Supporting Information

In situ detection of salicylate in *Ocimum Basilicum* plant leaves via reverse iontophoresis

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Experimental

Materials and Reagents

Salicylic acid (SA), potassium chloride, potassium monohydrogen phosphate and potassium hydroxide were purchased at their highest available purity from Sigma-Aldrich (UK) and were used as received. All solutions were prepared with deionized water (resistivity ≥ 18.2 MΩ·cm at 25°C) (Millipore, Watford, UK). A phosphate buffer solution (100 mM, pH = 7.0) was prepared with 100 mM potassium chloride added as the supporting electrolyte. *Ocimum Basilicum* (basil) plants were obtained locally and were used within a week of purchase. Each passive and iontophoresis measurement described in the work was repeated at least three times on a new leaf.

Instrumentation

Electrochemical experiments were performed using a computer-controlled potentiostat (μAUTOLAB Type III, ECO-chemie, NL) in a thermostatically controlled Faraday cage (25 ± 2) °C.

The vertical, glass iontophoresis cell (Figure 2) [1] comprises a lower chamber and an upper component with two electrode compartments separated by an intervening space. The basil leaf was interposed horizontally, with the abaxial side facing up, between the upper and lower parts of the cell (contact area: 1.6 cm^2). The anode compartment was filled with 1.0 mL of phosphate buffer (pH 7.0); the cathode contained either 1.0 ml of phosphate buffer, or a phosphate-buffered solution of

SA at either 1, 3, 7 or 10 mM. The lower chamber was charged with 7.0 mL of buffer. A constant current of 0.5 mA (with the voltage limited to 10V) was imposed for a period of between 8, 9 and 10 hours between the Ag/AgCl cathode and the silver wire anode, which were introduced into the electrode chambers prior to the initiation of the experiment.

Following iontophoresis, the extracted salicylate was quantified using cyclic voltammetry (50 $mV \cdot s^{-1}$) at a multi-walled carbon nanotube disposable screen-printed electrode (MWCNT-SPE, DropSens, Spain). The latter comprised a multi-walled carbon nanotube working electrode (diameter = 4.0 mm), a silver wire quasi-reference electrode, and a carbon counter electrode all printed on an inert substrate. Prior to performing the cyclic voltammetry, approximately 50 µL of solution was deposited onto the chip to ensure that all three electrodes were completely covered. For each extraction, it was accompanied by a new electrode.

Table S1. Analytical methods to measure salicylates in leaf extracts

Method	Plant	Concentration	Reference
	Arabidopsis Thaliana	SA = 29 ng/g FW SAG = 1603 ng/g FW	[2]
	Arabidopsis Thaliana and tobacco	*Tobacco* SA ≈ 4 µg/g FW SAG ≈ 20 µg/g FW *Arabidopsis* SA ≈ 0.1- 1 µg/g FW SAG ≈ 18 - 65 µg/g FW	[3]
HPLC-MS	*Hybrid Poplar*	SA ≈ 31.0 µg/ g FW	[4]
	Oilseed rape	SA ≈ 5-90 ng/g FW	[5]
	Arabidopsis Thaliana	SA≈30 ng/g FW MeSA ≈ 3 ng/g FW	[6]
	F G. Uralensis	SA ≈ 7 µg - 12 µg /g FW	[7]
	Oilseed rape	SA ≈1.1 - 5.8 ng/g FW	[8]
	Rose	SA ≈ 0.68 µg/g FW	[9]
	Coffea Arabica	SA ≈ 0.10 µg/g FW	[10]
Fluorescence	*Arabidopsis Thaliana*	SA+SAG ≈ 2 µg/g FW	[11]
Electrochemical	Oilseed rape	4 µM	[12]
	Tomato	0.3 µg/ g FW	[13]

Table S2. *In vivo* methods to quantify plant metabolites

Method	Sensor	Target	Plant	Reference
Electrochemical	POPD–Pt-MP–Pt electrode	H_2O_2	Oilseed rape leafstalk	[14, 15]
Electrochemical	SWCNTs and Hb modified carbon fiber ultramicroelectrode	H_2O_2	Aloe vera	[16]
Electrochemical	Self-reference Pt-CNT microelectrode	Indole-3-acetic acid	Maize roots	[17]
Fluorescence	Fluorescent proteins: mRFP1 and EGFP	H^+	*Arabidopsis Thaliana* leaves	[18]
Fluorescence	H_2DCFDA	Reactive oxygen species	*Arabidopsis Thaliana* leaves	[19]

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