Electronic Supplementary Information

Two Novel Innovanoside Dimers from *Daphne Aurantiaca* and a Concise Total Synthesis of Diinnovanoside A†

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**General Experimental Procedures.** NMR spectra were recorded on a Avance 400 NMR spectrometer with TMS as internal standard. ESIMS were measured on an Agilent LC/MSD Trap XCT mass spectrometer, whereas HRESIMS were measured using a Q-TOF micro mass spectrometer (Waters, USA). Optical rotations were acquired with Perkin-Elmer 341 polarimeter, whereas IR spectra were recorded on a Bruker Vector 22 spectrometer spectrometer with KBr pellets. Materials for CC were silica gel (100–200 mesh; Huiyou Silical Gel Development Co. Ltd. Yantai, P. R. China), silica gel H (10–40 μm; Yantai), Sephadex LH-20 (40–70 μm; Amersham Pharmacia Biotech AB, Uppsala, Sweden), and YMC-GEL ODS-A (50 μm; YMC, MA, U.S.A.). Prep. TLC (0.4–0.5 mm) was conducted with glass precoated silica gel GF254 (Yantai).

**Plant Material.** The plant material was collected in July 2006 in Lijiang City, Yunnan province, China, and identified as *Daphne aurantiaca* by Prof. Li-Shan Xie of Kunming Institute of Botany. A voucher specimen has been deposited in the Herbarium of the School of Pharmacy, Second Military Medical University, Shanghai (No. 200607-11).

**Isolation of compounds 1-3 from D. aurantiaca.** The air-dried and powdered stem bark of *D. aurantiaca* (7.0 kg) was extracted with MeOH for 3 ×50 L × 2 h. The solvent was evaporated under a vacuum. Then, the extract was suspended in H2O and partitioned with petroleum ether (5L×3), EtOAc (5L×3), and *n*-butanol (5L×3),
successively. The EtOAc extract (400g) was subjected to column chromatography on silica gel (200–300 mesh, 1000 g), eluted with gradient CHCl₃-MeOH (100:0-50:50) and separated into nine fractions (F₁-F₉). Fraction F₂ was rechromatographed on silica gel with CHCl₃-MeOH (50:1) and separated into four subfractions (F₂₁-F₂₄). F₂₂ was rechromatographed on ODS (CH₃OH-H₂O, 10:100-100:0) followed by Sephadex LH-20 with MeOH to give 3 (100 mg). Fraction F₅ was rechromatographed on silica gel with gradient mixture of CHCl₃-MeOH (10:1) and separated into six subfractions (F₅₁-F₅₆). F₅₃ was rechromatographed on ODS (CH₃OH-H₂O, 10:100-100:0) followed by Sephadex LH-20 with MeOH to give compound 1 (8 mg) and compound 2 (6 mg).

**Synthesis of compound 4**

![Structure diagram]

The compound was synthesized according to the published protocol.¹ Starting with 2, 3, 4, 6-tetra-O-acetyl-α-D-glucopyranosyl bromide and 3-hydroxy-2-methyl-4H-pyran-4-one, employed 2 steps in 47.5% yield as yellowish crystals: 

[^1]H NMR (600 MHz, DMSO-d₆) δ ppm 8.13 (dd, J = 5.64, 0.41 Hz, 1 H), 6.43 (d, J = 5.64 Hz, 1 H), 5.45 (d, J = 3.16 Hz, 1 H), 5.02 (d, J = 4.95 Hz, 1 H), 4.93 (d, J = 4.81 Hz, 1 H), 4.74 (d, J = 7.70 Hz, 1 H), 4.42 (s, 1 H), 3.64 (ddd, J = 11.76, 5.43, 1.65 Hz, 1 H), 3.37 - 3.49 (m, 1 H), 2.36 (s, 3 H); ¹³C NMR (150 MHz, DMSO-d₆) δ ppm 174.65, 161.77, 156.13, 142.23, 116.65, 104.08, 77.77, 76.81, 74.38, 70.10, 61.37, 15.69; HR-ESI-MS calcd for C₁₂H₁₆NaO₈ [M+Na]⁺ 311.0737, found 311.0753.

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Synthesis of compound 6

\[
\begin{align*}
\text{p-Coumaric acid} & \quad (6.56 \text{ g, 40 mmol}) \quad \text{and TBDMS triflate} & \quad (31.68 \text{ g, 120 mmol}) \quad \text{were dissolved in dichloromethane} (60 \text{ ml}), \\
\text{triethylamine} & \quad (16.16 \text{ g, 160 mmol}) \quad \text{was added dropwise to the mixture, stirred and cooled to } 0^\circ \text{C} \quad \text{in a flask fitted with dropping funnel. After completion of the addition, stirring was continued at room temperature for 48 h. Then a solution of HCl} \quad (1\text{N, 110 mL}) \quad \text{was added, and the mixture was stirred overnight at rt. Dichloromethane} \quad (60 \text{ ml}) \quad \text{was added, and the organic phase was washed three times with water, once with brine, dried, and finally concentrated. The residue was purified by fresh column chromatography} \quad (\text{Petro Ether/EtOAc} \quad 10:1) \quad \text{to afford white crystals} \quad (10 \text{ g, 36 mmol, 80%}): \\
\text{H NMR} \quad (600 \text{ MHz, DMSO-}d_6) & \quad \delta \quad ppm \\
7.58 & \quad (d, \ J = 8.67 \text{ Hz, 1 H}), \\
7.46 - 7.55 & \quad (m, 2 \text{ H}), \\
6.74 - 6.91 & \quad (m, 2 \text{ H}), \\
6.24 - 6.43 & \quad (m, 1 \text{ H}), \\
0.92 - 0.98 & \quad (m, 6 \text{ H}), \\
0.84 & \quad (s, 3 \text{ H}), \\
0.26 & \quad (s, 3 \text{ H}), \\
0.20 & \quad (d, \ J=1.10 \text{ Hz, 3 H}); \\
\text{C NMR} \quad (150 \text{ MHz, DMSO-}d_6) & \quad \delta \quad ppm \\
168.35, 160.02, 144.58, 130.49, 130.40, 128.15, 120.72, 120.70, 116.16, 26.23, 18.22, -2.77; \\
\text{HR-ESI-MS caled for} \quad \text{C}_{15}\text{H}_{22}\text{NaO}_3\text{Si} \quad [\text{M+Na}^+] & \quad 301.1230, \text{ found 301.1253.}
\end{align*}
\]

Synthesis of compound 7

\[
\begin{align*}
\text{A suspension of compound 6 crystals} \quad (2.78 \text{ g, 10.00 mmol}) \quad \text{in hexane contained in a Pyrex reactor was irradiated with a 400 W high-pressure mercury lamp for 60 h. The solvent was evaporated in vacuo, and the residue was purified by chromatography} \quad (\text{Petro Ether/EtOAc} \quad 15:1) \quad \text{to afford compound 7} \quad (2.23 \text{ g, 70%}) \quad \text{as a white solid:} \\
[\alpha]_D^\circ & \quad -4.8 \quad (c \quad 0.17, \text{ CH}_3\text{COCH}_3); \\
\text{H NMR} \quad (600 \text{ MHz, DMSO-}d_6) & \quad \delta \quad ppm \quad 12.03 \quad (\text{br. s., 2 H),}
\end{align*}
\]
7.21 (d, J = 7.89 Hz, 4 H), 6.78 (d, J = 7.89 Hz, 4 H), 4.17 (t, J = 8.53 Hz, 2 H), 3.64 -
3.75 (m, 2 H), 0.95 (s, 18 H), 0.18 (s, 12 H); ¹³C NMR (150 MHz, DMSO-d₆) δ ppm
172.96, 153.76, 132.20, 128.78, 119.29, 46.49, 40.28, 25.53, 17.86, -4.54;

**Synthesis of compound 1**

![Chemical Structure of Compound 1]

To a solution of compound 8 (300 mg, 0.17 mmol) in THF (20 mL) and AcOH
(1 ml) was added tetrabutylammonium fluoride (710 mg, 2.7 mmol). After stirring at
room temperature for 96 h, the organic solvent was removed under reduced pressure,
and the residue was dissolved in ethyl acetate (150 ml), then the organic phase was
washed with brine, dried, and finally concentrated. The residue was purified by
column chromatography (DCM/MeOH 10:1) to afford compound 1 (103 mg, 0.12
mmol, 70%) as a white solid. ¹H and ¹³C NMR spectroscopic data, see Table 1. [α]₂⁰
-54 (c 0.04, CH₃OH).

**Synthesis of compound 5**

![Chemical Structure of Compound 5]

Compound 4 (1.44 g, 5 mmol) and TBDMS triflate (7.92 g, 120 mmol) were
dissolved in DMF (50 ml), anhydrous pyridine (30 ml) was added dropwise to the
mixture, stirred and cooled to 0°C in a flask fitted with dropping funnel. After completion of the addition, stirring was continued at room temperature for 48 h. Ethyl acetate (150 mL) was added, and the organic phase was washed three times with saturated copper sulfate solution (50 mL×3), twice with water, once with brine, dried, and finally concentrated. The residue was no need to further purify and could be used directly in the next reaction.

A solution of the residue (3.0 g, 4 mmol), CBr₄ (265.2 mg, 0.8 mmol) and anhydrous MeOH (40 mL) in a Pyrex round flask was irradiated by a TLC lamp (Uvltec Limited, 245 nm, 8 W) for 0.5 h, followed by stirring without irradiation at room temperature. After the reaction was complete (TLC), the organic solvent was removed under reduced pressure. The residue was purified by column chromatography (Petro Ether/EtOAc 6:1) to afford compound 5 (2.3 g, 3.6 mmol, 72%) as a yellow solid: ¹H NMR (600 MHz, DMSO-d₆) δ ppm 7.91 - 8.15 (m, 1 H), 6.23 - 6.47 (m, 1 H), 5.60 - 5.79 (m, 1 H), 3.79 - 3.92 (m, 2 H) 4.61 (s, 1 H), 3.74 (s, 1 H), 3.53 - 3.61 (m, 1 H), 3.45 - 3.52 (m, 1 H), 3.41 (d, J=5.64 Hz, 1 H), 2.28 (d, J=0.69 Hz, 3 H), 0.85 - 0.88 (m, 27 H), 0.05 - 0.11 (m, 18 H); ¹³C NMR (150 MHz, DMSO-d₆) δ ppm 173.53, 160.03, 155.21, 141.25, 116.96, 100.14, 79.57, 79.07, 76.53, 71.33, 62.02, 26.09, 18.15, 18.10, 18.01, 15.35, -4.07, -4.46, -4.55; HR-ESI-MS calcd for C₃₀H₅₈NaO₆Si₃ [M+Na]⁺ 653.3332, found 653.3329.

Synthesis of compound 8
To a solution of compound 7 (150 mg, 0.27 mmol), compound 5 (510 mg, 0.81 mmol), and EDCI (576 mg, 3.0 mmol) in CH₂Cl₂ (30 mL) was added DMAP (122 mg, 1.0 mmol), and the mixture was stirred at room temperature for 24 h. Ethyl acetate (60 mL) was added, and the organic phase was washed three times with water, once with brine, dried, and finally concentrated. The residue was purified by column chromatography (Petro Ether/EtOAc 10:1) to give compound 8 (385 mg, 0.22 mmol, 80%) as a white solid: ¹H NMR (600 MHz, CDCl₃) δ ppm 7.48 (dd, J = 13.00, 5.71 Hz, 2 H), 7.05 (t, J = 7.57 Hz, 4 H), 6.71 (dd, J = 8.12, 4.68 Hz, 4 H), 6.25 (d, J = 5.64 Hz, 2 H), 5.67 (d, J = 3.58 Hz, 1 H), 5.61 (d, J = 3.58 Hz, 1 H), 4.15 - 4.31 (m, 2 H), 4.00 (dd, J = 11.28, 7.29 Hz, 1 H), 3.91 (dd, J = 13.75, 2.48 Hz, 2 H), 3.62 - 3.84 (m, 8 H), 3.57 (dd, J = 11.49, 4.06 Hz, 1 H), 3.44 (dd, J = 11.42, 6.19 Hz, 1 H), 2.27 (s, 3 H), 2.15 (s, 3 H), 0.96 (s, 20 H), 0.90 (s, 13 H), 0.85 - 0.88 (m, 29 H), 0.83 (s, 10 H), 0.02 - 0.19 (m, 48 H); ¹³C NMR (150 MHz, CDCl₃) δ ppm 175.43, 173.09, 172.96, 161.72, 156.07, 154.55, 143.14, 132.72, 132.54, 129.94, 121.34, 118.65, 102.39, 101.85, 80.00, 79.67, 77.06, 76.97, 76.87, 76.62, 73.31, 73.04, 66.39, 65.98, 48.38, 48.29, 41.97, 27.26, 27.21, 27.09, 19.59, 19.42, 19.31, 19.28, 16.83, 16.67, -2.68, -2.72, -2.72, -2.75, -2.79, -3.01, -3.10, -3.47; HR-ESI-MS calcd for C₉₀H₁₅₆NaO₂₀Si₈ [M+Na]⁺ 1803.9236, found 1803.9241.

**Synthesis of compound 9**

![Diagram of compound 9]

To a solution of compound 7 (750 mg, 1.35 mmol) and EDCI (2.8 g, 15.0 mmol) in methanol (30 mL) was added DMAP (610 mg, 5.0 mmol), and the mixture was stirred at room temperature for 12 h. The organic solvent was removed under reduced pressure, and the residue was dissolved in ethyl acetate (50 ml), then the organic
phase was washed with brine, dried, and finally concentrated. The residue was purified by column chromatography (P Petro Ether/EtOAc 30:1) to afford compound 9 (755 mg, 1.3 mmol, 96%) as a white solid: \([\alpha]_D^{25} -2.2 \text{ (c 0.22, CH}_3\text{COCH}_3\text{); } \) \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) ppm 7.14 (d, \(J=8.39\) Hz, 4 H), 6.79 (d, \(J=8.67\) Hz, 4 H), 4.31 - 4.40 (m, 2 H), 3.85 - 3.91 (m, 2 H), 3.30 (s, 6 H), 0.97 (s, 18 H), 0.17 (s, 12 H); \(^{13}\)C NMR (150 MHz, CDCl\(_3\)) \(\delta\) ppm 173.83, 156.14, 132.91, 129.92, 121.41, 52.77, 48.48, 42.14, 27.10, 19.66, -3.01; HR-ESI-MS calcd for C\(_{32}\)H\(_{48}\)NaO\(_6\)Si\(_2\) [M+Na]\(^+\) 607.2882, found 607.2918.

**Synthesis of compound 10**

![Diagram](image)

To a solution of compound 9 (584 mg, 1 mmol) in THF (20 mL) and AcOH (1 ml) was added tetrabutylammonium fluoride (710 mg, 2.7 mmol). After stirring at room temperature for 2 h, the organic solvent was removed under reduced pressure, and the residue was dissolved in ethyl acetate (150 ml), then the organic phase was washed with brine, dried, and finally concentrated. The residue was purified by column chromatography (P Petro Ether/EtOAc 6:1) to afford compound 10 (320 mg, 0.9 mmol, 90%) as a white solid: \([\alpha]_D^{25} -2.6 \text{ (c 0.33, CH}_3\text{COCH}_3\text{); } \) \(^1\)H NMR (600 MHz, DMSO-\(d_6\)) \(\delta\) ppm 7.07 (d, \(J=8.53\) Hz, 4 H), 6.68 (dt, \(J=8.53, 1.65\) Hz, 4 H), 4.17 (dd, \(J=10.39, 7.36\) Hz, 2 H), 3.68 - 3.88 (m, 2 H), 3.23 (s, 6 H); \(^{13}\)C NMR (150 MHz, DMSO-\(d_6\)) \(\delta\) ppm 173.81, 158.09, 130.68, 130.33, 116.81, 52.96, 48.23, 42.09, 41.96; HR-ESI-MS calcd for C\(_{20}\)H\(_{20}\)NaO\(_6\) [M+Na]\(^+\) 379.1152, found 379.1168.

**Synthesis of compound 11**

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To a solution of compound 10 (178 mg, 0.5 mmol) in anhydrous pyridine (20 mL) was added acetic anhydride (153 mg, 1.5 mmol), and the mixture was stirred at room temperature (overnight). Then ethyl acetate (50 mL) was added, and the organic phase was washed three times with saturated copper sulfate solution (20 ml×3), twice with water, once with brine, dried, and finally concentrated. The residue was purified by column chromatography (Petro Ether/EtOAc 20:1) to afford compound 11 (210mg, 0.48mmol, 95%) as a white solid: $\left[\alpha\right]_{D}^{25} -5.6$ (c 0.20, CH$_3$COCH$_3$); $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ ppm 7.29 (d, $J$=8.53 Hz, 4 H), 7.05 (d, $J$=8.53 Hz, 4 H), 4.38 - 4.49 (m, 2 H), 3.84 - 3.99 (m, 2 H), 3.32 (s, 6 H), 2.28 (s, 6 H); $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ ppm 173.46, 170.75, 151.19, 137.53, 129.88, 122.95, 52.99, 48.21, 42.31, 22.51; HR-ESI-MS calcd for C$_{24}$H$_{25}$O$_8$ [M+H]$^+$ 441.1544, found 441.1560.
### Crystallographic data of compound 11

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Colorless prism crystals of 11 were obtained by recrystallization in CH$_2$Cl$_2$. Crystal data were obtained on Bruker SMART APEX II CCD area detector with graphite monochromated Mo-K$_\alpha$ radiation ($\lambda =1.54178$ Å) at 133(2) and operating in the $\phi$-$\omega$ scan mode. The structure was solved by direct methods and refined with full-matrix
least-squares calculations of $F^2$ using SHELX-97. The collected data were reduced by using the program SAINT and empirical absorption correction was made by using the SADABS program. The hydrogen atom positions were geometrically idealized and allowed to ride on their parent atoms. Crystallographic data for 11 have been deposited at the Cambridge Crystallographic Data Centre (deposition no. CCDC 907651). Copies of these data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK. [fax: (+44) 1223-336-033; or email: deposit@ccdc.cam.ac.uk].
Figure 1. $^{13}$C NMR spectrum of compound 1
Figure 2. H NMR spectrum of compound 1
Figure 3. HSQC spectrum of compound 1
Figure 4. H- H COSY spectrum of compound 1
Figure 5. HMBC spectrum of compound 1
Figure 6. NOESY spectrum of compound 1
Elemental Composition Report

Single Mass Analysis

Tolerance = 10.0 PPM   /   DBE: min = -1.5, max = 50.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

319 formula(e) evaluated with 5 results within limits (all results (up to 1000) for each mass)

Elements Used:

C: 0-100    H: 0-100    O: 0-50

Minimum:                                  - 1 . 5

Maximum:                 5.0     10.0    50.0

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Figure 7. HR-ESI-MS spectrum of compound 1
Figure 8. $^{13}$C NMR spectrum of compound 2
Figure 9. H NMR spectrum of compound 2
Figure 10. HSQC spectrum of compound 2
Figure 11. $^1$H- $^1$H COSY spectrum of compound 2
Figure 12. HMBC spectrum of compound 2.
Figure 13. NOESY spectrum of compound 2.
Elemental Composition Report

Single Mass Analysis

Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

319 formula(e) evaluated with 5 results within limits (all results (up to 1000) for each mass)

Elements Used:

C: 0-100    H: 0-100    O: 0-50

Minimum:                                  - 1.5

Maximum:                 5.0     10.0    50.0

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Figure 14. HR-ESI-MS spectrum of compound 2
Figure 15. $^{13}$C NMR spectrum of compound 4
Figure 16. $^1$H NMR spectrum of compound 4
Figure 17. Carbon-13 NMR spectrum of compound 5
Figure 18. $^1$H NMR spectrum of compound 5
Figure 19. $^{13}$C NMR spectrum of compound 6
Figure 20. $^1$H NMR spectrum of compound 6
Figure 21. $^{13}$C NMR spectrum of compound 7
Figure 22. $^1$H NMR spectrum of compound 7
Figure 23. $^{13}$C NMR spectrum of compound 8
Figure 24. $^1$H NMR spectrum of compound 8
Figure 25. $^{13}$C NMR spectrum of compound 9
Figure 26. $^1$H NMR spectrum of compound 9
Figure 27.  $^{13}$C NMR spectrum of compound 10
Figure 28. $^1$H NMR spectrum of compound 10
Figure 29. $^{13}$C NMR spectrum of compound 11
Figure 30. $^1$H NMR spectrum of compound 11