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Synthesis of a benzyl-protected analog of arenarioside, a trisaccharide phenylpropanoid glycoside

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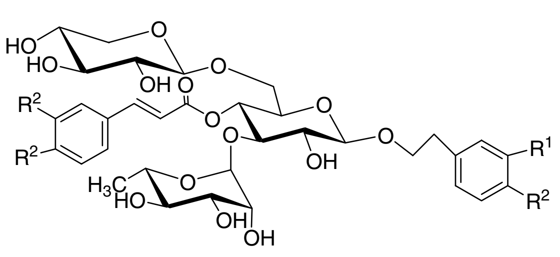
Abstract—A benzyl-protected analog of the phenylpropanoid glycoside arenarioside, (4-benzyloxyphenyl)ethyl α-L-rhamnopyranosyl-(1→3)-4-*O*-[(*E*)-3,4-di-*O*-benzyl-caffeoyl]-[β-D-xylopyranosyl-(1→6)]-β-D-glucopyranoside (**22**), was synthesized through two different routes from D-glucose. This is the first approach on the synthesis of a trisaccharide phenylpropanoid glycoside, although the benzyl-protecting group in the backbone of the arenarioside analog could not be removed by conventional debenzylation procedures.

Keywords: Phenylpropanoid glycosides; Arenarioside analog; Synthesis

1. Introduction

Phenylpropanoid glycosides are an interesting group of natural products that exist widely in herbal plants, and most of them possess strong biological activities. (3,4-Dihydroxylphenyl)ethyl α-L-rhamnopyranosyl-(1→3)-[β-D-xylopyranosyl-(1→6)]-4-*O*-caffeoyl-β-D-glucopyranoside (**1**) was first extracted from *Orobancbe arenaria* and named 'arenarioside' by Andary et al. in 1985.[1] It has also been found in other plant species such as *Jasminum nudiflorum*,[2] *Ballota nigra*,[3] *Scrophularia nodosa*,[4] and *Verbascum sinaiticum*.[5] This natural product has been shown to exhibit extensive bioactivities and pharmaceutical activities, such as inhibiting atherosclerosis development,[6] antioxidant activity,[7] antitumor activity,[8] xanthine oxidase inhibitory actvity,[9] and antibacterial activity.[10] However, the low content of arenarioside in each plant species has limited the further investigation of these activities and the chemical synthesis of phenylpropanoid glycosides is thus an important target.

Recently, several monosaccharide phenylpropanoid glycosides,[11] such as grayanoside A, isoacteoside and syringalide B, and disaccharide phenylpropanoid glycosides,[12] such as verbascoside, conandroside, and eutigoside A, were synthesized. To the best of our knowledge, no synthetic approach toward phenylpropanoid glycoside bearing a trisaccharide residue has been reported so far. As part of our effort to synthesize trisaccharide phenylpropanoid glycosides,[13] we herein report our results toward the synthesis of an arenarioside analog, (4-hydroxylphenyl)ethyl α-L-rhamnopyranosyl-(1→3)-[β-D-xylopyranosyl-(1→6)]-4-*O*-caffeoyl-β-D-glucopyranoside (**2**).



	R¹	R²
1	OH	OH
2	H	OH

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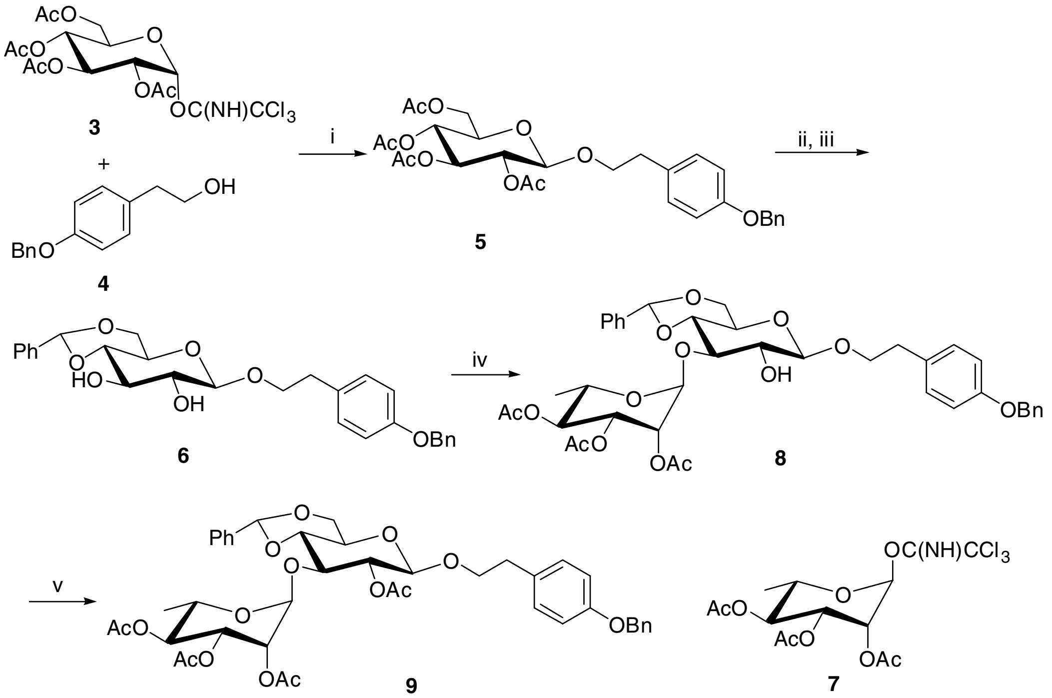
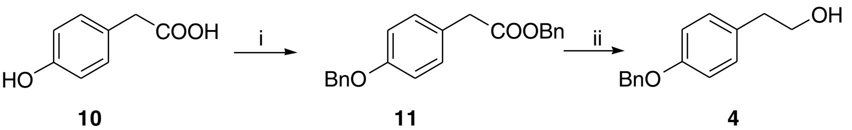
2. Results and discussion

Our strategy for the total synthesis of the arenarioside analog **2** involved a key disaccharide intermediate (4-benzyloxyphenyl)ethyl α-L-rhamnopyranosyl (1→3)-2-*O*-acetyl-4,6-*O*-benzylidene-β-D-glucopyranoside (**9**) (Scheme 1). Previously, we demonstrated that the rhamnose donor **7** reacted with 4,6-*O*-benzylidene-β-D-glucopyranoside in the presence of a catalytic amount of TMSOTf in CH_2Cl_2 at −35 °C to afford (1→3)-linked disaccharides in good yields with excellent regio- and stereoselectivity.[14] As an application of this methodology, an approach to the intermediate **9** was designed (Scheme 1). 2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl trichloroacetimidate (**3**) was prepared from D-glucose in three steps according to a literature method (76% overall yield).[15] (4-Benzyloxyphenyl)ethanol (**4**), prepared from (4-hydroxylphenyl) acetic acid (**10**) by an esterification/reduction sequence (Scheme 2), was glycosylated with **3** in the presence of a catalytic amount of trimethylsilyl triflate (TMSOTf) at −35 °C to give the β-linked monosaccharide derivative **5** as the major product in 62% yield. Deacetylation of **5**, followed by treatment with benzaldehyde dimethyl acetal under the catalysis of TsOH, gave diol **6** (82% overall yield). Glycosylation of **6** with 2,3,4-tri-*O*-acetyl-α-L-rhamnopyranosyl trichloroacetimidate **7**[14] in the presence of a catalytic amount of TMSOTf in CH_2Cl_2 at −35 °C resulted in the β-(1→3)-linked disaccharide derivative **8** (68% yield), which was acetylated with acetic anhydride to give the key intermediate **9** in 92% yield. Thus, the synthesis of **9** was achieved from D-glucose in 24% overall yield and eight steps.

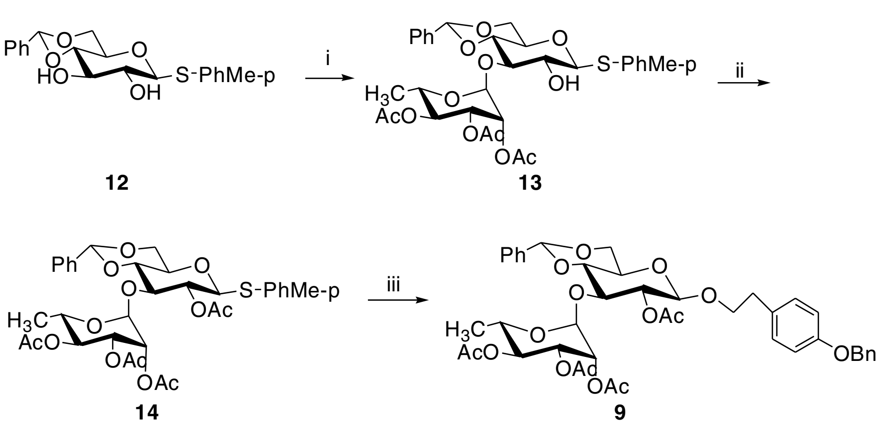
We also got the intermediate **9** through another route as outlined in Scheme 3. Compound **12** was prepared from D-glucose by sequential acetylation (93% yield), *p*-methylphenyl thioglycosidation (94.3%), deacetylation, and benzylidene acetalation (88% over two steps) according to the published process.[16] It was then glycosylated with **7** using TMSOTf as a catalyst to give the β-(1→3)-linked disaccharide **13** in 85% yield. Treating **13** with acetic anhydride in pyridine afforded **14** in 92% yield. Glycosylation of **14** with **4** in the presence of NIS and a catalytic amount of TMSOTf in CH_2Cl_2 at



Scheme 1. Reagents and conditions: (i) TMSOTf, 4 Å Ms, CH_2Cl_2, −35 °C, 62%; (ii) MeONa, MeOH; (iii) $PhCH(OCH_3)_2$, *p*-TsOH, MeCN, 82% over two steps; (iv) **7**, TMSOTf, 4 Å Ms, CH_2Cl_2, −35 °C, 68%; (v) Ac_2O, pyridine, 92%.



Scheme 2. Reagents and conditions: (i) BnBr, acetone, K_2CO_3, reflux, 92%; (ii) $LiAlH_4$, THF, 0 °C–reflux, 85%.



Scheme 3. Reagents and conditions: (i) **7**, TMSOTf, 4 Å Ms, CH_2Cl_2, −35 °C, 85%; (ii) Ac_2O, pyridine, 92%; (iii) **4**, NIS, TMSOTf, 4 Å Ms, CH_2Cl_2, −40 → −20 °C, 67%.

−40 °C gave **9** in 67% yield. Thus, intermediate **9** was prepared from D-glucose in 41% overall yield after seven steps.

With the key intermediate **9** in our hand, we began to construct the backbone of the arenarioside analog **2**. As shown in Scheme 4, removing the benzylidene group of **9** using 80% acetic acid gave diol **15** in 89% yield. The primary OH group of **15** was selectively protected with *tert*-butyldimethylsilyl chloride (TBDMSCl) to give **16** in 97% yield. The coupling of 3,4-di-*O*-benzylcoffeic acid **17**[17] with **16** in the presence of *N*,*N*-dicyclohexylcarbodiimide (DCC) and 4-dimethylaminopyridine (DMAP) afforded ester **18** in 94% yield. The TBDMS group of **18** was removed using 3 M HCl–THF to give alcohol **19** in 89% yield. Glycosylation of **19** with 2,3,4-tri-*O*-acetyl-α-D-xylopyranosyl trichloroacetimidate (**20**) in the presence of a catalytic amount of TMSOTf gave the β-(1→6)-linked trisaccharide phenylpropanoid glycoside **21** in 85% yield. Deacetylation of **21** with a saturated solution of NH_3 in MeOH at 13 °C provided the benzyl protected target molecule **22** in 58% yield.

In the last step, catalytic hydrogenation with 1,4-cyclohexadiene/Pd–C according to Kawada et al.[12c,d] was employed to remove the benzyl-protecting groups of **22**. We screened the amount of 1,4-cyclohexadiene and 5% Pd/C catalyst at 40 °C in 1:1 EtOH–DMF. Unfortunately, due to the poor chemical selectivity of this procedure, we only obtained a complex mixture, which was composed of the target molecule **2** (~5%) and its derivatives bearing one and two benzyl groups as well as the C=C bond hydrogenation products as indicated by the HPLC/MS analysis. We also tried the Li/NH_3 debenzylation procedure, but this also failed.

In summary, we have synthesized a benzyl protected derivative of the phenylpropanoid glycoside arenarioside, (4-benzyloxyphenyl)ethyl α-L-rhamnopyranosyl-(1→3)-4-*O*-[(*E*)-3,4-di-*O*-benzyl]caffeoyl-[β-D-xylopyranosyl-(1→6)]-β-D-glucopyranoside (**22**), through two different routes. This is the first approach on the synthesis of a trisaccharide phenylpropanoid glycoside, although the benzyl-protecting groups in the backbone of this arenarioside analog could not be removed by conventional debenzylation procedures. Further work is in progress to complete the total synthesis of **2** using other protecting groups.

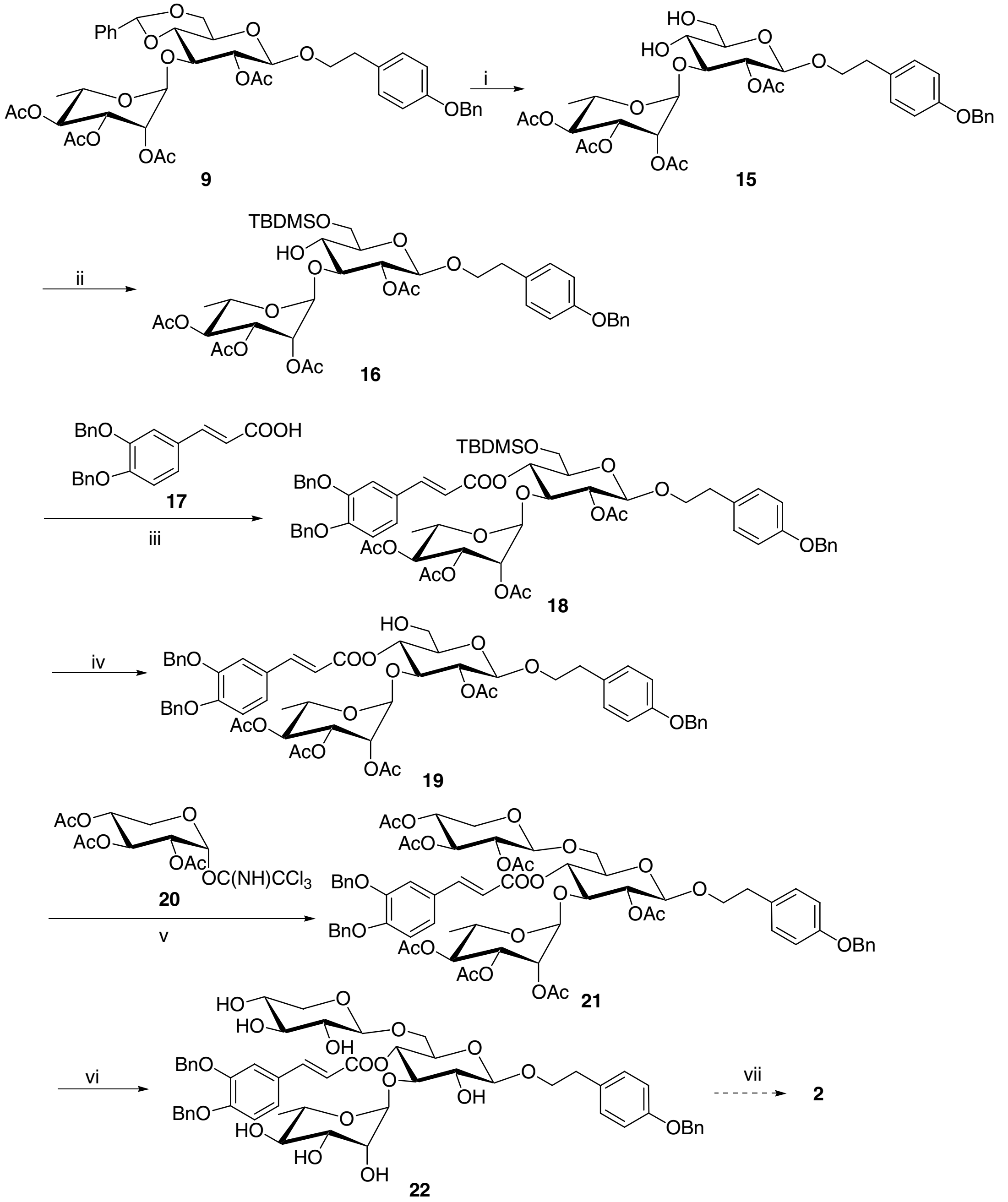
3. Experimental

3.1. General methods

^1H NMR, ^{13}C NMR, ^1H–^1H COSY, and HMQC spectra were recorded with a Bruker AVANCE DMX 500 spectrometer. Mass spectra were recorded on a Bruker Esquire 3000 Plus mass spectrometer through electron spray ionization. HRMS data were recorded with a BRUKER DALTONICS APEX III mass spectrometer in ESI mode. Optical rotations were measured at 20 °C and 589 nm in a PERKIN–ELMER 341 polarimeter. Elemental analyses were performed on a Carlo Erba 1110 instrument. The reactions were monitored by TLC on Silica Gel GF254. Detection was done by both UV light and charring with 20% concd H_2SO_4 in EtOH, and heating. Column chromatography was performed on Silica Gel H.

3.2. (4-Benzyloxyphenyl)ethanol (4)

To a soln of (4-hydroxyphenyl)acetic acid (**10**) (1.52 g, 10.0 mmol) in acetone (60 mL) were added benzyl bromide (2.8 mL, 30 mmol) and anhyd K_2CO_3 (4.2 g, 30 mmol). The reaction mixture was refluxed for 10 h, and then filtered over a short pad of silica gel and concentrated. The residue was subjected to chromatography on a silica gel column with 20:1 hexane–EtOAc to give **11** (3.06 g, 92.2%) as a white solid. To a suspension of $LiAlH_4$ (2.28 g, 60 mmol) in THF (45 mL) at 0 °C under N_2 was added dropwise a soln of **11** (4.98 g, 15 mmol) in



Scheme 4. Reagents and conditions: (i) 80% AcOH/water, 80 °C, 89%; (ii) TBDMSCl, DMAP, CH_2Cl_2, 97%; (iii) DCC, DMAP, CH_2Cl_2, 0 °C, 94%; (iv) 3 M HCl, THF, 89%; (v) TMSOTf, 4 Å Ms, CH_2Cl_2, −35 °C, 85%; (vi) NH_3/MeOH (saturated), 13 °C, 58%; (vii) 1,4-cyclohexadiene, 5% Pd–C, DMF–EtOH.

THF. The mixture was refluxed for 4 h, and then quenched by dropwise addition of MeOH, filtered over a short pad of silica gel, and diluted with EtOAc. The organic layer was dried over $MgSO_4$ and concentrated under diminished pressure. Silica gel column chromatography (5:1 hexane–EtOAc) of the residual oil afforded **4** (2.89 g, 85%) as a white solid. ^1H NMR (500 MHz, $CDCl_3$): δ 7.43–6.92 (9H, ArH), 5.05 (2H, s, $PhCH_2O$), 3.83 (2H, t, $PhCH_2CH_2O$), 2.82 (2H, t, $PhCH_2CH_2O$). ^{13}C NMR (125 MHz, $CDCl_3$): δ 157.6, 137.2 (ArC), 131.0, 130.1, 128.7, 128.1, 127.6, and 115.1 (ArCH), 70.1 ($PhCH_2O$), 63.8 ($PhCH_2CH_2$), 38.4 ($PhCH_2CH_2$). ESIMS: *m*/*z* 251 ($[M+Na]^+$).

3.3. (4-Benzyloxyphenyl)ethyl 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranoside (5)

To a mixture of **4** (0.57 g, 2.5 mmol), **3** (1.85 g, 3.75 mmol), and 4 Å molecular sieves (1.0 g) in anhyd CH_2Cl_2 (30 mL) was added trimethylsilyl triflate

(0.25 mmol) at −35 °C under N_2. The reaction mixture was stirred under the same conditions for 2 h, and then was neutralized with Et_3N. The mixture was filtered over a short pad of silica gel and concentrated. The residue was subjected to chromatography on a silica gel column (3:1 hexane–EtOAc) to give **5** (0.87 g, 62%) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.31–6.78 (9H, ArH), 5.12–5.08 (1H, t, J 9.5 Hz), 5.00–4.96 (1H, t, J 9.5 Hz), 4.91–4.88 (3H, m, $PhCH_2O$ and H-2 Glc), 4.40 (1H, d, $J_{1,2}$ 8.0 Hz), 4.18–4.16 (1H, m, $PhCH_2CH_2O$), 4.03–3.96 (2H, m, H-6 Glc and $PhCH_2CH_2O$), 3.58–3.52 (2H, m, H-5 Glc and H-6 Glc), 2.70–2.69 (2H, m, $PhCH_2CH_2O$), 1.94, 1.89, 1.87, and 1.76 (12H, 4s, CH_3CO–). ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.1, 169.7, 169.0, and 168.8 (–$COCH_3$), 157.1, 137.0 (ArC), 130.6, 129.7, 128.3, 127.6, 127.1, 114.5 (ArC), 100.3 (C-1 Glc), 34.7 ($PhCH_2CH_2O$), 20.3, 20.2 (CH_3CO–), other signals at δ 72.5, 71.4, 70.9, 70.4, 69.5, 68.2, and 61.7. ESIMS: *m*/*z* 581 ([M+Na]$^+$).

3.4. (4-Benzyloxyphenyl)ethyl 4,6-*O*-benzylidene-β-D-glucopyranoside (6)

To a soln of **5** (11.16 g, 20 mmol) in MeOH (100 mL) was added $NaOCH_3$ (0.54 g, 10 mmol). After stirring for 5 h, the deacetylation was completed (TLC). The reaction was neutralized with Dowex AG 50W X8 (H$^+$ form), filtered, and concentrated under diminished pressure. The resulting solid was repeatedly diluted with dry toluene and concentrated under diminished pressure. The residue was dissolved in MeCN (100 mL). To the soln were added benzaldehyde dimethyl acetal (6.9 mL, 45.6 mmol) and *p*-toluenesulfonic acid (0.38 g). After stirring for 30 min, the reaction mixture was neutralized with Et_3N and concentrated under diminished pressure. The crude product was crystallized from hexane–EtOAc to give pure **6** (7.84 g, 82%) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.52–6.93 (14H, ArH), 5.51 (1H, s, benzylidene), 5.05 (2H, s, $PhCH_2O$), 4.38 (1H, d, $J_{1,2}$ 8.0 Hz, H-1 Glu), 4.34–4.31 (1H, dd, J 5.0, 10.5 Hz), 4.12–4.07 (1H, m), 3.78–3.70 (3H, m), 3.55–3.46 (3H, m), 3.43–3.38 (1H, m), 3.25 (1H, br, OH), 2.93–2.89 (2H, m). ^{13}C NMR (125, MHz, $CDCl_3$): δ 157.7, 137.3, 137.2 (ArC), 130.6, 130.1, 129.4, 128.8, 128.5, 128.1, 127.7, 126.5, 115.1 (ArCH), 103.5 (benzylidene CH), 102.0 (C-1 Glc), 35.4 ($PhCH_2CH_2O$), other signals at δ 80.7, 74.7, 73.2, 71.4, 70.2, 68.8, 66.6. ESIMS: *m*/*z* 501 ([M+Na]$^+$).

3.5. (4-Benzyloxyphenyl)ethyl (2,3,4-tri-*O*-acetyl-α-L-rhamnopyranosyl)-(1→3) 4,6-*O*-benzylidene-β-D-glucopyranoside (8)

To a mixture of **6** (4.1 g, 8.2 mmol), **7** (4.41 g, 10.0 mmol), and 4 Å molecular sieves (2.0 g) in anhyd CH_2Cl_2 (60 mL) was added trimethylsilyl triflate (20 μL) at −35 °C under N_2. The mixture was stirred for 2 h, and then was neutralized with Et_3N. The mixture was filtered over a short pad of silica gel and concentrated. The residue was subjected to chromatography on a silica gel column with 4:1→2:1 hexane–EtOAc to give **8** (4.29 g, 68%) as a colorless oil. $[\alpha]_D$ −74.5 (*c* 1.38, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.48–6.92 (14H, ArH), 5.56 (1H, s, benzylidene), 5.34 (1H, s, H-2 Rha), 5.29 (1H, dd, $J_{2,3}$ 3.0 Hz, $J_{3,4}$ 10.0 Hz, H-3 Rha), 5.18 (1H, s, H-1 Rha), 5.06 (2H, s, $PhCH_2O$), 4.98 (1H, dd, t, $J_{3,4} = J_{4,5}$ 10.0 Hz, H-4 Rha), 4.35 (1H, m, H-6b Glc), 4.32 (1H, d, $J_{1,2}$ 8.0 Hz, H-1 Glc), 4.21–4.12 (2H, m, H-5 Rha and $PhCH_2CH_2O$), 3.86 (1H, t, $J_{2,3} = J_{3,4}$ 9.0 Hz, H-3 Glc), 3.80 (1H, t, $J_{5,6a} = J_{6a,6b}$ 10.5 Hz, H-6a Glc), 3.70–3.55 (3H, m, H-2 Glc, H-4 Glc and $PhCH_2CH_2O$), 3.45 (1H, m, H-5 Glc), 2.87 (2H, m, $PhCH_2CH_2O$), 2.20 (1H, br, OH), 2.13, 1.98, 1.96 (9H, 3 × s, Ac), 0.85 (3H, d, $J_{5,6}$ 6.0 Hz, H-6 Rha). ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.4 and 170. 1 (–$COCH_3$), 157.6, 137.3, 137.2 (ArC), 130.6, 130.0, 129.2, 128.7, 128.2, 128.1, 127.6, 126.4, and 115.1 (ArC), 103.7 (PhCH, benzylidene), 101.7 (C-1 Glc), 97.8 (C-1 Rha), 35.3 ($PhCH_2CH_2O$), 21.10, 20.94, and 20.92 (–$COCH_3$), 16.9 (C-6 Rha), other signals at δ 79.0, 76.3, 75.7, 71.4, 71.3, 70.2, 69.8, 69.4, 68.8, 66.9, and 66.1. ESIMS: *m*/*z* 773 ([M+Na]$^+$).

3.6. (4-Benzyloxyphenyl)ethyl (2,3,4-tri-*O*-acetyl-α-L-rhamnopyranosyl)-(1→3)-2-*O*-acetyl-4,6-*O*-benzylidene-β-D-glucopyranoside (9): Method A

To a soln of pyridine and Ac_2O (2:1, 90 mL) was added **8** (7.65 g, 10.0 mmol). The mixture was stirred at room temperature for 12 h, and then concentrated under diminished pressure. The residue was applied to a silica gel column with 4:1 hexane–EtOAc to give **9** (7.46 g, 92%) as a white solid. $[\alpha]_D$ −72.0 (*c* 1.06, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.48–6.91 (14H, ArH), 5.52 (1H, s, benzylidene), 5.31 (1H, dd, $J_{2,3}$ 3.5 Hz, $J_{3,4}$ 10.0 Hz, H-3 Rha), 5.07–5.04 (3H, m, H-2 Glc, $PhCH_2O$–), 4.99 (1H, dd, $J_{1,2}$ 1.5 Hz, $J_{2,3}$ 3.5 Hz, H-2 Rha), 4.94 (1H, t, $J_{3,4} = J_{4,5}$ 10.0 Hz, H-4 Rha), 4.88 (1H, d, $J_{1,2}$ 1.5 Hz, H-1 Rha), 4.58 (1H, d, $J_{1,2}$ 7.5 Hz, H-1 Glc), 4.35 (1H, dd, $J_{5,6b}$ 5.0 Hz, $J_{6a,6b}$ 10.5 Hz, H-6b Glc), 4.07 (2H, m, H-5 Rha, $PhCH_2CH_2O$), 3.87 (1H, t, $J_{2,3} = J_{3,4}$ 9.5 Hz, H-3 Glc), 3.78 (1H, t, $J_{5,6a} = J_{6a,6b}$ 10.5 Hz, H-6a Glc), 3.64 (2H, m, H-4 Glc, $PhCH_2CH_2O$), 3.47 (1H, m, H-5 Glc), 2.83 (2H, m, $PhCH_2CH_2O$), 2.11, 1.99, 1.97 (12H, 4 × s, Ac), 0.67 (3H, d, $J_{5,6}$ 6.5 Hz, H-6 Rha). ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.3, 170.2, 170.1, and 169.7 (–$COCH_3$), 137.3 (ArC), 131.1, 130.3, 129.4, 128.8, 128.4, 128.2, 127.7, 126.6, and 115.0 (ArC), 102.2 (PhCH, benzylidene), 101.5 (C-1 Glc), 97.7 (C-1 Rha), 35.4 ($PhCH_2CH_2O$), 21.2, 21.0, and 20.9 (–$COCH_3$), 16.8 (C-6 Rha), other signals at δ 79.3, 77.1, 73.6, 71.6, 70.9, 70.8, 70.3, 69.0, 68.7, 66.8, and 66.5. HRESIMS: calcd for $C_{42}H_{48}O_{15}Na$ ($[M+Na]^+$): 815.2891. Found: 815.2888. Anal. Calcd for $C_{42}H_{48}O_{15}$: C, 63.63; H, 6.10. Found: C, 63.70; H, 5.96.

3.7. *p*-Methylphenyl (2,3,4-tri-*O*-acetyl-α-L-rhamnopyranosyl)-(1→3)-4,6-*O*-benzylidene-1-thio-β-D-glucopyranoside (13)

To a mixture of **12** (3.08 g, 8.2 mmol), **7** (4.41 g, 10.0 mmol), and 4 Å molecular sieves (2.0 g) in anhyd CH_2Cl_2 (60 mL) was added trimethylsilyl triflate (20 μL) at −35 °C under N_2. The reaction mixture was stirred for 2 h, and then was neutralized with Et_3N. The mixture was filtered over a short pad of silica gel and concentrated. The residue was subjected to chromatography on a silica gel column with 4:1→2:1 hexane–EtOAc to give **13** (5.42 g, 85%) as a colorless oil. $[\alpha]_D$ −99.1 (*c* 0.98, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ 7.46–7.16 (9H, ArH), 5.54 (1H, s, benzylidene), 5.32 (1H, dd, $J_{1,2}$ 1.5 Hz, $J_{2,3}$ 3.5 Hz, H-2 Rha), 5.24 (1H, dd, $J_{2,3}$ 3.5 Hz, $J_{3,4}$ 10.0 Hz, H-3 Rha), 5.21 (1H, d, $J_{1,2}$ 5 Hz, H-1 Rha), 4.97 (1H, t, $J_{3,4} = J_{4,5}$ 10.0 Hz, H-4 Rha), 4.50 (1H, d, $J_{1,2}$ 9.5 Hz, H-1 Glu), 4.39 (1H, dd, $J_{5,6b}$ 4.5 Hz, $J_{6a,6b}$ 0.5 Hz, H-6b Glc), 4.18 (1H, m, H-5 Rha), 3.90 (1H, t, $J_{2,3} = J_{3,4}$ 8.5 Hz, H-3 Glc), 3.78 (1H, t, $J_{4,5} = J_{5,6a}$ 10.0 Hz, H-5 Glc), 3.57–3.46 (3H, m, H-2 Glc, H-4 Glc, H-6a Glc), 2.62 (1H, s, –OH), 2.38 (3H, s, CH_3PhS), 2.13, 1.97, 1.95 (9H, 3 × s, Ac), 0.83 (3H, d, $J_{5,6}$ 6.0 Hz, H-6 Rha). ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.5 and 170.1 (–$COCH_3$), 139.3, 137.4 (ArC), 134.1, 130.3, 129.3, 128.3, and 126.5 (ArC), 101.9 (Ph*C*H, benzylidene), 97.9 (C-1 Rha), 89.4 (C-1 Glc), 21.5, 21.2, and 21.0 (3 × –$COCH_3$), 17.0 (C-6 Rha), other signals at δ 78.9, 77.8, 73.6, 71.34, 71.29, 69.9, 69.5, 68.9, and 66.3. ESIMS: *m*/*z* 669 ($[M+Na]^+$).

3.8. *p*-Methylphenyl (2,3,4-tri-*O*-acetyl-α-L-rhamnopyranosyl)-(1→3)-4,6-*O*-benzylidene-2-*O*-acetyl-1-thio-β-D-glucopyranoside (14)

Compound **13** (6.46 g, 10.0 mmol) was dissolved in a mixture of pyridine and Ac_2O (2:1, 90 mL). After stirring for 12 h, the mixture was concentrated under diminished pressure. The residue was then eluted from a silica gel column (4:1 hexane–EtOAc) to give **14** (6.36 g, 92%) as a white solid. $[\alpha]_D$ −56.0 (*c* 0.6, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ 7.47–7.14 (9H, ArH), 5.54 (1H, s, benzylidene), 5.28 (1H, dd, $J_{2,3}$ 3.5 Hz, $J_{3,4}$ 10.0 Hz, H-3 Rha), 5.04 (1H, m, H-2 Glc), 4.91 (3H, m, H-4 Rha, H-2 Rha, H-1 Rha), 4.63 (1H, d, $J_{1,2}$ 10.0 Hz, H-1 Glc), 4.39 (1H, dd, $J_{5,6b}$ 5.0 Hz, $J_{6a,6b}$ 10.5 Hz, H-6b Glc), 4.06 (1H, m, H-5 Rha), 3.92 (1H, t, $J_{2,3} = J_{3,4}$ 9.5 Hz, H-3 Glc), 3.80 (1H, t, $J_{5,6a} = J_{6a,6b}$ 10.5 Hz, H-6a Glc), 3.65 (1H, t, $J_{3,4} = J_{4,5}$ 9.5 Hz, H-4 Glc), 3.51 (1H, m, H-5 Glc), 2.37 (3H, s, $SPhCH_3$), 2.18, 2.11, 1.99, 1.96 (12H, 4 × s, Ac), 0.63 (3H, d, $J_{5,6}$ 6.0 Hz, H-6 Rha). ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.24, 170.17, 170.1, and 169.79 (–$COCH_3$), 138.8, 137.2 (ArC), 133.5, 130.0, 129.5, 128.6, 128.3, and 126.7 (ArCH), 102.3 (Ph*C*H, benzylidene), 97.8 (C-1 Rha), 87.5 (C-1, Glc), 29.9 ($SPhCH_3$), 21.4, 21.13, 21.12, and 20.96 (4 × –$COCH_3$), 16.7 (C-6 Rha), other signals at δ 79.1, 78.6, 72.4, 71.6, 71.1, 70.9, 68.8, 68.6, and 66.6. HRESIMS: calcd for $C_{34}H_{40}O_{13}SNa$ ($[M+Na]^+$): 711.2087. Found: 711.2089.

3.9. (4-Benzyloxyphenyl)ethyl (2,3,4-tri-*O*-acetyl-α-L-rhamnopyranosyl)-(1→3)-2-*O*-acetyl-4,6-*O*-benzylidene-β-D-glucopyranoside (9): Method B

To a mixture of **14** (6.88 g, 10 mmol), **4** (4.56 g, 20 mmol), and 4 Å molecular sieves (5.0 g) in anhyd CH_2Cl_2 (150 mL) were added NIS (5.63 g, 25 mmol) and trimethylsilyl triflate (20 μL) at −40 °C under N_2. The reaction mixture was stirred for 2 h and then neutralized with Et_3N. The mixture was filtered over a short pad of silica gel, washed in turn with a saturated $Na_2S_2O_3$ soln, a saturated NaCl soln, and then dried and concentrated. The residue was subjected to chromatography on a silica gel column with 4:1 → 2:1 hexane–EtOAc to give **9** (5.3 g, 67%) as a colorless oil.

3.10. (4-Benzyloxyphenyl)ethyl (2,3,4-tri-*O*-acetyl-α-L-rhamnopyranosyl)-(1→3)-2-*O*-acetyl-β-D-glucopyranoside (15)

Compound **9** (1.58 g, 2.0 mmol) was dissolved in 4:1 AcOH–water (30 mL). The soln was stirred at 80 °C for 2 h. Toluene was added and the soln was concentrated under diminished pressure. The residue was applied to a silica gel column with 3:2–1:1 hexane–EtOAc to give **15** (1.25 g, 89%) as a colorless oil. $[\alpha]_D$ −28.0 (*c* 1.02, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ 7.44–6.89 (9H, ArH), 5.23–5.20 (1H, m, H-3 Rha), 5.12–5.09 (2H, m, H-2 Rha and H-4 Rha), 5.04 (2H, s, $PhCH_2O$), 4.98–4.94 (1H, t, $J_{1,2}$ 8.5 Hz, $J_{2,3}$ 9.0 Hz), 4.88 (1H, s, H-1 Rha), 4.43 (1H, d, $J_{1,2}$ 8.5 Hz, H-1 Glc), 4.15–4.12 (1H, m, H-5 Rha), 4.06–4.03 (1H, m, $PhCH_2CH_2O$), 3.92 (1H, br, OH), 3.82–3.80 (1H, m, H-6 Glc), 3.65–3.54 (4H, m, H-3 Glc, H-4 Glc, H-6 Glc and $PhCH_2CH_2O$), 3.36–3.32 (1H, m, H-5 Glc), 2.82–2.81 (2H, m, $PhCH_2CH_2O$), 2.15, 2.06, 2.03, and 1.99 (12H, 4 × s, Ac), 1.25 (3H, d, $J_{5,6}$ 6.0 Hz, H-6 Rha). ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.3, 170.2, 169.9, and 169.7 (–$COCH_3$), 157.6 and 137.4 (aromatic C), 131.1, 130.2, 128.8, 128.1, 127.6, 115.0 (aromatic C), 100.9 (C-1 Glu), 99.1 (C-1 Rha), 35.4 ($PhCH_2CH_2O$), 21.1, 20.97, 20.87, and 20.83 (–$COCH_3$), 17.7 (C-6 Rha), other signals at δ 85.2, 75.4, 71.6, 70.9, 70.2, 70.2, 70.1, 68.8, 67.9, and 62.5. HRESIMS: calcd for $C_{35}H_{44}O_{15}Na$ ([M+Na]$^+$), 727.2572. Found: 727.2549.

3.11. (4-Benzyloxyphenyl)ethyl (2,3,4-tri-*O*-acetyl-α-L-rhamnopyranosyl)-(1→3)-2-*O*-acetyl-6-*O*-*tert*-butyldimethylsilyl-β-D-glucopyranoside (16)

To a soln of **15** (1.41 g, 2.0 mmol) in CH_2Cl_2 (20 mL) were added DMAP (0.36 g, 2.94 mmol) and TBDMSCl (0.46 g, 2.94 mmol). The soln was stirred for 3.5 h. After concn of the solution, the residue was applied to a column of silica gel (5:2 hexane–EtOAc) to give **16** (1.58 g, 97%) as a colorless oil. $[\alpha]_D$ −34.0 (*c* 1.00, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.44–6.88 (9H, ArH), 5.26 (1H, dd, $J_{2,3}$ 3.5 Hz, $J_{3,4}$ 10.0 Hz, H-3 Rha), 5.09–5.06 (2H, m, H-2 Rha and H-4 Rha), 5.04 (2H, s, 4-$PhCH_2O$), 4.94 (1H, t, $J_{1,2} = J_{2,3}$ 8.5 Hz, H-2 Glc), 4.89 (1H, s, H-1 Rha), 4.35 (1H, d, $J_{1,2}$ 8.5 Hz, H-1 Glc), 4.24–4.21 (1H, m, H-5 Rha), 4.04–4.09 (1H, m, $PhCH_2CH_2O$), 3.92–3.86 (2H, m, H-6 Glc and OH), 3.64–3.57 (4H, m, H-3 Glc, H-4 Glc, H-6 Glc and $PhCH_2CH_2O$), 3.32–3.31 (1H, m, H-5 Glc), 2.82–2.79 (2H, m, $PhCH_2CH_2O$), 2.14, 2.05, 2.02, and 1.99 (12H, 4 × s, Ac), 1.21 (3H, d, $J_{5,6}$ 6.0 Hz, H-6 Rha), 0.91 (9H, s, Me_3C–), 0.11 (6H, 2 × s, Me_2SiBu–). ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.3, 170.3, 169.9, and 169.8 (carbonyl), 157.5, 137.4 (ArC), 131.2, 130.2, 128.8, 128.1, 127.7, 114.9 (ArC), 100.7 (C-1 Glc), 98.8 (C-1 Rha), 35.4 ($PhCH_2CH_2O$), 26.1 (Me_3C–), 21.2, 21.1, and 20.9 (–$COCH_3$), 18.6 (Me_3C–), 17.5 (C-6 Rha), −5.1 and −5.2 (Me_2SiBu–), other signals at δ 84.0, 74.9, 72.0, 71.7, 71.2, 70.5, 70.4, 70.2, 68.1, 67.4, and 64.3. HRESIMS: calcd for $C_{41}H_{58}O_{15}SiNa$ ([M+Na]$^+$), 841.3437. Found: 841.3403. Anal. Calcd for $C_{41}H_{58}O_{15}Si$: C, 60.13; H, 7.14. Found: C, 60.13; H, 7.13.

3.12. (4-Benzyloxyphenyl)ethyl (2,3,4-tri-*O*-acetyl-α-L-rhamnopyranosyl)-(1→3)-2-*O*-acetyl-4-*O*-[(*E*)-3,4-di-*O*-benzyl]caffeoyl-6-*O*-*tert*-butyldimethylsilyl-β-D-glucopyranoside (18)

To a soln of 3,4-di-*O*-benzylcoffeic acid (**17**) (0.88 g, 2.4 mmol) and **16** (1.0 g, 1.22 mmol) were added DCC (0.5 g, 2.4 mmol) and DMAP (0.3 g, 2.4 mmol) at 0 °C. The soln was stirred for 36 h. The mixture was concentrated and applied to a column of silica gel (5:1→2:1 hexane–EtOAc) to give **18** (1.33 g, 94%) as a colorless oil. $[\alpha]_D$ −51.4 (*c* 1.27, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.61 (1H, d, *J* 16.0 Hz, alkene H), 7.44–6.89 (22H, ArH), 6.23 (1H, *J* 16.0 Hz, alkene H), 5.21, 5.18, and 5.05 (6H, 3 × s, $PhCH_2O$), 5.14–5.04 (4H, m, H-4 Glc, H-3 Rha, H-2 Glc and H-2 Rha), 4.94 (1H, t, $J_{3,4} = J_{4,5}$ 10.0 Hz, H-4 Rha), 4.86 (1H, s, H-1 Rha), 4.39 (1H, d, $J_{1,2}$ 8.0 Hz, H-1 Glc), 4.09–4.07 (1H, m, $PhCH_2CH_2O$), 3.90–3.81 (2H, m, H-3 Glc and H-5 Rha), 3.74–3.69 (2H, m, H-6 Glc), 3.63–3.61 (1H, m, $PhCH_2CH_2O$), 3.51–3.49 (1H, m, H-5 Glc), 2.85–2.81 (2H, m, $PhCH_2CH_2O$), 2.10, 2.00, 1.95, and 1.75 (12H, 4 × s, Ac), 1.00 (3H, d, $J_{5,6}$ 6.0 Hz, H-6 Rha), 0.87 (9H, s, Me_3C–), 0.035 and 0.025 (6H, 2 × s, Me_2SiBu–). ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.3, 170.3, 169.7, and 169.7 (carbonyl C), 165.8, 157.5, 151.6, 149.2 (ArC), 146.0 and 115.3 (alkene C), 137.0, 136.8, 131.3, 130.2, 128.9, 128.8, 127.8, 127.7, 127.7, 127.5, 127.4, 127.4, 123.3, 115.0, 114.4, 114.1 (ArC), 100.8 (C-1 Glc), 99.2 (C-1 Rha), 26.1 (Me_3C–), 35.4 ($PhCH_2CH_2O$), 21.1, 21.0, 20.9, and 20.8 (–$COCH_3$), 18.6 (Me_3C–), 17.8 (C-6 Rha), −5.0 and −5.1 (Me_2SiBu–), other signals at δ 81.0, 75.6, 72.8, 71.6, 71.2, 71.1, 70.4, 70.3, 70.2, 68.9, 67.4, and 63.2. HRESIMS: calcd for $C_{64}H_{76}O_{18}SiNa$ ([M+Na]$^+$), 1183.4693. Found: 1183.4640. Anal. Calcd for $C_{64}H_{76}O_{18}Si$: C, 66.19; H, 6.60. Found: C, 66.26; H, 6.54.

3.13. (4-Benzyloxyphenyl)ethyl (2,3,4-tri-*O*-acetyl-α-L-rhamnopyranosyl)-(1→3)-2-*O*-acetyl-4-*O*-[(*E*)-3,4-di-*O*-benzyl]caffeoyl-β-D-glucopyranoside (19)

To a soln of **18** (1.75 g, 1.51 mmol) in THF (20 mL) was added HCl (3 M, 5 mL). After stirring for 3 h, TLC indicated completion, and TEA was added to neutralize the reaction. The reaction mixture was concentrated and applied to a silica gel column with (2:1→1:1) hexane–EtOAc to give **19** (1.41 g, 89%) as a colorless oil. $[\alpha]_D$ −73.4 (*c* 1.29, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.62 (1H, d, *J* 16 Hz, alkene H), 7.44–6.88 (22H, ArH), 6.21 (1H, d, *J* 16 Hz, alkene H), 5.20, 5.17, and 5.04 (6H, 3 × s, $PhCH_2O$), 5.12–5.04 (4H, m, H-4 Glc, H-2 Rha, H-2 Glc and H-3 Rha), 4.96 (1H, t, $J_{3,4} = J_{4,5}$ 9.5 Hz, H-4 Rha), 4.88 (1H, s, H-1 Rha), 4.43 (1H, d, $J_{1,2}$ 8.0 Hz, H-1 Glc), 4.09–4.07 (1H, m, $PhCH_2CH_2O$), 3.94 (1H, t, $J_{2,3} = J_{3,4}$ 9.5 Hz, H-3 Glc), 3.84–3.81 (1H, m, H-5 Rha), 3.70–3.57 (3H, m, H-6 Glc and $PhCH_2CH_2O$), 3.43–3.41 (1H, m, H-5 Glc), 2.83–2.80 (2H, m, $PhCH_2CH_2O$), 2.42–2.40 (1H, m, OH), 2.11, 2.09, 2.00, and 1.84 (12H, 4 × s, $COCH_3$), 1.01 (3H, d, $J_{5,6}$ 6.0 Hz, H-6 Rha). ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.3, 170.3, 169.7, and 169.6 ($C{=}O$), 166.7, 157.6, 151. 8, 149.2 (ArC), 146.8 and 115.0 (alkene C), 137.4, 136.9, 136.7, 131.1, 130.2, 128.8, 128.8, 128.3, 128.1, 127.6, 127.6, 127.5, 127.4, 127.4, 123.5, 114.6, 114.4, and 114.2 (ArC), 100.9 (C-1 Glc), 99.0 (C-1 Rha), 35.3 ($PhCH_2CH_2O$), 21.1, 20.9, 20.9, and 20.8 ($COCH_3$), 17.7 (C-6 Rha), other signals at δ 80.5, 74.7, 72.6, 71.6, 71.1, 71.0, 70.7, 70.4, 70.2, 69.9, 68.8, 67.4, and 61.6. HRESIMS: calcd for $C_{58}H_{62}O_{18}Na$ ([M+Na]$^+$), 1069.3828. Found: 1069.3781. Anal. Calcd for $C_{58}H_{62}O_{18}$: C, 66.53; H, 5.97. Found: C, 66.50; H, 6.14.

3.14. (4-Benzyloxyphenyl)ethyl (2,3,4-tri-*O*-acetyl-α-L-rhamnopyranosyl)-(1→3)-2-*O*-acetyl-4-*O*-[(*E*)-3,4-di-*O*-benzyl]caffeoyl-[(2,3,4-tri-*O*-acetyl-β-D-xylopyranosyl)-(1→6)]-β-D-glucopyranoside (21)

To a mixture of **19** (0.86 g, 8.2 mmol), **20** (4.19 g, 10.0 mmol), and 4 Å molecular sieves (2.0 g) in anhyd CH_2Cl_2 (60 mL) was added trimethylsilyl triflate (20 µL) at −35 °C under N_2. The reaction mixture was stirred under the same conditions for 2 h, and then neutralized with Et_3N. The mixture was filtered over a short pad of silica gel and then concentrated. The residue was chromatographed on a silica gel column (4:1→2:1 hexane–EtOAc) to give **21** (0.91 g, 85%) as a colorless oil. $[\alpha]_D$ −47.6 (*c* 1.04, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.61 (1H, d, *J* 16.0 Hz, alkene H), 7.46–6.90 (22H, m, ArH), 6.21 (1H, d, *J* 16.0 Hz, alkene H), 5.21, 5.19, and 5.05 (6H, 3 × s, PhCH_2O), 5.15–5.09 (2H, m, H-2 Glc and H-2 Rha), 5.03–4.88 (6H, m, H-4 Glc, H-3 Rha, H-4 Rha, H-2 Xyl and HH′-5 Xyl), 4.86 (1H, d, *J* 1.5 Hz, H-1 Rha), 4.52 (1H, d, *J* 7.5 Hz, H-1 Xyl), 4.38 (1H, J 8.0 Hz, H-1 Glc), 4.10–4.06 (2H, m, H-6 Glc and $PhCH_2$CH_2O), 3.89 (1H, t, *J* 9.5 Hz, H-3 Glc), 3.83–3.78 (2H, m, H-3 Xyl and H-5 Rha), 3.63–3.59 (3H, H-4 Xyl, H-5 Glc and $PhCH_2$CH_2O), 3.31 (1H, dd, *J* 9.0, 12.0 Hz, H-6 Glc), 2.84 (2H, t, *J* 6.5 Hz, PhC$H_2$$CH_2$O), 2.10, 2.032, 2.029, 1.99, 1.95, 1.94, and 1.83 (21H, 7 × s, –COCH_3), 1.00 (3H, d, *J* 6.0 Hz, H-6 Rha). ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.0, 169.9, 169.5, and 169.4 (*C*═O), 165.8, 157.4, 151.5, and 149.0 (ArC), 146.2 and 114.8 (alkene C), 137.2, 136.8, 136.6, 131.0, 130.0, 128.6, 128.6, 128.5, 128.1, 127.9, 127.5, 127.4, 127.4, 127.3, 127.2, 127.1, 123.2, 114.7, 114.2, and 113.9 (ArC), 100.8 (C-1 Xyl), 100.6 (C-1 Glc), 98.9 (C-1 Rha), 35.1 (Ph*C*$H_2$$CH_2$O), 20.9, 20.8, 20.7, 20.7, 20.6, and 20.6 (–CO*C*H_3), 17.5 (C-6 Rha), other signals at δ 80.2, 73.9, 72.5, 71.37, 71.36, 71.0, 70.78, 70.75, 70.5, 70.2, 70.0, 69.8, 68.9, 68.6, 68.3, 67.2, and 62.0. HRESIMS: calcd for $C_{69}H_{76}O_{25}Na$ ($[M+Na]^+$), 1327.4568. Found: 1327.4513. Anal. Calcd for $C_{69}H_{76}O_{25}$: C, 63.49; H, 5.87. Found: C, 63.50; H, 5.87.

3.15. (4-Benzyloxyphenyl)ethyl α-L-rhamnopyranosyl-(1→3)-4-*O*-[(*E*)-3,4-di-*O*-benzyl]caffeoyl-[β-D-xylopyranosyl-(1→6)]-β-D-glucopyranoside (22)

To a saturated soln of NH_3 in MeOH was added compound **21** (0.66 g, 5.1 mmol) at 13 °C. The reaction mixture was stirred with the introduction of NH_3 to saturate the soln for 8 h, and then further stirred at 13 °C for 4 h. The NH_3 was drawn out under diminished pressure and the reaction mixture was concentrated and subjected to chromatography on a silica gel column with 1:15 MeOH–CH_2Cl_2 to give **22** (0.30 g, 58%) as a colorless oil. $[\alpha]_D$ −34.6 (*c* 0.86, $CHCl_3$). ^{1}H NMR (500 MHz, CD_3OD): δ 7.66 (1H, d, *J* 16.0 Hz, alkene H), 7.44–6.89 (22H, m, ArH), 6.39 (1H, *J* 16 Hz, alkene H), 5.21 (1H, d, *J* 1.0 Hz, H-1 Rha), 5.114, 5.117, and 5.01 (6H, 3 × s, PhCH_2O), 5.11 (1H, m, H-4 Glc), 4.37 (1H, d, *J* 8.0 Hz, H-1 Glc), 4.24 (1H, d, *J* 7.5 Hz, H-1 Xyl), 4.06–4.04 (1H, dd, *J* 7.5, 9.5 Hz, $PhCH_2$CH_2O), 3.94 (1H, dd, *J* 1.0, 3.0 Hz, H-2 Rha), 3.88 (1H, m, H-3 Glc), 3.83–3.80 (2H, H-6 Glc and H-5 Xyl), 3.74–3.71 (2H, m, H-5 Glc and $PhCH_2$CH_2O), 3.61–3.55 (3H, m, H-6 Glc, H-3, H-5 Rha), 3.47–3.45 (1H, m, H-4 Xyl), 3.40 (1H, d, *J* 8.5 Hz, H-2 Glc), 3.33–3.29 (2H, m, H-3 Xyl and H-4 Rha), 3.24–3.21 (1H, dd, *J* 7.5, 9.0 Hz, H-2 Xyl), 3.14 (1H, t, *J* 11.0 Hz, H-5 Xyl), 2.86 (2H, t, *J* 7.0 Hz, PhC$H_2$$CH_2$O), 1.09 (3H, d, *J* 6.0 Hz, H-6 Rha). ^{13}C NMR (125 MHz, CD_3OD): δ 168.1 (*C*═O), 158.7, 152.7, and 150.2 (ArC), 147.5 and 116.2 (alkene C), 138.8, 138.4, 138.3, 132.3, 131.0, 129.50, 129.47, 128.97, 128.95, 128.9, 128.8, 128.7, 128.5, 124.6, 115.9, 115.3, and 115.0 (ArC), 105.3 (C-1 Glc), 104.2 (C-1 Xyl), 103.0 (C-1 Rha), 18.6 (C-6 Rha), 36.3 (Ph*C*$H_2$$CH_2$O–), other signals at δ 81.6, 77.5, 76.0, 74.8, 74.7, 73.7, 72.3, 72.2, 72.0, 71.9, 71.0, 70.9, 70.6, 70.4, 69.3, and 66.9. HRESIMS: calcd for $C_{55}H_{62}O_{18}Na$ ($[M+Na]^+$), 1033.3828. Found: 1033.3795. Anal. Calcd for $C_{55}H_{62}O_{18}$: C, 65.34; H, 6.18. Found: C, 65.25; H, 6.23.

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