79 (d, 1H, H-1, $J_{1,2}$ 9.8 Hz), 4.99 (d, 1H, H-2'), 5.26 (d, 1H, H-1', $J_{1',2'}$ 0.7 Hz), 5.40 (t, 1H, H-4, $J_{4,5}$ 9.7 Hz), 5.45 (t, 1H, H-2, $J_{2,3}$ 9.5 Hz), 5.87 (t, 1H, H-3, $J_{3,4}$ 9.6 Hz), 7.23-7.53 (m, 14H, Bz, Bn), 7.78-7.96 (m, 6H, Bz); δ_C (200 MHz, $CDCl_3$) 14.9 (CH_3, SEt), 20.3, 21.0 (2 × CH_3, Ac), 24.0 (CH_2, SEt), 66.2 (C-6), 69.3, 73.1 (CH_2, Bn, C-5'), 72.2, 74.3, 77.6, 78.2, 79.8, 81.6, 84.8 (C-2, C-3, C-4, C-5, C-2', C-3', C-4'), 86.5 (C-1), 105.3 (C-1'), 127.5-128.4 (CH, arom.), 137.9, 138.4 (Cq, Bn), 164.7, 165.2, 165.6 (C=O, Bz), 169.5, 169.7 (C=O, Ac).

Ethyl 6-*O*-(2,3-di-*O*-acetyl-5-*O*-benzyl-β-D-ribofuranosyl)-2,3,4-tri-*O*-benzyl-1-thio-β-D-glucopyranoside (21a)

N-Iodosuccinimide (0.63 mmol, 142 mg) and a catalytic amount of triflic acid (0.06 mmol, 5 μL) was added to a mixture of donor **19a** (0.60 mmol, 221 mg) acceptor **17** (0.50 mmol, 239 mg) and powdered molecular sieves in 1,2-dichloroethane/Et_2O (12 mL, 1/1, v/v) at 0°C under an atmosphere of N_2. After 2 min, the reaction was filtered, diluted with CH_2Cl_2, washed successively with 1 M $Na_2S_2O_3$, 1 M $NaHCO_3$ and H_2O, dried ($MgSO_4$), and concentrated *in vacuo*. Purification of the crude product by flash chromatograpy (12% EtOAc/toluene) followed by gel-filtration using an LH20 column (50% CH_2Cl_2/MeOH) gave the *title compound* **21a** (232 mg, 58%) as an oil; [Found: C, 67.3; H, 6.6. $C_{45}H_{52}O_{11}S$ requires C, 67.48; H, 6.54%]; $[\alpha]_D^{20}$ +3.4° (*c* 1, $CHCl_3$); R_f (50% Et_2O/light petroleum) 0.4; *m/z* 801.5 $(M+H)^+$; δ_H (300 MHz, $CDCl_3$) 1.25 (3H, t, CH_3, SEt), 2.05, 2.07 (2 × s, CH_3, Ac), 2.70 (m, 2H, CH_2, SEt), 4.46 (d, 1H, H-1, $J_{1,2}$ 10.2 Hz), 5.35 (d, 1H, H-1', $J_{1',2'}$ 0.3 Hz), 7.24-7.44 (m, 20H, Bn); δ_C (200 MHz, $CDCl_3$) 15.0 (CH_3, SEt), 20.5 (CH_3, Ac), 24.9 (CH_2, SEt), 66.7 (C-6), 71.4 (C-5'), 73.2, 74.9, 75.4, 75.6 (4 × CH_2, Bn), 72.2, 74.3, 77.6, 78.2, 79.8, 81.6, 84.8 (C-2, C-3, C-4, C-5, C-2', C-3', C-4'), 86.5 (C-1), 105.3 (C-1'), 127.5-128.4 (CH, arom.), 137.9, 138.4 (Cq, Bn), 169.5, 169.7 (C=O, Ac).

3,4,5-Trimethoxyphenyl 2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranoside (27)

To a stirred solution of 2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranose (**23**, 540.7 mg, 1 mmol) and 3,4,5-trimethoxyphenol (267 mg, 1.5 mmol) in THF (3 mL) at 0 °C was added Ph_3P (262 mg, 1 mmol) and a solution of diethyl azodicarboxylate (164 μL, 1 mmol) in THF. The mixture was stirred overnight (15 h). The solution was concentrated under reduced pressure and the residue was dissolved in CH_2Cl_2 (25 mL) and washed with 10% aq. $NaHCO_3$ and water. The organic layer was dried over $MgSO_4$, filtered and concentrated. The product was purified by silica gel column chromatography. Elution was effected with Et_2O/light petroleum, (1/2 → 1/1, v/v) to afford the *title compound* **27** (437 mg, 62%) as a colourless oil; [Found: C, 72.8; H, 6.6. $C_{43}H_{46}O_9$ requires C, 73.07; H, 6.56%]; R_f (Et_2O/light petroleum, 1/1, v/v) 0.25; $[\alpha]_D^{20}$ +1.3° (*c* 2, $CHCl_3$); *m/z* 706.4 $(M+H)^+$; δ_H (600 MHz, $CDCl_3$) 3.7-3.9 (m, 6H, H-2', H-3', H-4', H-5', H-6a', H-6b') 3.74 (s, 6H, 3-OMe, 5-OMe), 3.84 (s, 3H, 4-OMe), 4.70 (AB, 2H, CH_2, Bn), 4.84 (AB, 2H, CH_2, Bn), 4.93 (AB, 2H, CH_2, Bn), 4.97 (d, 1H, H-1', $J_{1',2'}$ 7.4 Hz), 5.00 (AB, 2H, CH_2, Bn), 6.40 (s, 1H, H-2, H-6), 7.20-7.36 (m, 20H, 4 × Bn); δ_C (200 MHz, $CDCl_3$) 56.3 (3-OMe, 5-OMe), 61.3 (4-OMe), 69.5 (C-6'), 74.0, 75.4, 76.2 (CH_2, Bn), 75.5, 78.3, 82.5, 85.1, 95.5 (C-2', C-3', C-4', C-5'), 95.5 (C-2, C-6), 103.0 (C-1'), 128.1-128.8 (CH, Bn), 138.3, 138.7, 138.8 (Cq, Bn), 133.8 (C-4), 153.9, 154.5 (C-1, C-3, C-5).

3,4,5-Trimethoxyphenyl 2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranoside (28) and 1-(2,3,4,6-tetra-*O*-benzoyl-1-deoxy-β-D-glucopyranosyl)-2-oxo-4,5,6-trimethoxy-1,4-cyclohexadiene (30)

A mixture of trichloroacetimidate donor **26** (748 mg, 1.00 mmol) and 3,4,5-trimethoxyphenol (267 mg, 1.5 mmol) was dissolved in CH_2Cl_2 (12 mL) and pulverized molecular sieves (4 Å, 2 g) were added. The resulting mixture was stirred for 20 min under an atmosphere of argon and then 1 mL of a 0.25 M solution of $BF_3{\bullet}OEt_2$ in CH_2Cl_2 was slowly added over a period of 30 min. TLC analysis (CH_2Cl_2/MeOH, 50/1, v/v) showed the disappearance of the imidate **26** and the formation of two lower running products. The reaction mixture was neutralized with Et_3N, filtered and the filtrate was washed with 10% aq. $NaHCO_3$ and water. The organic phase was dried ($MgSO_4$), filtered and concentrated *in vacuo*. Purification of the crude syrup was accomplished using a silica gel column (CH_2Cl_2/MeOH 0→1%) to afford homogeneous **28** (312 mg, 41%) as a white amorphous solid; [Found: C, 67.5; H, 4.9. $C_{43}H_{38}O_{13}$ requires C, 67.71; H, 5.02%]; R_f (CH_2Cl_2/MeOH, 100/1, v/v) 0.65; $[\alpha]_D^{20}$ –12.6° (*c* 0.5, $CHCl_3$); *m/z* 785.3 $(M+Na)^+$; δ_H (300 MHz, $CDCl_3$) 3.60 (s, 6H, 3-OMe, 5-OMe), 3.74 (s, 3H, 4-OMe), 4.35 (m, 2H, H-5'), 4.54 (dd, 1H, H-6'a, $J_{5,6a'}$ 6.0 Hz, $J_{6a',6b'}$ 12.1 Hz), 4.70 (dd, 1H, H-6'b, $J_{5,6b'}$ 3.0 Hz), 5.36 (d, 1H, H-1', $J_{1',2'}$ 7.7 Hz), 5.75 (m, 1H, H-2', H-4'), 6.01 (t, 1H, H-3', $J_{3',4'} \approx J_{2',3'}$ 9.6 Hz), 6.23 (s, 1H, H-2, H-6), 7.27-7.42 (m, 12H, 4 × Bz), 7.85-8.00 (m, 8H, 4 × Bz); δ_C (200 MHz, $CDCl_3$) 55.9 (3-OMe, 5-OMe), 60.9 (4-OMe), 63.3 (C-6'), 69.5, 71.8, 72.7, 76.6 (C-2', C-3', C-4', C-5'), 95.6 (C-2, C-6), 100.6 (C-1'), 128.4-133.5 (CH, Bz), 128.9 129.0, 129.3 (Cq, Bz), 133.8 (C-4), 153.5, 153.4 (C-1, C-3, C-5), 165.0, 165.2, 165.7, 166.1 (C=O, Bz). Furter elution with 5% methanol in CH_2Cl_2 gave *C*-aryl glycoside **30** (137 mg, 18%) as a syrup; [Found: C, 67.7; H, 5.1. $C_{43}H_{38}O_{13}$ requires C, 67.71; H, 5.02%]. R_f (5% MeOH/CH_2Cl_2) 0.35; $[\alpha]_D^{20}$ –83.9° (*c* 1, $CHCl_3$); *m/z* 785.2 $(M+Na)^+$; δ_H (300 MHz, $CDCl_3$) 2.89 (s, 3H, 5-OMe), 3.58, 3.70 (2 × s, 2 × 3H, 4-OMe, 6-OMe), 4.05 (m, 2H, H-5'), 4.31 (dd, 1H, H-6'a, $J_{5,6a'}$ 6.0 Hz, $J_{6a',6b'}$ 12.1 Hz), 4.42 (d, 1H, H-1', $J_{1',2'}$ 9.7 Hz), 4.53 (dd, 1H, H-6'b, $J_{5,6b'}$ 3.1 Hz), 5.48 (t, 1H, H-4', $J_{4',5'}$ 9.6 Hz), 5.48 (d, 1H, H-3 or H-5, $J_{3,5}$ 1.4 Hz), 5.57 (d, 1H, H-3 or H-5), 5.78 (t, 1H, H-3', $J_{3',4'}$ 9.6 Hz), 5.89 (t, 1H, H-2', $J_{2',3'}$ 9.6 Hz), 7.26-7.42 (m, 12H, 4 × Bz), 7.85-8.00 (m, 8H, 4 × Bz); δ_C (200 MHz, $CDCl_3$) 52.1 (5-OMe), 55.9, 56.5 (4-OMe, 6-OMe), 66.6, 69.1 (C-6'), 73.0, 73.1, 75.1, 75.8, 78.3, 78.4 (C-1', C-2', C-3', C-4', C-5', C-2"), 79.9 (C-1), 104.7, 105.4 (C-3, C-5), 128.0-133.4 (CH, Bz), 128.7 129.0, 130.1 (Cq, Bz), 165.1, 165.3, 165.6, 165.8 (C=O, Bz), 166.7, 167.4 (C-4, C-5), 186.7 (C-2).

1-(2,3,4,6-Tetra-*O*-acetyl-1-deoxy-β-D-glucopyranosyl)-2-oxo-4,5,6-trimethoxy-1,4-cyclohexadiene (29)

1,2,3,4,6-penta-*O*-acetyl-β-D-glucopyranose (**25**, 390.4 mg, 1 mmol) and 3,4,5-trimethoxyphenol (267 mg, 1.5

mmol) were dissolved in CH_2Cl_2 (3 mL). BF_3•OEt_2 (126 μL, 1 mmol) was added and the reaction mixture was stirred for 15 h. The mixture was diluted with CH_2Cl_2 and washed with 10% aq. $NaHCO_3$ and water. The organic layer was dried over $MgSO_4$, filtered and concentrated. The crude product was purified by silica gel column chromatography and elution was effected with methanol in dichloromethane (0→10%) to afford the *title compound* **29** (453 mg, 88%) as a white solid; [Found: C, 53.6; H, 5.8. $C_{23}H_{30}O_{13}$ requires C, 53.70; H, 5.88%]; R_f (10% MeOH/CH_2Cl_2) 0.35; $[\alpha]_D^{20}$ –96.3° (*c* 0.5, $CHCl_3$); *m/z* 537.3 $(M+Na)^+$; δ_H (600 MHz, $CDCl_3$) 1.99 (s, 3H, CH_3, Ac), 2.00 (s, 3H, CH_3, Ac), 3.05 (s, 3H, 5-OMe), 3.57 (m, 2H, H-5'), 3.77, 3.79 (2 × s, 2 × 3H, 4-OMe, 6-OMe), 3.90 (dd, 1H, H-6'a, $J_{5,6a'}$ 3.3 Hz, $J_{6a',6b'}$ 12.1 Hz), 4.06 (m, 2H, H-6'b, H-1', $J_{1',2'}$ 9.7 Hz), 4.95 (t, 1H, H-4', $J_{4',5'}$ 9.6 Hz), 5.13 (t, 1H, H-3', $J_{3',4'}$ 9.6 Hz), 5.43 (t, 1H, H-2', $J_{2',3'}$ 9.6 Hz), 5.61 (s, 2H, H-3, H-5); δ_C (200 MHz, $CDCl_3$ 20.3, 20.5 (4 × CH_3, Ac), 52.1 (5-OMe), 55.8, 56.1 (4-OMe, 6-OMe), 61.8 (C-6'), 68.0, 69.0, 74.6, 75.6, 77.4 (C-1', C-2', C-3', C-4', C-5'), 79.5 (C-1), 104.3, 104.8 (C-3, C-5), 166.7, 167.3 (C-4, C-5), 168.9, 169.2, 169.9 (C=O, Ac), 186.6 (C-2).

6-*O*-(2,3-Di-*O*-acetyl-5-*O*-benzyl-β-D-*erythro*-apiofuranosyl)-2,3,4-tri-*O*-benzoyl-α-D-glucopyranosyl trichloroacetimidate (31)

To a stirred solution of compound **14** (1.66 g, 1.97 mmol) in dichloromethane/water (20.20 mL, 100/1, v/v) was added in approximately 45 min a 0.1 M stock-solution of NIS/cat. TfOH (25 ± 3 mL) and the progress of the reaction was followed by TLC-analysis (5% MeOH/CH_2Cl_2). After complete disappearance of the starting material the reaction was stopped by adding a 10% aq. $Na_2S_2O_3$ solution. The organic layer was separated and washed with 10% aq. $NaHCO_3$ solution and water then dried ($MgSO_4$), filtered and concentrated. The crude product was purified by silica gel column chromatography (CH_2Cl_2/MeOH, 100/0 → 95/5, v/v) and after concentration of the appropriate fractions the corresponding hemiacetal was obtained. R_f 0.3 (5% MeOH/CH_2Cl_2). The compound was dried by evaporation of toluene (3 × 10 mL) and dissolved in CH_2Cl_2 (10 mL). Subsequently, cesium carbonate (0.2 mmol, 64 mg) and trichloroacetonitrile (6 mmol, 600 μL) were added. After stirring the resulting mixture for 1 h, TLC-analysis indicated that the starting material was completely converted into a higher running product. The reaction mixture was filtered, concentrated and the resulting oil was purified by silica gel chromatography (toluene/ethyl acetate/triethylamine, 100/0/0.5 → 90/10/0.5, v/v/v) to give the *title compound* **31** (1.60 g, 86%) as a light yellow syrup; [Found: C, 57.1; H, 4.5 $C_{45}H_{42}Cl_3NO_{15}$ requires C, 57.31; H, 4.49%]; R_f (toluene/ethyl acetate/triethylamine, 90/10/1, v/v/v) 0.45; $[\alpha]_D^{20}$ +7.2° (*c* 1, $CHCl_3$); δ_H (200 MHz, $CDCl_3$) 2.05, 2.07 (2 × s, CH_3, Ac), 3.85 (m, 3H, H-6a, H-6b, H-5), 3.95 (AB, 2H, H-4a', H-4b' or H-5a', H-5b'), 4.12 (AB, 2H, H-4a', H-4b' or H-5a', H-5b'), 4.64 (s, 2H, CH_2, Bn), 5.03 (d, 1H, H-2'), 5.37 (d, 1H, H-1', $J_{1',2'}$ 0.7 Hz), 5.41 (t, 1H, H-4, $J_{4,5}$ 9.7 Hz), 5.58 (dd, 1H, H-2, $J_{2,3}$ 9.6 Hz), 6.01 (t, 1H, H-3, $J_{3,4}$ 9.6 Hz), 6.78 (d, 1H, H-1, $J_{1,2}$ 3.7 Hz), 7.24-7.55 (m, 14H, Bz, Bn), 7.78-7.96 (m, 6H, Bz); δ_C (200 MHz,) 20.2, 20.9 (2 × CH_3, Ac), 66.0, 69.1, 73.0 (C-4", C-5", C-6', CH_2, Bn), 68.4, 69.9, 70.4, 71.7, 76.1 (C-2', C-3', C-4', C-5', C-2"), 84.9 (C-3"), 90.3 (CCl_3), 92.7 (C-1'), 106.2 (C-1"), 127.3-133.2 (CH, arom.), 129.2, 129.4 (Cq, Bz), 137.5 (Cq, Bn), 159.8 (C=NH), 164.7, 164.9 (C=O, Bz), 168.8, 169.5 (C=O, Ac).

3,4,5-Trimethoxyphenyl 6-*O*-(2,3-di-*O*-acetyl-5-*O*-benzyl-β-D-*erythro*-apiofuranosyl)-2,3,4-tri-*O*-benzoyl-β-D-glucopyranoside (32) and 1-(2,3,4-tri-*O*-benzoyl-6-*O*-(2,3-di-*O*-acetyl-5-*O*-benzyl-β-D-*erythro*-apiofuranosyl)-1-deoxy-β-D-glucopyranosyl)-2-oxo-4,5,6-trimethoxy-1,4-cyclohexadiene (33)

Trichloroacetimidate donor **31** (943 mg, 1.00 mmol) and 3,4,5-trimethoxyphenol (267 mg, 1.5 mmol) were dissolved in a mixture of CH_2Cl_2 and THF (11 mL, 10/1, v/v) and powdered molecular sieves (4 Å, 2 g) were added. The mixture was stirred for 30 min under an atmosphere of argon and then 1 mL of a 0.25 M solution of BF_3•OEt_2 in CH_2Cl_2 was slowly added over a period of 30 min. TLC analysis (20% EtOAc/toluene) showed the disappearance of the imidate **31** and the formation of two lower running products. The reaction mixture was neutralized with Et_3N, filtered and the filtrate was washed with 10% aq. $NaHCO_3$ and water. The organic phase was dried ($MgSO_4$), filtered

and concentrated *in vacuo*. The crude mixture was purified by silica gel column chromatography (0→1% MeOH/CH_2Cl_2) to afford homogeneous **32** (607 mg, 63%) as a coulorless syrup; [Found: C, 64.4; H, 5.4 $C_{52}H_{52}O_{18}$ requires C, 64.72; H, 5.43%]; R_f (20% EtOAc/toluene) 0.45; $[\alpha]_D^{20}$ –6.8° (*c* 0.5, $CHCl_3$); *m/z* 964.4 $(M+H)^+$; δ_H (300 MHz, $CDCl_3$) 2.01 (s, 3H, CH_3, Ac), 2.02 (s, 3H, CH_3, Ac), 3.70 (s, 6H, 3-OMe, 5-OMe), 3.72 (m, 1H, H-6'a), 3.77 (s, 3H, 4-OMe), 3.85 (m, 1H, H-6'b), 3.97 (AB, 2H, CH_2, Bn), 4.00 (m, 2H, H-5'), 4.14 (AB, 2H, H-5"), 4.53 (AB, 2H, H-4"), 5.00 (d, 2H, H-2"), 5.26 (d, 1H, H-1', $J_{1',2'}$ 7.8 Hz), 5.28 (d, 1H, H-1", $J_{1",2"}$ 0.8 Hz), 5.55 (t, 1H, H-4', $J_{4',5'}$ 9.6 Hz), 5.71 (dd, 1H, H-2', $J_{2',3'}$ 9.6 Hz), 5.96 (t, 1H, H-3', $J_{3',4'}$ 9.6 Hz), 6.26 (s, 1H, H-2, H-6), 7.27-7.38 (m, 17H, 3 × Bz, Bn), 7.85-8.00 (m, 6H, 3 × Bz). δ_C (200 MHz, $CDCl_3$) 20.3, 21.1 (2 × CH_3, Ac), 55.9 (3-OMe, 5-OMe), 60.7 (4-OMe), 65.9, 69.0, 73.1 (C-4", C-5", C-6', CH_2, Bn), 69.1, 71.6, 72.5, 73.7, 76.2 (C-2', C-3', C-4', C-5', C-2"), 85.0 (C-3"), 95.5 (C-2, C-6), 100.4 (C-1'), 105.8 (C-1"), 127.6-133.5 (CH, arom.), 128.8, 128.9 (Cq, Bz), 133.6 (C-4), 137.6 (Cq, Bn), 152.7 (C-1), 153.4 (C-3, C-5), 164.9, 165.6 (C=O, Bz), 169.0, 169.7 (C=O, Ac). Further elution of the column resulted in the isolation of compound **33** (38 mg, 4%) as an light yellow syrup; [Found: C, 64.7; H, 5.4 $C_{52}H_{52}O_{18}$ requires C, 64.72; H, 5.43%]; R_f (20% EtOAc/toluene) 0.15; $[\alpha]_D^{20}$ –107.2° (*c* 1, $CHCl_3$); *m/z* 964.4 $(M+H)^+$; δ_H (300 MHz, $CDCl_3$) 2.05, 2.21 (2 × s, 6H, CH_3, Ac), 2.91 (s, 3H, 5-OMe), 3.48 (m, 2H, H-6'a, H-6'b), 3.72, 3.80 (2 × s, 6H, 4-OMe, 6-OMe), 3.75 (m, 1H, H-5'), 3.86 (d, 1H, H-4a'), 4.05 (d, 1H, H-4b'), 4.12 (s, 2H, CH_2, Bn), 4.35 (d, 1H, H-1', $J_{1',2'}$ 9.7 Hz), 4.53 (AB, 2H, CH_2, Bn), 4.84 (d, 2H, H-2"), 5.21 (t, 1H, H-4', $J_{4',5"}$ 9.8 Hz), 5.34 (d, 1H, H-1", $J_{1",2"}$ 0.8 Hz), 5.60 (d, 1H, H-3 or H-5, $J_{3,5}$ 1.4 Hz), 5.63 (d, 1H, H-3 or H-5), 5.21 (t, 1H, H-3', $J_{3',4'}$ 9.8 Hz), 5.21 (t, 1H, H-2', $J_{2',3"}$ 9.8 Hz), 7.27-7.38 (m, 17H, 3 × Bz, Bn), 7.85-8.00 (m, 6H, 3 × Bz); δ_C (300 MHz, $CDCl_3$) 20.7, 21.2 (2 × CH_3, Ac), 52.1 (5-OMe), 55.9, 56.5 (4-OMe, 6-OMe), 66.6, 69.1 (C-4", C-5", C-6', CH_2, Bn), 73.0, 73.1, 75.1, 75.8, 78.3, 78.4 (C-1', C-2', C-3', C-4', C-5', C-2"), 79.8 (C-1), 85.3 (C-3"), 104.5, 105.4, 106.3 (C-1", C-3, C-5), 128.0-133.4 (CH, Bz), 128.7 129.0, 130.1 (Cq, Bz), 165.7, 165.1, 165.7 (C=O, Bz), 166.6, 167.7 (C-4, C-6), 169.0, 169.7 (C=O, Ac), 186.7 (C-2).

3,4,5-Trimethoxyphenyl 6-*O*-(5-*O*-benzyl-β-D-*erythro*-apiofuranosyl)-β-D-glucopyranoside (34)

Sodium methanolate (20 mg) was added to a solution of compound **32** (777 mg, 0.81 mmol) in a mixture of methanol and dichloromethane (5/1, v/v). After stirring for 2 h, the deacylation was complete, as judged by TLC-analysis. The reaction was neutralized with Dowex 50W X4 (H^+-form), filtered and concentrated. The crude product was applied to a column of silica gel and eluted with ethyl acetate/methanol (100/0 →95/5, v/v) to furnish the *title compound* **34** (405 mg, 88%) as a white amorphous solid; [Found: C, 57.2; H, 6.5 $C_{27}H_{36}O_{13}$ requires C, 57.04; H, 6.38%]; R_f (12% MeOH/CH_2Cl_2) 0.35; $[\alpha]_D^{20}$ –57.7° (*c* 1, MeOH); δ_H (200 MHz, $CDCl_3$/ CD_3OD) 3.65 (s, 3H, 4-OMe), 3.74 (s, 6H, 3-OMe, 5-OMe), 3.86 (d, 1H, H-2", $J_{2",3"}$ 2.1 Hz), 4.76 (d, 1H, H-1', $J_{1',2'}$ 7.6 Hz), 4.95 (d, 1H, H-1", $J_{1",2"}$ 2.6 Hz), 6.38 (s, 1H, H-2, H-6), 7.32 (m, 5H, Bn); δ_C (200 MHz, $CDCl_3$) 56.0 (3-OMe, 5-OMe), 60.3 (4-OMe), 60.7, 70.3, 71.9, 73.3 (CH_2, Bn, C-6', C-5", C-4"), 69.9, 75.7, 76.2, 76.9, 80.1 (C-2', C-3', C-4', C-5", C-2"), 78.3 (C-3"), 95.2 (C-2, C-6), 101.3 (C-1'), 108.6 (C-1"), 127.5, 127.6 (CH, Bn), 133.7 (C-4), 137.2 (Cq, Bn), 153.4 (C-3, C-5), 154.7 (C-1).

3,4,5-Trimethoxyphenyl 6-*O*-(β-D-*erythro*-apiofuranosyl)-β- D-glucopyranoside (1)

Compound **34** (145 mg, 0. 26 mmol) was dissolved in isopropanol/water (5.5 mL, 10/1, v/v) and, under a N_2 atmosphere, palladium on carbon was added. After applying a brief vacuum, the mixture was brought under a H_2-atmosphere for 12 h. The hydrogen gas was removed by application of a brief vacuum and the suspension was filtered, concentrated and the residue was purified on silica gel (CH_2Cl_2/MeOH, 85/15 → 80/20, v/v) to give the *title compound* **1** (113 mg, 91%) as a white amorphous solid ; [Found: C, 50.2; H, 6.3 $C_{20}H_{30}O_{13}$ requires C, 50.21; H, 6.32%]; R_f (20% MeOH /CH_2Cl_2) 0.6; *m/z* 501.2 $(M+Na)^+$; δ_H (600 MHz, CD_3OD) 3.25 (m, 2H, H-2', H-4'), 3.36 (t, 1H, H-3', $J_{3',4'} \approx J_{4',5'}$ 9.6 Hz), 3.48 (s, 2H, H-5"), 3.53 (m, 2H, H-6'a, H-5'), 3.63 (s, 3H, 4-OMe), 3.69 (d, 1H, H-4"b,

$J_{4"a,4"b}$ 9.6 Hz), 3.74 (s, 6H, 3-OMe, 5-OMe), 3.81 (d, 1H, H-2", $J_{2",3"}$ 2.1 Hz), 3.88 (d, 1H, H-4"a), 3.98 (dd, 1H, H-6'a, $J_{6'a,6'b'}$ 9.3 Hz, $J_{6'a,5'}$ 3.9 Hz), 4.73 (d, 1H, H-1', $J_{1',2'}$ 7.3 Hz), 4.90 (d, 1H, H-1", $J_{1",2"}$ 2.4 Hz), 6.39 (s, 1H, H-2, H-6); δ_C (600 MHz, CD_3OD) 55.7 (3-OMe, 5-OMe), 60.5 (4-OMe), 64.4 (C-5"), 66.7 (C-6'), 69.1 (C-4'), 72.8 (C-2'), 73.5 (C-4"), 74.8 (C-5'), 76.0 (C-2"), 76.4 (C-3'), 78.9 (C-3"), 95.0 (C-2, C-6), 101.4 (C-1'), 108.9 (C-1"), 133.2 (C-4), 153.0 (C-3, C-5), 154.7 (C-1); $[\alpha]_D^{20}$ -87° (c 1.0, MeOH). Lit.[1,2] $[\alpha]_D^{25}$ -99.8° (c 0.5, MeOH)[1] and $[\alpha]_D^{21}$ -81.7° (c 0.9, MeOH)[2]. The *title compound* was acetylated according to Miyamura[2] to afford 3,4,5-trimethoxyphenyl 6-*O*-(2,3,5-tri-*O*-acetyl-β-D-*erythro*-apiofuranosyl)-2,3,4-tri-*O*-acetyl-β-D-glucopyranoside as white crystals, m.p. 138 °C; Lit.[2] m.p. 132-134 °C.

3,4,5-Trimethoxyphenyl 2,3,4-tri-*O*-phenoxyacetyl-6-*O*-(2,3-di-*O*-phenoxyacetyl-5-*O*-benzyl-β-D-*erythro*-apiofuranosyl)-β-D-glucopyranoside (35)

Phenoxyacetyl chloride (660 μL, 4.75 mmol) was added dropwise in a period of 30 min to a stirred solution of **34** (416 mg, 0.732 mmol) and pyridine (680 μL, 9 mmol) in 10 mL CH_2Cl_2. After stirring for 1 h TLC analysis (toluene/ethyl acetate, 8/1, v/v) showed the formation of one major spot. The reaction was quenched by addition of methanol and diluted with dichloromethane and washed with water. The organic layer was dried ($MgSO_4$) and concentrated under reduced pressure. The resulting syrup was purified with silica gel column chromatography. Elution was performed with toluene/ethyl acetate (100/0 → 80/20, v/v), to furnish, after concentration of the appropriate fractions, pure **35** (797 mg, 88%) as a light yellow oil; [Found: C, 64.8; H, 5.4 $C_{67}H_{66}O_{23}$ requires C, 64.94; H, 5.37%]; R_f (12.5% EtOAc/toluene) 0.5; $[\alpha]_D^{20}$ –23.2° (*c* 1, $CHCl_3$); δ_H (300 MHz, $CDCl_3$) 3.43 (dd, 1H, H-6'a, $J_{5,6a'}$ 3.1 Hz, $J_{6a',6b'}$ 12.1 Hz), 3.49 (dd, 1H, H-6'b, $J_{5,6b'}$ 6.2 Hz), 3.75 (s, 6H, 3-OMe, 5-OMe), 3.78 (s, 3H, 4-OMe), 3.99 (dd, 2H, H-4"), 4.19 (s, 2H, CH_2, Bn), 4.47 (s, 2H, CH_2, PhOAc), 4.48 (s, 2H, CH_2, PhOAc), 4.50 (s, 2H, CH_2, PhOAc), 4.51 (s, 2H, CH_2, PhOAc), 4.54 (s, 2H, CH_2, PhOAc), 4.90 (d, 2H, H-2"), 5.03 (d, 1H, H-1', $J_{1',2'}$ 7.7 Hz), 5.25 (t, 1H, H-4', $J_{4',5'}$ 9.6 Hz), 5.29 (dd, 1H, H-2', $J_{2',3'}$ 9.7 Hz), 5.37 (d, 1H, H-1", $J_{1",2"}$ 1.7 Hz), 5.46 (t, 1H, H-3', $J_{3',4'}$ 9.6 Hz), 6.19 (s, 1H, H-2, H-6), 6.81-6.88 (m, 20H, OPh, Bn), 7.22-7.28 (m, 10H, OPh); δ_C (200 MHz, $CDCl_3$) 56.1 (3-OMe, 5-OMe), 60.9 (4-OMe), 64.3, 64.6, 64.7, 65.4 (5 × CH_2, PhOAc), 71.0, 71.6, 73.1, 74.4 (C-4", C-5", C-6', CH_2, Bn), 69.0, 71.7, 72.6, 73.3, 77.2 (C-2', C-3', C-4', C-5', C-2"), 86.3 (C-3"), 95.2 (C-2, C-6), 99.0 (C-1'), 105.8 (C-1"), 114.3, 114.4, 114.5, 114.6 (CH, PhOAc), 121.7, 121.8, 121.9 (CH, PhOAc), 127.6-129.5 (CH, Bn, PhOAc), 133.6 (C-4), 137.3 (Cq, Bn), 152.7 (C-1), 153.6 (C-3, C-5), 157.3, 157.4 (Cq, PhOAc), 167.5, 167.6, 167.7, 167.8, 168.3 (C=O, PhOAc).

3,4,5-Trimethoxyphenyl 2,3,4-tri-*O*-phenoxyacetyl-6-*O*-(2,3-di-*O*-phenoxyacetyl-β-D-*erythro*-apiofuranosyl)-β-D-glucopyranoside (36)

Palladium on carbon (10%) was added to a solution of **34** (793 mg, 0.64 mmol) in a mixture of isopropanol/ethyl acetate/acetic acid (12/8/1, v/v/v, 15 mL). The mixture was vigorously stirred for 48 hours under hydrogen atmosphere. The reaction mixture was filtered and the filtrate was concentrated. The residual oil was applied onto a column of silica gel and elution was effected with toluene/ethyl acetate (100/0 → 70/30, v/v) to give pure **36** (0.632 g, 86%) as an oil; [Found: C, 62.5; H, 5.3 $C_{60}H_{60}O_{23}$ requires C, 62..72; H, 5.26%]; R_f (4% MeOH/CH_2Cl_2) 0.4; *m/z* 1150.2 $(M+H)^+$, 1177.3 $(M+Na)^+$; $[\alpha]_D^{20}$ –12.0° (*c* 1.1, $CHCl_3$); δ_H (300 MHz, $CDCl_3$) 3.50 (m, 2H, H-6'a, H-6'b), 3.77 (s, 6H, 3-OMe, 5-OMe), 3.78 (s, 3H, 4-OMe), 4.05 (AB, 2H, H-4"), 4.45 (s, 2H, CH_2, PhOAc), 4.52 (s, 2H, CH_2, PhOAc), 4.58 (s, 2H, CH_2, PhOAc), 4.68 (s, 2H, CH_2, PhOAc), 4.75 (s, 2H, CH_2, PhOAc), 4.96 (s, 2H, H-2"), 5.00 (d, 1H, H-1", $J_{1",2"}$ 1.6 Hz), 5.09 (d, 1H, H-1', $J_{1',2'}$ 7.5 Hz), 5.19 (t, 1H, H-4', $J_{4',5'}$ 9.6 Hz), 5.36 (dd, 1H, H-2', $J_{2',3'}$ 9.7 Hz), 5.44 (t, 1H, H-3', $J_{3',4'}$ 9.6 Hz), 6.21 (s, 1H, H-2, H-6), 6.81-6.92 (m, 15H, OPh), 7.22-7.27 (m, 10H, OPh); δ_C (200 MHz, $CDCl_3$) 56.2 (3-OMe, 5-OMe), 60.9 (4-OMe), 64.5, 64.8, 64.9, 65.0, 65.6 (5 × CH_2, PhOAc), 67.3, 74.1, 78.5 (C-4", C-5", C-6'), 68.9, 71.8, 72.9, 73.4, 78.7 (C-2', C-3', C-4', C-5', C-2"), 87.0 (C-3"), 95.3 (C-2,

C-6), 99.0 (C-1'), 106.1 (C-1"), 114.3, 114.4, 114.5, 114.6 (CH, PhOAc), 121.8, 122.0, 122.1 (CH, PhOAc), 129.6 (CH, PhOAc), 133.6 (C-4), 152.7 (C-1), 153.7 (C-3, C-5), 157.3, 157.4 (Cq, PhOAc), 167.6, 167.8, 168.4, 168.5, 169.1 (C=O, PhOAc).

3,4,5-Trimethoxyphenyl 2,3,4-tri-*O*-phenoxyacetyl-6-*O*-(2,3-di-*O*-phenoxyacetyl-5-*O*-(3,4-di-*O*-acetylcaffeoyl)-β-D-*erythro*-apiofuranosyl)-β-D-glucopyranoside (37)

To a solution of compound **36** (230 mg, 0.20 mmol) in CH_2Cl_2 (5 mL) and pyridine was added (50 μL, 0.60 mmol), was added a 1 mL of 0.4 M stock-solution of 3,4-di-*O*-acetylcaffeoyl chloride in CH_2Cl_2. Monitoring the reaction by TLC-analysis showed the formation of a new spot. After 2 h the reaction mixture was diluted with CH_2Cl_2 and washed with 10% $NaHCO_3$ solution and water. The organic layer was separated and then dried ($MgSO_4$), filtered and concentrated. The crude product was purified by silica gel column chromatography (toluene/ethyl acetate, 8/2 → 5/5, v/v) and after concentration of the appropriate fractions, **37** (215 mg, 77%) was obtained as a syrup; [Found: C, 62.7; H, 5.1 $C_{73}H_{70}O_{28}$ requires C, 62.84; H, 5.06%]; R_f (4% MeOH/CH_2Cl_2) 0.4; $[\alpha]_D^{20}$ –33.2° (*c* 1, $CHCl_3$); δ_H (300 MHz, $CDCl_3$) 2.31 (s, 6H, 2 × CH_3, Ac), 3.51 (dd, 1H, H-6'a, $J_{5,6a'}$ 6.0 Hz, $J_{6a',6b'}$ 12.1 Hz), 3.75 (m, 1H, H-6'b), 3.77 (s, 3H, 4-OMe), 3.78 (s, 6H, 3-OMe, 5-OMe), 3.85 (m, 1H, H-5'), 4.20 (dd, 2H, H-5", J 10.8 Hz, J 18.3 Hz), 4.33 (s, 2H, CH_2, PhOAc), 4.50 (s, 2H, CH_2, PhOAc), 4.55 (d, 1H, H-4a", J 12.6 Hz), 4.57 (s, 2H, CH_2, PhOAc), 4.58 (s, 2H, CH_2, PhOAc), 4.76 (dd, 2H, CH_2, PhOAc), 4.97 (s, 2H, H-2"), 5.09 (d, 1H, H-4"b), 5.12 (d, 1H, H-1', $J_{1',2'}$ 7.6 Hz), 5.28 (t, 1H, H-4', $J_{4',5'}$ 9.7 Hz), 5.36 (dd, 1H, H-2', $J_{2',3'}$ 9.7 Hz), 5.45 (t, 1H, H-3', $J_{3',4'}$ 9.7 Hz), 5.46 (s, 1H, H-1"), 6.21 (s, 1H, H-2, H-6), 6.31 (d, 1H, H-8'", $J_{7'",8'"}$ 15.9 Hz), 6.73-6.96 (m, 16H, OPh, H-5'"), 7.16-7.27 (m, 12H, OPh, H-6'", H-2'"), 7.68 (d, 1H, H-7'"); δ_C (300 MHz, $CDCl_3$) 20.6 (CH_3, Ac), 56.2 (3-OMe, 5-OMe), 60.9 (4-OMe), 64.4, 64.7, 64.8, 64.9 (5 × CH_2, PhOAc), 63.2, 65.3, 72.1 (C-4", C-5", C-6'), 69.0, 71.8, 72.7, 73.4, 76.0 (C-2', C-3', C-4', C-5', C-2"), 84.9 (C-3"), 95.3 (C-2, C-6), 99.0 (C-1'), 105.3 (C-1"), 114.3, 114.4, 114.5, 114.6 (CH, PhOAc), 117.5 (C-3'"), 121.6, 121.8, 121.9, 122.9, 124.0 (CH, PhOAc, C-2'", C-5'", C-6'"), 129.4, 129.6 (CH, PhOAc), 132.7 (C-1'"), 142.5 (C-3'"), 144.1 (C-4'"), 144.5 (C-7'"), 152.7 (C-1), 153.7 (C-3, C-5), 157.2, 157.3, 157.5 (Cq, PhOAc), 164.7 (C-9'"), 167.5, 167.6, 167.8 (C=O, PhOAc), 168.4, 168.9 (C=O, Ac).

3,4,5-Trimethoxyphenyl 6-*O*-(5-*O*-caffeoyl-β-D-*erythro*-apiofuranosyl)-β- D-glucopyranoside (2)

To a stirred solution of compound **37** (181 mg, 0.13 mmol) in CH_2Cl_2 (2 mL) was added dropwise 1 mL of a 0.01 M K_2CO_3 solution in MeOH. Monitoring the deacylation by TLC-analysis showed that after adding 0.1 mL of the stock solution a new major spot occurred, in which both phenolic acetyl functions are cleaved as indicated by NMR-spectroscopy. After adding the total volume (1 mL) of K_2CO_3 solution TLC-analysis revealed the formation of a low running product. The solution was neutralized with a small amount of acetic acid and the solution was concentrated. The crude product was applied to a column of silica gel and eluted with dichloromethane/methanol (92/8 → 80/20, v/v) to furnish the *title compound* (40 mg, 49%) as white amorphous solid; [Found: C, 54.6; H, 5.5 $C_{29}H_{36}O_{16}$ requires C, 54.73; H, 5.66%]; R_f (12% MeOH/CH_2Cl_2) 0.30; *m/z* 663.0 $(M+Na)^+$; δ_H (600 MHz, CD_3OD) 3.41 (t, 1H, H-4', $J_{4',5'}$ 9.6 Hz), 3.44 (dd, 1H, H-2', $J_{2',3'}$ 9.6 Hz), 3.47 (t, 1H, H-3', $J_{3',4'}$ 9.6 Hz), 3.60 (m, 1H, H-6'b), 3.65 (s, 3H, 4-OMe), 3.68 (m, 1H, H-5'), 3.80 (s, 6H, 3-OMe, 5-OMe), 3.82 (d, 1H, H-4a, $J_{4a",4b"}$ Hz), 3.98 (d, 1H, H-2", $J_{1",2"}$ 2.1 Hz), 4.05 (d, 1H, H-4"a), 4.12 (dd, 1H, H-6'a, $J_{6'a,6'b'}$ 10.5 Hz, $J_{6'a,5'}$ 1.3 Hz), 4.25 (AB, 2H, H-5"), 4.99 (d, 1H, H-1', $J_{1',2'}$ 7.3 Hz), 5.01 (d, 1H, H-1", $J_{1",2"}$ 2.1 Hz), 6.33 (d, 1H, H-8'", $J_{7'",8'"}$ 15.9 Hz), 6.45 (s, 1H, H-2, H-6), 6.86 (d, 1H, H-5'", $J_{5'",6'"}$ 8.1 Hz), 7.06 (dd, 1H, H-6'"), 7.20 (d, 1H, H-2'", $J_{7'",8'"}$ 15.9 Hz), 7.70 (d, 1H, H-7'"); δ_C (600 MHz, CD_3OD) 55.5 (3-OMe, 5-OMe), 59.6 (4-OMe), 66.7 (C-5"), 67.2 (C-6'), 70.2 (C-4'), 73.4 (C-2'), 73.6 (C-4"), 75.6 (C-5'), 76.5 (C-2"), 76.9 (C-3'), 79.0 (C-3"), 95.3 (C-2, C-6), 101.4 (C-1'), 109.3 (C-1"), 114.0 (C-8'"), 114.5 (C-2'"), 115.4 (C-5'"), 122.0 (C-6'"), 127.1 (C-1'"), 133.5 (C-4), 145.3 (C-3'"), 145.3 (C-7'"), 148.0 (C-4'"), 153.6 (C-3, C-5), 154.2 (C-1), 166.5 (C-9'"); $[\alpha]_D^{20}$ -74° (c 1.0, MeOH). Lit.[3] $[\alpha]_D^{26}$ –70.3° (c 0.8, MeOH).

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