

## Supplementary Materials:

# JA-Ile-macrolactone 5b induces tea plant (*Camellia sinensis*) resistance to both herbivore *Ectropis obliqua* and pathogen *Colletotrichum camelliae*

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## Supplementary Methods

**NMR data of JA-Ile-macrolactones. JA-Ile-macrolactone 5a.** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 5.76 (d, *J* = 8.8 Hz, 1H), 5.35 (ddd, *J* = 10.4, 7.7, 5.6, 2.1 Hz, 1H), 5.10 (dt, *J* = 11.7, 6.3 Hz, 1H), 4.49 (ddd, *J* = 10.8, 4.4, 3.1 Hz, 1H), 4.41 (dd, *J* = 8.8, 6.7 Hz, 1H), 3.83 (td, *J* = 11.0, 1.9 Hz, 1H), 2.64 – 2.51 (m, 1H), 2.51 – 2.30 (m, 4H), 2.29 – 1.95 (m, 7H), 1.84 (dtd, *J* = 9.3, 6.8, 3.9 Hz, 1H), 1.58 (qd, *J* = 11.5, 9.3 Hz, 1H), 1.41 (dq, *J* = 15.0, 7.5, 4.0 Hz, 1H), 1.08 (ddt, *J* = 14.4, 9.2, 7.3 Hz, 1H), 0.90 – 0.81 (m, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 220.30, 171.04, 170.69, 128.82, 128.37, 77.37, 77.26, 77.05, 76.73, 63.32, 57.30, 53.38, 42.98, 38.33, 37.50, 36.43, 28.59, 27.82, 25.60, 25.04, 15.73, 11.31.

**JA-Ile-macrolactone 5b.** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 5.68 (d, *J* = 8.1 Hz, 1H), 5.42 – 5.32 (m, 2H), 4.41 – 4.29 (m, 2H), 3.88 (ddd, *J* = 10.9, 6.3, 2.8 Hz, 1H), 2.59 – 2.47 (m, 2H), 2.42 (dtd, *J* = 14.6, 8.5, 2.6 Hz, 1H), 2.36 – 2.24 (m, 3H), 2.24 – 2.10 (m, 3H), 2.07 – 1.99 (m, 1H), 1.93 (dd, *J* = 5.9, 3.8 Hz, 2H), 1.63 – 1.46 (m, 1H), 1.39 (dtd, *J* = 14.8, 7.4, 4.3 Hz, 1H), 1.25 – 1.16 (m, 1H), 1.12 (ddd, *J* = 13.7, 9.3, 7.2 Hz, 1H), 0.94 – 0.80 (m, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 219.84, 171.53, 171.05, 129.24, 127.77, 77.36, 77.25, 77.04, 76.73, 64.21, 57.64, 55.82, 42.64, 37.78, 37.27, 36.10, 28.10, 27.04, 25.17, 25.10, 15.94, 11.48.

## Supplementary Legends:

**Table S1.** Primers used in this investigation.

**Table S2.** MRM transitions and retention times of 12 flavonoids

**Figure S1.** Calibration curves of 12 flavonoids

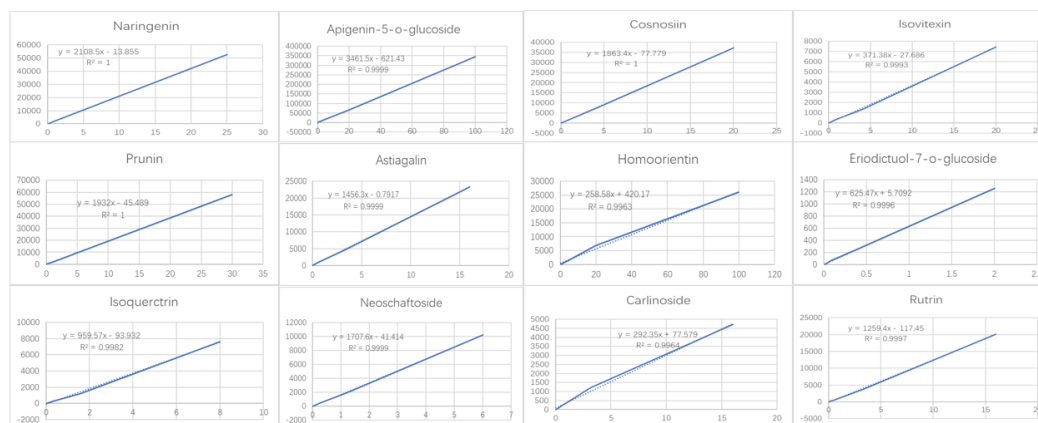
**Figure S2.** <sup>1</sup>H and <sup>13</sup>C NMR Spectra of compounds

**Table S1.** Primers used in this investigation.

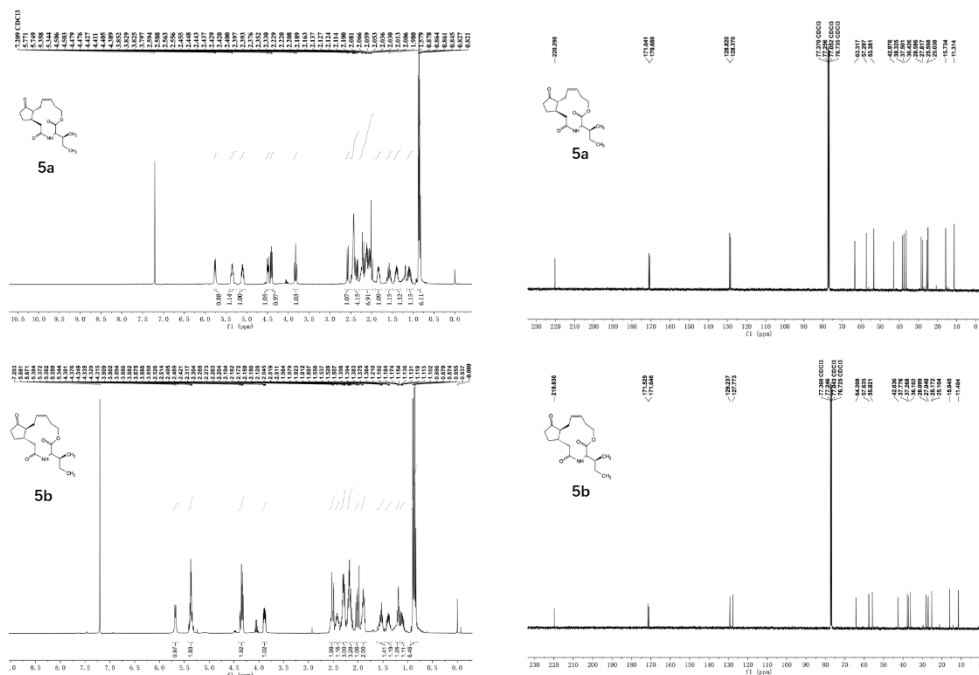
Name	GeneBank Accession Number	Primer Sequence (5'-3') Forward/Reverse	Ref.
<i>CsEF1</i>	KA280301.1	TTGGACAAGCTCAAGGCTGAACG ATGGCCAGGAGCATCAATGACAGT	[1]
<i>CsCLATHRIN1</i>	KA291473.1	TAGAGCGGGTAGTGGAGACCTCGTT TACCAAAGCCGGCTCGTATGAGATT	[1]
<i>CsACTIN1</i>	KA280216.1	TGGGCCAGAAAGATGCTTATGTAGG ATGCCAGATCTTTTCCATGTCATCC	[2]
<i>CsGAPDH1</i>	KA295375.1	TTTTTGGCCTTAGGAACCCAGAGG GGGCAGCAGCCTTATCCTTATCAGT	[3]
<i>CsSAND1</i>	KM057790	TCCAATTGCCCCCTTAATGACTCA GTAAGGGCAGGCAAACACCAGGTA	[1]
<i>CsTIP41</i>	AT4G34270	TGGAGTTGGAAGTGGACGAGACCGA CTCTGGAAAGTGGGATGTTGAAGC	[4]
<i>CsUBC1</i>	KA281185.1	TGCTGGTGGGGTTTTTCTGTACC AAGGCATATGCTCCCATTGCTGTTT	[1]
<i>CsPTB1</i>	GAAC01052498.1	TGACCAAGCACACTCCACACTATCG TGCCCCCTTATCATCATCCACAA	[1]
<i>CsTUA1</i>	JN399223.1	TCACTGTTTACCCATCTCCC GTAGGTGGGTGCGTCAATAT	[3]
<i>CsTBP</i>	AT1G55520	GGCGGATCAAGTGTGGAAGGGAG ACGCTTGGGATTGTATTCGGCATT	[4]
<i>CsOPR3</i>	XM_028243785.1	CGATCAACAGCCGGTGGATT GCGTGGACAGCATCAACCAC	[5]

**Table S2.** MRM transitions and retention times of 12 flavonoids.

Flavonoid Name	Transitions (m/z)	Retention Time (min)
Naringenin	273>153	9.37
Apigenin-5-o-glucoside	433>271	6.23
Cosmosiin	433>271	7.22
Isovitexin	433>283	5.73
Prunin	435>273	7.25
Astiagaln	449>287	6.95
Homoorientin	449>298	4.79
Eriodictuol-7-o-glucoside	451>289	5.99
Isoquertrn	465>303	6.03
Neoschaftoside	565>271	6.87
Carlinoside	581>273	6.63
Rutin	611>303	5.60



**Figure S1.** Calibration curves of 12 flavonoids.



**Figure S2.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR Spectra of compounds.

## References

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2. Wang, M.L.; Li, Q.H.; Xin, H.H.; Chen, X.; Zhu, X.J.; Li, X.H. Reliable reference genes for normalization of gene expression data in tea plants (*Camellia sinensis*) exposed to metal stresses. *Plos ONE* **2017**, *12*, e0175863.
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