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Total synthesis of cucurbitoside A using a novel fluorous protecting group

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ABSTRACT

The first total synthesis of cucurbitoside A was achieved using a new fluorous *N*-phenylcarbamoyl (^{F}Car) protecting group. The ^{F}Car group was introduced into carbohydrates in high yield and was selectively removed with Bu_4NNO_2 without damaging other acyl protecting groups. The synthetic intermediates were easily isolated by fluorous solid-phase extraction.

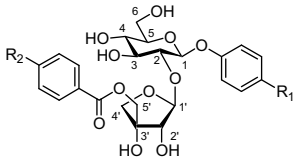
Fluorous protecting groups[1] have become increasingly popular in organic synthesis because they not only fulfill all the requirements for traditional protecting groups, but are also readily separated from non-fluorous by-products by solid-phase extraction with a fluorous reverse-phase silica gel column (fluorous solid-phase extraction (FSPE)).[2] To date, we have synthesized new fluorous protecting groups for functional groups in order to apply the technologies to total, parallel, and combinatorial syntheses of complex molecules.[3] By utilizing these protecting groups, efficient and expeditious syntheses of natural products, including peptides,[4] oligosaccharides,[3a] and modified monosaccharides, have been accomplished.

Five new acylated phenolic glycosides, cucurbitosides A–E (Fig. 1), were isolated from the seeds of *Cucurbita moschata* in 2005.[5] Although pharmacological studies have demonstrated that the seeds exhibit hepatoprotective and antitumor activities,[6] it has not yet been confirmed that the biological activities are attributable to cucurbitosides. The cucurbitosides have a β-D-apiofuranosyl-(1→2)-β-D-glucopyranose sugar chain and an ester linkage of benzoyl or 4-hydroxybenzoyl moiety at C-5′ of apiofuranose. Apiofuranose-containing glycosides, such as saponins, flavinoids, or phenolic glycosides, play a crucial role in the biochemistry of plants.[7] Among them, sequinosides A–K and M-LMF (leaf movement factor) and kelampayosides A and B are structurally similar to cucurbitosides, and most of them possess interesting biological activities.[8] Although M-LMF and kelampayosides A and B have previously been synthesized,[8c,d] total synthesis of cucurbitosides has not yet been reported. Therefore, the chemical synthesis of cucurbitosides is an important step in elucidating the relationship between the partially acylated structures and the promising biological activities of the natural products.

In the synthesis of acylated phenolic glycosides, the removal of protecting groups, other than acyl groups, is a key step. Specifically, protecting groups that are chemoselectively removed and stable under a wide range of reaction conditions are efficient and convenient. Recently, Sato et al. have proposed a *N*-phenylcarbamoyl (Car) group as a useful protecting group for the synthesis of natural products such as partially acylated oligosaccharide esters.[9] The Car group is stable from pH 1 to pH 12 in aqueous solutions[10] and is selectively removed with Bu_4NNO_2 without damaging other common protecting groups. Hence, the fluorous *N*-phenylcarbamoyl (^{F}Car) group is considered to be a valuable tool in the expeditious synthesis of acylated phenolic glycoside, because the fluorous separation technique and the unique chemical properties of the Car group can be utilized for synthesis.

We describe herein the synthesis of fluorous *N*-phenylcarbamoyl (^{F}Car) protecting reagent and its application to the synthesis of cucurbitoside A.

Fluorous carboxylic acid **2** was prepared via fluorous methyl benzoate **1**[3a] by the route shown in Scheme 1. Compound **1,**



Cucurbitoside A: $R_1 = CH_2CH_2OH$, $R_2 = H$
B: $R_1 = CH_2CH_2OH$, $R_2 = OH$
C: $R_1 = CH_2OH$, $R_2 = H$
D: $R_1 = CH_2OH$, $R_2 = OH$
E: $R_1 = OH$, $R_2 = H$

Figure 1. The structures of cucurbitosides A–E.

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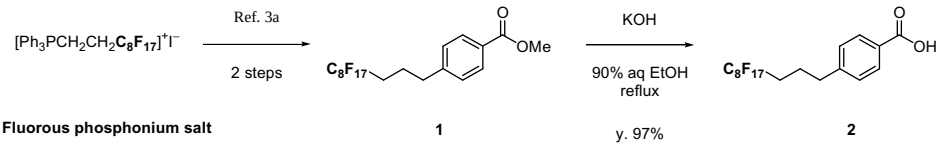
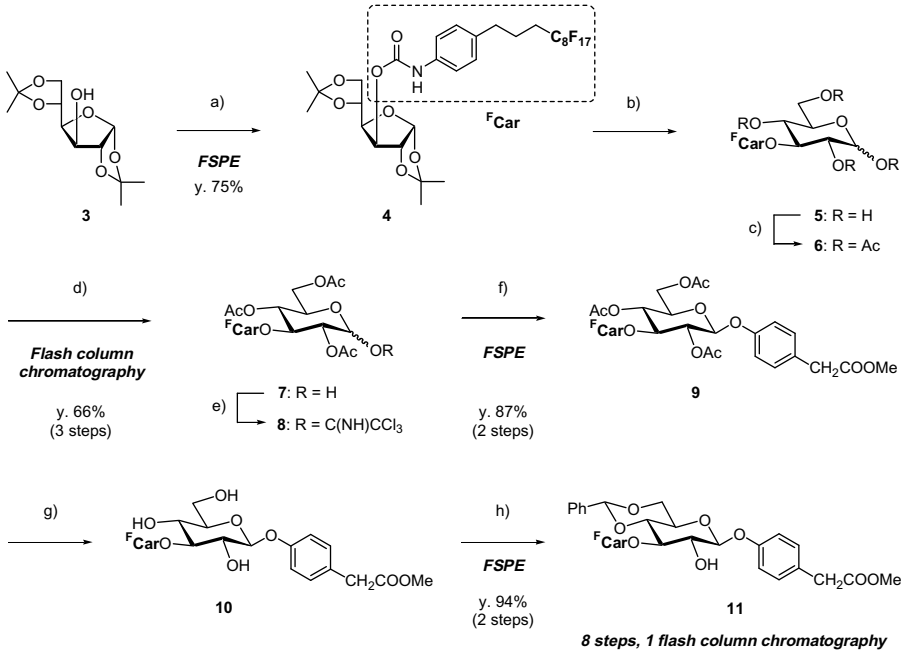


Scheme 1. Preparation of fluorous carboxylic acid **2**.

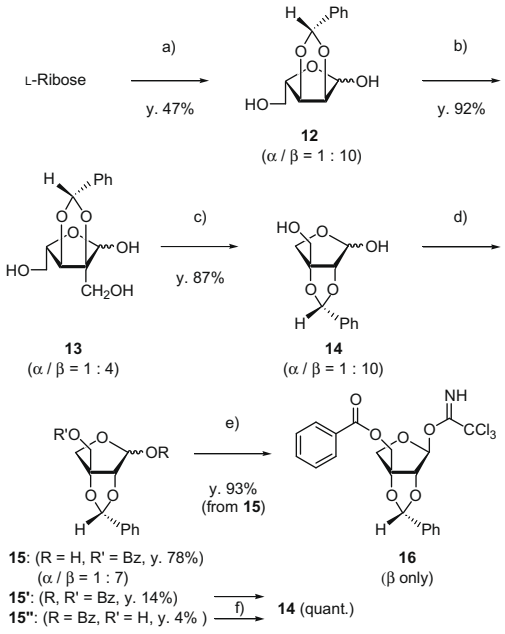
which was prepared from fluorous phosphonium salts in two steps, was hydrolyzed with potassium hydroxide in 90% aq EtOH to give the corresponding crystalline fluorous carboxylic acid **2** in 97% yield.

Initially, we examined the fluorous synthesis of phenyl β-D-glucopyranosyl acceptor from 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (**3**) by using ^{F}carboxylic acid **2** (Scheme 2). In order to simplify the introduction of a ^{F}Car group into the carbohydrates, we chose the direct conversion of the carboxylic acid **2** to its urethane derivative using a base and diphenylphosphoryl azide (DPPA).[11] ^{F}Carboxylic acid **2** (1.0 equiv) was reacted with diacetone glucose **3** (2.0 equiv) in the presence of DPPA (1.2 equiv) and triethylamine (2.2 equiv) in toluene under reflux. The completed reaction was quenched with saturated aq NH_4Cl and the reaction mixture was then extracted with EtOAc. The EtOAc layer was washed, dried, and concentrated. To separate the fluorous product from excess diacetone glucose **3**, the residue was loaded onto a fluorous reverse-phase silica gel (Fluoro*Flash*®)[12] column and eluted successively with 80% aq MeOH and MeOH.[13] The MeOH fraction was concentrated to give ^{F}Car-protected compound **4** in 75% yield. Acid hydrolysis of the isopropylidene groups of **4** using 80% aq TFA proceeded smoothly and gave compound **5**. Treatment of **5** with Ac_2O in pyridine gave tetra-O-acetylated compound **6**, which was reacted with $BnNH_2$ in THF. After the reaction was completed, the THF solvent was removed and the residue was purified by silica gel column chromatography to provide 2,3,4-tri-*O*-acetyl derivative **7** in 66% overall yield from **4**. Compound **7** was reacted with trichloroacetonitrile in the presence of DBU to give the corresponding imidate **8**, which was glycosylated with methyl 4-hydroxyphenylacetate (3.0 equiv) and a catalytic amount of $BF_3{\cdot}Et_2O$ (0.5 equiv) in CH_2Cl_2. Although the phenol derivatives are generally removed by washing with a large volume of a basic aqueous solution, treatment of the liquid waste is resource consuming. Therefore, we chose FSPE for the separation of desired glycoside **9** from excess phenol derivatives. The crude product was purified by FSPE and phenyl β-D-glucopyranoside **9** was subsequently obtained in 87% overall yield from **7**. Acetyl groups of **9** were removed with NaOMe in MeOH to give compound **10**. Finally, deacetylated derivative **10** was reacted with benzaldehyde dimethylacetal in the presence of *p*-TsOH·H_2O in DMF at 60 °C. After monitoring the disappearance of **10** on TLC, the reaction was quenched with Et_3N, and excess water was then added into the reaction mixture. After 15 min, the solution was loaded directly onto a Fluoro*Flash*® column and eluted successively with 80% aq MeOH and EtOAc.[14] The EtOAc fraction was concentrated to give glucosyl acceptor **11** in 94% overall yield from **9**. In these reaction steps, FSPE was utilized three times for speedy purification of the fluorous intermediates and products. Standard flash column chromatography was used only once, but the acceptor **11** was successfully prepared in 40% overall yield from **3** with sufficient purity for the next use.

Another component of cucurbitoside A, D-apiofuranose donor **16**, was prepared from L-ribose[15] via a five-step reaction as shown in Scheme 3. Numerous synthesis methods of apiose and its 2,3-*O*-isopropylidene-protected derivative have been published.[16] However, it was reported by Zhu et al. and Gin et al. that the 2,3-*O*-isopropylidene group on apiofuranose could not be removed without the acid hydrolysis of glycosidic linkages of the oligosaccharide.[17] Therefore, we chose the benzylidene group as the protecting group



Scheme 2. Reagents and conditions: (a) ^{F}carboxylic acid **2**, DPPA, Et_3N/toluene, reflux; (b) 80% aq TFA/CH_2Cl_2, rt; (c) Ac_2O, pyridine, rt; (d) $BnNH_2$/THF, rt; (e) CCl_3CN, DBU/CH_2Cl_2, 0 °C; (f) methyl 4-hydroxyphenylacetate, $BF_3{\cdot}Et_2O$, MS-4 Å CH_2Cl_2, −20 °C; (g) NaOMe/MeOH, rt; (h) benzaldehyde dimethylacetal, *p*-TsOH·H_2O/DMF, 60 °C.

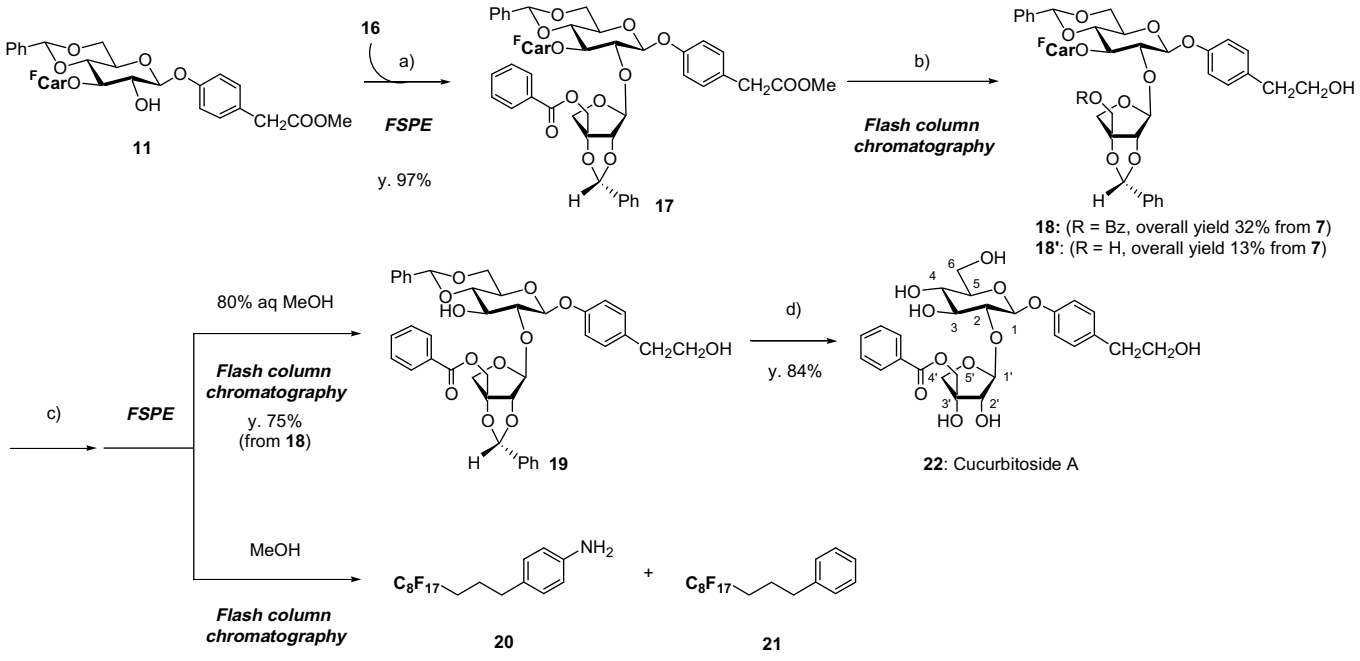


Scheme 3. Reagents and conditions: (a) benzaldehyde, $CuSO_4$, CSA/DMF, rt; (b) 37% aq HCHO, K_2CO_3/MeOH, 85 °C; (c) $NaBH_4$/MeOH then $NaIO_4/H_2O$, rt; (d) BzCl, pyridine/CH_2Cl_2, −78 °C; (3) CCl_3CN, DBU/CH_2Cl_2, 0 °C; (f) NaOMe/MeOH, rt.

for the 2,3-hydroxyl group on D-apiose because the protecting group is selectively introduced into the 2,3-hydroxyl group on L-ribose and removed under mild neutral conditions. 2,3-*O*-benzylidene-L-ribose **12** (α/β = 1:10) was synthesized according to the method described by Chan and Just.[18] K_2CO_3-catalyzed aldol condensation of **12** with formaldehyde gave the corresponding 2-*C*-hydroxymethyl derivative **13** (α/β = 1:4) in 92% yield. Reduction of **13** followed by oxidative cleavage with $NaIO_4$ afforded the 2,3-*O*-benzylidene-protected D-apiofuranose **14** (α/β = 1:10) in 87% yield. Finally, compound **15** (α/β = 1:7), obtained by selective benzoylation of **14**, was reacted with trichloroacetonitrile in the presence of DBU to give the apiosyl donor **16** (β only) in 93% yield. In selective benzoylation of **14**, 1,6-O-di-benzoylated **15′** (y. 14%) and 1-O-benzoylated **15″** (y. 4%) derivatives were obtained as side products. Benzoyl groups of compounds **15′** and **15″** were removed with NaOMe to give **14** in quantitative yield.

Using the fluorous acceptor **11** and the donor **16** obtained thus far, cucurbitoside A was synthesized via the route shown in Scheme 4. To a stirred mixture of **11** (1.0 equiv), **16** (1.5 equiv), and MS-4 Å in CH_2Cl_2 was added trimethylsilyl trifluoromethansulfonate (TMSOTf, 0.2 equiv) at −20 °C. After monitoring the disappearance of acceptor **11** on TLC, the reaction was quenched with Et_3N, and the reaction mixture was filtered off and the filtrate was subsequently concentrated. The residue was purified by FSPE to give the corresponding disaccharide **17** in 97% yield.[19] Reduction of **17** with $NaBH_4$ gave a crude product which included the alcohol **18**. The crude product was purified by standard silica gel column chromatography to give the pure compound **18** in 32% overall yield from **7**. In addition to the main product, debenzoylated derivative **18′** (13% overall yield) was obtained as a side product. The fluorous carbamoyl group of **18** was removed with Bu_4NNO_2 (3.0 equiv) in DMF at 120 °C. After 2 h, the reaction was quenched with saturated aq $NaHCO_3$ and the reaction mixture was then extracted with EtOAc. The EtOAc layer was washed, dried, and concentrated. To separate the disaccharide **19** from the fluorous compounds, the residue was loaded onto a Fluoro*Flash*® column and eluted successively with 80% aq MeOH and MeOH. The 80% aq MeOH fraction was concentrated to give the precursor **19**. From the MeOH fraction, 4-(1*H*, 1*H*, 2*H*, 2*H*, 3*H*, 3*H*-perfluoroundecyl)aniline **20** and 1*H*, 1*H*, 2*H*, 2*H*, 3*H*, 3*H*-perfluoroundecylbenzene **21**[20] were recovered as main products. Currently, an examination of the reuse or recycling of compound **20** is in progress. Finally, hydrogenolysis of compound **19** was carried out using $Pd(OH)_2$.The reaction proceeded smoothly to give cucurbitoside A in 84% yield. The optical rotation, ^1H and ^{13}C NMR data of the product agreed well with previous reports.[21]

In conclusion, the first total synthesis of cucurbitoside A has been accomplished using a novel fluorous protecting group, fluorous *N*-phenylcarbamoyl (Car) group. The fluorous intermediates were easily and quickly isolated from non-fluorous by-products



Scheme 4. Reagents and conditions: (a) TMSOTf, MS-4 Å/CH_2Cl_2, −20 °C; (b) $NaBH_4$/1,4-dioxane–H_2O (20:1), rt; (c) Bu_4NNO_2/DMF, 120 °C; (d) $Pd(OH)_2$, H_2 gas/MeOH, rt.

by FSPE. The fluorous Car group was selectively removed without damaging the benzoyl and benzylidene groups under common reaction conditions for a non-fluorous Car group. In order to demonstrate the versatility of ^{F}Car groups, studies examining its application to fluorous syntheses of other bioactive oligosaccharides are currently underway.

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12. Fluoro*Flash*® Silica Gel 40 μm is available from Fluka.
13. Typical procedure of FSPE. *Washing*: A new Fluoro*Flash*® silica gel (5 g) column was washed with acetone (10 ml). *Preconditioning*: The column was washed with 80% aq MeOH (15 ml). *Sample loading*: The residue, including compound **4**, (610 mg) was dissolved in 2 ml of CH_2Cl_2. To the solution was added Fluoro*Flash*® silica gel (1 g), and the solvent was then evaporated. The powder was loaded onto the column. *Fluorophobic elution*: The column was eluted with 80% aq MeOH (30 ml) to give a fraction containing the organic compound **3**. *Fluorophilic elution*: The column was eluted with MeOH (30–50 ml) to give a fraction containing the fluorous compound **4** (516 mg, y. 75%). *Final washing*: To regenerate the Fluoro*Flash*® silica gel for reuse, the column was washed with acetone (10 ml).
14. Usually MeOH is used to elute fluorous compounds from a Fluoro*Flash*® column. When the fluorous compounds were sparingly soluble in MeOH, EtOAc was used to quickly elute the fluorous compounds from the column.
15. L-Ribose is commercially available from Tokyo Chemical Industry Co., Ltd.
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19. *Physical data of disaccharide* **17**: $[\alpha]_D^{23}$ −27.6 (*c* 0.51, $CHCl_3$); ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.99–6.89 (23H, m, aromatic protons), 6.73 (1H, br s, –N*H*), 5.91 (1H, s, PhC*H*–), 5.56 (1H, s, PhC*H*–), 5.51 (1H, s, H-1′(Api)), 5.39 (1H, t, $J_{3,4}$ = 9.3 Hz, H-3(Glc)), 5.06 (1H, d, $J_{1,2}$ = 7.3 Hz, H-1(Glc)), 4.65 (1H, s, H-2′(Api)), 4.59, 4.48 (2H, each d, $J_{5,5'}$ = 11.9 Hz, $J_{5',5}$ = 11.9 Hz, H-5, 5′(Api)), 4.37 (1H, dd, $J_{6eq,5}$ = 4.7 Hz, $J_{6eq,6ax}$ = 10.3 Hz, H-6eq(Glc)), 4.25 (2H, s, H-4′(Api)), 4.11 (1H, dd, $J_{2,1}$ = 7.4 Hz, $J_{2,3}$ = 8.6 Hz, H-2(Glc)), 3.79 (1H, t, $J_{6ax,5}$ = 10.2 Hz, $J_{6ax,6eq}$ = 10.2 Hz, H-6ax(Glc)), 3.77 (1H, t, $J_{4,3}$ = 9.4 Hz, $J_{4,5}$ = 9.4 Hz, H-4(Glc)), 3.68 (3H, s, –COOC*H*$_3$), 3.66–3.57 (1H, m, H-5(Glc)), 3.52 (2H, s, –C*H*$_2$COOCH$_3$), 2.63 (2H, t, *J* = 7.4 Hz, C*H*$_2$CH$_2$CH$_2$C$_8$F$_{17}$), 2.16–1.82 (4H, m, CH$_2$C*H*$_2$C*H*$_2$C$_8$F$_{17}$); ^{13}C NMR (63 MHz, $CDCl_3$) δ 172.0, 165.8, 155.6, 152.3, 136.7, 136.1, 135.7, 135.6, 133.3, 130.6, 129.9, 129.7, 129.4, 129.1, 128.8, 128.7, 128.6, 128.5, 128.4, 128.2, 127.0, 126.2, 126.1, 119.4, 116.5, 107.0, 106.3, 101.4, 89.9, 87.0, 78.4, 77.2, 75.7, 75.0, 73.6, 68.6, 66.2, 64.5, 52.0, 40.3, 34.3, 30.2 (t), 21.4. MS (ESI-pos.) calcd for $C_{59}H_{49}F_{17}O_{14}Na$ (M+Na)$^+$ 1342.2857, found: 1342.2901.
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21. *Physical data of synthetic cucurbitoside A*: $[\alpha]_D^{17}$ −75.5 (*c* 1.1, MeOH) [lit. $[\alpha]_D^{24}$ −76.1 (*c* 1.1, MeOH)[5]]; ^{1}H NMR (250 MHz, CD_3OD) δ 7.92 (2H, dd, *J* = 8.5, 1.4 Hz, benzoyl), 7.58 (1H, tt, *J* = 8.1, 1.3 Hz, benzoyl), 7.41 (2H, t, *J* = 7.8 Hz, benzoyl), 6.93 (2H, d, *J* = 9.2 Hz, aromatic protons), 6.88 (2H, d, *J* = 9.1 Hz, aromatic protons), 5.51 (1H, d, $J_{1,2}$ = 1.0 Hz, H-1′(Api)), 4.91 (1H, d, $J_{1,2}$ = 7.4 Hz, H-1(Glc)), 4.35, 4.27 (2H, each d, $J_{5,5'}$ = 11.5 Hz, $J_{5',5}$ = 11.4 Hz, H-5′(Api)), 4.34, 3.92 (2H, each d, $J_{4,4'}$ = 9.7 Hz, $J_{4',4}$ = 9.5 Hz, H-4′(Api)), 3.98 (1H, d, $J_{2,1}$ = 1.1 Hz, H-2′(Api)), 3.86 (1H, br d, $J_{6,6'}$ = 12.7 Hz, H-6(Glc)), 3.70–3.55 (2H, m, H-3, 6′(Glc)), 3.63 (1H, dd, $J_{2,3}$ = 9.4 Hz, $J_{2,1}$ = 7.5 Hz, H-2(Glc)), 3.60 (2H, t, *J* = 7.3 Hz, Ph-CH$_2$C*H*$_2$OH), 3.43–3.34 (2H, m, H-4, 5(Glc)), 2.63 (t, *J* = 7.3 Hz, Ph-C*H*$_2$CH$_2$OH); ^{13}C NMR (63 MHz, CD_3OD) δ 167.6, 157.3, 134.3, 133.9, 131.1, 130.9, 130.7, 129.5, 117.2, 110.3 (C-1′ (Api)), 100.7 (C-1(Glc)), 79.2 (C-3′ (Api)), 78.8 (C-3(Glc)), 78.6 (C-2′(Api)), 78.1 (C-2(Glc)), 78.0 (C-5(Glc)), 75.4 (C-4′(Api)), 71.5 (C-4(Glc)), 68.5 (C-5′(Api)), 62.5 (C-6(Glc)), 64.3 (PhCH$_2$CH$_2$OH), 39.4 (PhCH$_2$CH$_2$OH). MS (ESI-pos.) calcd for $C_{26}H_{32}O_{12}Na$ (M+Na)$^+$ 559.1791, found: 559.1798.