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Synthesis of a partially benzylated derivative of the anhydro-D-altro-heptulose found in *Coriaria japonica* A

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Abstract—A partially benzylated derivative of the anhydro-D-altro-heptulose found in *Coriaria japonica* A, which is a synthetically useful unit, was successfully synthesized from a D-mannose derivative by a novel synthetic approach involving an intramolecular O-ketopyranosylation.
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1. Introduction

In *Coriaria japonica* A is found a tannin, which binds with an anhydro-D-altro-heptulose having a 6,8-dioxabicyclo[3.2.1] octane structure **1** via an ester linkage (Fig. 1), and its analogs show biologically important antitumor and antivirus activities.[1] Several methods for synthesizing **1** have been reported such as the enzymatic transketolization reaction of hydroxypyruvic acid with D-ribose,[2] the molybdic acid treatment of 2-*C*-hydroxymethyl-allofuranose,[3] and the radical intramolecular cyclization of a *C*-altropyranoside derivative via the intramolecular hydrogen abstraction reaction.[4] These methods require complicated processes or specific compounds.

We have studied the Lewis acid- or Brønsted acid-promoted O-ketosylations of 1-*C*-alkylated hexopyranose derivatives, which are ketopyranoses carrying alkyl groups at their anomeric centers.[5] Some studies have reported the intramolecular O-ketosylation method of these hexopyranoses catalyzed by trifluoromethanesulfonic acid (TfOH) to afford various anhydroketopyranoses having the 6,8-dioxabicyclo[3.2.1] octane structures.[6]

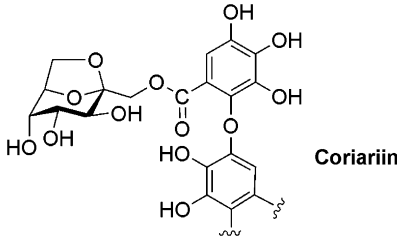

Figure 1.

In order to apply the intramolecular O-ketosylation method to the synthesis of a naturally occurring anhydroketopyranose having a 6,8-dioxabicyclo[3.2.1] octane structure, we investigated the synthesis of a partially benzylated derivative, (1,6-anhydro-2,3,4-tri-*O*-benzyl-1-*C*-hydroxymethyl-D-altropyranose, **2**), of an anhydro-D-altro-heptulose found in *Coriaria japonica* A from a D-mannopyranose derivative. Compound **2** is synthetically useful because it has a C-1′ free hydroxy function, which can be used for direct binding with a tannin.

Our synthetic approach involves the following key reaction steps: (1) the steric inversion at the C-3 position of the D-mannopyranose derivative to form the D-altropyranose derivative, (2) the introduction of the vinyl group into the C-1 position of the altropyranose derivative to produce a 1-*C*-vinylated D-altropyranose derivative, (3) the intramolecular O-glycosidation of the 1-*C*-vinylated D-altropyranose derivative to form the anhydroketopyranose structure, and (4) the conversion of the vinyl

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group of the anhydroketopyranose to the hydroxymethyl group.

This Letter describes the synthesis of the partially benzylated anhydro-D-altro-heptulose derivative **2** by a novel synthetic approach involving an intramolecular O-ketosylation developed by us.

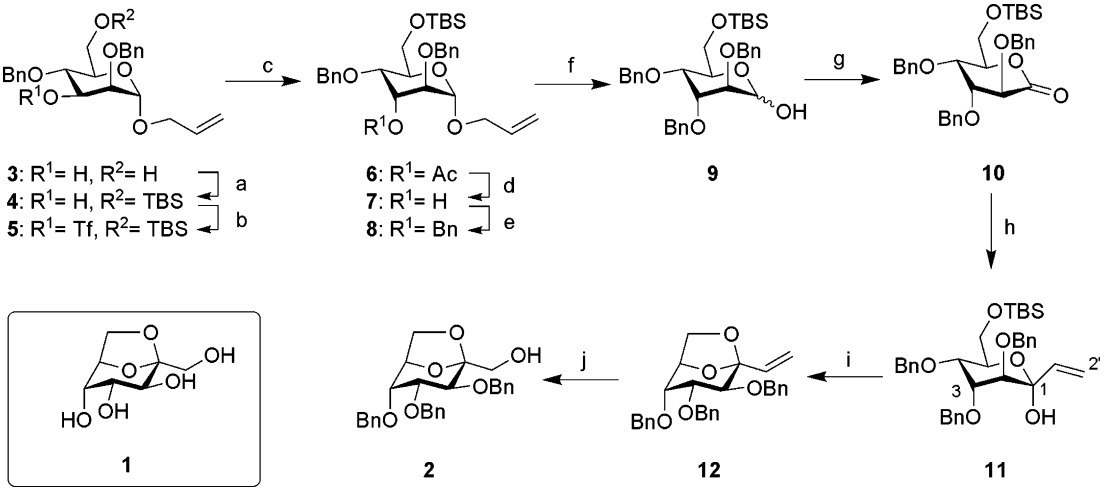
2. Results and discussion

Our synthetic approach to **2** is shown in Scheme 1. The TBS group was introduced into the C-6 of the allyl 2,4-di-*O*-benzyl-D-mannopyranoside (**3**)[7] by an ordinary procedure using TBSCl and imidazole in CH_2Cl_2 to afford the allyl 2,4-di-*O*-benzyl-6-*O*-*tert*-butyldimethylsilyl-α-D-mannopyranoside (**4**) in 88% yield. The reaction of **4** with Tf_2O in pyridine produced the allyl 2,4-di-*O*-benzyl-6-*O*-*tert*-butyldimethylsilyl-3-*O*-trifluoromethanesulfonyl-α-D-mannopyranoside (**5**) in 93% yield. The steric inversion at C-3 of **5**, which was the first key reaction step in our synthetic approach, was made by the reaction of **5** with AcOCs (2 equiv) in the presence of 18-crown-6 (2 equiv) in toluene at 30 °C for 24 h under ultrasonic conditions.[8] The reaction afforded the allyl 3-*O*-acetyl-2,4-di-*O*-benzyl-6-*O*-*tert*-butyldimethylsilyl-α-D-altropyranoside (**6**), which was purified by preparative silica-gel TLC (hexane/ethyl acetate = 6/1) in 62% yield. The assignment of the altropyranoside structure was done by measurement of the ^{1}H NMR spectrum of **6**. The signal of H-3 of **6** was observed at 5.33 ppm with a triplet peak ($J_{2,3} = 3.4$ Hz, $J_{3,4} = 3.4$ Hz), and their spin coupling constants indicated the dihedral angles of the H-2_{eq}–H-3_{eq} and the H-3_{eq}–H-4_{ax}, which supported the ring conformation of the altropyranoside.

The allyl 2,4-di-*O*-benzyl-6-*O*-*tert*-butyldimethylsilyl-α-D-altropyranoside (**7**) was obtained in 95% yield by the ordinary deprotection of the acetyl group of **6** using NaOMe in MeOH, and the following typical benzylation of **7** using NaH and benzyl bromide in DMF gave the allyl 2,3,4-tri-*O*-benzyl-6-*O*-*tert*-butyldimethylsilyl-α-D-altropyranoside (**8**) in 96% yield. The removal of the allyl group of **8** was carried out using $PdCl_2$ (3 equiv) in AcOH–AcONa at 30 °C for 4 h under ultrasonic conditions[9] to afford the 2,3,4-tri-*O*-benzyl-6-*O*-*tert*-butyldimethylsilyl-D-altropyranose (**9**) in 87%, and the oxidation of **9** using DMSO and Ac_2O[10] produced 2,3,4-tri-*O*-benzyl-6-*O*-*tert*-butyldimethylsilyl-D-altrono-1,5-lactone (**10**) in 99% yield. The introduction of the vinyl group into the C-1 of **10**, which was the second key reaction step, was successfully achieved by the reaction of **10** with vinylmagnesium chloride (1.2 equiv) in toluene in the presence of $CeCl_3$[11] (1.2 equiv) at −78 °C for 1 h. The reaction afforded the 2,3,4-tri-*O*-benzyl-6-*O*-*tert*-butyldimethylsilyl-1-*C*-vinyl-D-altropyranose (**11**), which was purified by preparative silica-gel TLC (toluene/ethyl acetate = 19/1) in 62% yield.

The intramolecular O-glycosidation of **11**, which was the third key reaction step in our synthetic approach, smoothly proceeded using 5 mol % TfOH in the presence of $CaSO_4$ in CH_3CN at 0 °C for 2 h, which was the same reaction conditions as previously reported.[6] The reaction afforded the 1,6-anhydro-2,3,4-tri-*O*-benzyl-1-*C*-vinyl-D-altropyranose (**12**), which was purified by preparative silica-gel TLC (benzene/ethyl acetate = 10/1) in 88% yield. The deprotection of the TBS group at C-6 of **11** before the intramolecular O-glycosidation was not necessary because the TBS group was removed under the acidic conditions during the intramolecular O-glycosidation, as we previously observed.[6] The NMR and mass spectra supported the formation of **12**.

The conversion of the vinyl functional group of **12** into the hydroxymethyl functional group, which was the final key reaction step, was carried out by the ozone oxidation of **12** at −78 °C for 45 min and treatment with triphenylphosphine (5 equiv), and the following reduction



Scheme 1. Reagents and conditions: (a) TBSCl (2 equiv), imidazole (2 equiv), CH_2Cl_2, rt, 2 h, 88%; (b) Tf_2O (1.5 equiv), pyridine, −20 °C to rt, 2.5 h, 93%; (c) CsOAc (2 equiv), 18-crown-6 (2 equiv), toluene, sonication, 30 °C, 24 h, 62%; (d) NaOMe, MeOH, rt, overnight, 95%; (e) BnBr (1.5 equiv), NaH (4 equiv), DMF, 0 °C to rt, overnight, 96%; (f) $PdCl_2$ (3 equiv), AcOH–AcONa buffer, sonication, 30 °C, 4 h, 87%; (g) DMSO, Ac_2O, rt, overnight, 99%; (h) vinylMgCl (1.2 equiv), $CeCl_3$ (1.2 equiv), toluene, −78 °C, 1 h, 62%; (i) TfOH (0.05 equiv), CH_3CN, 0 °C, 88%; (j) O_3, Ph_3P (5 equiv), CH_2Cl_2, −78 °C, 45 min., then $NaBH_4$ (8 equiv), THF, 0 °C, 3 h, 72%.

using $NaBH_4$[12] (8 equiv) at 0 °C for 3 h to successfully afford the desired **2**, which was purified by preparative silica-gel TLC (hexane/ethyl acetate = 4/1) in 72% yield as amorphous crystals. The NMR and mass spectra supported the formation of **2**.[13]

In summary, the partially benzylated anhydro-D-altroheptulose derivative **2** could be successfully synthesized from the D-mannopyranoside derivative by a novel synthetic approach involving the intramolecular O-glycosidation developed by us. An investigation of the preparation of several analogs of **2** by a similar synthetic approach is now in progress.

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13. *Spectroscopic data for* **4**: ^{1}H NMR ($CDCl_3$, 600 MHz): δ 0.07 (3H, s, $Si(CH_3)_2$), 0.08 (3H, s, $Si(CH_3)_2$), 0.91 (9H, s, $C(CH_3)_3$), 2.35 (1H, d, $J = 9.6$ Hz, OH), 3.57–3.60 (1H, m, H-5), 3.65 (1H, t, $J = 9.6$ Hz, H-4), 3.74 (1H, dd, $J = 1.4$ Hz, $J = 3.4$ Hz, H-2), 3.83–3.88 (2H, m, H-6), 3.92 (1H, dt, $J = 4.1$ Hz, $J = 9.6$ Hz, H-3), 3.93 (1H, dd, $J = 6.2$ Hz, $J = 13.1$ Hz, Ha-1′), 4.01 (1H, ddd, $J = 1.4$ Hz, $J = 5.5$ Hz, $J = 13.1$ Hz, Hb-1′), 4.93 (1H, d, $J = 1.4$ Hz, H-1), 5.16 (1H, dd, $J = 1.4$ Hz, $J = 10.3$ Hz, Ha-3′), 5.25 (1H, dd, $J = 1.4$ Hz, $J = 17.2$ Hz, Hb-3′), 5.86 (1H, m, H-2′). ^{13}C NMR ($CDCl_3$, 150 MHz): δ −5.3, −5.1, 18.3, 25.9, 62.6, 67.6, 71.8, 72.3, 72.7, 74.8, 76.6, 78.6, 95.7, 117.2, 133.8. Compound **5**: ^{1}H NMR ($CDCl_3$, 600 MHz): δ 0.069 (3H, s, $(CH_3)_2Si$), 0.073 (3H, s, $(CH_3)_2Si$), 0.89 (9H, s, $C(CH_3)_3$), 3.62 (1H, dd, $J = 2.8$ Hz, $J = 12.4$ Hz, H-5), 3.49 (1H, d, $J = 11.7$ Hz, Ha-1′), 3.88–3.93 (2H, m, Ha-6, Hb-1′), 3.97 (1H, dd, $J = 2.1$ Hz, $J = 2.7$ Hz, H-2), 4.10 (1H, dd, $J = 5.5$ Hz, $J = 13.1$ Hz, Hb-6), 4.19 (1H, t, $J = 9.6$ Hz, H-4), 4.59–4.82 (4H, m, CH_2Ph), 4.86 (1H, s, H-1), 5.16–5.23 (2H, m, H-3′), 5.27 (1H, dd, $J = 3.4$ Hz, $J = 9.6$ Hz, H-3), 5.81 (1H, m, H-2′). ^{13}C NMR ($CDCl_3$, 150 MHz): δ −5.4, −5.2, 18.2, 25.8, 61.8, 67.9, 72.5, 73.1, 73.2, 75.2, 76.8, 88.3, 96.3, 117.8, 133.2. Compound **6**: ^{1}H NMR ($CDCl_3$, 600 MHz): δ 0.07 (3H, s, $Si(CH_3)_2$), 0.08 (3H, s, $Si(CH_3)_2$), 0.91 (9H, s, $C(CH_3)_3$), 2.01 (3H, s, CH_3CO), 3.71 (1H, dd, $J = 1.4$ Hz, $J = 3.4$ Hz, H-2), 3.80 (1H, dd, $J = 5.5$ Hz, $J = 11.0$ Hz, Ha-6), 3.88 (1H, dd, $J = 3.4$ Hz, $J = 8.9$ Hz, H-4), 3.85–3.93 (2H, m, Ha-1′, Hb-6), 4.03 (1H, m, H-5), 4.23 (1H, m, Hb-1′), 4.80 (1H, d, $J = 1.4$ Hz, H-1), 5.13 (1H, ddd, $J = 1.4$ Hz, $J = 3.4$ Hz, $J = 10.3$ Hz, Ha-3′), 5.28 (1H, ddd, $J = 1.4$ Hz, $J = 2.1$ Hz, $J = 18.6$ Hz, Hb-3′), 5.33 (1H, t, $J = 3.4$ Hz, H-3), 5.87 (1H, m, H-2′). ^{13}C NMR ($CDCl_3$, 150 MHz): δ −5.4 ($Si(CH_3)_2$), −5.2 ($Si(CH_3)_2$), 18.2 ($C(CH_3)_3$), 21.0 (CH_3CO), 25.8 ($C(CH_3)_3$), 62.7 (C-6), 67.3 (C-3), 67.4 (C-1′), 68.9 (C-5), 70.7 (C-4), 71.5 (CH_2Ph), 72.4 (CH_2Ph), 75.6 (C-2), 97.5 (C-1, $J_{C1-H1} = 164.7$ Hz), 116.3 (C-3′), 134.1 (C-2′), 170.7 (CH_3CO). HRMS (ESI): m/z calcd for $C_{31}H_{44}O_7Si{\cdot}Na^+$: 579.2749. Found: 579.2795. Compound **7**: ^{1}H NMR ($CDCl_3$, 600 MHz): δ 0.05 (3H, s, $Si(CH_3)_2$), 0.08 (3H, s, $Si(CH_3)_2$), 0.84 (9H, s, $C(CH_3)_3$), 3.61 (1H, dd, $J = 1.4$ Hz, $J = 3.8$ Hz, H-2), 3.71 (1H, dd, $J = 3.3$ Hz, $J = 9.5$ Hz, H-4), 3.76 (1H, dd, $J = 5.7$ Hz, $J = 11.5$ Hz, Ha-6), 3.83–3.85 (2H, m, H-5, Hb-6), 3.93 (1H, dtd, $J = 1.2$ Hz, $J = 6.2$ Hz, $J = 12.9$ Hz, Ha-1′), 4.04–4.06 (1H, m, H-3), 4.16 (1H, dtd, $J = 1.4$ Hz, $J = 5.3$ Hz, $J = 12.9$ Hz, Hb-1′), 4.82 (1H, d, $J = 0.2$ Hz, H-1), 5.11 (1H, ddd, $J = 1.2$ Hz, $J = 2.6$ Hz, $J = 10.3$ Hz, Ha-3′), 5.18 (1H, ddd, $J = 1.5$ Hz, $J = 3.1$ Hz, $J = 17.2$ Hz, Hb-3′), 5.81 (1H, m, H-2′). ^{13}C NMR ($CDCl_3$, 150 MHz): δ −5.4, −5.2, 18.2, 25.9, 62.8, 66.6, 68.0, 68.2, 71.2, 71.9, 72.1, 76.6, 97.3 (C-1, $J_{C1-H1} = 168.3$ Hz), 117.9, 133.3. Compound **8**: ^{1}H NMR ($CDCl_3$, 600 MHz): δ 0.04 (6H, s, $Si(CH_3)_2$), 0.89 (9H, s, $C(CH_3)_3$), 3.74–3.83 (5H, m, H-2, H-6, H-3, H-4 or H-5), 3.98 (1H, dd, $J = 6.2$ Hz, $J = 13.1$ Hz, Ha-1′), 4.09–4.12 (2H, m, H-3, H-4 or H-5), 4.26 (1H, dd, $J = 4.8$ Hz, $J = 13.1$ Hz, Hb-1′), 4.83 (1H, d, $J = 0.7$ Hz, H-1), 5.15 (1H, dd, $J = 1.4$ Hz, $J = 10.3$ Hz, Ha-3′), 5.29 (1H, dd, $J = 1.4$ Hz, $J = 19.2$ Hz, Hb-3′), 5.91 (1H, m, H-2′). ^{13}C NMR ($CDCl_3$, 150 MHz): δ −5.4, −5.2, 18.3, 25.9, 63.0, 67.9, 70.2, 71.7, 72.0, 72.6, 72.8, 74.3, 76.5, 98.6 (C-1, $J_{C1-H1} = 167.5$ Hz), 116.7, 134.4. Compound **9**: β form: ^{1}H NMR ($CDCl_3$, 600 MHz): δ 0.07 (3H, s, $(SiCH_3)_2$), 0.09 (3H, s, $Si(CH_3)_2$), 0.91 (9H, s, $C(CH_3)_3$), 3.47 (1H, t, $J = 2.1$ Hz, H-2), 3.75 (1H, dd, $J = 2.1$ Hz, $J = 2.8$ Hz, H-3), 3.85–3.90 (2H, m, H-4, Ha-6), 3.99–4.03 (2H, m H-5, Hb-6), 4.33–4.77 (6H, m, CH_2Ph), 5.06 (1H, d, $J = 2.1$ Hz, H-1). ^{13}C NMR ($CDCl_3$, 150 MHz): δ −5.4, −5.1, 18.3, 25.9, 62.6, 68.2, 71.7, 71.9, 72.4, 74.0, 75.5, 77.3, 92.8; α form: ^{1}H NMR ($CDCl_3$, 600 MHz): δ 0.07 (3H, s, $(CH_3)_2Si$), 0.09 (3H, s, $(CH_3)_2Si$), 0.91 (9H, s, $C(CH_3)_3$), 3.53 (1H, dd, $J = 2.1$ Hz, $J = 12.4$ Hz, H-2), 3.59 (1H, d, $J = 4.1$ Hz, H-4), 3.85–3.90 (2H, m, H-3 and Ha-6), 3.99–4.03 (2H, m, H-5 and Hb-6), 4.33–4.68 (6H, m, CH_2Ph), 5.04–5.08 (1H, m, H-1), 7.18–7.33 (15H, m Ph). ^{13}C NMR ($CDCl_3$, 150 MHz): δ −5.3, −5.0, 18.3, 25.9, 62.8, 68.2, 72.2, 73.065, 73.074, 73.5, 75.2, 77.3, 91.6. Compound **10**: ^{1}H NMR ($CDCl_3$, 600 MHz): δ 0.08 (3H, s, $Si(CH_3)_2$), 0.09 (3H, s, $Si(CH_3)_2$), 0.91 (9H, s, $C(CH_3)_3$), 3.86 (2H, d, $J = 3.2$ Hz, H-6), 4.06 (1H, dd, $J = 2.7$ Hz, $J = 6.3$ Hz, H-3), 4.23 (1H, dd, $J = 2.7$ Hz, $J = 6.3$ Hz, H-4), 4.26 (1H, d, $J = 6.3$ Hz, H-2), 4.57–4.59 (1H, m, H-5), 4.47–4.94 (6H, m, CH_2Ph). ^{13}C NMR ($CDCl_3$, 150 MHz): δ −5.4, −5.2, 18.3, 25.9, 62.0, 71.9, 72.6, 72.7, 73.6, 74.9, 75.7, 79.0, 168.7. Compound **11**: ^{1}H NMR ($CDCl_3$, 600 MHz): δ 0.08 (3H, s, $Si(CH_3)_2$), 0.09 (3H, s, $Si(CH_3)_2$), 0.91 (9H, s,

$C(CH_3)_3$), 3.33 (1H, d, J = 3.4 Hz, H-2), 3.80 (1H, dd, J = 2.1 Hz, J = 3.4 Hz, H-3), 3.89 (1H, d, J = 11.0 Hz, Ha-6), 3.98–4.12 (3H, m, H-4, H-5, Hb-6), 5.22 (1H, dd, J = 2.1 Hz, J = 11.0 Hz, Ha-2′), 5.58 (1H, dd, J = 2.1 Hz, J = 17.9 Hz, Hb-2′), 5.98 (1H, m, H-1′). ^{13}C NMR ($CDCl_3$, 150 MHz): δ −5.3 ($Si(CH_3)_2$), −5.0 ($Si(CH_3)_2$), 18.3 ($C(CH_3)_3$), 21.0 (CH_3CO), 25.9 (($CH_3)_3C$), 62.6 (C-6), 68.9 (C-4 or C-5), 71.2 (C-4 or C-5), 72.6 (CH_2Ph), 73.1 (CH_2Ph), 73.9 (CH_2Ph), 75.4 (C-3), 78.4 (C-2), 96.5 (C-1), 116.3 (C-2′), 138.1 (C-1′). HRMS (ESI): m/z calcd for $C_{35}H_{46}O_6Si{\cdot}Na^+$: 613.2950. Found: 613.2968. Compound **12**: ^{1}H NMR ($CDCl_3$, 600 MHz): δ 3.62 (1H, dd, J = 0.7 Hz, J = 7.6 Hz, Ha-6), 3.66 (1H, dd, J = 2.4 Hz, J = 3.6 Hz, H-4), 3.78–3.82 (2H, m, H-2, H-3), 3.80 (1H, dd, J = 0.7 Hz, J = 6.9 Hz, Hb-6), 4.59–4.65 (1H, m, H-5), 4.62–4.81 (6H, m, CH_2Ph), 5.33 (1H, dd, J = 2.1 Hz, J = 11.0 Hz, Ha-2′), 5.70 (1H, dd, J = 2.1 Hz, J = 17.9 Hz, Hb-2′), 6.10 (1H, dd, J = 11.0 Hz, J = 17.2 Hz, H-1′). ^{13}C NMR ($CDCl_3$, 150 MHz): δ 66.1 (C-6), 72.1 (CH_2Ph), 72.7 (CH_2Ph), 74.7 (C-4), 75.2 (C-5), 75.3 (CH_2Ph), 78.5 (C-3), 82.9 (C-2), 106.7 (C-1), 118.3(C-2′), 133.0 (C-1′). HRMS (ESI): m/z calcd for $C_{29}H_{30}O_5{\cdot}Na^+$: 481.1985. Found: 481.1999. Compound **2**: $[\alpha]_D^{23}$ −45.0 (c 0.80, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 3.63 (1H, dd, J = 0.7 Hz, J = 8.3 Hz, Ha-6), 3.67–3.68 (1H, m, H-4), 3.74–3.83 (4H, m, H-2, Hb-6, H-1′), 3.93 (1H, d, J = 8.9 Hz, H-3), 4.57–4.63 (1H, m, H-5), 4.65–4.90 (6H, m, CH_2Ph). ^{13}C NMR ($CDCl_3$): δ 62.0 (C-1′), 66.6 (C-6), 72.1 (CH_2Ph), 72.5 (CH_2Ph), 74.6 (C-4), 75.2 (CH_2Ph), 75.5 (C-5), 78.9 (C-2), 79.8 (C-3), 107.9 (C-1). HRMS (ESI): m/z calcd for $C_{28}H_{30}O_6{\cdot}Na^+$: 485.1935. Found: 485.1950.