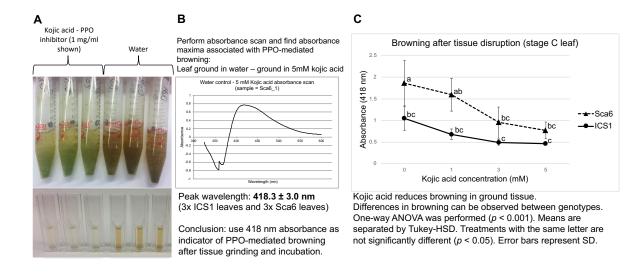
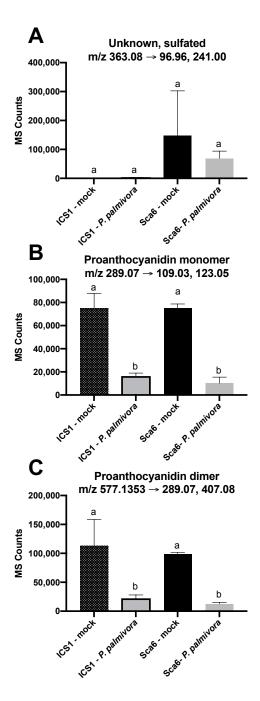
80-L ICS1 -0.6 nkatal/mg protein Sca6 Abs (412 nm)/min 60-40bc cd bcd :de 0.2 20de е e Ē 0.0 t clovanide Protein

Quinone formation (PPO activity)

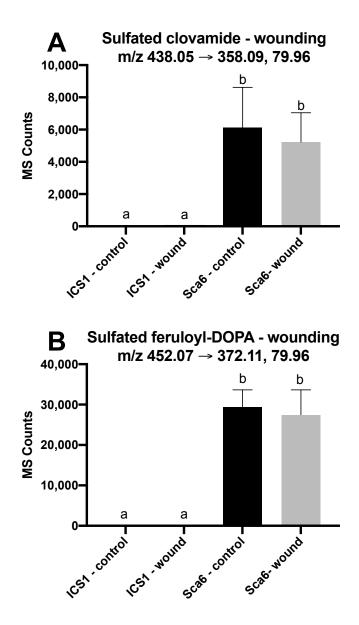
Supplemental Figure 1. Polyphenol oxidase (PPO) activity assay of stage C leaf protein extracts with controls. "Buffer" is control (McIlvaine's buffer, pH 7). "SDS" = sodium dodecyl sulfate. "-Clovamide" represents protein only with no substrate. "-Protein" represent clovamide only with no added protein. One-way ANOVA was performed (p < 0.001) and pairwise student's t-test were used for multiple comparisons. Groups with the same letter are not significantly different (p < 0.1). Error bars represent standard deviation.



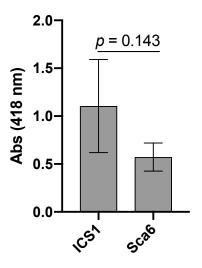
Supplemental Figure 2. Development of browning assay used for Figure 4C,D. (A) Example of supernatant browning of ground 'Sca6' stage C leaf with and without kojic acid (PPO inhibitor). (B) Example absorbance scan (325-600 nm) of stage C leaf disc ground in water minus stage C leaf disc ground in 5 mM kojic acid solution. Absorbance maximum (~418 nm) indicates PPO-mediated browning. (C) Demonstration that kojic acid reduces browning measurement (Abs_{418nm}) in concentration-dependent manner and that 'Sca6' leaf discs produce more browning that 'ICS1'.



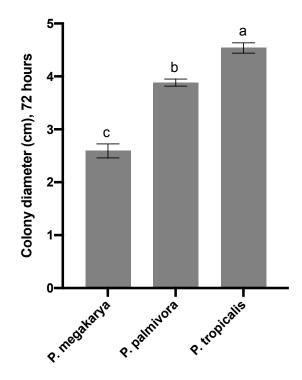
Supplemental Figure 3. Other metabolite features from LC-MS metabolomics of *P*. *palmivora* infection of pod that were indicated in the Loadings Chart (*Fig. 7B*). (A) Unknown sulfated metabolite. (B) A proanthocyanidin monomer (catechin or epicatechin). (C) A proanthocyanidin dimer (B type). MS Counts represent mass spectrometer signal intensity of peaks integrated in XCMS Online (Tautenhahn et al., 2012). Shared letters mean no difference by Tukey-HSD (p < 0.05, n = 3). Parent ion m/z values are suspected molecular ions ([M-H]⁻) in (B) and (C). Error bars represent standard deviation.



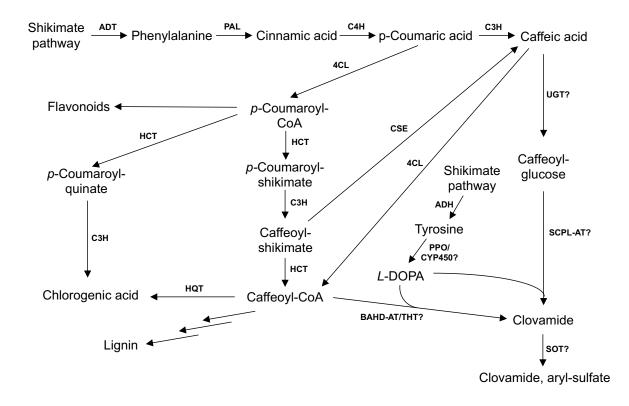
Supplemental Figure 4: Effect of wounding on two sulfated HCAAs in fruit/pod peel. (A) MS Signal of clovamide, arylsulfate in 'ICS1' and 'Sca6' control and wounded pods. (B) MS Signal of Feruloyl-DOPA, arylsulfate in 'ICS1' and 'Sca6' control and wounded pods. No induction of either compound by wounding was observed. Shared letters mean no difference by Tukey-HSD (p < 0.05, n = 3). Parent ion m/z values are suspected molecular ions ([M-H]⁻). Error bars represent standard deviation.



Supplemental Figure 5: Supernatant browning (Abs_{418nm}) from grinding 'ICS1' or 'Sca6' pod tissue in water. T-test, n = 3. Error bars represent standard deviation.



Supplemental Figure 6. Colony diameter of *P. megakarya, P. palmivora, P. tropicalis* in V8 media after 72 hours of growth. Shared letters mean no difference by Tukey-HSD (p < 0.01, n = 8). Error bars represent standard deviation.



Supplemental Figure 7. Hypothetical biosynthetic pathways to clovamide from precursors derived from the Shikimate pathway. ADT = arogenate dehydratase, PAL = phenylalanine ammonia lyase, C4H = cinnamic acid 4-hydroxylase, C3H = *p*-coumaroyl 3' hydroxylase, 4CL = 4-coumaroyl CoA ligase, HCT = hydroxycinnamoyl-CoA shikimate/guinate hydroxycinnamoyl transferase, HQT = hydroxycinnamoyl-CoA guinate transferase, CSE = caffeoyl shikimate esterase, ADH = arogenate dehydrogenase, PPO = polyphenol oxidase, CYP450 = cytochrome p450 (tyrosine hydroxylase), L-DOPA = L-3, 4-dihydroxyphenylalanine, UGT = UDP-glucose dependent glycosyltransferase, SCPL-AT = serine carboxypeptidase-like acyltransferase, THT = hydroxycinnamoyl-CoA:tyramine-N-hydroxycinnamoyl transferase, BAHD-AT = BAHD acyltransferase -BAHD is acronym for first four substrates identified for this class - see Petersen (2016), SOT = sulfotransferase. Figure is based on: (Araji et al., 2014; Bouchez et al., 2019; Hirschmann et al., 2014; Knollenberg et al., 2018; Payyavula et al., 2015; Petersen, 2016; Polturak et al., 2016; Qian et al., 2019; Vanholme et al., 2013). Clovamide biosynthesis is known to occur from caffeoyl-CoA and L-DOPA via BAHD-AT in Trifolium pratense (Bouchez et al., 2019; Sullivan and Bonawitz, 2018), however the THT and UGT/SCPL-AT pathways presented are purely hypothetical and are provided as alternative hypotheses. Hypothetical pathways are based on similar acylations by hydroxycinnamoyl groups reported in the literature (D'Auria, 2006; Petersen, 2016). L-DOPA formation from tyrosine is catalyzed by a CYP450 in *Beta vulgaris* (Polturak et al., 2016) and likely by PPO in Juglans regia (Araji et al., 2014), although the responsible enzyme in cacao is currently unknown.

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