Supplementary data

Verification of the Versatility of the *In Vitro* Enzymatic Reaction Giving (+)-*cis*-12-Oxo-phytodienoic Acid

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**EXPERIMENTAL SECTION**

1. **General Experimental Procedures**

Optical rotations were obtained with a JASCO P-2200 polarimeter. NMR spectra were recorded in CDCl3 using a JNM-EX 270 FT-NMR spectrometer (JEOL; 1H NMR: 270 MHz, 13C NMR: 67.5 MHz) and AMX 500 spectrometer (Bruker; 1H NMR: 500 MHz, 13C NMR: 126 MHz). FDMS and FIMS analyses were performed on a JMS-T100GCV instrument (JEOL), and CIMS was performed on a JMS-SX102A instrument (JEOL).

1. **Synthesis of LA amino acid conjugates** 1

To a stirred mixture of LA (0.88 mmol, 245.0 mg) and N(CH2CH3)3 (0.98 mmol, 0.14 mL) in THF (11 mL) at -10°C was added a solution of ethyl chloroformate (0.98 mmol, 0.098 mL), and the mixture was further stirred for 20 min. To this reaction mixture was added a solution of an amino acid (1.77 mmol) in 0.3 M NaOH (6.9 mL), and the reaction mixture was further stirred for 25 min at 25°C. The volatile component of the reaction mixture was removed under reduced pressure to give a crude oil. The resulting oil was washed with the following solutions: 0.1 M HCl (30 mL) and EtOAc (30 mL×3). The combined organic layers were dried over Na2SO4 and filtered. The volatile component of the solution was removed under reduced pressure to give a crude oil, and the resulting oil was subjected to silica gel column chromatography, whose conditions are described in each section for each synthesized compound.

LA-L-Gly (212.6 mg, 72%), purified using a solution of CH3COOH:EtOAc:*n*-hexane = 1:70:30 by silica gel (30 g) column chromatography.

FD-HR-MS: *m/z* 336.25467 [M+H]+; calculated *m/z* 335.24604 for C20H33NO3.

1H-NMR (CDCl3, 270 MHz): H 10.51 (s, 1H), 6.28 (s, 1H), 5.44-5.20 (m, 6H), 4.18-3.97 (m, 2H), 2.84-2.66 (m, 4H), 2.26 (t, *J*=8.0 Hz, 2H), 2.08-1.94 (m, 4H), 1.70-1.50 (m, 2H), 1.40-1.10 (m, 8H), 0.92 (t, *J­*=8.0 Hz, 3H).

LA- L-Ala (262.2 mg, 85%), purified using a solution of CH3COOH:EtOAc:*n*-hexane = 1:60:40 by silica gel (30 g) column chromatography.

FD-HR-MS: *m/z* 350.27110 [M+H]+; calculated *m/z* 350.26952 for C21H36NO3.

1H-NMR (CDCl3, 270 MHz): H 7.18-6.85 (br.s, 1H), 5.45-5.18 (m, 6H), 3.70 (q, *J*=7.0 Hz, 1H), 2.87-2.66 (m, 4H), 2.21 (t, *J*=7.2 Hz, 2H), 2.10-1.95 (m, 4H), 1.69-1.52 (m, 2H), 1.43 (d, *J*=7.2 Hz, 3H), 1.34-1.15 (m, 8H), 0.98 (t, *J*=7.6 Hz, 3H).

LA- L-Val (355.3 mg, quantitative), purified using a solution of CH3COOH:EtOAc:*n*-hexane = 1:40:60 by silica gel (40 g) column chromatography.

FD-HR-MS: *m/z* 378.29933 [M+H]+; calculated *m/z* 378.30820 for C23H40NO3.

1H-NMR (CDCl3, 270 MHz): H 10.46 (s, 1H), 5.53-4.99 (m, 6H), 4.73-4.14 (m, 1H), 2.92-2.52 (m, 4H), 2.36-2.08 (m, 3H), 2.08-1.84 (m, 4H), 1.77-1.43 (m, 2H), 1.40-1.10 (m, 8H), 1.05-0.53 (m, 9H).

LA- L-Leu (254.2 mg,74%), purified using a solution of CH3COOH:EtOAc:*n*-hexane = 1:40:60 by silica gel (45 g) column chromatography.

FD-HR-MS: *m/z* 392.29 [M+H]+; calculated *m/z* 392.31647 for C24H42NO3.

1H-NMR (CDCl3, 270 MHz): H 5.54-5.00 (m, 6H), 4.54-4.00 (m, 1H), 2.89-2.72 (m, 4H), 2.31-2.17 (m, 2H), 2.12-2.00 (m, 4H), 1.82-1.51 (m, 5H), 1.43-1.18 (m, 8H), 1.04-0.84 (m, 9H).

LA- L-Ile (261.9 mg,76%), purified using a solution of CH3COOH:EtOAc:*n*-hexane = 1:40:60 by silica gel (40 g) column chromatography.

FD-HR-MS: *m/z* 392.31498 [M+H]+; calculated *m/z* 392.31647 for C24H42NO3.

1H-NMR (CDCl3, 270 MHz): H 10.66 (s, 1H), 5.49-5.15 (m, 6H), 4.59 (dd, *J*=4.6, 8.6 Hz, 1H), 2.94-2.58 (m, 4H), 2.28 (t, *J*=8.1 Hz, 2H), 2.02-1.80 (m, 5H), 1.60-1.44 (m, 2H), 1.40-1.10 (m, 10H), 1.04-0.59 (m, 9H).

LA- L-Phe (374.2 mg, quantitative), purified using a solution of CH3COOH:EtOAc:*n*-hexane = 1:50:50 by silica gel (50 g) column chromatography.

FD-HR-MS: *m/z* 426.30099 [M+H]+; calculated *m/z* 425.29299 for C27H39NO3.

1H-NMR (CDCl3, 270 MHz): H 7.70-7.48 (br.s, 1H), 7.28-7.04 (m, 5H), 5.51-5.16 (m, 6H), 4.98-4.74 (m, 1H), 3.26-2.98 (m, 2H), 2.94-2.52 (m, 4H), 2.23-2.08 (m, 2H), 2.06-1.92 (m, 4H), 1.65-1.42 (m, 2H), 1.39-1.10 (m, 8H), 0.94 (t, *J*=7.5 Hz, 3H).

LA- L-Tyr (113.1 mg, 29.7%), purified using a solution of CH3COOH:EtOAc:*n*-hexane = 1:80:20 by silica gel (50 g) column chromatography.

FD-HR-MS: *m/z* 442.29487 [M+H]+; calculated *m/z* 442.29573 for C27H40NO4.

1H-NMR (CDCl3, 270 MHz): H 6.92 (d, *J*=7.5 Hz, 2H), 6.66 (d, *J*=7.5 Hz, 2H), 5.42-5.12 (m, 6H), 4.92-4.71 (m, 1H), 3.12-2.88 (m, 2H), 2.86-2.64 (m, 4H), 2.21-1.94 (m, 4H), 2.06-1.92 (m, 4H), 1.67-1.40 (m, 2H), 1.37-1.07 (m, 8H), 0.94 (t, *J*=7.5 Hz, 3H).

LA- L-Trp (198.5 mg, 49.4%), purified using a solution of CH3COOH:EtOAc:*n*-hexane = 1:80:20 by silica gel (50 g) column chromatography.

FD-HR-MS: *m/z* 464.30427 [M]+; calculated *m/z* 464.30389 for C29H40N2O3.

1H-NMR (CDCl3, 270 MHz): H 7.55 (d, *J*=7.5 Hz, 2H), 7.33 (d, *J*=7.5 Hz, 2H), 7.27-7.04 (m, 3H), 7.03-6.96 (m, 2H), 5.44-5.16 (m, 6H), 4.97-4.82 (m, 1H), 3.39-3.18 (m, 2H), 2.82-2.59 (m, 4H), 2.15-1.84 (m, 6H), 1.58-1.37 (m, 2H), 1.36-1.08 (m, 8H), 0.95 (t, *J*=7.5 Hz, 3H).

LA- L-Glu (230.8 mg, 64%), purified using a solution of CH3COOH:CHCl3:MeOH = 1:88:12 by silica gel (50 g) column chromatography.

FD-HR-MS: found *m/z* 408.27544 [M-H]-; calculated *m/z* 406.27500 for C23H38NO5.

1H-NMR (CDCl3, 270 MHz): H 8.81-8.16 (br.s, 1H), 5.48-5.16 (m, 6H), 4.74-4.54 (m, 1H), 2.86-2.66 (m, 4H), 2.56-2.41 (m, 2H), 2.32-2.20 (m, 2H), 2.20-2.10 (m, 2H), 2.10-1.92 (m, 4H), 1.70-1.48 (m, 2H), 1.41-1.15 (m, 8H), 0.95 (t, *J*=7.5 Hz, 3H).

LA- L-Gln (283.1 mg, 79%), purified using a solution of CH3COOH:CHCl3:MeOH= 1:82:18 by silica gel (30 g) column chromatography.

FD-HR-MS: found *m/z* 407.29035 [M+H]-; calculated *m/z* 407.29098 for C23H39N2O4.

1H-NMR (CDCl3, 270 MHz): H 5.45-5.2 (m, 6H), 4.50-4.37 (m, 1H), 2.85-2.63 (m, 4H), 2.54-2.33 (m, 2H), 2.32-2.18 (m, 2H), 2.16-2.04 (m, 2H), 2.03-1.94 (m, 4H), 1.69-1.51 (m, 2H), 1.40-1.20 (m, 8H), 0.95 (t, *J*=7.5 Hz, 3H).

1. **Synthesis of OPDA amino acid conjugates**

*Preparation of acetone powder using flax seeds (Linum usitatissimum)* 2*.*

Seeds (200 g) of flax (*Linum usitatissimum*) were crushed into a powder using a mixer and stirred with a solution of acetone (2 L) at -30°C. The mixture was filtered using a vacuum filtration apparatus to give a powder, and to the resulting powder, a solution of acetone (2 L) was added at -30°C. The mixture was further stirred for 20 min and filtered using a vacuum filtration apparatus to remove the acetone, which afforded an acetone powder (approximately 40 g). The powder was kept at -20°C until being used for the experiments.

*Preparation of a solution to convert LA amino acid conjugates into OPDA amino acid conjugates*

Preparation of recombinant *Escherichia coli* with the *PpAOC2* geneand a solution containing the PpAOC2 protein were performed according to a reported method 3. The acetone powder derived from flax seed (1250 mg) was added to the prepared solution containing PpAOC2 protein (100 μg/mL, 10 mL), and the mixture was stirred for 1 hour at 4°C. The resulting mixture was centrifuged (15000 rpm, 30 min, 4°C), and the supernatant (Sup-A) was used as the solution to convert LA-amino acid conjugates into OPDA-amino acid conjugates.

*Preparation of OPDA-amino acid conjugates* 4

To a solution of LA-amino conjugate (0.17 mmol) in EtOH (40 L) was added buffer solution (50 mM Tris-HCl, pH 8.0) containing 20 mM NaCl and Tween 20 (approximately 40 L), and the solution was vigorously mixed until the emulsion disappeared, and in some cases, additional Tween 20 solution (approximately 60 L) was added until the emulsion disappeared. Then, a solution of Sup-A (100 L) prepared previous section was added, and the mixture was further stirred for 3 hours at 23°C. The resulting solution was washed with solutions of 0.1 M HCl (30 mL) and EtOAc (30 mL×3). The combined organic layers were dried over Na2SO4 and filtered. The volatile component of the solution was removed under reduced pressure to give a crude oil, and the resulting oil was subjected to silica gel column chromatography, whose conditions are described in each section for each synthesized compound.

OPDA- L-Gly (26%), purified using a solution of CH3COOH:CHCl3:MeOH = 1:95:5 by silica gel (15 g) column chromatography.

FD-HR-MS: *m/z* 350.23279 [M+H]+; calculated *m/z* 350.23313 for C20H32NO4.

1H-NMR (CDCl3, 270 MHz): H 8.77-8.27 (m, 1H), 7.74-7.51 (m, 1H), 6.28-6.02 (m, 1H), 5.44-5.11 (m, 2H), 3.70-3.44 (m, 2H), 3.00-2.82 (m, 1H), 2.56-2.30 (m, 2H), 2.29-2.13 (m, 3H), 2.13-1.78 (m, 3H), 1.78-1.45 (m, 2H), 1.44-1.00 (m, 9H), 0.99-0.62 (m, 3H).

OPDA- L-Ala (24%), purified using a solution of CH3COOH:CHCl3:MeOH = 1:97:3 by silica gel (15 g) column chromatography.

FD-HR-MS: *m/z* 364.24790 [M+H]+; calculated *m/z* 364.24878 for C21H34NO4.

1H-NMR (CDCl3, 270 MHz): H 7.88-7.44 (m, 1H), 6.32-5.82 (m, 2H), 5.52-5.00 (m, 2H), 3.73-3.38 (m, 1H), 3.01-2.25 (m, 3H), 2.23-2.02 (m, 3H), 2.01-1.76 (m, 3H), 1.75-1.42 (m, 2H), 1.41-0.96 (m, 12H), 0.95-0.70 (m, 3H).

OPDA- L-Val (25%), purified using a solution of CH3COOH:EtOAc:*n*-hexane = 1:50:50 by silica gel (15 g) column chromatography.

FD-HR-MS: *m/z* 392.28104 [M+H]+; calculated *m/z* 392.28008 for C23H38NO4.

1H-NMR (CDCl3, 270 MHz): H 11.32-10.00 (br.s, 1H), 7.90-7.65 (m, 1H), 6.40-6.20 (m, 1H), 6.20-6.10 (d, *J*=5.4 Hz, 1H), 5.60-5.12 (m, 2H), 4.77-4.31 (m, 1H), 3.11-2.82 (m, 1H), 2.62-2.34 (m, 2H), 2.32-2.11 (m, 4H), 2.11-1.92 (m, 5H), 1.80-1.48 (m, 3H), 1.43-1.03 (m, 9H), 1.00-0.62 (m, 9H).

OPDA- L-Leu (15%), purified using a solution of CH3COOH:CHCl3:MeOH = 1:98:2 by silica gel (15 g) column chromatography.

FD-HR-MS: *m/z* 406.29511 [M+H]+; calculated *m/z* 406.29573 for C24H40NO4.

1H-NMR (CDCl3, 270 MHz): H 6.13 (dd, *J*=5.9, 1.7 Hz, 2H), 5.69-5.07 (m, 2H), 4.40-4.00 (m, 1H), 3.50-2.92 (m, 1H), 2.81-2.34 (m, 2H), 2.33-2.13 (m, 3H), 2.13-1.92 (m, 3H), 1.91-1.45 (m, 6H), 1.45-1.11 (m, 9H), 1.10-0.68 (m, 9H).

OPDA- L-Ile (14%), purified using a solution of CH3COOH:EtOAc:*n*-hexane = 1:50:50 by silica gel (20 g) column chromatography.

FD-HR-MS: *m/z* 406.29491 [M+H]+; calculated *m/z* 406.29573 for C24H40NO4.

1H-NMR (CDCl3, 270 MHz): H 7.74-7.46 (m, 1H), 6.35-5.91 (m, 2H), 5.46-5.06 (m, 2H), 4.48-4.18 (m, 1H), 2.96-2.76 (m, 1H), 2.55-2.27 (m, 2H), 2.20-2.06 (m, 2H), 2.05-2.00 (m, 1H), 1.99-1.89 (m, 2H), 1.88-1.73 (m, 1H), 1.70-1.58 (m, 1H), 1.58-1.46 (m, 2H), 1.45-1.33 (m, 2H), 1.32-0.98 (m, 9H), 0.93-0.63 (m, 9H).

OPDA- L-Phe (16%), purified using a solution of CH3COOH:EtOAc:*n*-hexane = 1:50:50 by silica gel (20 g) column chromatography.

FD-HR-MS: *m/z* 440.2813 [M+H]+; calculated *m/z* 440.28008 for C27H38NO4.

1H-NMR (CDCl3, 270 MHz): H 7.63-7.42 (m, 1H), 7.12-6.96 (m, 5H), 6.87-6.60 (m, 1H), 6.14-6.00 (m, 1H), 5.47-5.14 (m, 2H), 4.54-4.32 (m, 1H), 3.63-3.05 (m, 2H), 2.93-2.75 (m, 1H), 2.50-2.25 (m, 2H), 2.11-1.75 (m, 6H), 1.74-1.49 (m, 2H), 1.32-0.93 (m, 9H), 0.84 (t, *J*=7.5 Hz, 3H).

OPDA- L-Tyr (4%), purified using a solution of CH3COOH:EtOAc:*n*-hexane = 1:60:40 by silica gel (20 g) column chromatography.

FD-HR-MS: *m/z* 456.27435 [M+H]+; calculated *m/z* 456.27500 for C27H38NO5.

1H-NMR (CDCl3, 270 MHz): H 7.63-7.42 (m, 1H), 7.12-6.96 (m, 5H), 6.87-6.60 (m, 1H), 6.14-6.00 (m, 1H), 5.47-5.14 (m, 2H), 4.54-4.32 (m, 1H), 3.63-3.05 (m, 2H), 2.93-2.75 (m, 1H), 2.50-2.25 (m, 2H), 2.11-1.75 (m, 6H), 1.74-1.49 (m, 2H), 1.32-0.93 (m, 9H), 0.84 (t, *J*=7.5 Hz, 3H).

OPDA- L-Glu (38%), purified using a solution of CH3COOH:CHCl3:MeOH = 1:88:12 by silica gel (20 g) column chromatography.

HR-EI-MS: found *m/z* 420.2390 [M-H]-; calculated *m/z* 420.2386 for C23H34NO6.

1H-NMR (CDCl3, 270 MHz): H 6.63-6.55 (m, 1H), 5.59-5.20 (m, 2H), 4.58-4.20 (m, 1H), 3.29-3.00 (m, 1H), 2.58-2.30 (m, 3H), 2.29-2.12 (m, 3H), 2.10-1.82 (m, 5H), 1.70-1.42 (m, 3H), 1.38-1.08 (m, 9H), 0.90 (t, *J*=7.5 Hz, 3H).

OPDA- L-Gln (48%), purified using a solution of CH3COOH:CHCl3:MeOH = 1:82:18 by silica gel (20 g) column chromatography.

HR-EI-MS: found *m/z* 419.2585 [M-H]-; calculated *m/z* 419.2546 for C23H35N2O5.

1H-NMR (CDCl3, 270 MHz): H 7.80-7.65 (m, 1H), 6.55-6.12 (m, 1H), 5.59-5.14 (m, 2H), 4.57-4.35 (m, 1H), 3.04-2.70 (m, 1H), 2.60-2.27 (m, 4H), 2.26-2.18 (m, 2H), 2.18-1.88 (m, 5H), 1.75-1.63 (m, H), 1.62-1.45 (m, 2H), 1.44-1.04 (m, 9H), 0.89 (t, *J*=7.5 Hz, 3H).

1. **Synthesis of (7*R*,11*S*)-dn-*cis*-OPDA**

*Isolation of (7Z,10Z,13Z)-hexadeca-7,10,13-trienoic acid*

Radish leaves (2 kg) were extracted using EtOH (5 L), and the volatile components of the extract was removed under reduced pressure to give a crude material, which was washed with solutions of H2O (1 L) and EtOAc (1 L × 3). The volatile components of the combined organic layers were removed under reduced pressure to give a crude oil, which was subjected to silica gel (300 g) column chromatography using *n*-hexane:EtOAc = 2:3 as the eluent to give a crude material containing 2,3-dihydroxypropyl (7*Z*,10*Z*,13*Z*)-hexadeca-7,10,13-trienoate. To a solution of the obtained crude material in EtOH was added a solution of 1 M KOH in EtOH, and the mixture stirred for 24 hours at 25°C. The volatile component of the reaction mixture was removed under reduced pressure to give a crude oil. The resulting oil was washed with solutions of 0.1 M HCl (100 mL) and EtOAc (100 mL × 3). The combined organic layers were dried over Na2SO4 and filtered. The volatile components of the solution were removed under reduced pressure to give a crude oil, which was subjected to silica gel column chromatography (*n*-hexane:EtOAc = 4:1) followed by purification by HPLC (YM-Pack ODS-AM, 5 M,  10 mm × 300 mm, MeOH containing 0.1% AcOH) to give (7*Z*,10*Z*,13*Z*)-hexadeca-7,10,13-trienoic acid (28 mg, 0.11 mmol).

(7*Z*,10*Z*,13*Z*)-Hexadeca-7,10,13-trienoic acid

1H NMR (270 MHz, CDCl3) δH: 5.37-5.30 (6H, m）, 2.81 (4H, m), 2.36 (2H, m), 2.08 (4H, m), 1.65 (2H, m), 1.38-1.26 (6H, m), 0.98 (3H, t, *J* = 7.6 Hz). FD-MS: *m/z* 250.14 (rel. int., 89.7490%); FD-HR-MS: *m/z*: calcd. for C16H26O2, 250.19328; found 250.19271.

*Preparation of (7R,11S)-dn-cis-OPDA*

Preparation of (7*R*,11*S*)-dn-*cis*-OPDA was performed by the method described in the previous section “Preparation of OPDA-amino acid conjugates” with some modification. Before being added the solution of Sup-A, (7*Z*,10*Z*,13*Z*)-Hexadeca-7,10,13-trienoic acid (28 mg, 0.11 mmol) was converted into sodium salt using 2M NaOH solution (40 L) in order to improve the solubility of the compound into the solution, and the reaction was accomplished to give a oil. The oil was purified using a silica gel column chromatography (4 g, CH3COOH:EtOAc:*n*-hexane = 1:70:30) to give (7*R*,11*S*)-dn-*cis*-  
OPDA (6.7 mg, 0.025 mmol).

(7*R*,11*S*)-dn-*cis*-OPDA

1H NMR (270 MHz, CDCl3): δH 7.73 (1H, dd, *J* = 6.2, 2.7 Hz), 6.19 (1H, dd, J = 6.2, 2.7 Hz), 5.44-5.36 (2H, m), 2.98 (1H, m), 2.54-2.43 (2H, m), 2.39-2.34 2H, t, J = 7.6 Hz), 2.13-2.03 (2H, m), 1.65 (2H, m), 1.40-1.19 (6H, m), 0.97 (3H, J = 7.6 Hz). FD-MS: *m/z* 265.18 [M + H]+ (rel. int., 88%); []D23 + 110.5 (c 0.3, CHCl3); FD-HR-MS: *m/z*: calcd. for C16H24O3, 264.17254; found 264.17298.

1. **Synthesis of LA monoglyceride**

The synthesis of LA monoglyceride was performed according to a reported method 1.

1. **Synthesis of OPDA monoglyceride**

The synthesis of OPDA monoglyceride was performed according to a reported method 1, except OPDA was used instead of LA.

OPDA monoglyceride

1H NMR (500 MHz, CDCl3) δH: 7.75 (1H, dd, *J* = 5.9, 2.8 Hz), 6.19-6.17 (1H, dd, *J* = 5.9, 1.8 Hz), 5.54-5.21 (2H, m), 4.22-4.13 (2H, m), 3.93 (1H, m), 3.72-3.56 (2H, m), 2.98 (1H, m), 2.67-2.41 (2H, m), 2.35 (2H, t, *J* = 7.3 Hz), 2.19-1.99 (2H, m), 1.63 (2H, m), 1.31 (8H, m), 0.97 (3H, t, *J* = 7.7 Hz). FD-MS: *m/z* 367.23 [M + H]+ (rel. int., 100%); FD-HR-MS: *m/z*: calcd. for C21H34O5, 366.24062; found 366.24118.

1. **Synthesis of (9*Z*,12*Z*,15*Z*)-*N*-(2,3-dihydroxypropyl) octadeca-9,12,15-trienamide**

The synthesis of (9*Z*,12*Z*,15*Z*)-*N*-(2,3-dihydroxypropyl) octadeca-9,12,15-trienamide was performed according to a reported method 1 except (2,2-dimethyl-1,3-dioxolan-4-yl)methanamine was used instead of propane-1,2,3-triol.

1H NMR (270 MHz, CDCl3) δH: 6.18 (1H, s), 5.37-5.35 (6H, m), 3.76 (1H, m), 3.54 (2H, m), 3.40 (2H, m), 2.79 (4H, m), 2.22 2H, t, *J* = 7.6 Hz), 2.10-1.95 (4H, m), 1.62 (2H, m), 1.31 (8H, m), 0.98 (3H, t, *J* = 7.6 Hz). FD-MS: *m/z* 351.25 (rel. int., 23%); FD-HR-MS: *m/z*: calcd. for C21H37NO3, 351.27734; found 351.27619.

1. **Synthesis of *N*-(2,3-dihydroxypropyl)-8-((1*S*,5*S*)-4-oxo-5-((*Z*)-pent-2-en-1-  
   yl)cyclopent-2-en-1-yl)octanamide.**

The synthesis of *N*-(2,3-dihydroxypropyl)-8-((1*S*,5*S*)-4-oxo-5-((*Z*)-pent-2-en-1-  
yl)cyclopent-2-en-1-yl)octanamide was performed according to the method 3 described in the section of “*Preparation of OPDA-amino acid conjugates*”

1H NMR (270 MHz, CDCl3) δH: 7.73 (1H, dd, *J=* 6.2, 2.7 Hz), 6.19 (1H, dd, *J*= 6.2, 2.7 Hz), 5.44-5.36 (2H, m), 2.98 (1H, m), 2.54-2.43 (2H, m), 2.39-2.34 (2H, t, *J*= 7.6 Hz), 2.13-2.03 (2H, m), 1.65 (2H, m), 1.40-1.19 (6H, m), 0.97 (3H, *J*= 7.6 Hz); FD-MS: *m/z* 265.18 [M+H]+ (rel. Int., 88%); FD-HR-MS: *m/z* 264.17298 (calcd. for, C16H24O3, 264.17254).

1. **UPLC MS/MS analysis of OPDA and OPDA monoglyceride**

Measurements of OPDA and OPDA monoglycerides were accomplished according to a reported method 5 except the following parameters to measure OPDA monoglyceride in positive mode were used: precursor ion [M+ H]+: *m/z* 367.43, transition ion: *m/z* 275.20, cone voltage: 43 V, collision energy: 12.5 eV; and OPDA in negative mode: precursor ion [M- H]-: *m/z* 291.37, transition ion: *m/z* 164.99 6, cone voltage: 50 V, collision energy: 22 eV.

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