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Title	Potato tuber-inducing activities of jasmonic acid and related-compounds (II)
Author(s)	Miyawaki, Kanji; Inoue, Shiro; Kitaoka, Naoki et al.
Citation	Bioscience biotechnology and biochemistry, 85(12), 2378-2382 https://doi.org/10.1093/bbb/zbab161
Issue Date	2021-12
Doc URL	https://hdl.handle.net/2115/87357
Rights	This is a pre-copyedited, author-produced version of an article accepted for publication in Bioscience biotechnology and biochemistry following peer review. The version of record Kanji Miyawaki, Shiro Inoue, Naoki Kitaoka, Hideyuki Matsuura, Potato tuber-inducing activities of jasmonic acid and related-compounds (II), Bioscience, Biotechnology, and Biochemistry, Volume 85, Issue 12, December 2021, Pages 2378-2382, is available online at: https://doi.org/10.1093/bbb/zbab161 .
Type	journal article
File Information	33_Supplementary data_03.pdf



Supplementary data

Potato Tuber-inducing Activities of Jasmonic acid and Related-Compounds (II)

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References

I. 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 (Bruker, ¹H NMR: 500 MHz, ¹³C NMR: 126 MHz). FDMS and FIMS analyses were performed on a JMS-T100GCV (JEOL). Silica gel 60 F₂₅₄ TLC plates (0.25 and 0.5 mm thickness: Merck, Darmstadt, Germany) were used for analytical and preparative TLC, respectively, and silica gel column chromatography was carried out using silica gel (Wako-gel C-200) provided by Wako Pure Chem. (Japan).

II. Synthesis of *cis*-(-)-OPDA

Synthesis of *cis*-(-)-OPDA was performed according to a previously reported method (Kajiwara *et al.* 2012).

III. Synthesis of *iso*-OPDA

Synthesis of *cis*-OPDA was performed according to a previously reported method (Dabrowska and Boland 2007).

IV. Synthesis of *cis*-(+)-OPDA-L-Ile

The synthesis of *cis*-(+)-OPDA-L-Ile was performed according to a previously reported method (Uchiyama *et al.* 2018).

V. Synthesis of (+)-4,5-didehydroJA

The synthesis of (+)-4,5-didehydroJA was performed according to a previous paper (Monte *et al.* 2019) using (-)-JA isolated from the culture filtrate of *Lasiodiplodia theobormae* (Aldridge *et al.* 1971; Nakamori *et al.* 1994).

In brief, diethyl allyl phosphate (100 μ L, 0.56 mmol), Na₂CO₃ (71 mg, 0.67 mmol), and palladium acetate (7.56 mg, 0.036 mmol) were added to a stirred solution of (+)-MeJA (67 mg, 0.3 mmol) originated from the culture filtrate of *L. theobromae* in DMF (3 mL) at 80 °C, and the reaction mixture was further stirred for 12 hours. A usual work-up was performed for purification to give methyl (+)-4,5-didehydrojasmonate (35 mg, 0.17 mmol, 56%).

(+)-Methyl 4,5-didehydrojasmonate:

¹H NMR (CDCl₃, 270 MHz) δ_{H} : 7.61 (1H, dd, $J=5.8, 2.5$ Hz), 6.19 (1H, dd, $J=5.8, 1.1$ Hz), 5.45 (1H, m), 5.21 (1H, m), 3.64 (3H, s), 2.60-1.98 (8H, m), 0.94 (3H, t, $J=7.9$ Hz).

To a stirred mixture of methyl (+)-4,5-didehydrojasmonate (8 mg, 0.036 mmol) in 0.1 M phosphate buffer (8 mL, pH 8.0) and MeOH (1.5 mL), esterase was added from porcine liver (Sigma), and the reaction mixture was further stirred for 5 hours at 30°C. A usual work-up was performed for purification to generate (+)-4,5-dhidehydroJA (4.6 mg, 0.022 mmol, 61%).

(+)-4,5-DihidehydroJA:

FD-MS: m/z 208 $[M]^+$; $^1\text{H NMR}$ (CDCl_3 , 270 MHz) δ_{H} : 7.61 (1H, dd, $J=5.9$, 2.1 Hz), 6.19 (1H, dd, $J=5.9$, 1.9 Hz), 5.45 (1H, m), 5.21 (1H, m), 2.99-2.0 (8H, m), 0.95 (3H, t, $J=6.9$ Hz).

VI. Synthesis of 3,7-didehydroJA

The synthesis of 3,7-didehydroJA was performed according to a previous paper (Monte *et al.* 2018) using MeJA as a starting compound. To a solution of methyl 4,5-didehydrojasmonate (93 mg, 0.41 mmol) synthesized from MeJA in MeOH (15 mL) in a pressure-resistant glass reaction vessel, NaOMe (44 mg, 0.82 mmol) was added, and the reaction mixture was further stirred for 12 hours at 80°C. To quench MeONa, NH_4Cl powder was directly added to the solution, and a usual work-up was performed for purification to give methyl 3,7-didehydrojasmonate (55 mg, 0.24 mmol, 59%).

Methyl 3,7-didehydrojasmonate:

$^1\text{H NMR}$ (CDCl_3 , 270 MHz) δ_{H} : 7.61 (1H, dd, $J=5.8$, 2.5 Hz), 6.19 (1H, dd, $J=5.8$, 1.1 Hz), 5.45 (1H, m), 5.21 (1H, m), 3.64 (3H, s), 2.60-1.98 (8H, m), 0.94 (3H, t, $J=7.9$ Hz).

To a stirred mixture of methyl 3,7-didehydrojasmonate (30 mg, 0.14 mmol) in 0.1 M phosphate buffer (10 mL, pH 8.0) and MeOH (2.0 mL), esterase from porcine liver (5 mg) (Sigma) was added, and the reaction mixture was further stirred for 3 days at 25°C. A usual work-up was performed for purification to generate 3,7-didehydroJA (29 mg, quantitative).

3,7-dihydroJA:

FD-MS: m/z 208 $[M]^+$; ^1H NMR (CDCl_3 , 270 MHz) δ_{H} : 7.61 (1H, dd, $J=5.8, 2.5$ Hz), 6.19 (1H, dd, $J=5.8, 1.1$ Hz), 5.45 (1H, m), 5.21 (1H, m), 3.64 (3H, s), 2.60-1.98 (8H, m), 0.94 (3H, t, $J=7.9$ Hz).

VII. Synthesis of the JA amino acid conjugates

The synthesis of JA amino acid conjugates was performed according to a previously reported method (Kramell *et al.* 1988).

VIII. Evaluation of the potato tuber inducing activity

The evaluation of potato tuber-inducing activity was performed according to the reported method using potato single node stems (Koda and Okazawa 1988).

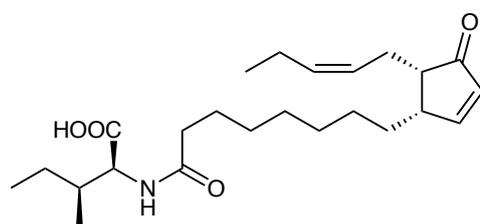
IX. Evaluation of endogenous amounts of JA, 12-hydroxyJA, and 12-*O*- β -D-glucopyranosyloxyJA

Evaluation of endogenous amounts of JA, 12-hydroxyJA, and 12-*O*- β -D-glucopyranosyloxyJA were accomplished according reported method (Matsuura *et al.* 2009).

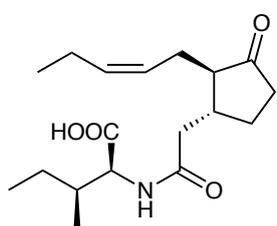
Table S1. Endogenous amounts of JA, 12OHJA, and 12OGlcJA in the single node stems (pmol/g fresh weight).

Treated compounds to single node stems	Endogenous amounts		
	JA	12OHJA	12OGlcJA
(-)-JA	3436 ± 2217	77236 ± 19205	45081 ± 12348
(+)-4,5-didehydro JA	689 ± 107	18042 ± 3102	8400 ± 1023
<i>iso</i> -OPDA	9 ± 3	62 ± 19	205 ± 53
3,7-didehydro JA	17 ± 1	138 ± 39	192 ± 47
control (non-treated)	10 ± 1	60 ± 34	180 ± 41

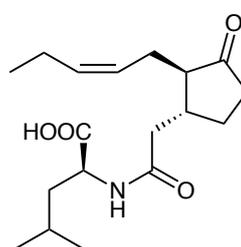
Three node stems of *S. tuberosum* L. cv Dansyaku were implanted in one flask, and the endogenous amounts of target compounds in the nodes were calculated using UPLC MS/MS system. The values represented average ± STDEV using 4 replicates (n= 4).



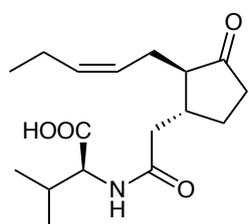
cis-(+)-OPDA-L-Ile



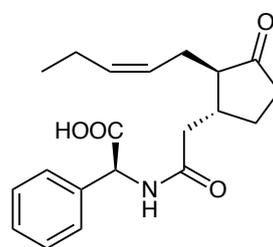
(-)-JA-L-Ile



(-)-JA-L-Leu



(-)-JA-L-Val



(-)-JA-L-Phe

Figure S1. Chemical structures of (-)-JA-L-Ile, -Leu, -Phe, -Val, and *cis*-(+)-OPDA-L-Ile.

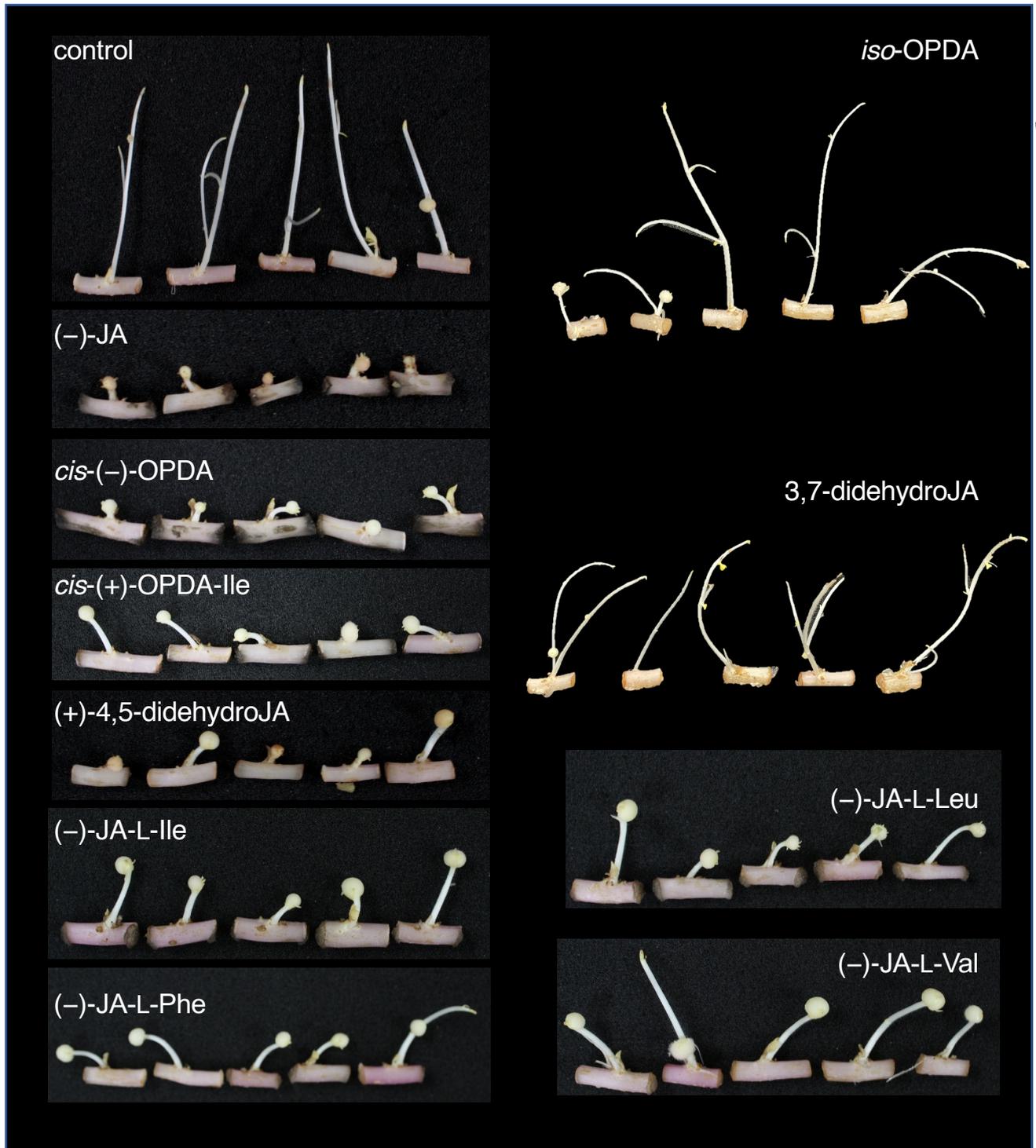


Figure S2. Potato tuber inducing activities.

Single node stems of *S. tuberosum* cv. Dansyaku were transplanted onto modified 1/2 white medium containing of target compound ($1 \times 10^{-4}M$), and left for 3 weeks at 22 °C under the dark.

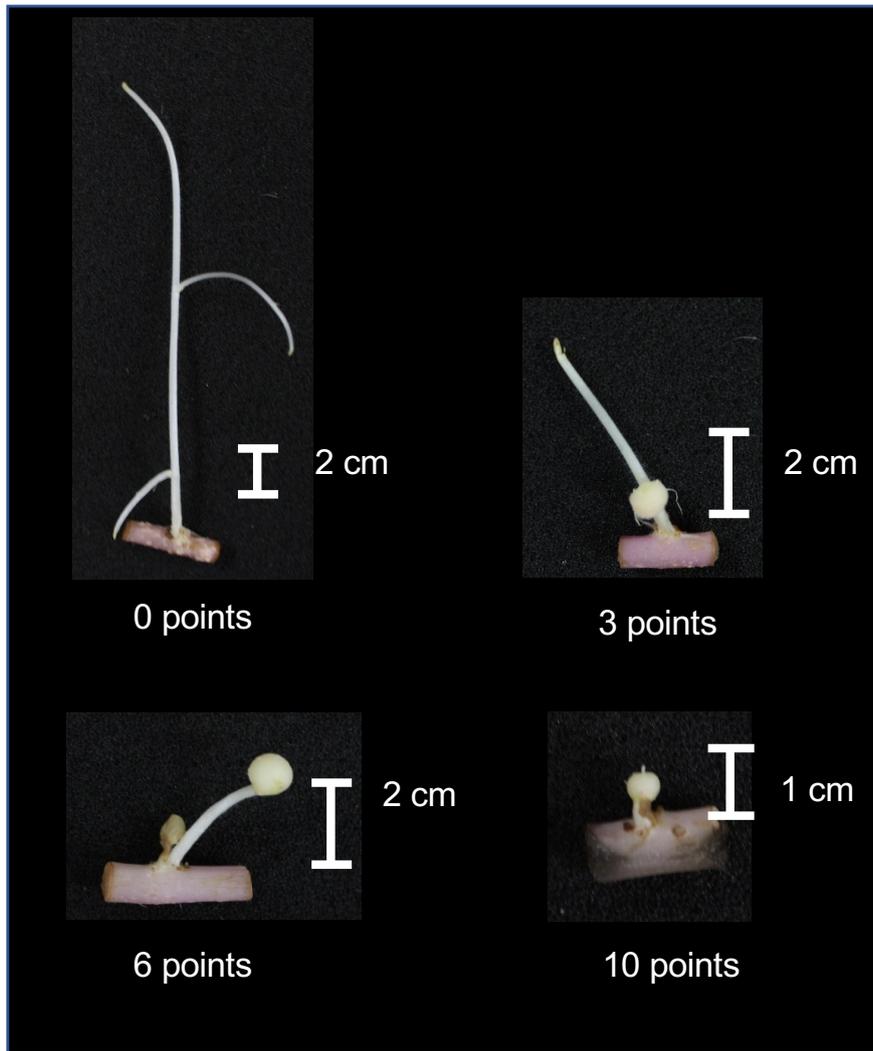


Figure S3. Grading scales to evaluate potato tuber inducing activity.

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