Enantioselective Total Synthesis of Semperoside A

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Supporting Information

General Experimental Procedure: For a general experimental procedure of preparation of acetate **9** see previous papers.¹

[4a*S*,5*Z*,7*S*,7a*R*]-7-Methyl-4,4a,7,7a-tetrahydro-1*H*-cyclopenta[*c*]pyran-3-one (**10**).

MeMgBr (3M in Et₂O, 2.5 mL) was added dropwise to a stirred solution of CuBrMe₂S (1.55 g, 7.5 mmol) in dry THF (15 mL) and Me₂S (8.2 mL) at –20°C (cryostat). The yellow cuprate suspension was kept at –20°C for 10 min, then cooled to –45°C, and acetate (**-**)-**9** (500 mg, 2.5 mmol), in dry THF was slowly added by syringe. After 3 h the mixture was warmed to room temperature, poured onto a 1N NaOH solution, and stirring was continued for an additional 1 h. The solution was acidified to pH = 2 with 1N

HCl and then extracted with Et₂O. The organic layer was concentrated to about 15 mL; a catalytic amount of *p*-TsOH was added and the solution was stirred until complete lactonisation (8 h). The solution was diluted with CH₂Cl₂ and washed with 5% aq. NaHCO₃. The aqueous layer was extracted with CH₂Cl₂. The combined organic layers were dried over MgSO₄ and solvent was removed. Separation of the residue by column chromatography (10 g of silica gel, hexane / EtOAc = 8:2) gave lactone **10** (317 mg, 2.1 mmol, yield = 85%); m.p.: 77°-78°C. [α]_D = +191.3 (*c*=1.3, CH₂Cl₂); IR (nujol): 3047, 2925, 1728, 1461, 1238, 1065 cm⁻¹; ¹H-NMR (300MHz, CDCl₃) δ 5.70 (dt, *J* = 5.5, 2.0 Hz, 1H), 5.52 (dt, *J* = 5.5, 2.0 Hz, 1H), 4.32 (dd, *J* = 4.5, 11.5 Hz, 1H), 4.08 (dd, *J* = 6.5, 11.5 Hz, 1H), 3.33-3.45 (m, 1H), 2.68 (dd, *J* = 7.0, 15.0 Hz, 1H), 2.55-2.75 (m, 1H), 2.34 (dd, *J* = 6.0, 15.0 Hz, 1H), 2.20-2.28 (m, 1H), 1.11 (d, *J* = 7.0 Hz, 3H); ¹³C-NMR (75.2 MHz, CDCl₃) δ 173.3 (CO), 137.1 (CH), 130.6 (CH), 69.5 (CH₂), 43.7 (CH), 42.9 (CH), 41.5 (CH), 33.7 (CH₂), 21.2 (CH₃). Anal. Calcd for C₉H₁₂O₂: C, 71.03; H, 7.95. Found: C, 71.14; H, 7.87.

[3a*R*,4*S*,5*R*,6*R*,6a*R*]-4-Hydroxymethyl-6-iodo-5-methyl-hexahydro-cyclopenta[*b*]furan-2-one (**11**).

Lactone **10** (280 mg, 1.8 mmol) was added to a hydro-alcoholic solution (H₂O-EtOH 1:1) of NaOH (72 mg, 1.8 mmol) and the mixture was refluxed overnight, monitoring the reaction by TLC (hexane/EtOAc = 3:7). Solvent was evaporated under reduced pressure by aiding with addition of CH₃CN. The residue was washed with Et₂O to remove unreacted olefin and the suspension was filtered. The

recovered sodium salt was dissolved in H₂O (20 mL) and acidified to pH = 7 by the addition of dry ice. The neutralized solution was then added portionwise to a stirred solution of KI (996 mg, 6

¹ G. Zanoni; A. Porta; A. Meriggi; M. Franzini; G. Vidari *J.Org.Chem.*, **2002**, 67, 60-64
G. Zanoni; F. Agnelli; A. Meriggi; G. Vidari *Tetrahedron Asymmetry*, **2001**, 12, 1779

mmol) and I_2 (1.47 g, 5.8 mmol) in H_2O (100 mL) at $0^\circ C$. The resulting mixture was stirred overnight. Solid Na_2SO_3 was added to destroy excess iodine. Solvent was evaporated and the residue was partitioned between CH_2Cl_2 and H_2O . The aqueous layer was reextracted with CH_2Cl_2 . The combined organic layers were dried over $MgSO_4$ and evaporated to give iodide **11** as nice colorless crystals (504 mg, 1.71 mmol, yield = 95%). $[\alpha]_D = +38.02$ ($c = 1.075$, CH_2Cl_2); IR (nujol) 3260, 2929, 1784, 1460, 1376, 1166, 1039, 1020, 995, 886 cm^{-1} ; 1H NMR (300 MHz, $CDCl_3$) δ 5.30 (d, $J = 6$ Hz, 1H), 4.60 (d, $J = 4.3$ Hz, 1H), 3.71 (dd, $J = 5.7$, 11 Hz, 1H), 3.88 (dd, $J = 6.9$, 11 Hz, 1H), 3.28-3.4 (m, 1H), 2.85 (dd, $J = 2$, 18.6 Hz, 1H), 2.70 (dd, $J = 10$, 18.6 Hz, 1H), 2.15-2.3 (m, 1H), 1.24-1.38 (m, 1H), 1.08 (d, $J = 6.2$ Hz, 3H); ^{13}C NMR (75.2 MHz, $CDCl_3$) δ 177.1 (C=O), 90.9 (CH), 59.8 (CH_2), 47.0 (CH), 42.7 (CH), 38.5 (CH), 36.9 (CH), 30.4 (CH_2), 19.2 (CH_3). Anal. Calcd for $C_9H_{13}IO_3$: C, 36.51; H, 4.43. Found: C, 36.39; H, 4.35.

[3aR,4R,5S,6aS]-4-Hydroxymethyl-5-methyl-hexahydro-cyclopenta[b]furan-2-one (7).

Excess Raney®-nickel [25 ml of an aqueous suspension (Fluka)] was decanted and the solid washed with EtOH (3 x 1.5 mL). CH_2Cl_2 (3 mL) and three drops of EtOH were then added. Under N_2 , a solution of lactone **11** (110 mg, 0.37 mmol) in CH_2Cl_2 (1 mL) was added, and the mixture was stirred for 1h at room temperature, monitoring the reaction by TLC (hexane/EtOAc = 3:7). The mixture was diluted with CH_2Cl_2 and filtered. Solvent

was evaporated and the residue was separated by column chromatography (hexane/ EtOAc = 1:1) to yield lactone **7** (45 mg, 0.26 mmol, yield = 71%). $[\alpha]_D = +14.73$ ($c = 0.9$, CH_2Cl_2); IR (Nujol) 3450, 2968, 1756, 1306, 1186, 1028, 742 cm^{-1} ; 1H NMR (300 MHz, $CDCl_3$) δ 5.02 (t, $J = 6$ Hz, 1H), 3.88 (dd, $J = 4$, 10.6 Hz, 1H), 3.62 (dd, $J = 8.8$, 10.6 Hz, 1H), 3.10-3.22 (m, 1H), 2.64-2.69 (m, 2H), 2.23 (dd, $J = 5$, 14 Hz, 1H), 1.72-1.90 (m, 2H), 1.6 (brs, OH), 1.40-1.52 (ddd, $J = 5.5$, 11.9, 17.4 Hz, 1H), 1.05 (d, $J = 6.5$ Hz, 3H); ^{13}C NMR (75.2 MHz, $CDCl_3$) δ 178.5 (C=O), 84.9 (CH), 60.8 (CH_2), 50.4 (CH), 41.4 (CH_2), 40.0 (CH), 32.5 (CH), 29.5 (CH_2), 17.3 (CH_3); mass (%): 170 (M^+ , 10), 140 (85), 95 (47), 81 (100), 69 (35), 55 (40), 41 (41). Anal. Calcd for $C_9H_{14}O_3$: C, 63.51; H, 8.29. Found: C, 63.62; H, 8.37.

[3aR,4R,5S,6aS]-5-Methyl-4-(2-trimethylsilanyl-ethoxymethoxymethyl)-hexahydro-cyclopenta[b] furan-2-one (12).

To a solution of lactone **7** (90 mg, 0.53 mmol) in dry CH_2Cl_2 (2 mL), under Argon, were added, in the order, tetrabutylammonium fluoride (216 mg, 0.58 mmol), diisopropylethyl amine (450 μL , 2.65 mmol) and trimethylsilyloxyethyl chloride (280 μL , 1.6 mmol). The mixture was stirred at room temperature for 3 h (TLC: hexane /EtOAc = 3:7). The reaction was diluted with CH_2Cl_2 and washed

with aq. $NaHSO_4$. The aqueous layer was extracted with CH_2Cl_2 . The organic layer was dried over Na_2SO_4 and solvent was evaporated. Separation of the residue by column chromatography (20 mg of silica gel, hexane/EtOAc = 8:2) afforded **12** as colorless oil (154 mg; yield = 97%). $[\alpha]_D = +23.94$ ($c = 1.3$, CH_2Cl_2); IR (film) 2950, 1770, 1380, 1280, 1250, 1170, 1040, 940, 860, 840, 740 cm^{-1} ; 1H NMR (300 MHz, $CDCl_3$) δ 5.0 (t, $J = 6.1$ Hz, 1H), 4.66 (ABq, $J = 6.9$ Hz, 2H), 3.70 (dd, $J = 10.2$, 3.8 Hz, 1H), 3.58-3.68 (m, 2H), 3.42-3.52 (m, 1H), 3.06-3.18 (br qu, $J = 7$ Hz, 1H), 2.58-2.64 (m, 2H), 2.22 (dd, $J = 5$, 13.8 Hz, 1H), 1.78-1.92 (m, 2H), 1.45 (ddd, $J = 5.5$, 11.9, 17.4 Hz, 1H), 1.04 (d, $J = 6.5$ Hz, 3H), 0.93-1.00 (m, 2H), 0.02 (s, 9H, 3xMe); ^{13}C NMR (75.2 MHz, CD_2Cl_2) δ 176.3 (CO), 93.6 (CH_2), 83.3 (CH), 65.1 (CH_2), 63.9 (CH_2), 47.4 (CH), 40.4 (CH_2), 39.3

(CH), 31.7 (CH), 28.3 (CH₂), 16.7 (CH₂), 15.9 (CH₃), -3.1 (3xCH₃); ESI: 323.2 ([M+Na]⁺), 622.9 ([2M+Na]⁺). Anal. Calcd for C₁₅H₂₈O₄Si: C, 59.96; H, 9.39. Found: C, 59.83; H, 9.45.

[3a*S*,4*R*,5*S*,6a*S*]-3-Hydroxymethylene-5-methyl-4-(2-trimethylsilyl-ethoxymethoxymethyl)-hexahydro-cyclopenta[*b*]furan-2-one (6).

Lactone **12** (150 mg, 0.5 mmol) in dry Et₂O (7 mL) was added to NaH (60% dispersion in oil, 62 mg, 1.5 mmol) in dry Et₂O (3 mL) under argon at room temperature. After five minutes, freshly distilled HCOOEt (600 μL, 7.4 mmol) was added and the solution was stirred for 20 h, during which time the color turned to orange. The solution was acidified with 0.6N HCl and the aq layer was extracted with EtOAc. The combined organic layers were dried

over MgSO₄ and solvent was evaporated under reduced pressure. Separation of the residue by column chromatography [i) hexane; ii) hexane/EtOAc = 1:1] gave enol **6** as colorless oil (158 mg, yield = 96%); [α]_D = -37.9 (*c*=1.1, CH₂Cl₂); IR (film) 3600-2600, 2955, 1744, 1648, 1375, 1248, 1194, 1110, 1027, 985, 938, 836, 767 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 9.10 (d, *J* = 13.3 Hz, 1H), 7.59 (dd, *J* = 1.9, 13.3 Hz, 1H), 4.94-5.10 (m, 1H), 4.64-4.81 (m, 2H), 3.88 (dd, *J* = 4.3, 10.5 Hz, 1H); 3.60-3.74 (m, 3H), 3.36-3.46 (m, 1H), 2.24 (dd, *J* = 5.2, 13.3 Hz, 1H), 1.80-2.00 (m, 2H), 1.4-1.5 (m, 1H), 1.02 (d, *J* = 6.2 Hz, 3H), 0.94-1.02 (m, 2H), 0.05 (s, 9H, 3xMe); ¹³C NMR (75.2 MHz, CDCl₃) δ 193.7 (C), 176.5 (C), 173.2 (C), 159.7 (CH), 156.3 (CH), 102.1 (C), 99.7 (C), 94.9 (CH₂), 94.7 (CH₂), 84.5 (CH), 81.2 (CH), 67.0 (CH₂), 66.5 (CH₂), 66.3 (CH₂), 65.6 (CH₂), 50.6 (CH), 50.3 (CH), 42.8 (CH), 42.7 (CH), 42.1 (CH₂), 41.8 (CH₂), 32.6 (CH), 32.3 (CH), 18.0 (CH₂), 17.9 (CH₂), 17.1 (CH₃), 16.8 (CH₃), -1.5 (3xCH₃), -1.8 (3xCH₃); ESI: 351.2 ([M+Na]⁺), 679.0 ([2M+Na]⁺). Anal. Calcd for C₁₆H₂₈O₅Si: C, 58.50; H, 8.59. Found: C, 58.62; H, 8.68.

2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl bromide (5).

Oxalyl bromide (2M in CH₂Cl₂, 3.0 mmol, 1.6 mL) was added to a stirred solution of 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranose (1.3 g, 2.3 mmol) dissolved in dry CH₂Cl₂ (15 mL) and DMF (0.84 mL). The mixture was stirred under argon at room temperature for 30 min and then cooled to 0°C. The organic layer was washed with cold H₂O and then dried over MgSO₄. Solvent was evaporated and the residual product was immediately used in the following step.

[3*E*,3a*S*,4*R*,5*S*,6a*S*]-5-Methyl-4-(2-trimethylsilyl-ethoxymethoxymethyl)-3-([2*R*,3*R*,4*S*,5*R*,6*R*]-3,4,5-tris-benzyloxy-6-benzyloxymethyl-tetrahydro-pyran-2-yloxymethylene)-hexahydro-cyclopenta[*b*]furan-2-one (13).

Dry K₂CO₃ (250 mg, 1.8 mmol) was added to enol **6** (148 mg, 0.45 mmol) dissolved in dry NMP (10 mL) under argon. Five minutes later, 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl bromide (**5**) (1.4 g, 2.25 mmol), dissolved in NMP (3 mL), was added dropwise. The reaction

was checked by TLC (hexane/EtOAc = 7:3) and went to completion 4 h later. The mixture was diluted with Et₂O and washed with H₂O, followed by 5% aq NaHCO₃. The aqueous phase was extracted with EtOAc and the combined organic layers were dried over MgSO₄, filtered, and evaporated. Separation of the residue by column chromatography with hexane/ EtOAc = 8:2 yielded lactone **13** (364 mg, yield = 95%) as colorless solid, m.p. = 86°C-90°C; [α]_D = -70.3 (*c*=1.1, CH₂Cl₂); IR (nujol) 3033, 2952, 1750, 1676, 1478, 1361, 1209, 1071, 835, 736, 697, 678 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 7.56 (d, *J* = 1.9 Hz, 1H), 7.12-7.48 (m, 20H), 4.74-5.00 (m, 7H), 4.46-4.66 (m, 5H), 3.45-3.85 (m, 11H), 2.24 (dd, *J* = 4.8, 13.6 Hz, 1H), 1.80-2.00 (m, 2H), 1.43 (ddd, *J* =

5, 11.2, 16.2 Hz, 1H), 1.08 (d, $J = 6.0$ Hz, 3H), 0.88-0.96 (m, 2H), 0.05 (s, 9H, 3xMe); ^{13}C NMR (75.2 MHz, CD_2Cl_2) δ 173.1 (CO), 153.6 (CH), 139.4 (C), 139.0 (C), 129.0 (CH), 128.7 (CH), 128.6 (CH), 128.57 (CH), 128.53 (CH), 128.33 (CH), 109.3 (C), 105.1 (anomeric CH, $J_{\text{CH}}^1 = 162$ Hz), 95.8 (CH_2), 84.9 (CH), 83.8 (CH), 82.3 (CH), 78.0 (CH), 76.4 (CH), 76.3 (CH_2), 75.7 (CH), 74.2 ($2\times\text{CH}_2$), 69.2 (CH_2), 67.3 (CH_2), 65.5 (CH_2), 51.5 (CH_2), 44.4 (CH), 42.2 (CH), 34.8 (CH_2), (CH), 18.9 (CH_2), 18.3 (CH_3), -0.9 ($3\times\text{CH}_3$); ESI: 873.5 ($[\text{M}+\text{Na}]^+$), 1723.2 ($[2\text{M}+\text{Na}]^+$). Anal. Calcd for $\text{C}_{50}\text{H}_{62}\text{O}_{10}\text{Si}$: C, 70.56; H, 7.34. Found: C, 70.67; H, 7.42.

[3E,3aS,4R,5S,6aS]-4-Hydroxymethyl-5-methyl-3-([2R,3R,4S,5R,6R]-3,4,5-tris-benzyloxy-6-benzyloxymethyl-tetrahydro-pyran-2-yloxymethylene)-hexahydro-cyclopenta[b]furan-2-one (4).

nBuSH (30 μL , 0.225 mmol) and MgBr_2 (56 mg, 0.27 mmol) were added in the order to lactone **13** (80 mg, 0.09 mmol) dissolved in dry Et_2O (1.5 mL) and CH_2Cl_2 (1.5 mL). The mixture was stirred for 7 h at rt, monitored by TLC (hexane/ $\text{EtOAc} = 6:4$), diluted with CH_2Cl_2 , and

washed with 5% aq NaHCO_3 . The aqueous layer was extracted with CH_2Cl_2 . The combined organic layers were dried over Na_2SO_4 , filtered, and evaporated. The residue was separated by column chromatography. Elution with hexane/ $\text{EtOAc} = 75:25$ afforded free alcohol **4** (48 mg, yield = 75%) as a pale yellow oil; $[\alpha]_{\text{D}} = -57.8$ ($c = 0.495$, CH_2Cl_2); IR (film) 3583, 3031, 2872, 1738, 1676, 1454, 1372, 1308, 1242, 1070, 847, 738, 699 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 7.57 (d, $J = 2.1$ Hz, 1H), 7.15-7.40 (m, 20H), 4.74-4.96 (m, 7H), 4.48-4.66 (m, 3H), 3.44-3.80 (m, 9H), 2.68 (dd, $J = 8.0, 6.6$ Hz, 1H), 2.23 (dd, $J = 5.4, 13.8$ Hz, 1H), 1.76-1.92 (m, 1H), 1.35-1.65 (m, 2H), 1.04 (d, $J = 6.2$ Hz, 3H); ^{13}C NMR (75.2 MHz, CD_2Cl_2) δ 172.7 (CO), 153.7 (CH), 139.3 (C), 138.98 (C), 138.93 (C), 138.8 (C), 129.1 (CH), 129.0 (CH), 128.74 (CH), 128.70 (CH), 128.6 (CH), 128.5 (CH), 128.4 (CH), 128.35 (CH), 109.6 (C), 105.3 (CH), 84.8 (CH), 83.7 (CH), 82.1 (CH), 77.8 (CH), 76.6 (CH), 76.2 (CH_2), 75.8 (CH_2), 75.7 (CH_2), 74.2 (CH_2), 69.0 (CH_2), 61.7 (CH_2), 54.8 (CH), 43.9 (CH), 42.3 (CH_2), 33.3 (CH), 17.9 (CH_3); ESI: 743.5 ($[\text{M}+\text{Na}]^+$). Anal. Calcd for $\text{C}_{44}\text{H}_{48}\text{O}_9$: C, 73.31; H, 6.71. Found: C, 73.12; H, 6.81.

[2aS,4S,4aR,7R,7aS,7bS]-4-Methyl-7-([2S,3R,4S,5R,6R]-3,4,5-tris-benzyloxy-6-benzyloxymethyl-tetrahydro-pyran-2-yloxy)-octahydro-2,6-dioxo-cyclopenta[cd]inden-1-one (15).

$\text{Hg}(\text{OCOCF}_3)_2$ (136 mg, 0.32 mmol) was added to alcohol **4** (58 mg, 0.08 mmol) dissolved in dry THF (2 mL) under argon, and the mixture was stirred at rt for 4 d, monitored by TLC (hexane/ $\text{EtOAc} = 6:4$). Solvent was evaporated and the crude product was dissolved in degassed THF/

5% aq NaOH , giving an orange solution. NaBH_4 was added until complete discoloration, followed by acetone to destroy excess NaBH_4 . Mercury was separated and the supernatant solution was diluted with EtOAc and brine. The aq layer was extracted with EtOAc and the combined organic layers were washed with brine, dried over Na_2SO_4 , and evaporated. Separation of the residue by column chromatography (hexane/ $\text{EtOAc} = 8:2$) yielded lactone **15** as colorless solid (30 mg, yield = 50%), m.p. = 125°C - 130°C ; $[\alpha]_{\text{D}} = +50.2$ ($c = 0.8$, CH_2Cl_2); IR (nujol) 3033, 2918, 1763, 1453, 1354, 1073, 1000, 909, 732 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.1-7.4 (m, 20H), 5.52 (s, 1H, 3-H), 4.5-5.0 (m, 10H), 4.35 (dd, $J = 4, 13$ Hz, 1H, 1 β -H), 3.6-3.8 (m, 4H), 3.45-3.6 (m, 3H), 3.15

(ddd, $J = 6.6, 10.3, 13$ Hz, 1H, 5-H), 2.63 (d, $J = 10.3$ Hz, 1H, 4-H), 2.25 (dd, $J = 6.7, 13.4$ Hz, 1H, 7 α -H), 1.95-2.10 (m, 1H, 8-H), 1.25-1.40 (m, 2H, 7 β -H and 9-H), 1.05 (d, $J = 6.4$ Hz, 3H, CH₃); ¹³C NMR (75.2 MHz, CD₂Cl₂) δ 175.8 (CO), 139.6 (C), 139.3 (C), 139.2 (C), 139.1 (C), 129.51 (CH), 129.13 (CH), 129.04 (CH), 129.02 (CH), 128.82 (CH), 128.63 (CH), 128.61 (CH), 128.50 (CH), 128.43 (CH), 128.38 (CH), 128.32 (CH), 128.26 (CH), 103.1 (CH), 98.2 (CH), 85.5 (CH), 84.5 (CH), 83.2 (CH), 78.4 (CH), 76.2 (CH₂), 75.8 (CH₂), 75.7 (CH), 75.6 (CH₂), 74.0 (CH₂), 69.6 (CH₂), 57.0 (CH₂), 42.2 (CH₂), 42.1 (CH), 42.0 (CH), 36.6 (CH), 33.3 (CH), 17.1 (CH₃); ESI: 743.5 ([M+Na]⁺). Anal. Calcd for C₄₄H₄₈O₉: C, 73.31; H, 6.71. Found: C, 73.42; H, 6.81.

[2a*S*,4*S*,4a*R*,7*R*,7a*S*,7b*S*]-4-Methyl-7-([2*S*,3*R*,4*R*,5*R*,6*R*]-3,4,5-trihydroxy-6-hydroxymethyl-tetrahydro-pyran-2-yloxy)-octahydro-2,6-dioxa-cyclopenta[*cd*]inden-1-one (1). (Semperoside A)

A catalytic amount of palladium, 5 wt. % on activated carbon, was added to lactone **15** (21 mg, 0.029 mmol) dissolved in EtOAc (2 mL) and MeOH (1 mL). The mixture was stirred under hydrogen at rt for 30 min, monitoring the reaction by TLC (EtOAc / EtOH / toluene = 4:2:1). The mixture was filtered and solvent was evaporated. Separation of the residue by column chromatography (EtOAc / EtOH / toluene = 4:1:1) afforded compound **1** (semperoside A) (10 mg, yield = 95%.) as colorless solid, mp 182-184 °C; $[\alpha]_D^{25} = +67.2$ ($c = 0.3$, MeOH); CD = 215 nm ($\Delta\epsilon = -1.3$; $c = 10^{-3}$ M in MeOH); ¹H NMR (400 MHz, D₂O) δ 5.3 (s, 1H, 3-H), 5.05 (dd, $J = 4.5, 5.5$ Hz, 1-H, 6-H), 4.6 (d, $J = 8$ Hz, 1H, 1'-H), 4.18 (dd, $J = 4.1, 12.7$ Hz, 1H, 1 β -H), 3.79 (dd, $J = 3, 11.4$ Hz, 1H, 6'-H), 3.65 (dd, $J = 4.6, 11.4$ Hz, 1H, 6'-H'), 3.57 (br d, $J = 12.7$ Hz, 1H, 1 α -H), 3.2-3.5 (m, 5H), 3.06 (d, $J = 10.5$ Hz, 1H, 4-H), 2.09 (dd, $J = 5.3, 14.2$ Hz, 1H, 7 α -H), 1.65-1.78 (m, 1H, 8-H), 1.43 (ddd, $J = 4, 10, 12$ Hz, 1H, 9-H), 1.35 (ddd, $J = 4.3, 13, 14$ Hz, 1H, 7 β -H), 0.92 (d, $J = 6.4$ Hz, 3H, CH₃); ¹³C NMR (75.2 MHz, D₂O) δ 178.9 (CO), 102.5 (CH), 97.5 (CH), 86.7 (CH), 76.6 (CH), 75.9 (CH), 73.6 (CH), 69.7 (CH), 60.8 (CH₂), 57.2 (CH₂), 41.7 (CH), 40.8 (CH₂), 40.7 (CH), 35.6 (CH), 32.8 (CH), 15.9 (CH₃); ESI: 383.2 ([M+Na]⁺), 743.1 ([2M+Na]⁺). Anal. Calcd for C₁₆H₂₄O₉: C, 53.33; H, 6.71. Found: C, 53.21; H, 6.63.

Iridoid atomic numbering in NMR-spectra: