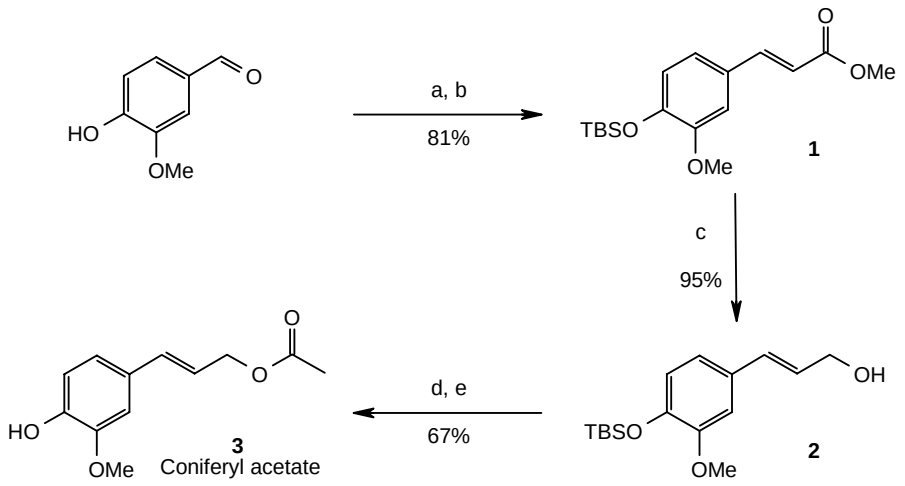
Supporting Text

GC-MS Analysis. A Shimadzu QP-5000 system (Shimadzu, Columbia, MD) equipped with Shimadzu GC-17 gas chromatograph was used for GC-MS analyses of volatile compounds. Separations were performed on a CP-SIL 5CB column (25 m × 0.25 mm i.d. × 0.4-μm film thickness; Varian, Lake Forest, CA). Ultrapure helium was used as the carrier gas at a rate of 1.4 ml min^{-1}. Separation conditions were as follows: 50°C for the initial temperature using a 2-min hold, and then a temperature gradient from 50°C to 275°C at 10°C min^{-1} was applied followed by a 2-min hold at 275°C. Injection and detector temperatures were set at 250°C and 280°C, respectively. Eluted compounds were identified by comparing their retention time and mass fragmentation patterns with authentic standards.

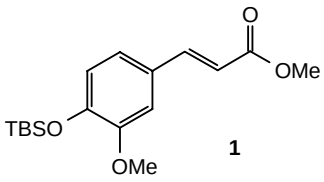
For GC-MS analyses of secretory gland substrate incubation experiments, a Thermo Electron Trace GC ultra coupled to a DSQ mass spectrometer equipped with an Alltech ECONO-CAP-EC-5 capillary column (30 m × 0.25 mm i.d. × 0.25-mm film thickness) was used. Ultrapure helium was used as the carrier gas at a flow rate of 1.2 ml/min. Oven temperature was set initially at 40°C for 2 min, then raised to 100°C using a temperature gradient of 8°C·min^{-1}, held at 100°C for 3.5 min, increased to 280°C at 3°C·min^{-1}, raised to 300°C at 10°C·min^{-1}, and finally held at 300°C for 3.5 min before column reequilibration at 40°C. The injector/transfer line/trap temperatures were 220/250/200°C, respectively. Electron impact ionization was carried out at 70 eV.

Synthesis of Acetate Ester of Coniferyl Alcohol. Unless stated otherwise, reactions were performed in flame-dried glassware under a positive pressure of nitrogen using freshly distilled solvent. Tetrahydrofuran (THF), toluene, and pyridine were freshly purified from a Seca Solvent System (GlassContour, Laguna Beach, CA). All reagents were used as shipped from their manufacturers without further purification. TLC was performed by using Silicycle silica gel 60 F_{254}-precoated plates (0.25 mm). Visualization of the developed chromatogram was performed by UV absorbance (254 or 365 nm), iodine stain, ethanolic potassium permaganate, or ethanolic 2,4-dinitrophenyl hydrazine

stain. Column chromatography and dry column vacuum chromatography were performed by using Silicyle silica gel (40- to 63-μm particle size, 40- or 60-E pore size, and 25- to 40-μm particle size, 60-Å pore size, respectively) using the indicated solvent system as eluent. NMR spectra were recorded in deuteriochloroform on a Varian NMR Systems 500 (^{1}H, 500 MHz; ^{13}C, 125 MHz) instrument. ^{1}H chemical shifts are reported in parts per million (ppm) on δ scale using residual nondeuterated solvent as an internal standard (7.26 ppm). Data for ^{1}H NMR are reported as follows: chemical shift, multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad), integration, and coupling constants. ^{13}C chemical shifts are reported in parts per million (ppm) on δ scale using the central peak of deuteriochloroform as an internal standard (77 ppm). All ^{13}C NMR spectra were recorded with complete proton decoupling. Proton and carbon spectra were recorded as 1D experiments using the standard protocols in VnmrJ. Proton integrations were measured at decreased pulse angle (30°) and increased relaxation time (5 sec). Spectral assignments were confirmed by homonuclear gradient COSY and heteronuclear gradient HSQC experiments. Low-resolution mass spectral analyses were performed by LC-MS on an Agilent 1100 LC system and an Agilent MSD/Trap (ESI±). Analytical chromatography columns used for LC-MS analysis include Phenomenex (Torrrance, CA) SYNERGY FUSION or GEMINI reverse-phase columns (150 × 4.6 mm, l × d) with matching guard cartridges. Typical LC-MS assay conditions for the Gemini column: mobile phase A: 0.1% HCO_2H in H_2O; mobile phase B: 0.1% HCO_2H in MeCN; gradient = 5–95% B in 25 min; 0.5 ml/min A/B with postcolumn injection of C: 20 mM NH_4OAc in H_2O, 0.1 ml/min; 5.0-μl injection volume (1.0-5.0 μM sample); DAD detection monitored at 215 and 254 nm plus up to two additional wavelengths (compound-specific). Ammonium acetate is coeluted postcolumn to enhance the phenolic ESI- signal (for phenols that ionize poorly in the ESI+ mode). LC/MSD TRAP software and DATAANALYSIS software were used for data analysis.



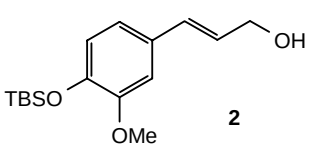
Scheme 1. Synthesis of coniferyl acetate. Reagents and conditions: a, *tert*-butyl dimethylsilylchloride (1.5 eq), imidazole (3.0 eq), THF, 0-25°C, 18 h, 93%. b, methyl diethylphosphonoacetate (1.1 eq), NaHMDS (1.1 eq), THF, 25°C, 18 h, 87% and 81% for two steps. c, Dibal-H (10.0 eq), THF, 0-25°C, 2 h, 95%. d, Ac_2O (2.0 eq), pyridine (10.0 eq), DMAP (0.01 eq), toluene, 1 h, *quant*. e, TBAF (1.2 eq), THF, 0°C, 1 h, 67% for two steps.



(1) (*E*)-methyl 3-(4-*tert*-butyldimethylsilyloxy-3-methoxyphenyl) acrylate: vanillin (1.52 g, 10.0 mmol) was placed in a round-bottom flask, and freshly distilled THF (100 ml, 0.1 M) and imidazole (2.05 g, 30.0 mmol, 3.0 eq) were added at room temperature. The reaction mixture was cooled to 0°C in an ice bath and stirred for 30 min, and then *tert*-butyl dimethylsilylchloride (2.26 g, 15.0 mmol, 1.5 eq) was added slowly by cannula to the cooled reaction mixture. The ice bath was removed, and the reaction mixture was allowed to warm to room temperature and stirred overnight. The reaction was quenched with saturated NaCl (50 ml) and extracted with ethyl acetate (3 × 50 ml), dried with Na_2SO_4, concentrated *in vacuo*, and subjected to dry column vacuum chromatography (90% hexanes/ethyl acetate → ethyl acetate) to afford a white solid (2.58 g, 96%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.87 (s, 1H), 7.43 (s, 1H), 7.39 (d, *J* = 8.3 Hz, 1H), 6.99 (d, *J* = 8.3 Hz, 1H), 3.90 (s, 3H), 1.03 (s, 9H), 0.22 (s, 6H); ^{13}C

NMR (125 MHz, $CDCl_3$) δ 191.0, 151.6, 151.3, 130.9, 126.2, 120.7, 110.1, 55.4, 25.6, 18.5, -4.6. LCMS $[M+H]^+$ calculated for $C_{14}H_{24}O_3Si$: 267.14, found: 267.4.

The TBS-protected vanillin (2.58 g, 9.6 mmol) was placed in a round-bottom flask. Freshly distilled THF (90 ml, 0.1 M) and methyl diethylphosphonoacetate (1.8 ml, 10.0 mmol, 1.1 eq) were added, and the reaction mixture was cooled to 0°C. Then sodium hexmethyldisilazide (NaHMDS, 1.0 M in THF, 10 ml, 1.1 eq) was added slowly by cannula to the cooled reaction mixture. The reaction was allowed to warm to room temperature and stirred overnight. The reaction mixture was quenched with saturated NH_4Cl, and then the THF was removed *in vacuo*. The crude product was then partitioned with ethyl acetate (50 ml) and extracted successively with 0.1 M HCl (2 × 50 ml), saturated $NaHCO_3$ (2 × 50 ml), and saturated NaCl (50 ml), dried with Na_2SO_4, concentrated *in vacuo*, and subjected to column chromatography (95% hexanes/ethyl acetate → 50% hexanes/ethyl acetate) to afford the (*E*)-isomer **1** as a colorless oil (1.92 g, 60% overall). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 (d, *J* = 15.8Hz, 1H), 7.03 (d, *J* = 8.3 Hz, 1H), 7.02 (s, 1H), 6.85 (d, *J* = 8.3 Hz, 1H), 6.30 (d, *J* = 15.8Hz, 1H), 3.84 (s, 3H), 3.79 (s, 3H), 1.00 (s, 9H), 0.20 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.8, 151.8, 147.6, 145.4, 128.6, 122.8, 121.6, 115.9, 111.2, 55.9, 52.0, 25.9, 18.7, -4.4. LCMS $[M+H]^+$ calculated for $C_{17}H_{27}O_4Si$: 323.17, found: 323.3.



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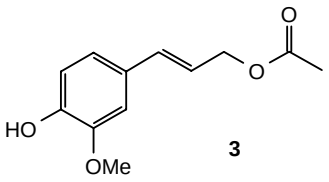
(2) (*E*)-3-(4-*tert*-butyldimethylsilyloxy-3-methoxyphenyl)prop-2-en-1-ol: **1** (1.61 g, 5.0 mmol) was placed in a round-bottom flask, and freshly distilled THF (50 ml, 0.1 M) was added at room temperature. The reaction mixture was cooled to 0°C in an ice-salt bath and stirred for 30 min, and then diisobutylaluminum hydride (DIBAL-H, 1.0 M in THF, 50.0 ml, 10.0 eq) was added slowly by dropping funnel to the cooled reaction mixture over the period of 1 h. The ice-salt bath was removed, and the reaction mixture was allowed to warm to room temperature and stirred an additional 1.5-2 h (until **1** was no longer detectable by TLC). The reaction was cooled to 0°C and quenched by slow addition of 100 mM Rochelle's salt (potassium sodium tartrate, 100 ml). The reaction mixture was then partitioned with ethyl acetate (50 ml), and the residual aluminum salts were

dissolved by the addition of diluted HCl (~10 ml). The biphasic mixture was then filtered through a pad of celite, diluted with saturated NaCl (100 ml), extracted with ethyl acetate (3 × 100 ml), dried with Na_2SO_4, concentrated *in vacuo*, and subjected to dry column vacuum chromatography (80% hexanes/ethyl acetate → ethyl acetate) to afford **2** as a colorless oil (1.51 g, 95%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.99 (s, 1H), 6.94 (d, *J* = 8.3 Hz, 1H), 6.89 (d, *J* = 8.3 Hz, 1H), 6.63 (d, *J* = 15.8 Hz, 1H), 6.32 (dt, *J* = 6.6, 15.8 Hz, 1H), 4.37 (d, *J* = 6.6 Hz, 2H), 3.89 (s, 3H), 1.06 (s, 9H), 0.24 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.3, 145.0, 131.4, 131.0, 126.7, 120.8, 119.6, 109.7, 64.2, 55.8, 25.8, 18.7, -4.5. LCMS $[M+H]^+$ calculated for $C_{16}H_{27}O_3Si$: 295.17, found: 295.5.



3

(3) (*E*)-4-hydroxy-3-methoxycinnamylacetate (coniferyl acetate): Alcohol **2** (1.51 g, 4.75 mmol) was placed in a round-bottom flask. Freshly distilled toluene (10 ml, 0.2 M), freshly distilled pyridine (4.0 ml, 47.5 mmol, 10.0 eq), acetic anhydride (Ac_2O, 0.94 ml, 9.5 mmol, 2.0 eq), and 4-dimethylaminopyridine (DMAP, 6 mg, 0.05 mmol, ~1.0 mol%) were added at room temperature, and the reaction mixture was stirred for 1.0 h until TLC showed the consumption of starting material. The crude reaction mixture was then concentrated under reduced pressure with successive portions of toluene (25 ml) to azeotropically remove the excess Ac_2O and pyridine. The resultant oil was dissolved in ethyl acetate (50 ml) and extracted with diluted HCl (3 × 50 ml) and saturated NaCl (2 × 50 ml). The aqueous layers were then back-extracted with ethyl acetate (2 × 50 ml), and the organic layers were then combined, dried with Na_2SO_4, concentrated *in vacuo*, and subjected to dry column vacuum chromatography (90% hexanes/ethyl acetate) to afford a colorless oil (1.59 g, 99%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.98 (s, 1H), 6.92 (d, *J* = 8.3 Hz, 1H), 6.88 (d, *J* = 8.3 Hz, 1H), 6.58 (d, *J* = 15.8 Hz, 1H), 6.22 (dt, *J* = 6.6, 15.8 Hz, 1H), 4.66 (d, *J* = 6.6 Hz, 2H), 3.77 (s, 3H), 2.06 (s, 3H), 1.00 (s, 9H), 0.16 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.0, 151.3, 146.1, 135.4, 130.5, 121.5, 121.2, 120.1, 109.8, 65.7, 56.0, 26.1, 21.4, 18.7, -4.3. LCMS $[M+H]^+$ calculated for $C_{18}H_{29}O_4Si$: 337.18, found: 337.5.

The TBS-protected 4-hydroxy-3-methoxycinnamylacetate (1.59 g, 4.75 mmol) was placed in a round-bottom flask. Freshly distilled THF (50 ml, 0.1 M) was added, and the reaction mixture was cooled to 0°C in an ice-salt bath and stirred for 30 min. Then tetrabutylammonium fluoride (TBAF, 1.2 M in THF, 10 ml, 1.2 eq) was added slowly by cannula to the cooled reaction mixture. The reaction was allowed to stir an additional 30 min, and then the reaction mixture was diluted with cold ethyl acetate (100 ml), extracted with diluted HCl (3 × 50 ml) and saturated NaCl (50 ml), dried with Na_2SO_4, concentrated *in vacuo*, and subjected to column chromatography (99% dichloromethane/methanol) to afford the coniferyl acetate **3** as a colorless oil (0.72 g, 68% overall). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.99 (s, 1H), 6.96 (d, *J* = 8.3 Hz, 1H), 6.93 (d, *J* = 8.3 Hz, 1H), 6.67 (d, *J* = 15.8 Hz, 1H), 6.36 (dt, *J* = 6.6, 15.8 Hz, 1H), 5.63 (br s, 1H), 4.78 (d, *J* = 6.6 Hz, 2H), 3.93 (s, 3H), 2.13 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.7, 151.6, 145.8, 135.2, 130.1, 121.6, 121.3, 119.8, 109.7, 64.9, 56.1, 21.5. LCMS $[M-H]^-$ calculated for $C_{12}H_{13}O_4$: 221.08, found: 221.1.

Synthesis of [8,9-^{13}C]-coniferyl alcohol. [8,9-^{13}C]-Ferulic acid (**4**) was synthesized as previously described (1), but with vanillin and U-^{13}C malonic acid used as reactants. Briefly, 0.47 mmol of [U-^{13}C]malonic acid and 0.5 mmol of dry vanillin were dissolved in 168 μl of dry pyridine in a small vial, which was subsequently capped with a rubber septum and sealed with parafilm. Piperidine (10.3 μl) was added as catalyst, and the reaction proceeded with gentle stirring under an inert nitrogen atmosphere at 40°C for 3 days. The reaction was quenched by addition of 1.1 ml of ice-cold 1.8 M sulfuric acid. The resulting precipitate was recovered by filtration through glass wool, dissolved in 100% ethanol, and purified by flash chromatography over a silica gel column (Silica Gel, 63-200 μm mesh). The carboxyl group of the resulting doubly ^{13}C-labeled hydroxycinnamic acid was ethylated overnight at room temperature in 4.5 ml of anhydrous ethanol containing 448 μl of acetyl chloride. The resulting 1-ethyl-[8,9-^{13}C]-ferulate was then reduced using the method of Quideau and Ralph (2), which utilizes DIBAL-H as the reducing agent, to afford [8,9-^{13}C]-coniferyl alcohol, which was purified by flash chromatography over silica gel.

1. Gang, D. R., Wang, J., Dudareva, N., Nam, K. H., Simon, J. E., Lewinsohn, E. & Pichersky, E. (2001) *Plant Physiol*. **125,** 539-555.

2. Quideau, S. & Ralph, J. (1992) *J. Agric. Food Chem.* **40,** 1108-1110.