Supplementary Methods

Synthesis of [phenyl-$^{13}C_6$]OxIAA

[phenyl-$^{13}C_6$]2-oxindol-3-yl acetic acid ([phenyl-$^{13}C_6$]OxIAA) was prepared from [phenyl-$^{13}C_6$]indole-3-acetic acid ($^{13}C_6$-IAA) according to the method of Tuominen et. al. with slight modifications (Schmidt and Michel 1985; Tuominen et al. 1994). $^{13}C_6$-IAA (20 mg, 0.11 mmol) was stirred in *t*-BuOH (0.6 mL) containing H_2O (0.01 mL) and then *N*-bromosuccinimide (15.7 mg IAA, 0.088 mmol) was gradually added over 15 min at room temperature. The mixture was stirred for 1 h at room temperature. The resulting solution was added into water (15 mL) and adjusted to pH 3.0. The mixture was extracted with EtOAc (15 mL x 3). The organic layer was dried over Na_2SO_4, the solvent was removed *in vacuo*. The residue was purified by a silica gel column chromatography with $CHCl_3$–MeOH (4:1) to give [phenyl-$^{13}C_6$]OxIAA (14.1 mg, 65% yield) as a yellow powder LC-ESI-MS *m/z* 198.09 $[M+H]^+$: $C_4{}^{13}C_6H_{10}NO_3$ The NMR spectrum was measured for non-labeled OxIAA that was synthesized with same procedure. ^{1}H-NMR (400 MHz, acetone-d_6) δ 2.75-2.80 (2H, m), 3.72-3.74 (1H, m), 6.92 (1H, d, J = 7.9 Hz), 6.96 (1H, dd, J = 7.3, 7.6 Hz), 7.19 (1H, dd, J = 7.5, 7.9 Hz), 7.30 (1H, d, J = 7.5 Hz), 9.48 (1H, s), ^{13}C-NMR (100 MHz, acetone-d_6) δ 34.42, 42.33, 121.90, 124.26, 128.23, 128.58, 129.81, 143.13, 172.15, 178.43.

Synthesis of [phenyl-$^{13}C_6$]OxIAA-Glc

To a solution of [phenyl-$^{13}C_6$]OxIAA (12.0 mg, 0.061 mmol) in anhydrous CH_2Cl_2 (5 mL) was added 2,3,4,6-tetra-*O*-(benzyl-D-glucopyranosyl)-trichloroacetimidate (104 mg, 0.15 mmol) under Ar atmosphere, and the reaction mixture was stirred at room temperature for 8 h. The resultant mixture was washed with water (1 mL) and then solvent was removed *in vacuo*. The residue was used for following reaction without further purification. Benzyl ether groups of OxIAA tetrabenzylglucoside was removed by catalytic hydrogenation with H_2 (2 atm) and 10% Pd/C (1 mg) in EtOAc:MeOH:AcOH = 2:2:1 (2 mL) for 4h at room temperature. After the filtration of Pd/C and evaporation of solvent, The residue was purified by a silica gel column chromatography with $CHCl_3$–MeOH (2:1) to yield [phenyl-$^{13}C_6$]-3,4,5-trihydroxy-6-(hydroxymethyl)-tetrahydro-2H-pyran-2-yl-2-(2-oxoindolin-3-yl)-acetate ([phenyl-$^{13}C_6$]OxIAA-Glc) as an amorphous powder (6.6 mg, 31 % yield). LC-ESI-MS *m/z* 360.13: $[M+H]^+$ for $C_{10}{}^{13}C_6H_{20}NO_8$. The NMR spectrum was measured for non-labeled OxIAA-Glc that was

synthesized with same procedure. ^{1}H-NMR (400 MHz, CD_3OD) δ 2.83-2.93 (1H, m), 3.08-3.20 (1H, m), 3.30-3.36 (4H, m), 3.65-3.83 (3H, m), 5.47 (0.5H, d, J = 8.0 Hz), 5.52 (0.5H, d, J = 7.6 Hz), 6.89 (1H, d, J = 7.6 Hz), 6.98 (1H, dd, J = 7.6, 7.8 Hz), 7.20 (1H, dd, J = 7.6, 7.8 Hz), 7.30 (1H, d, J = 7.6 Hz), ^{13}C-NMR (100 MHz, CD_3OD) δ 35.48, 35.61, 62.35, 71.05, 73.95, 74.00, 77.88, 78.86, 78.91, 96.09, 96.16, 110.90, 123.38, 123.43, 125.31, 129.33, 130.31, 130.36, 143.67, 143.74, 171.63, 181.08, 181.14.

Synthesis of OxIAA, OxIAA-Glc and IAA-Glc

OxIAA was synthesized as described in the synthesis of [phenyl-$^{13}C_6$]OxIAA using IAA as a starting material. OxIAA-Glc was synthesized as mentioned in the synthesis of [phenyl-$^{13}C_6$]OxIAA-Glc using OxIAA as a starting material. IAA-Glc was synthesized as previously published (Jakas et al. 1993; Keglevic and Pokorny 1969).

LC-ESI-MS/MS analysis of IAA and OxIAA

For analysis of OxIAA and IAA in *Arabidopsis* seedlings, 30–70 mg of fresh plants were quickly weighed, frozen with liquid nitrogen and stored at –80 °C. Plant material was homogenized in 80 % acetone/H_2O (0.2–1 mL) containing 2–4 ng of [phenyl-$^{13}C_6$]OxIAA, and 2–4 ng of IAA, with ceramic beads (3 mm) using a Tissue Lyser (Qiagen) for 3 min. The supernatants were centrifuged at 15,000 ×*g* for 3 min at 4 °C and transferred to test tubes. The extraction was repeated two times without the internal standards. The supernatants were combined and evaporated by nitrogen gas, and centrifuged at 15,000 ×*g* for 5 min after the volume was decreased to < 200 µL. The supernatant was applied to a 5-µm, 4.6 × 150 mm Symmetry shield C_{18} column (Waters) coupled to a 5-µm, 4.6 × 10 mm C_{18} guard column (Senshu Pak) connected to an HPLC system equipped with a 2475 multi λ-fluorescence detector (Waters). The samples were eluted at a flow rate of 1 mL/min with 0.01 M ammonium acetate (solvent A) and 100 % methanol (solvent B) by using 10 % solvent B for 1 min and a gradient of 10–50 % solvent B over 30 min.

For OxIAA analysis, HPLC fractions eluting at the retention time of OxIAA (7.5 - 8.5 min) were collected and evaporated by using a Speed Vac. The dried OxIAA fraction was redissolved with 1 % acetic acid/H_2O (1 mL) and applied to an Oasis HLB column (Waters). The column was washed with 20 % methanol/H_2O containing 1 % acetic acid (1 mL) before eluting the OxIAA with 70 % methanol/H_2O containing 1% acetic acid (1 mL). The eluate was then evaporated to

dryness by using a Speed Vac. The OxIAA fraction was re-dissolved in 50% acetonitrile/H_2O (20 μL) and injected to UPLC. Elution of the samples was carried out with solvent A2 and acetonitrile solvent B2 using 2% solvent B2 for 0.1 min, and a gradient ranging from 2–50% of solvent B2 for 7.4 min, at a flow rate of 0.2 mL/min. The temperature of UPLC column was 40 °C. The retention time of OxIAA and [phenyl-$^{13}C_6$]OxIAA were 3.67 min. OxIAA was analyzed by using the negative ion mode. MS/MS analysis conditions were as follows: capillary = 2.65 kV, source temperature = 100°C, desolvation temperature = 400°C, collision energy = 8 V, sampling cone voltage = 15 V, scan time 0.6 sec/scan (delay = 0.05 sec), and MS/MS transition (*m/z*): 190.1/146.1 for unlabeled OxIAA and 196.1/152.1 for [phenyl-$^{13}C_6$]OxIAA. Quantification was carried out using the extracted ion chromatogram of OxIAA and [phenyl-$^{13}C_6$]OxIAA. A standard curve was generated using OxIAA and [phenyl-$^{13}C_6$]OxIAA and prepared as described above, except for the omission of the HPLC purification step.

For IAA analysis, HPLC fractions were further purified and analyzed as described by *Mashiguchi et al*. (Mashiguchi et al. 2011). IAA was quantified by using [phenyl-$^{13}C_6$]IAA as previously described (Sugawara et al. 2009).

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