Electronic Supplementary Material (ESI) for Analyst.

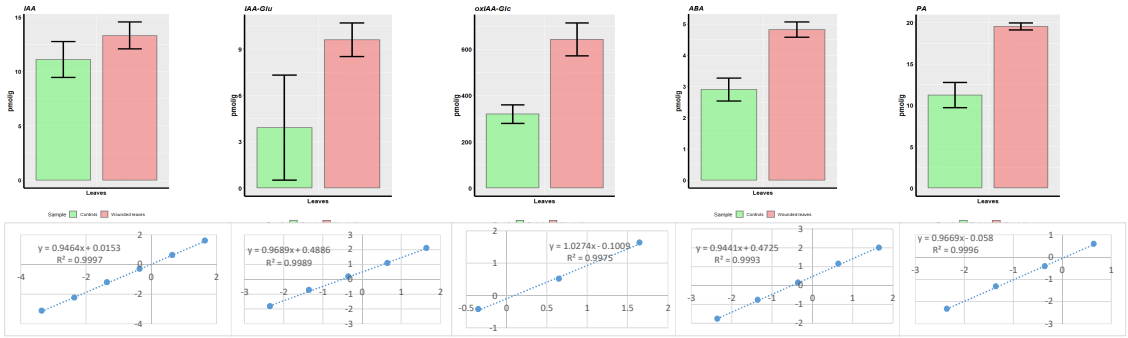
The protocol of isotopically labelled LC-MS/MS quantification analysis

For the quantification experiments, the amount of *Arabidopsis thaliana* (Col-0) leaves of 10 mg (fresh weight, FW) were freshly harvested transferred into 2 ml plastic Eppendorf tubes, containing 2-mm ceria-stabilized zirconium oxidebeads (Retsch GmbH & Co. KG, Haan, Germany). The frozen leaf material was homogenized in 1 ml of ice cold 10% MeOH/H_2O (v/v) extraction solution containing a cocktail of labelled standards (5 pmol of [$^2H_2$]JA-Ile, [$^{13}C_6$]IAA, [$^2H_5$]OPDA, and 10 pmol of [$^2H_6$]JA, [$^2H_6$]ABA, [$^2H_3$]PA, [$^2H_4$]SA) by an MM 301 vibration mill at a frequency of 27 Hz for 3 min. Samples were sonicated for 3 min in the ice bath and subsequently extracted using a benchtop laboratory rotator for 20 min at 4 ℃. After spin down, the supernatants were transferred into clean tubes and re-extracted with 1 ml of ice cold 10% MeOH/H2O (v/v) All samples were pre-concentrated by RP polymer-based solid phase extraction (Oasis HLB columns, 30 mg/1 ml, Waters). The SPE sorbent was activated by 1 ml of 100% MeOH and equilibrated with 0.1% HCOOH/H2O (v/v). After sample loading, the column was washed with 1 ml of extraction solution and eluted with 3 ml of 80% MeOH/H2O (v/v). and then evaporated to dryness under gentle stream of nitrogen, the samples were reconstructed in 20 µL of 15% acetonitrile: 85% 10 mM HCOOH (v/v) for the LC–MS/MS analysis

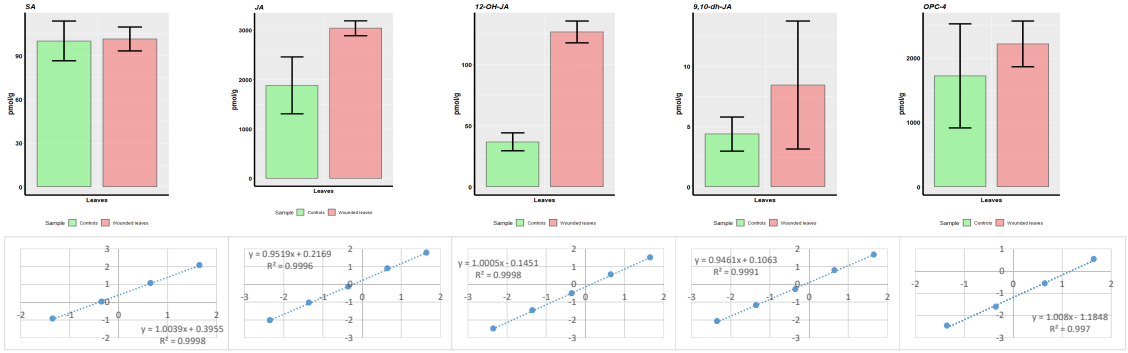
Targeted phytohormones and their related compounds were analysed by an Acquity UPLC System (Waters) coupled to a triple quadrupole mass spectrometer Xevo™ TQ MS (Waters MS), and 5 µL of each sample was injected onto a RP column (Acquity UPLC CSH™ C18; 2.1x100 mm; 1.7 µm) at a flow rate of 0.4 ml/min. Analytes were separated by a gradient elution using 10 mM HCOOH (A) and ACN (B) over 35 min. as follows: 0–5 min isocratic elution (15% A; v/v); 5–15 min linear gradient to 45% A; 15–28 min, logarithmic gradient to 48.6% A; 28–29 min linear gradient to 100% A. Finally, the column was washed with 100% ACN and then equilibrated to the initial conditions for 5 min. The eluate was introduced into the electrospray ion source of a tandem MS analyser and analysed using the following MS/MS conditions: source temperature, 120℃; cone/desolvation gas flow, 70/650 L/h; capillary voltage, 3 kV; cone voltage, 23–30 V; collision energy, 12–23 eV; collision gas flow (argon), 0.21 mL/min. The analysed compounds and appropriate internal standards quantified in multiple ion monitoring mode (MRM) using optimized MS conditions and continuous polarity-switching data measurements. MRM transitions were recorded over each chromatographic run in ten targeted scan windows to obtain the greatest possible MS signal intensity for each compound. The MassLynx™ software package (version 4.1, Waters, Milford, MA, USA) was used to control the instrument and to acquire and process all of the MS data.

Table 1. Absolute quantifications for the studied compounds determined through isotopically labelled LC-MS/MS analysis. Leaf samples (10 mg FW) were extracted, purified using the SPE procedure and analysed by LC–MS/MS. The standard curves with regression equations were also shown below.

Samples	pmol/g DW ± SD; RSD [%]																			
	IAA				IAA-Glu				oxIAA-Glc				ABA				PA			
Control leaves	10.21	11.08	±	1.65	5.53	5.86	±	0.48	365.14	319.08	±	39.91	2.78	2.90	±	0.37	9.69	11.23	±	1.53
	12.99		RSD [%]	14.87	6.20		RSD [%]	8.12	297.47		RSD [%]	12.51	3.31		RSD [%]	12.71	12.75		RSD [%]	13.62
	10.06				LOQ				294.65				2.60				11.25			
Wounded leaves	11.88	13.30	±	1.24	9.17	9.61	±	1.09	633.59	642.32	±	71.29	4.55	4.82	±	0.24	19.08	19.54	±	0.43
	13.82		RSD [%]	9.35	8.81		RSD [%]	11.33	575.79		RSD [%]	11.10	4.88		RSD [%]	5.03	19.93		RSD [%]	2.18
	14.20				10.85				717.58				5.02				19.60			



Samples	pmol/g DW ± SD; RSD [%]																			
	SA				JA				12-OH-JA				9.10-dh-JA				OPC-4			
Control leaves	86.00	100.07	±	13.72	1519.16	1876.94	±	575.87	29.08	36.67	±	7.32	3.04	4.38	±	1.42	1087.24	1721.84	±	808.35
	100.79		RSD [%]	13.71	2541.25		RSD [%]	30.68	37.25		RSD [%]	19.96	4.22		RSD [%]	32.42	2631.92		RSD [%]	46.95
	113.41				1570.42				43.69				5.87				1446.36			
Wounded leaves	92.31	101.39	±	8.12	2862.35	3035.38	±	149.88	134.16	126.52	±	8.97	14.39	8.45	±	5.32	1818.90	2217.49	±	356.00
	103.92		RSD [%]	8.01	3125.13		RSD [%]	4.94	128.74		RSD [%]	7.09	4.12		RSD [%]	62.99	2329.69		RSD [%]	16.05
	107.95				3118.66				116.64				6.84				2503.86			



Samples	pmol/g DW ± SD; RSD [%]																			
	OPC-6				OPC-8				*cis* -OPDA				dn-OPDA				Ja-Ile			
Control leaves	67.47	87.15	±	23.88	17.73	27.28	±	16.33	2381.14	7812.03	±	4973.49	3817.99	7218.97	±	3486.92	400.46	430.95	±	134.96
	113.72		RSD [%]	27.41	46.14		RSD [%]	59.89	12144.48		RSD [%]	63.66	10785.89		RSD [%]	48.30	578.55		RSD [%]	31.32
	80.25				17.95				8910.46				7053.02				313.83			
Wounded leaves	215.77	240.42	±	22.49	78.85	97.15	±	28.75	3136.48	6771.16	±	3173.00	5644.41	8023.95	±	2061.05	710.70	716.87	±	27.56
	245.68		RSD [%]	9.35	82.32		RSD [%]	29.59	8188.74		RSD [%]	46.86	9178.07		RSD [%]	25.69	746.99		RSD [%]	3.84
	259.81				130.29				8988.26				9249.38				692.91			

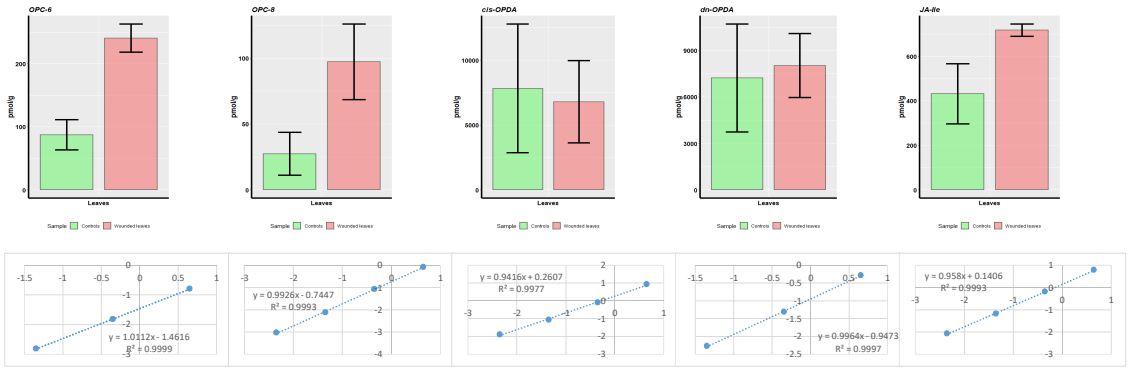


Table 2. Absolute quantifications for the studied compounds determined through isotopically labelled LC-MS/MS analysis. Separated tissue samples (10 mg FW) were extracted, purified using the SPE procedure and analysed by LC–MS/MS. The standard curves with regression equations were also shown below.

Sample	pmol/g DW ± SD; RSD [%] Levels in pmol/g FW																			
	cis- OPDA				OPC-6				OPC-4				JA				ABA			
Wounded regions	20089.24				2.08				8689.88				15469.51				38.94			
	N.D				N.D				N.D				N.D				37.91			
	12939.00				1.63				6102.50				19643.00				29.77			
	10530.56				2.15				5883.38				12069.07				N.D			
	10434.29	9638.26	±	4518.20	3.38	2.13	±	0.77	5538.64	5371.72	±	1699.49	8788.20	11715.18	±	3988.90	N.D	35.54	±	5.03
	8562.22		RSD [%]	0.47	2.69		RSD [%]	0.36	4379.00		RSD [%]	0.32	8872.83		RSD [%]	0.34	N.D		RSD [%]	0.14
	6424.41				1.71				3353.34				6875.72				N.D			
	8327.04				2.20				4251.67				7494.26				N.D			
	5253.40				2.81				7031.66				14586.14				N.D			
	4184.21				0.51				3115.37				11637.88				N.D			
Unwounded regions	8719.78				0.11				246.40				1949.09				9.63			
	9228.12				0.20				262.14				1494.97				17.15			
	8164.81				N.D				251.15				1967.08				14.21			
	9194.54				0.31				436.19				3057.81				N.D			
	4991.97	7445.23	±	2587.99	0.24	0.26	±	0.18	312.59	305.80	±	116.57	1277.50	1808.45	±	489.08	N.D	13.66	±	3.79
	3255.04		RSD [%]	0.35	0.13		RSD [%]	0.71	139.42		RSD [%]	0.38	1343.50		RSD [%]	0.27	N.D		RSD [%]	0.28
	9203.21				0.19				245.50				1421.75				N.D			
	9699.03				0.76				579.36				1945.06				N.D			
	2631.88				0.22				336.95				1710.20				N.D			
	9363.91				0.19				248.32				1917.52				N.D