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Note

Syntheses and Potato Tuber-inducing Activities of Unnatural Long-chain OPC-9:0 and OPC-10:0

Hiroaki TOSHIMA, Yuko TAKANO, Akitami ICHIHARA, Yasunori KODA,* and Yoshio KIKUTA*

*Department of Bioscience and Chemistry; *Department of Botany, Faculty of Agriculture, Hokkaido University, Sapporo 060-8589, Japan*

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The unnatural long-chain OPCs, OPC-9:0 and OPC-10:0, were respectively synthesized from the ethyl esters of OPC-7:0 and OPC-8:0. C_2-carbon elongation was achieved *via* alkylation of the enolate of *tert*-butyl acetate. The potato tuber-inducing activity of OPC-10:0, as well as OPC-8:0, -6:0 and -4:0, was similar to that of jasmonic acid. OPC-9:0 also exhibited weak tuber-inducing activity.

Key words: OPC; 12-oxo-PDA; jasmonic acid; tuber-inducing activity

We have recently reported syntheses of the homologous OPC series, OPC-1:0, -3:0, -4:0, -5:0, -6:0, -7:0 and -8:0, as a racemic and *trans*-rich (*ca.* 95%) mixture, *via* 1,4-conjugate addition of zinc-copper reagents for 2-[(*Z*)-2-pentenyl]-2-cyclopenten-1-one.[1] The esters of the homologous OPC series have been converted into 3-oxa-OPCs and 2-fluoro-OPCs.[2] These results show that OPC derivatives are promising intermediates for other OPC analogues and homologues possessing various chain lengths that are required for studies on the biological activity of endogenous compounds related to the octadecanoid signalling pathway in higher plants.[3] 12-Oxo-phytodienoic acid (12-oxo-PDA, **1**), dihydro-12-oxo-PDA (OPC-8:0, **2**), OPCs, and the oxa-analogues of OPCs have recently been shown to exhibit biological activities in some typical bioassay systems with 7-*epi*-jasmonic acid (7-*epi*-JA, **5**) and jasmonic acid (JA, **6**).[4] These results suggest that not only **5** and **6** but also their biosynthetic intermediates (**1**, **2**, **3** and **4**) are biologically active without needing to be converted into **5** or **6** *via* enzymatic reduction and β-oxidation, and that there are some independent receptors corresponding to the carbon-chain length of the signalling molecules (Fig. 1). We describe here the syntheses and potato tuber-inducing activities[5] of the unnatural long-chain OPCs, OPC-9:0 and OPC-10:0.

Two possible routes were planned for the syntheses of OPC-9:0 and OPC-10:0: (1) *via* 1,4-conjugate addition of the C_9- and C_{10}-zinc-copper reagents for 2-[(*Z*)-2-pentenyl]-2-cyclopenten-1-one,[1] and (2) *via* C_2-elongation as the enolate of *tert*-butyl acetate for the derivatives of OPC-7:0 and OPC-8:0. The former route was abandoned because the corresponding iodo-esters, which are not commercially available, must be prepared from appropriate compounds *via* several steps. In practice, ethyl 9-iodononanoate and ethyl 10-iododecanoate have been prepared from 9-decen-1-ol;[6] however, generation of the corresponding zinc-copper reagents was more difficult than that from short-chain iodo-esters because purification by vacuum distillation at relatively high temperature would promote the elimination of hydrogen iodide. So the latter route was followed. Ethyl ester (**7a**), as a mixture of *cis*- and *trans*-isomers (*cis*, *ca.* 25%), has been previously converted into acetal **8a** as a mixture of *cis*- and *trans*-isomers (*cis*, *ca.* 10%)[1,2,7] with 2-ethyl-2-methyl-1,3-dioxorane and *p*-toluenesulfonic acid in a 94% yield. The ester of **8a** was reduced with lithium aluminum hydride in tetrahydrofuran (THF) to give alcohol **9a** in a 92% yield. Treatment of **9a** with iodine, triphenylphosphine, and imidazole in benzene gave

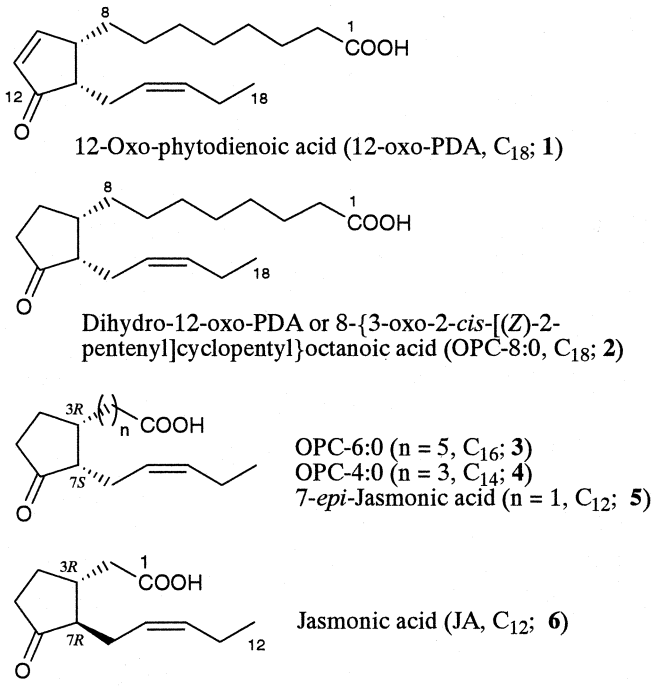
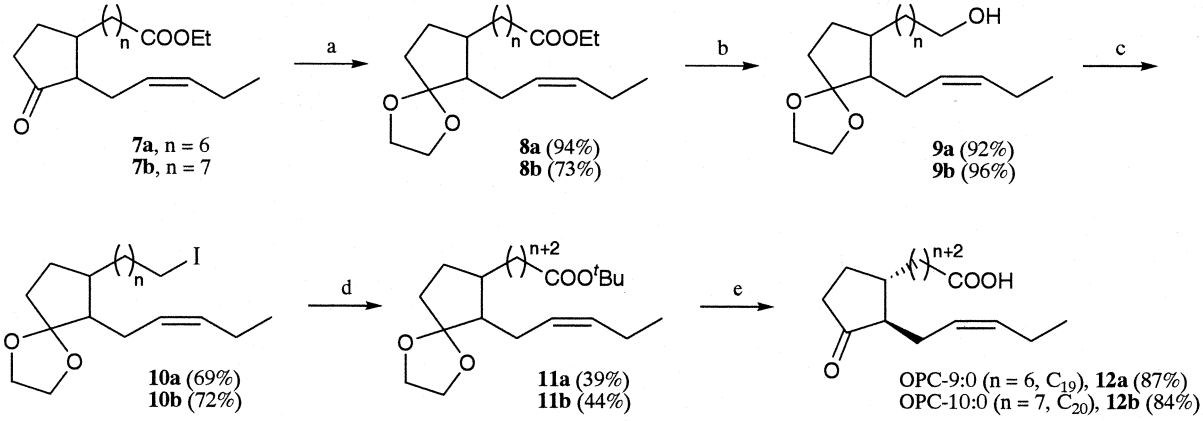


Fig. 1. Structures of Jasmonic acid and its Biosynthetic Intermediates.

To whom correspondence should be addressed. Hiroaki TOSHIMA; Fax: +81-11-706-2505; E-mail: toshima@chem.agr.hokudai.ac.jp

Abbreviations: JA, jasmonic acid; PDA, phytodienoic acid; OPC-8:0, 8-{3-oxo-2-*cis*-[(*Z*)-2-pentenyl]cyclopentyl}octanoic acid; the other OPC abbreviations follow the former and their numbers indicate corresponding carboxylic acids



Scheme 1. Syntheses of OPC-9:0 and OPC-10:0.
(a) *p*-TsOH, 2-ethyl-2-methyl-1,3-dioxorane/ethylene glycol; (b) $LiAlH_4$/THF; (c) I_2, Ph_3P, imidazole/benzene; (d) CH_3COO^tBu, LDA/THF-HMPA; (e) TFA-H_2O.

iodide **10a** as an alkylating agent in a 69% yield. Alkylation of the enolate of *tert*-butyl acetate with **10a** was next examined. When 3 eq. of the lithium enolate of *tert*-butyl acetate, which had been generated by treating with lithium diisopropylamide (LDA), in THF was used, alkylation procceded slightly to give desired C_2-elongated ester **11a** in a 9% yield with the recovery of most of **10a**. When 10 eq. of the lithium enolate was used in THF and hexamethylphosphoramide (HMPA), **11a** was obtained in a 39% yield with a slight amount of **10a**. Although the yield was significantly increased, even the use of excess lithium enolate did not result in a higher yield. The *tert*-butyl ester and acetal of **11a** were finally hydrolyzed with 50% aq. trifluoroacetic acid at the same time to give OPC-9:0 (**12a**)[8] as the predominantly *trans*-isomer (*ca.* 95%, based on the ^{13}C-NMR spectrum)[1,2] in an 87% yield. By following the same route, ethyl ester **7b** was converted into OPC-10:0 (**12b**) as the predominantly *trans*-isomer (*ca.* 95%).[1,2]

The tuber-inducing activities of synthetic unnatural long-chain OPC-9:0 (**12a**) and OPC-10:0 (**12b**) were examined by monitoring the rate of tuberization.[5] Both **12a** and **12b** exhibited activity in the range from a 10^{-6} to 10^{-4} M concentration. While the activity of **12b** was similar to that of the JA standard [a mixture of minor (±)-**5** (*ca.* 7%) and major (±)-**6** that was used as a positive control],[9] **12a** exhibited rather weak activity. The rate of tuberization of **12a** was 46% at the relatively high concentration of 10^{-4} M. In previous bioassays on tuber-inducing activity, the following results have been obtained:[1,2] (1) Even-numbered OPC-8:0, OPC-6:0, and OPC-4:0 exhibited activities at the same concentration ($>10^{-6}$ M) as that of the JA standard. (2) Unnatural odd-numbered OPC-7:0 exhibited slightly weaker activity than that of the JA standard. (3) Unnatural odd-numbered OPC-5:0 and 3-oxa-OPCs (-8:0, -6:0, and -4:0) exhibited weak activities. Their rate of tuberization was 36–46% at a 10^{-4} M concentration when that of the JA standard was 100%. (4) Unnatural odd-numbered OPC-3:0 and OPC-1:0 are considered to have exhibited almost no activity, because their rate of tuberization was below 17% at a 10^{-4} M concentration. Therefore, the order of the tuber-inducing activities of OPCs, including the unnatural odd-numbered and long-chain homologues was OPC-10:0, -8:0, -6:0, and -4:0 ≈ JA standard > OPC-7:0 > OPC-9:0 ≈ OPC-5:0 > OPC-3:0 ≈ OPC-1:0. It is not always considered that the activity of all even-numbered OPCs would only arise from **5** or **6** produced endogenously by β-oxidation in plant tissue because 3-oxa-OPCs exhibit activity as analogues of the corresponding OPCs. Futhermore, unnatural odd-numbered OPC-9:0, -7:0 and -5:0, which would undergo β-oxidation into OPC-3:0 and -1:0 in plant tissue, also exhibit activity. Considering the potent **5**/**6**-like activity and the molecular size of the phytotoxin, coronatine,[10] OPC-9:0 (**12a**, C_{19}) and -7:0 (C_{17}) might be recognized as mimics of OPC-8:0 (**2**, C_{18}) or its precursor, 12-oxo-PDA (**1**, C_{18}). Enzymatic reduction of **1** to **2** and β-oxidation of **2** to **5** might be not required to exhibit the various **5**/**6**-like biological activities. It is necessary to consider the roles of **1**, **2**, **3** and **4** as biologically active endogenous compounds. Other structually simple analogues of **1** and **2**, which do not undergo β-oxidation but exhibit potent biological activities, are required in studies of the octadecanoid signalling pathway.

In conclusion, long-chain OPCs **12a** and **12b** were synthesized in five steps from the ethyl esters of OPC-7:0 and OPC-8:0, respectively. It was proved that the esters of the homologous OPC series are useful intermediates for other homologues. Both unnatural long-chain OPCs exhibited potato tuber-inducing activity. The order of activity of the present OPCs has been presented. Plant physiological studies related to the octadecanoid signalling pathway will be assisted by OPC homologues and analogues that provide significant information.

Experimental

General methods. ^1H- and ^{13}C-NMR spectra were recorded with a JEOL JNM-EX-270 spectrometer (^1H at 270 MHz; ^{13}C at 67.5 MHz). In the ^1H-NMR spectra, chemical shifts are reported as δ (ppm) values relative to the residual proton (δ 7.26 ppm) of $CDCl_3$. In the ^{13}C-NMR spectra, chemical shifts are reported as δ (ppm) values relative to the carbon signal (δ 77.0 ppm) of

$CDCl_3$. IR spectra were measured with a Perkin Elmer System 2000 FT-IR spectrometer, and mass spectra were recorded with a JEOL JMS-AX500 or JEOL JMS-SX102A spectrometer. Column chromatography was carried out with silica gel 60 (spherical, 70-140 mesh ASTM; Kanto Chemical Co., Japan).

Ethyl 7-{6-[(Z)-2-pentenyl]-1,4-dioxaspiro[4.4]non-7-yl}heptanoate (**8a**). The synthesis and spectral data of **8a** have been described.[2] Since there are some errors in the assignment of the ^{1}H-NMR spectrum, the corrected data are described here. ^{1}H-NMR ($CDCl_3$) δ: 0.96 (3H, t, J=7.6 Hz, CH_2Me), 1.25 (3H, t, J=7.2 Hz, CO_2CH_2Me), 1.23–1.38 (6H, m), 1.52–1.80 (10H, m), 2.00–2.06 (4H, m, allyl-$CH_2\times2$), 2.28 (2H, t, J=7.3 Hz, CH_2CO_2Et), 3.84–3.89 (4H, m, OCH_2CH_2O), 4.12 (2H, q, J=7.2 Hz, CO_2CH_2Me), 5.37 (2H, m, vinyl-$H\times2$).

Ethyl 8-{6-[(Z)-2-pentenyl]-1,4-dioxaspiro[4.4]non-7-yl}octanoate (**8b**). According to the same synthetic method as that for **8a** and the corresponding short-chain esters,[2] **7b** (1.05 g, 3.30 mmol) was converted into **8b** (705 mg, 73%, based on consumed **7b**) as a colorless oil. IR ν_{max} (film) cm^{-1}: 2932, 2874, 1738, 1653, 1464, 1373, 1250, 1163, 1117, 1040; ^{1}H-NMR ($CDCl_3$) δ: 0.96 (3H, t, J=7.6 Hz, CH_2Me), 1.25 (3H, t, J=7.2 Hz, CO_2CH_2Me), 1.23–1.39 (8H, m), 1.52–1.79 (10H, m), 2.03–2.09 (4H, m, allyl-$CH_2\times2$), 2.28 (2H, t, J=7.3 Hz, CH_2CO_2Et), 3.87–3.90 (4H, m, OCH_2CH_2O), 4.12 (2H, q, J=7.2 Hz, CO_2CH_2Me), 5.37 (2H, m, vinyl-$H\times2$); EI-MS m/z: 366 (23, M^+), 321 (17 M-C_2H_5O), 195 (26), 99 (100). HR-MS m/z (M^+): calcd. for $C_{22}H_{38}O_4$, 366.2770; found, 366.2753.

7-{6-[(Z)-2-pentenyl]-1,4-dioxaspiro[4.4]non-7-yl}heptanol (**9a**). According to the same synthetic method as that for the corresponding short-chain alcohols,[2] **8a** (865 mg, 2.70 mmol) was converted into **9a** (770 mg, 92%) as a colorless oil. IR ν_{max} (film) cm^{-1}: 3356, 2929, 2856, 1652, 1462, 1324, 1153, 1043; ^{1}H-NMR ($CDCl_3$) δ: 0.96 (3H, t, J=7.6 Hz, CH_2Me), 1.19–1.40 (8H, m), 1.52–1.80 (10H, m), 2.01–2.06 (5H, m, allyl-$CH_2\times2$ and OH), 3.63 (2H, m, CH_2OH), 3.84–3.89 (4H, m, OCH_2CH_2O), 5.36 (2H, m, vinyl-$H\times2$); EI-MS m/z: 310 (11, M^+), 195 (18), 99 (100). HR-MS m/z (M^+): calcd. for $C_{19}H_{34}O_3$, 310.2758; found, 310.2743.

8-{6-[(Z)-2-pentenyl]-1,4-dioxaspiro[4.4]non-7-yl}octanol (**9b**). According to the same synthetic method as that for the corresponding short chain-alcohols,[2] **8b** (492 mg, 1.34 mmol) was converted into **9b** (419 mg, 96%) as a colorless oil. IR ν_{max} (film) cm^{-1}: 3357, 2928, 2856, 1653, 1458, 1325, 1152, 1044; ^{1}H-NMR ($CDCl_3$) δ: 0.96 (3H, t, J=7.6 Hz, CH_2Me), 1.19–1.39 (10H, m), 1.52–1.80 (10H, m), 2.01–2.06 (5H, m, allyl-$CH_2\times2$ and OH), 3.63 (2H, m, CH_2OH), 3.84–3.89 (4H, m, OCH_2CH_2O), 5.36 (2H, m, vinyl-$H\times2$); EI-MS m/z: 324 (11, M^+), 195 (18), 99 (100). HR-MS m/z (M^+): calcd. for $C_{20}H_{36}O_3$, 324.2665; found, 324.2663.

1-Iodo-7-{6-[(Z)-2-pentenyl]-1,4-dioxaspiro[4.4]non-7-yl}heptane (**10a**). To a stirred solution of **9a** (760 mg, 2.45 mmol) in benzene (10 ml) were successively added imidazole (417 mg, 6.13 mmol), triphenylphosphine (1.60 g, 6.13 mmol), and iodine (622 mg, 4.90 mmol) at room temperature. The mixture was stirred for 19 h, and the reaction was quenched by adding sat. aq. Na_2SO_3 (10 ml). After diluting with EtOAc (10 ml), the reaction mixture was successively washed with a 1:1 mixture of sat. aq. Na_2SO_3 and sat. aq. $NaHCO_3$ (20 ml), sat. aq. $NaHCO_3$ (20 ml), and brine (20 ml). The organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The resulting insoluble materials in hexane were filtered off, and the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography (hexane:Et_2O=10:1) to give **10a** (706 mg, 69%) as a colorless oil. IR ν_{max} (film) cm^{-1}: 2959, 2927, 2854, 1741, 1461, 1307, 1158, 1044; ^{1}H-NMR ($CDCl_3$) δ: 0.96 (3H, t, J=7.3 Hz, CH_2Me), 1.17–1.44 (8H, m), 1.52–1.84 (10H, m), 2.01–2.06 (4H, m, allyl-$CH_2\times2$), 3.19 (2H, t, J=6.9 Hz, CH_2I), 3.84–3.89 (4H, m, OCH_2CH_2O), 5.36 (2H, m, vinyl-$H\times2$); EI-MS m/z: 420 (20, M^+), 195 (28), 99 (100). HR-MS m/z (M^+): calcd. for $C_{19}H_{33}O_2I$, 420.1525; found, 420.1548.

1-Iodo-8-{6-[(Z)-2-pentenyl]-1,4-dioxaspiro[4.4]non-7-yl}octane (**10b**). According to the same synthetic method as that for **10a**, **9b** (419 mg, 1.29 mmol) was converted into **10b** (404 mg, 72%) as a colorless oil. IR ν_{max} (film) cm^{-1}: 2959, 2927, 2854, 1741, 1462, 1306, 1158, 1043; ^{1}H-NMR ($CDCl_3$) δ: 0.96 (3H, t, J=7.3 Hz, CH_2Me), 1.17–1.44 (10H, m), 1.52–1.84 (10H, m), 2.01–2.06 (4H, m, allyl-$CH_2\times2$), 3.19 (2H, t, J=6.9 Hz, CH_2I), 3.84–3.89 (4H, m, OCH_2CH_2O), 5.36 (2H, m, vinyl-$H\times2$); EI-MS m/z: 434 (16, M^+), 195 (27), 99 (100). HR-MS m/z (M^+): calcd. for $C_{20}H_{35}O_2I$, 434.1682; found, 434.1659.

tert-Butyl 9-{6-[(Z)-2-pentenyl]-1,4-dioxaspiro[4.4]non-7-yl}nonanoate (**11a**). To a stirred solution of diisopropylamine (2.20 ml, 15.7 mmol) in dry THF (15.7 ml) and dry HMPA (1.48 ml, 8.51 mmol) was added dropwise *n*-BuLi (a 1.60 M solution in hexane, 9.81 ml, 15.7 mmol) at −10°C under an argon atmosphere, and the mixture was stirred for 30 min at 4°C. To the resulting LDA solution was added dropwise *tert*-butyl acetate (2.12 ml, 15.7 mmol) at −78°C. The mixture was stirred for 40 min at the same temperature. To the resulting enolate solution was added dropwise **10a** (656 mg, 1.57 mmol) in dry THF (1.0 ml) at −78°C. The temperature was gradually allowed to warm to room temperature over 60 min. After adding sat. aq. NH_4Cl (30 ml), the reaction mixture was extracted with Et_2O (30 ml × 3). The combined organic layers were successively washed with water (30 ml) and brine (30 ml), dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography (hexane:Et_2O=2:1) to give **11a** (250 mg, 39%) as a colorless oil. IR ν_{max} (film) cm^{-1}: 2928, 2856, 1732, 1457, 1367, 1154, 1044; ^{1}H-NMR ($CDCl_3$) δ: 0.96

(3H, t, J=7.6 Hz, CH_2Me), 1.23–1.33 (10H, m), 1.44 (9H, s, CMe_3), 1.52–1.83 (10H, m), 2.01–2.07 (4H, m, allyl-$CH_2\times2$), 2.20 (2H, t, J=7.3 Hz, CH_2CO_2Bu), 3.84–3.89 (4H, m, OCH_2CH_2O), 5.36 (2H, m, vinyl-$H\times2$); EI-MS m/z: 408 (14, M^+), 335 (23, $M^+-C_4H_9O$), 195 (21), 99 (100). HR-MS m/z (M^+): calcd. for $C_{25}H_{44}O_4$, 408.3239; found, 408.3206.

tert-Butyl 10-{6-[(Z)-2-pentenyl]-1,4-dioxaspiro[**4.4**]*non-7-yl}decanoate* (**11b**). According to the same synthetic method as that for **11a**, **10b** (404 mg, 0.93 mmol) was converted into **11b** (172 mg, 44%) as a colorless oil. IR ν_{max} (film) cm^{-1}: 2929, 2856, 1732, 1458, 1367, 1154, 1044; ^{1}H-NMR ($CDCl_3$) δ: 0.96 (3H, t, J=7.6 Hz, CH_2Me), 1.23–1.34 (12H, m), 1.44 (9H, s, CMe_3), 1.51–1.83 (10H, m), 2.01–2.08 (4H, m, allyl-$CH_2\times2$), 2.20 (2H, t, J=7.3 Hz, CH_2CO_2Bu), 3.85–3.90 (4H, m, OCH_2CH_2O), 5.36 (2H, m, vinyl-$H\times2$); EI-MS m/z: 422 (15, M^+), 349 (20, $M^+-C_4H_9O$), 195 (21), 99 (100). HR-MS m/z (M^+): calcd. for $C_{26}H_{46}O_4$, 422.3247; found, 422.3235.

9-{3-oxo-2-[(Z)-2-pentenyl]cyclopentyl}nonanoic acid (OPC-9:0, **12a**). According to the same synthetic method as that for 3-oxa-OPCs,[2] **11a** (250 mg, 0.61 mmol) was hydrolyzed with 50% aq. TFA to give **12a** (164 mg, 87%) as a colorless oil. IR ν_{max} (film) cm^{-1}: 3450-2670, 3010, 2923, 2856, 1733, 1715, 1652, 1456, 1162, 941; ^{1}H-NMR ($CDCl_3$) δ: 0.96 (3H, t, J=7.6 Hz, CH_2Me), 1.26–1.40 (12H, m), 1.62–1.82 (5H, m), 2.01–2.07 (4H, m, allyl-$CH_2\times2$), 2.28–2.39 (5H, m), 5.27 (1H, m, vinyl-H), 5.40 (1H, m, vinyl-H); ^{13}C-NMR ($CDCl_3$) δ: 14.1, 20.5, 24.6, 25.3, 26.8, 26.9, 28.9, 29.1, 29.2, 29.6, 34.0, 34.6, 38.0, 41.0, 55.0, 125.3, 133.4, 179.9, 221.1; EI-MS m/z: 308 (10, M^+), 290 (29, M^+-H_2O) 151 (69), 83 (100). HR-MS m/z (M^+): calcd. for $C_{19}H_{32}O_3$, 308.2352; found, 308.2314.

10-{3-oxo-2-[(Z)-2-pentenyl]cyclopentyl}decanoic acid (OPC-10:0, **12b**). According to the same synthetic method as that for 3-oxa-OPCs,[2] **11b** (171 mg, 0.41 mmol) was hydrolyzed with 50% aq. TFA to give **12b** (110 mg, 84%) as a colorless oil. IR ν_{max} (film) cm^{-1}: 3450-2660, 3009, 2927, 2855, 1740, 1710, 1652, 1463, 1163, 941; ^{1}H-NMR ($CDCl_3$) δ: 0.96 (3H, t, J=7.6 Hz, CH_2Me), 1.29–1.39 (14H, m), 1.59–1.85 (5H, m), 2.01–2.07 (4H, m, allyl-$CH_2\times2$), 2.28–2.38 (5H, m), 5.27 (1H, m, vinyl-H), 5.40 (1H, m, vinyl-H); ^{13}C-NMR ($CDCl_3$) δ: 14.1, 20.5, 24.6, 25.3, 26.9, 27.0, 29.0, 29.2, 29.3, 29.4, 29.7, 34.0, 34.6, 38.0, 41.0, 55.0, 125.4, 133.4, 179.9, 221.2; EI-MS m/z: 322(10, M^+), 304 (29, M^+-H_2O) 151 (69), 83 (100). HR-MS m/z (M^+): calcd. for $C_{20}H_{34}O_3$, 322.2508; found, 322.2462.

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References and Notes

1) Toshima, H., Nara, S., Aramaki, H., Ichihara, A., Koda, Y., and Kikuta, Y., Efficient syntheses of the OPC homologous series, OPC-1:0, -3:0, -4:0, -5:0, -6:0, -7:0, and -8:0. *Biosci. Biotechnol. Biochem.*, **61**, 1724–1728 (1997).

2) Toshima, H., Fujino, Y., Ichihara, A., Koda, Y., and Kikuta, Y., Syntheses of 3-oxa-OPC and 2-fluoro-OPC homologues. *Biosci. Biotechnol. Biochem.*, **62**, 689–694 (1998).

3) Sembdner, G. and Parthier, B., The biochemistry and the physiological and molecular actions of jasmonates. *Annu. Rev. Plant Physiol. Plant Mol. Biol.*, **44**, 569–589 (1993) and references cited therein.

4) (a) Farmer, E. E. and Ryan, C. A., Octadecanoid precursors of jasmonic acid activate the synthesis of wound-inducible proteinase inhibitors. *The Plant Cell*, **4**, 129–134 (1992); (b) Weiler, E. W., Kutchan, T. M., Gorba, T., Brodschelm, W., Niesel, U., and Bublitz, F., The Pseudomonas phytotoxin coronatine mimics octadecanoid signalling molecules of higher plants. *FEBS Lett.*, **345**, 9–13 (1994); (c) Schierle, K., Hopke, J., Niedt, M.-L., Boland, W., and Steckhan, E., Homologues of dihydro-12-oxophytodienoic acid and jasmonic acid by mixed Kolbe electrolysis. *Tetrahedron Lett.*, **48**, 8715–8718 (1996); (d) Blechert, S., Boeklmann, C., Brummer, O., Fublein, M., Gundlach, H., Haider, G., Holder, S., Kutchan, T. M., Weiler, E. M., and Zenk, M. H., Structural separation of biological activities of jasmonates and related compounds. *J. Chem. Soc., Perkin Trans. 1*, 3549–3559 (1997); (e) Stelmach, B. A., Muller, A., Hennig, P., Laudert, D., Andert, L., and Weiler, E. W., Quantification of the octadecanoid 12-oxo-phytodienoic acid, a signalling compound in plant mechanotransduction. *Phytochemistry*, **347**, 539–546 (1998) and references cited therein.

5) Koda, Y. and Okazawa, Y., Detection of potato tuber-inducing activity in potato leaves and old tubers. *Plant Cell Physiol.*, **29**, 969–974 (1988).

6) Ethyl 9-iodononanoate was prepared in 3 steps: (1) tosylation, (2) oxidation with RuO_4 and $NaIO_4$, and (3) ethyl esterification with EtI and K_2CO_3. Ethyl 10-iododecanoate was prepared in 4 steps: (1) tosylation, (2) hydroboration with 9-borabicyclo[3.3.1]nonane (9-BBN) and then alkaline H_2O_2, (3) oxidation with RuO_4 and $NaIO_4$, and (4) ethyl esterification with EtI and K_2CO_3.

7) Crombie, L. and Mistry, K. M., Synthesis of 12-oxo-phytodienoic acid (12-oxo-PDA) and the compounds of its enzymatic degradation cascade in plants, OPC-8:0, -6:0, -4:0, -2:0 (epi-jasmonic acid), as their methyl esters. *J. Chem. Soc., Perkin Trans. 1*, 1981–1991 (1991).

8) OPC-9:0 has been synthesized *via* mixed Kolbe electolysis in a low yield (see ref. 4c).

9) Racemic and *trans*-rich JA (JA standard) was prepared *via* alkaline hydrolysis of commercially available racemic methyl jasmonate.

10) Toshima, H., Nara, S., Ichihara, A., Koda, Y., and Kikuta, Y., Syntheses and potato tuber-inducing activity of coronafacic acid analogues. *Biosci. Biotechnol. Biochem.*, **62**, 681–688 (1998) and references cited therein.