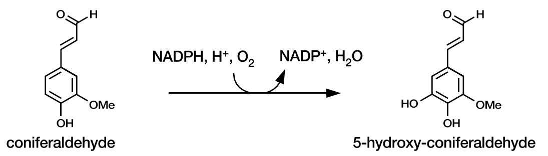
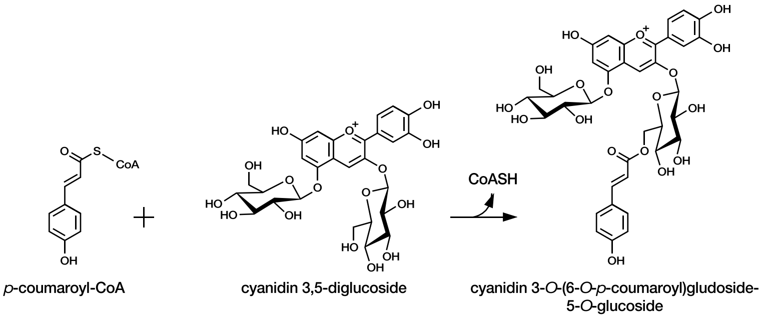
**Table S1.** List of genes used for lignin modification.

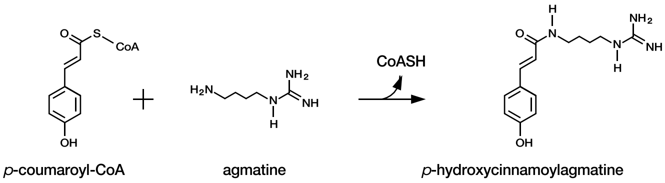
| Gene | Function | Organism | Kingdom | Locus tag/ Gene symbol | Accession | Reference |
|---|---|---|---|---|---|---|
| *F5H* | ferulic acid 5-hydroxylase | *Arabidopsis thaliana* | Viridiplantae | AT4G36220 | AEE86636 | [1] |
| *3AT2* | coumaroyl-CoA:anthocyanidin 3-*O*-glucoside-6''-*O*-coumaroyltransferase | *Arabidopsis thaliana* | Viridiplantae | AT1G03495 | AAF86513 | [2] |
| *ACT* | agmatine coumaroyltransferase | *Hordeum vulgare* | Viridiplantae | – | BAF97626 | [3] |
| *AT208* | anthocyanidin 3-*O*-glucoside 6'-*O*-acyltransferase | *Perilla frutescens* | Viridiplantae | – | BAA93475 | [4] |
| *Atu1417* | enoyl-CoA hydratase | *Agrobacterium fabrum* C58 | Bacteria | Atu1417 | AAK87210 | [5] |
| *Balat_0669* | chlorogenic acid esterase | *Bifidobacterium animalis* DSM 10140 | Bacteria | Balat_0669 | ACS47609 | [6] |
| *BrRCD* | caffeic acid 4,5-dioxygenase | *Bradyrhizobium* sp. ORS278 | Bacteria | BRADO_RS26060 | WP_012029184 | [7] |
| *C2H* | *p*-coumaroyl 2'-hydroxylase | *Ipomoea batatas* | Viridiplantae | – | BAL22347 | [8] |
| *CA9OMT* | coniferyl alcohol 9-*O*-methyltransferase | *Linum nodiflorum* | Viridiplantae | – | ABX71750 | [9] |
| *CADH* | coniferyl alcohol dehydrogenase | *Streptomyces* sp. NL15-2K | Bacteria | – | BAN09098 | [10] |
| *CALipB* | lipase B | *Moesziomyces antarcticus* | Fungi | – | CAA83122 | [11] |
| *calA* | coniferyl alcohol dehydrogenase | *Pseudomonas* sp. HR199 | Bacteria | – | CAB69495 | [12] |
| *calB* | coniferyl aldehyde dehydrogenase | *Pseudomonas* sp. HR199 | Bacteria | – | CAA06926 | [13] |
| *CASHT* | hydroxycinnamoyl-CoA: serotonin *N*-(hydroxycinnamoyl)transferase | *Capsicum annuum* | Viridiplantae | LOC107839132 | AAK15312 | [14] |
| *CCMT1* | cinnamic acid/*p*-coumaric acid carboxyl methyltransferase | *Ocimum basilicum* | Viridiplantae | – | ABG75942 | [15] |
| *CGT* | chlorogenic acid: glucaric acid caffeoyltransferase | *Solanum lycopersicum* | Viridiplantae | LOC101265588 | CBV37053 | [16] |
| *CHS5* | chalcone synthase | *Glycine max* | Viridiplantae | GLYMA_08G109200 | AAB01004 | [17] |
| *couA* | *hydroxycinnamoyl-CoA hydratase-lyase* | *Rhodopseudomonas palustris* CGA009 | Bacteria | RPA1786 | CAE27227 | [18] |
| *CURS3* | curcumin synthase | *Curcuma longa* | Viridiplantae | – | BAH85781 | [19] |
| *CYP84A4* | *p*-coumaraldehyde 3-hydroxylase | *Arabidopsis thaliana* | Viridiplantae | At5g04330 | AED90728 | [20] |
| *CYP98A22* | *p*-coumaroyl 2'-hydroxylase | *Ruta graveolens* | Viridiplantae | CYP98A22 | AEG19446 | [21] |
| *F6H1* | feruloyl-CoA 6'-hydroxylase | *Arabidopsis thaliana* | Viridiplantae | AT3G13610 | AEE75382 | [22] |
| *FDC1* | phenacrylic acid decarboxylase | *Saccharomyces cerevisiae* S288C | Fungi | YDR539W | DAA12368 | [23] |
| *HCALDH* | hydroxycinnamaldehyde dehydrogenase | *Arabidopsis thaliana* | Viridiplantae | AT3G24503 | AEE76907 | [24] |
| *HCBT* | anthranilic acid *N*-hydroxycinnamoyl /benzoyltransferase | *Dianthus caryophyllus* | Viridiplantae | – | CAB06427 | [25] |
| *HCT2* | malic acid *O*-hydroxycinnamoyl transferase | *Trifolium pratense* | Viridiplantae | – | ACI16631 | [26] |
| *HHT1* | omega-hydroxypalmitic acid *O*-feruloyl transferase | *Arabidopsis thaliana* | Viridiplantae | AT5G41040 | AED94628 | [27] |
| *ligL* | β-aryl ether Cα-dehydrogenase | *Sphingobium* sp. SYK-6 | Bacteria | SLG_33660 | BAK68041 | [28] |
| *OsHCT4* | glycerol *O*-hydroxycinnamoyltransferase | *Oryza sativa* | Viridiplantae | OSNPB_060185500 | BAS96510 | [29] |
| *padC* | phenolic acid decarboxylase | *Bacillus subtilis* 168 | Bacteria | BSU34400 | CAB15445 | [30] |
| *pcaHG* | protocatechuic acid 3,4-dioxygenase | *Stenotrophomonas maltophilia* KB2 | Bacteria | – | AFH89645 (*pcaH*)<br>AFH89644 (*pcaG*) | [31] |
| *pcaH2G2* | protocatechuic acid 3,4-dioxygenase | *Hydrogenophaga intermedia* | Bacteria | BN948_05072<br>BN948_05073 | AAK84297 (*pcaH2*)<br>AAK84298 (*pcaG2*) | [32] |
| *pdc* | *p*-coumaric acid decarboxylase | *Lactobacillus plantarum* | Bacteria | LPU63827 | AAC45282 | [33] |
| *PFOMT* | phenylpropanoid/flavonoid *O*-methyltransferase | *Mesembryanthemum crystallinum* | Viridiplantae | – | AAN61072 | [34] |
| *PKS1* | *p*-coumaroyl-diketide-CoA synthase | *Wachendorfia thyrsiflora* | Viridiplantae | – | AAW50921 | [35] |
| *RAS* | rosmarinic acid synthase | *Melissa officinalis* | Viridiplantae | – | CBW35684 | [36] |
| *rpaI* | acyl-homoserine lactone synthases | *Rhodopseudomonas palustris* CGA009 | Bacteria | RPA0320 | CAE25764 | [37] |
| *SDT* | spermidine disinapoyl acyltransferase | *Arabidopsis thaliana* | Viridiplantae | AT2G23510 | AEC07460 | [38] |
| *slr0095* | caffeoyl-CoA *O*-methyltransferase | *Synechocystis* sp. PCC 6803 | Bacteria | SYNGTS_2605 | BAK51353 | [39] |
| *SNG1* | sinapoylglucose:malic acid *O*-sinapoyltransferase | *Arabidopsis thaliana* | Viridiplantae | AT2G22990 | AEC07390 | [40] |
| *SPC4* | cationic peroxidase | *Sorghum bicolor* | Viridiplantae | LOC8074114 | EES02106 | [41] |
| *STS2* | resveratrol synthase | *Vitis vinifera* | Viridiplantae | VIT_00010554001 | ABC84860 | [42] |
| *THT10* | tyramine hydroxycinnamoyltransferase | *Nicotiana tabacum* | Viridiplantae | LOC107822189 | CAB55502 | [43] |
| *tyrB* | tyrosine aminotransferase | *Escherichia coli* K-12 | Bacteria | b4054 | NP_418478 | [44] |
| *UGT72E1* | coniferaldehyde UDP-glucosyl transferase | *Arabidopsis thaliana col* | Viridiplantae | AT3G50740 | AEE78703 | [45] |
| *UGT84A2* | sinapic acid-1-glucosyltransferase | *Arabidopsis thaliana* | Viridiplantae | AT3G21560 | AEE76523 | [46] |
| *VpVAN* | vanillin synthase | *Vanilla planifolia* | Viridiplantae | – | AKG47593 | [47] |
| *ydiB* | quinic acid/shikimic acid 5-dehydrogenase | *Escherichia coli* K-12 | Bacteria | b1692 | NP_416207 | [48] |

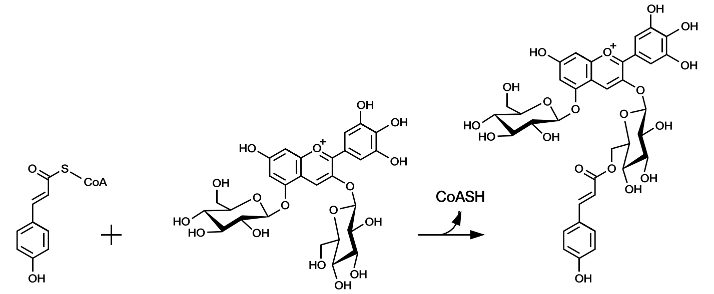
**Table S2.** Summary of enzyme properties for the conversion of metabolites in the shikimate, general phenylpropanoid, flavonoid, or monolignol biosynthetic pathways.

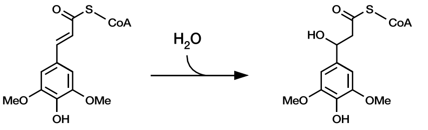
Reaction scheme, coenzyme requirement, enzyme activity (kinetic parameters, specific activity, or substrate range), and reference(s) are shown.

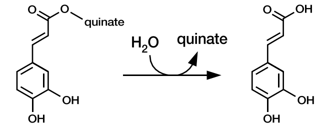
| | |
|---|---|
| Gene | *F5H* |
| Enzyme | ferulic acid 5-hydroxylase |
| Reaction |  |
| Coenzyme | NADPH |
| Kinetics<br>$V_{\max}$ and $K_m$ | coniferaldehyde, 5 pkat·mg$^{-1}$ and 1 (μM)<br>coniferyl alcohol, 6 pkat·mg$^{-1}$ and 3 (μM)<br>ferulic acid, 4 pkat·mg$^{-1}$ and 1,000 (μM) |
| Reference | [1] |

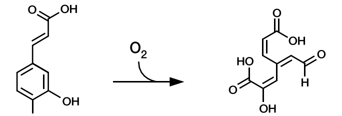
| | |
|---|---|
| Gene | *3AT2* |
| Enzyme | anthocyanin acyltransferase |
| Reaction |  |
| Coenzyme | unnecessary |
| Kinetics<br>$k_{cat}$ and $K_m$ | *p*-coumaroyl-CoA, 6.9 sec$^{-1}$ and 6.6 μM<br>feruloyl-CoA, 7.7 sec$^{-1}$ and 9.4 μM<br>caffeoyl-CoA, 8.5 sec$^{-1}$ and 4.9 μM<br>sinapoyl-CoA, not determined |
| Reference | [2] |

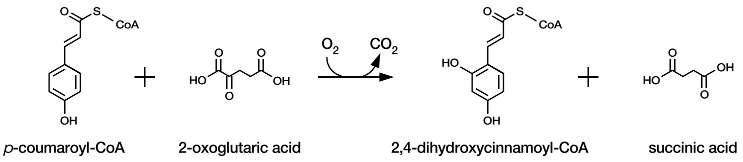
| | |
|---|---|
| Gene | *ACT* |
| Enzyme | agmatine coumaroyltransferase |
| Reaction |  |
| Coenzyme | unnecessary |
| Specific activity and $K_m$ | *p*-coumaroyl-CoA, 9.9 kat·M$^{-1}$·g$^{-1}$ and 1.0 μM<br>feruloyl-CoA, 1.4 kat·M$^{-1}$·g$^{-1}$ and 6.1 μM<br>caffeoyl-CoA, 5.9 kat·M$^{-1}$·g$^{-1}$ and 5.8 μM |
| Reference | [3] |

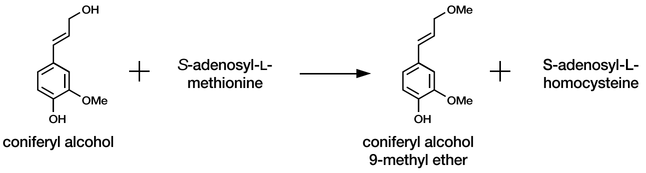
| | |
|---|---|
| Gene | *AT208* |
| Enzyme | anthocyanidin 3-*O*-glucoside 6'-*O*-acyltransferase |
| Reaction |  |
| Coenzyme | unnecessary |
| Kinetics<br>$V_{\max}$ and $K_{\mathrm{m}}$ | *p*-coumaroyl-CoA, 138 nkat·mg$^{-1}$ and 24 μM<br>caffeoyl-CoA, 168 nkat·mg$^{-1}$ and 45 μM |
| Reference | [49] |

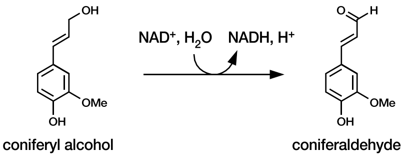
| | |
|---|---|
| Gene | *Atu1417* |
| Enzyme | enoyl-CoA hydratase |
| Reaction |  |
| Coenzyme | unnecessary |
| Substrate range | feruloyl-CoA, *p*-coumaroyl-CoA, caffeoyl-CoA |
| Reference | [5] |

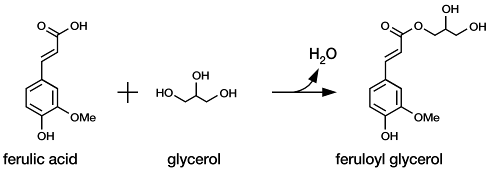
| | |
|---|---|
| Gene | *Balat_0669* |
| Enzyme | chlorogenic acid esterase |
| Reaction |  |
| Coenzyme | unnecessary |
| Specific activity | chlorogenic acid, 2.5 μmol·min$^{-1}$·mg$^{-1}$ |
| Reference | [6] |

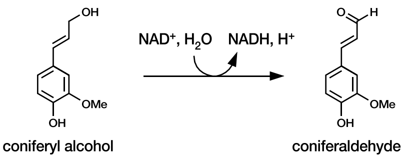
| | |
|---|---|
| Gene | *BrRCD* |
| Enzyme | caffeic acid 4,5-dioxygenase |
| Reaction |  |
| Coenzyme | unnecessary |
| Substrate range | caffeic acid, homoprotocatechuic acid, protocatechuic acid, catechol |
| Reference | [7] |

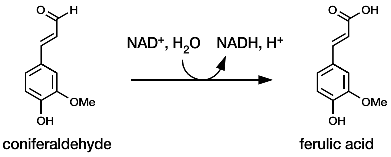
| | |
|---|---|
| Gene | *C2H* |
| Enzyme | *p*-coumaroyl 2'-hydroxylase |
| Reaction |  |
| Coenzyme | ascorbate |
| Kinetics<br>$k_{\text{cat}}$ and $K_{\text{m}}$ | *p*-coumaroyl-CoA, 0.64 sec$^{-1}$ and 15.25 μM<br>feruloyl-CoA, 0.55 sec$^{-1}$ and 14.06 μM |
| Reference | [8] |

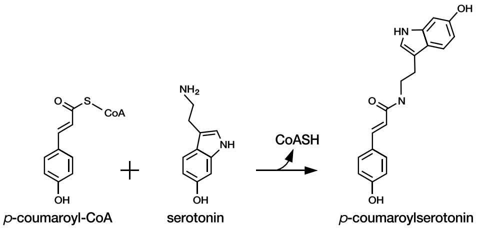
| | |
|---|---|
| Gene | *CA9OMT* |
| Enzyme | coniferyl alcohol 9-*O*-methyltransferase |
| Reaction |  |
| Coenzyme | unnecessary |
| Kinetics<br>$k_{\text{cat}}$ and $K_{\text{m}}$ | coniferyl alcohol, 0.029 sec$^{-1}$ and 7.23 μM |
| Reference | [9] |

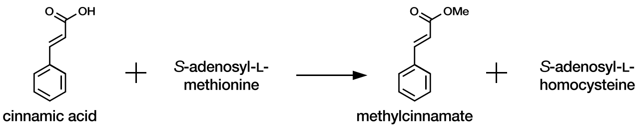
| | |
|---|---|
| Gene | *CADH* |
| Enzyme | coniferyl alcohol dehydrogenase |
| Reaction |  |
| Coenzyme | $NAD^+$ |
| Kinetics<br>$k_{\text{cat}}$ and $K_{\text{m}}$ | coniferyl alcohol, 69.7 sec$^{-1}$ and 130 μM<br>coniferyl alcohol, 116 sec$^{-1}$ and 1700 μM |
| Reference | [10, 50] |

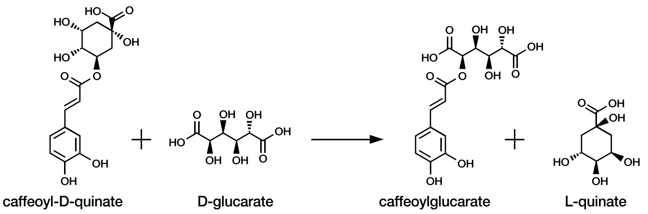
| | |
|---|---|
| Gene | *CALipB* |
| Enzyme | lipase B |
| Reaction |  |
| Coenzyme | unnecessary |
| Substrate range | ferulic acid, *p*-coumaric acid, caffeic acid |
| Reference | [51, 52] |

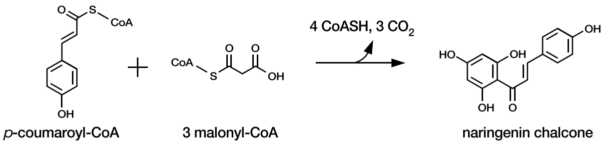
| | |
|---|---|
| Gene | *calA* |
| Enzyme | coniferyl alcohol dehydrogenase |
| Reaction |  |
| Coenzyme | NAD$^+$ |
| Substrate | Only reported for coniferyl alcohol |
| Reference | [12] |

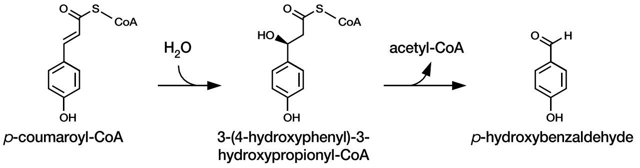
| | |
|---|---|
| Gene | *calB* |
| Enzyme | coniferyl aldehyde dehydrogenase |
| Reaction |  |
| Coenzyme | NAD$^+$ |
| Specific activity and $K_\mathrm{m}$ | coniferaldehyde, 36.5 μmol·min$^{-1}$·g$^{-1}$ and 7–12 μM<br>sinapaldehyde, 28.1 μmol·min$^{-1}$·g$^{-1}$ |
| Reference | [13] |

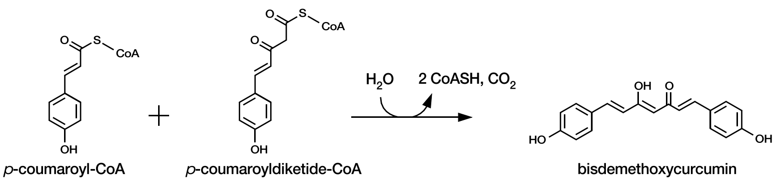
| | |
|---|---|
| Gene | *CASHT* |
| Enzyme | hydroxycinnamoyl-CoA: serotonin *N*-(hydroxycinnamoyl)transferase |
| Reaction |  |
| Coenzyme | unnecessary |
| Kinetics<br>$V_\mathrm{max}$ and $K_\mathrm{m}$ | *p*-coumaroyl-CoA, 35 nkat·mg$^{-1}$ and 23.2 μM<br>feruloyl-CoA, 7 nkat·mg$^{-1}$ and 3.5 μM)<br>caffeoyl-CoA, 31 nkat·mg$^{-1}$ and 12.7 μM |
| Reference | [14, 53] |

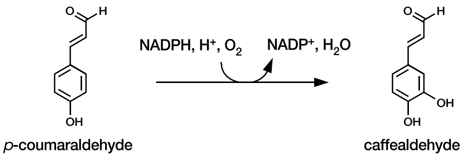
| | |
|---|---|
| Gene | *CCMT1* |
| Enzyme | cinnamic acid/*p*-coumaric acid carboxyl methyltransferase |
| Reaction |  |
| Coenzyme | unnecessary |
| Kinetics<br>$k_\mathrm{cat}$ and $K_\mathrm{m}$ | cinnamic acid, 0.188 sec$^{-1}$ and 124 μM<br>*p*-coumaric acid, 116 sec$^{-1}$ and 70.4 μM |
| Reference | [15] |

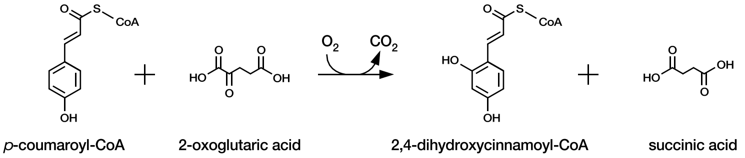
| | |
|---|---|
| Gene | *CGT* |
| Enzyme | chlorogenic acid: glucaric acid caffeoyltransferase |
| Reaction |  |
| Coenzyme | unnecessary |
| Kinetics<br>$V_{\mathrm{max}}$ and $K_{\mathrm{m}}$ | D-glucaric acid, 624 nkat·mg$^{-1}$ and 400 μM<br>D-galactaric acid, 310 nkat·mg$^{-1}$ and 1,700 μM |
| Reference | [16, 54] |

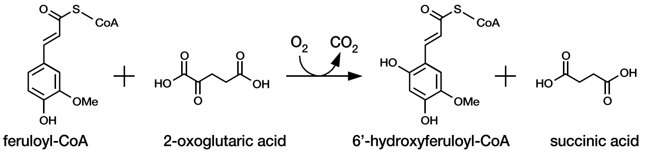
| | |
|---|---|
| Gene | *CHS5* |
| Enzyme | chalcone synthase |
| Reaction |  |
| Coenzyme | unnecessary |
| Substrate range | *p*-coumaroyl-CoA, caffeoyl-CoA, feruloyl-CoA |
| Reference | [17, 55] |

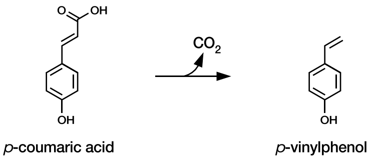
| | |
|---|---|
| Gene | *couA* |
| Enzyme | hydroxycinnamoyl-CoA hydratase-lyase |
| Reaction |  |
| Coenzyme | unnecessary |
| Substrate range | *p*-coumaroyl-CoA, caffeoyl-CoA, feruloyl-CoA |
| Reference | [18] |

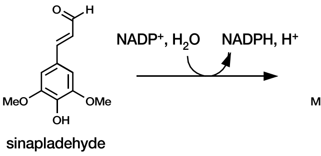
| | |
|---|---|
| Gene | *CURS3* |
| Enzyme | curcumin synthase |
| Reaction |  |
| Coenzyme | unnecessary |
| Kinetics<br>$k_{\mathrm{cat}}$ and $K_{\mathrm{m}}$ | *p*-coumaroyl-CoA, 0.006 sec$^{-1}$ and 3.4 μM<br>(*p*-coumaroyl-CoA + cinnamoyldiketide-*N*-acetylcysteamine)<br>feruloyl-CoA, 0.003 sec$^{-1}$ and 2.2 μM<br>(feruloyl-CoA + cinnamoyldiketide-*N*-acetylcysteamine) |
| Reference | [19] |

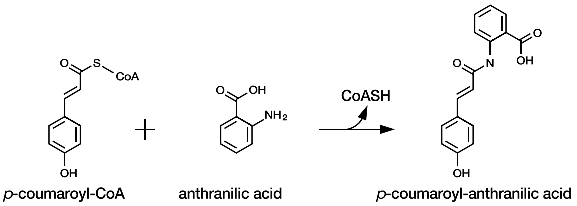
| | |
|---|---|
| Gene | *CYP84A4* |
| Enzyme | *p*-coumaraldehyde 3-hydroxylase |
| Reaction |  |
| Coenzyme | NADPH |
| Kinetics<br>$V_{\mathrm{max}}$ and $K_{\mathrm{m}}$ | *p*-coumaraldehyde, 0.69 pkat·mg$^{-1}$ and 41 µM |
| Reference | [20] |

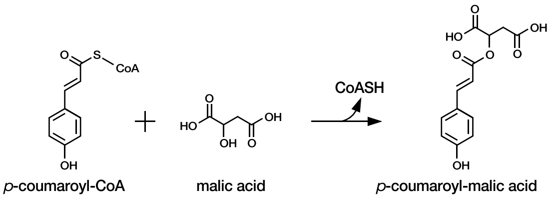
| | |
|---|---|
| Gene | *CYP98A22* |
| Enzyme | *p*-coumaroyl 2'-hydroxylase |
| Reaction |  |
| Coenzyme | ascorbate |
| Kinetics<br>$k_{\mathrm{cat}}$ and $K_{\mathrm{m}}$ | *p*-coumaroyl-CoA, 0.71 sec$^{-1}$ and 50 µM<br>feruloyl-CoA, 0.46 sec$^{-1}$ and 37 µM |
| Reference | [21] |

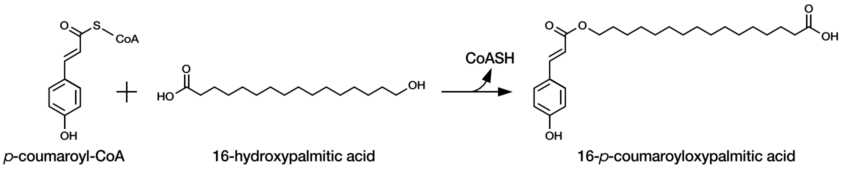
| | |
|---|---|
| Gene | *F6H1* |
| Enzyme | feruloyl-CoA 6′-hydroxylase |
| Reaction |  |
| Cofactor | ascorbate |
| Kinetics<br>$k_{\mathrm{cat}}$ and $K_{\mathrm{m}}$ | feruloyl-CoA, 11.0 sec$^{-1}$ and 36 µM<br>*p*-coumaroyl-CoA, trace reaction |
| Reference | [22] |

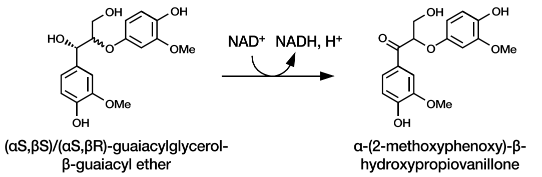
| | |
|---|---|
| Gene | *FDC1* |
| Enzyme | phenacrylic acid decarboxylase |
| Reaction |  |
| Cofactor | prenylated FMNH$_2$ |
| Kinetics<br>$k_{\mathrm{cat}}$ and $K_{\mathrm{m}}$ | *p*-coumaric acid, 1.5 sec$^{-1}$ and 110 µM<br>cinnamic acid, 4.6 sec$^{-1}$ and 180 µM<br>ferulic acid, 3.8 sec$^{-1}$ and 180 µM |
| Reference | [56] |

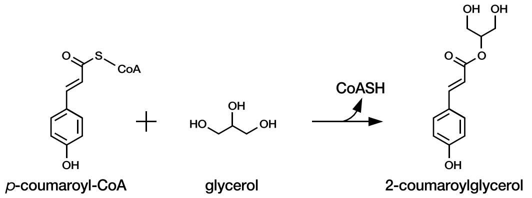
|  |  |
|---|---|
| Gene | *HCALDH* |
| Enzyme | hydroxycinnamaldehyde dehydrogenase |
| Reaction |  |
| Coenzyme | $NADP^+$ |
| Kinetics<br>$V_{max}$ and $K_m$ | coniferaldehyde, 560 pkat·$mg^{-1}$ and 43 µM<br>sinapaldehyde, 1700 pkat·$mg^{-1}$ and 150 µM<br>*p*-coumarladehyde, 310 pkat·$mg^{-1}$ and 19 µM |
| Reference | [57] |

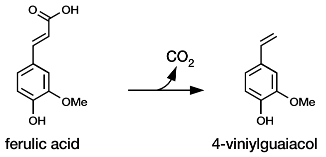
|  |  |
|---|---|
| Gene | *HCBT* |
| Enzyme | anthranilic acid *N*-hydroxycinnamoyl/benzoyltransferase |
| Reaction |  |
| Coenzyme | unnecessary |
| Substrate range | *p*-coumaroyl-CoA, caffeoy-CoA, feruloyl-CoA, sinapoyl-CoA |
| Reference | [25, 58] |

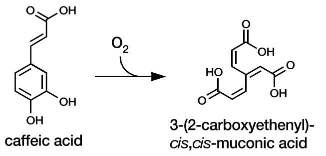
|  |  |
|---|---|
| Gene | *HCT2* |
| Enzyme | malic aicd *O*-hydroxycinnamoyl transferase |
| Reaction |  |
| Coenzyme | unnecessary |
| Specific activity | *p*-coumaroyl-CoA, 34 nkat·$mg^{-1}$<br>caffeoyl-CoA, 5.1 nkat·$mg^{-1}$ |
| Reference | [26] |

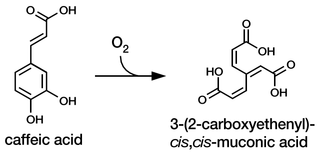
|  |  |
|---|---|
| Gene | *HHT1* |
| Enzyme | omega-hydroxypalmitic acid *O*-feruloyl transferase |
| Reaction |  |
| Coenzyme | unnecessary |
| Kinetics<br>$k_{cat}$ and $K_m$ | *p*-coumaroyl-CoA, 0.0136 $sec^{-1}$ and 36.7 µM<br>feruloyl-CoA, 0.0173 $sec^{-1}$ and 9.7 µM |
| Reference | [27] |

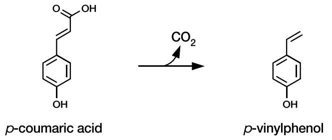
| | |
|---|---|
| Gene | *ligL* |
| Enzyme | β-aryl ether Cα-dehydrogenase |
| Reaction |  |
| Coenzyme | NAD$^+$ |
| Substrate range | β-O-4 dimers and oligomers with guaiacyl and syringyl structure |
| Reference | [28, 59] |

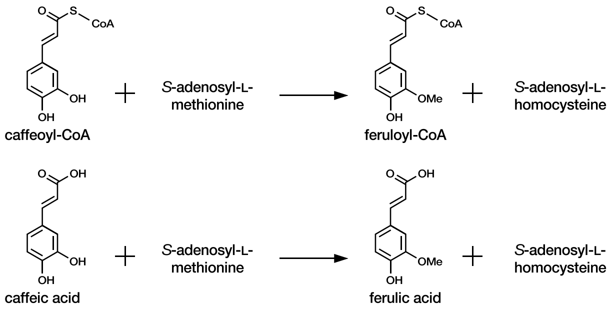
| | |
|---|---|
| Gene | *OsHCT4* |
| Enzyme | glycerol *O*-hydroxycinnamoyltransferase |
| Reaction |  |
| Coenzyme | unnecessary |
| Kinetics<br>$k_{cat}$ and $K_m$ | *p*-coumaroyl-CoA, 0.037 sec$^{-1}$ and 60 μM<br>feruloyl-CoA, 0.071 sec$^{-1}$ and 72 μM<br>caffeoyl-CoA, 0.082 sec$^{-1}$ and 102 μM |
| Reference | [29] |

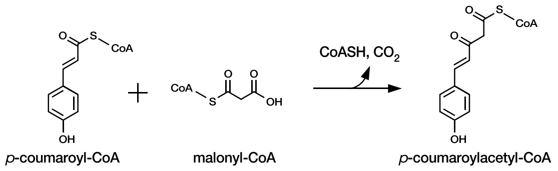
| | |
|---|---|
| Gene | *padC* |
| Enzyme | phenolic acid decarboxylase |
| Reaction |  |
| Coenzyme | prenylated FMNH$_2$ ? |
| Kinetics<br>$V_{max}$ and $K_m$ | ferulic acid, 280 μmol·min$^{-1}$·mg$^{-1}$ and 1100 μM<br>*p*-coumaric acid, 265 μmol·min$^{-1}$·mg$^{-1}$ and 1300 μM<br>caffeic acid, 180 μmol·min$^{-1}$·mg$^{-1}$ and 2600 μM |
| Reference | [30] |

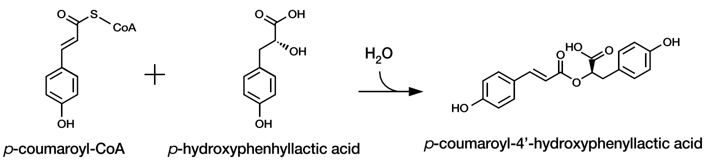
| | |
|---|---|
| Gene | *pcaG* + *pcaH* |
| Enzyme | protocatechuic acid 3,4-dioxygenase |
| Reaction |  |
| Coenzyme | unnecessary |
| Substrate range | caffeic acid and dihydrocaffeic acid |
| Reference | [31] |

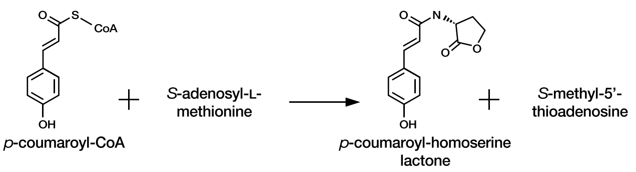
| | |
|---|---|
| Gene | *pcaG2* + *pcaH2* |
| Enzyme | protocatechuic acid 3,4-dioxygenase |
| Reaction |  |
| Coenzyme | unnecessary |
| Substrate range | caffeic acid and 3,4-dihydroxyphenylacetic acid |
| Reference | [32] |

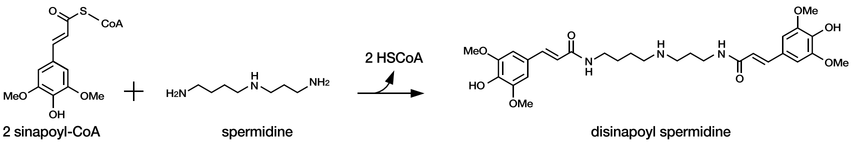
| | |
|---|---|
| Gene | *pdc* |
| Enzyme | *p*-coumaric acid decarboxylase |
| Reaction |  |
| Coenzyme | prenylated $FMNH_2$ |
| Kinetics<br>$V_{max}$ and $K_m$ | *p*-coumaric acid, 766 μmol·min$^{-1}$·mg$^{-1}$ and 1400 μM |
| Reference | [33] |

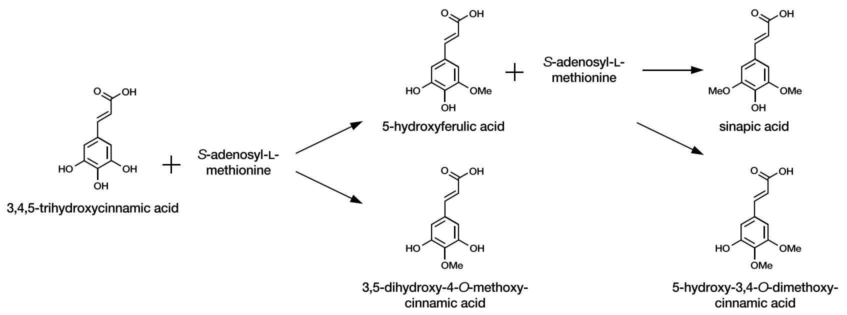
| | |
|---|---|
| Gene | *PFOMT* |
| Enzyme | phenylpropanoid/flavonoid *O*-methyltransferase |
| Reaction |  |
| Coenzyme | unnecessary |
| Kinetics<br>$V_{max}$ and $K_m$ | caffeoyl-CoA, 0.025 μmol·min$^{-1}$·mg$^{-1}$ and 25 μM<br>caffeic acid, 0.005 μmol·min$^{-1}$·mg$^{-1}$ and 44 μM<br>quercetin, 0.034 μmol·min$^{-1}$·mg$^{-1}$ and 6.4 μM |
| Reference | [34] |

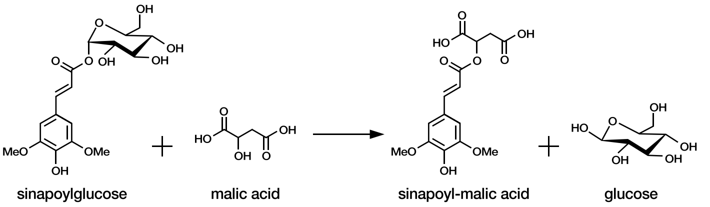
| | |
|---|---|
| Gene | *PKS1* |
| Enzyme | *p*-coumaroyl-diketide-CoA synthase |
| Reaction |  |
| Coenzyme | unnecessary |
| Kinetics<br>$k_{cat}$ and $K_m$ | *p*-coumaroyl-CoA, 0.00048sec$^{-1}$ and 85 μM<br>phenylpropionyl-CoA, 0.0025 sec$^{-1}$ and 40 μM<br>cinnamoyl-CoA, 0.00053 sec$^{-1}$ and 28 μM |
| Reference | [35] |

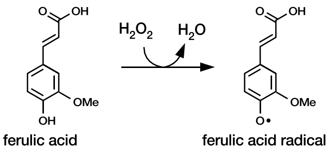
| | |
|---|---|
| Gene | *RAS* |
| Enzyme | rosmarinic acid synthase |
| Reaction |  |
| Coenzyme | unnecessary |
| Kinetics<br>$V_{\mathrm{max}}$ and $K_{\mathrm{m}}$ | *p*-coumaroyl-CoA (+*p*-hydroxyphenhyllactic acid), 1076 pkat·mg$^{-1}$ and 9.4 μM<br>*p*-coumaroyl-CoA (+3,4-dihydroxyphenhyllactic acid), 294 pkat·mg$^{-1}$ and 3.2 μM<br>caffeoyl-CoA (+*p*-hydroxyphenhyllactic acid), 283 pkat·mg$^{-1}$ and 2.3 μM<br>caffeoyl-CoA (+3,4-dihydroxyphenhyllactic acid), 103 pkat·mg$^{-1}$ and 3.3 μM |
| Reference | [37] |

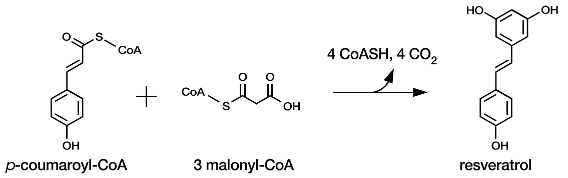
| | |
|---|---|
| Gene | *rpaI* |
| Enzyme | acyl-homoserine lactone synthases |
| Reaction |  |
| Coenzyme | unnecessary |
| Reference | [36] |

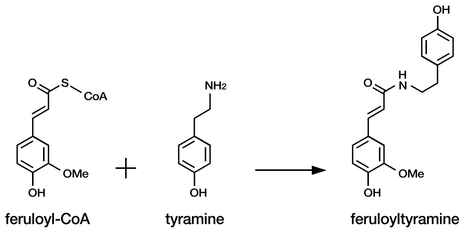
| | |
|---|---|
| Gene | *SDT* |
| Enzyme | spermidine disinapoyl acyltransferase |
| Reaction |  |
| Coenzyme | unnecessary |
| Kinetics<br>$k_{\mathrm{cat}}$ and $K_{\mathrm{m}}$ | sinapoyl-CoA, 5.1 sec$^{-1}$ and 8.3 μM |
| Reference | [38] |

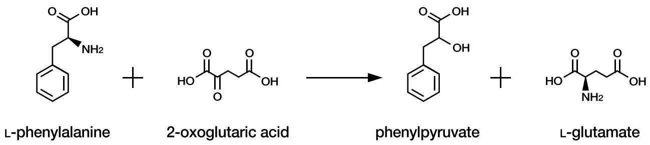
| | |
|---|---|
| Gene | *slr0095* |
| Enzyme | caffeoyl-CoA *O*-methyltransferase |
| Reaction |  |
| Coenzyme | unnecessary |
| Kinetics<br>$k_{\mathrm{cat}}$ and $K_{\mathrm{m}}$ | 3,4,5-tryhydroxycinnamic acid, 0.0104 liter·sec$^{-1}$ and 20.7 μM<br>caffeoyl-CoA, 0.0245 liter·sec$^{-1}$ and 32.9 μM<br>caffeic acid, 0.0055 liter·sec$^{-1}$ and 69.3 μM<br>5-hydroxyferulic acid, 0.0250 liter·sec$^{-1}$ and 74.0 μM |
| Reference | [39] |

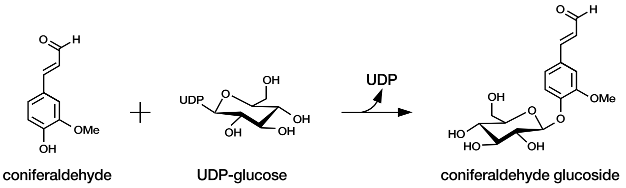
| | |
|---|---|
| Gene | *SNG1* |
| Enzyme | sinapoylglucose:malic acid *O*-sinapoyltransferase |
| Reaction |  |
| Coenzyme | unnecessary |
| Kinetics<br>$V_{\mathrm{max}}$ and $K_{\mathrm{m}}$ | sinapoylglucose, 0.528 μmol·min$^{-1}$·mg$^{-1}$ and 460 μM |
| Reference | [40] |

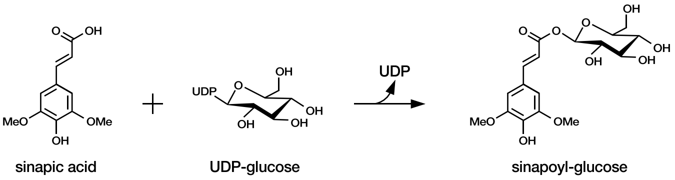
| | |
|---|---|
| Gene | *SPC4* |
| Enzyme | cationic peroxidase |
| Reaction |  |
| Coenzyme | unnecessary |
| Kinetics<br>$V_{\mathrm{max}}$ /$K_{\mathrm{m}}$ | ferulic acid, 0.92 M$^{-1}$·s$^{-1}$<br>*p*-coumaric acid, 0.23 M$^{-1}$·s$^{-1}$ |
| Reference | [41] |

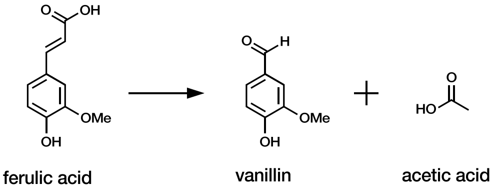
| | |
|---|---|
| Gene | *STS2* |
| Enzyme | resveratrol synthase |
| Reaction |  |
| Coenzyme | unnecessary |
| Reference | [42] |

| | |
|---|---|
| Gene | *THT10* |
| Enzyme | tyramine hydroxycinnamoyltransferase |
| Reaction |  |
| Coenzyme | unnecessary |
| Kinetics<br>$V_{\mathrm{max}}$ and $K_{\mathrm{m}}$ | feruloyl-CoA, 69960 pkat·mg$^{-1}$ and 0.6 μM<br>sinapoyl-CoA, 76000 pkat·mg$^{-1}$ and 1 μM<br>*p*-coumaroyl-CoA, 19200 pkat·mg$^{-1}$ and 2 μM<br>cinnamoyl-CoA, 120320 pkat·mg$^{-1}$ and 4.7 μM |
| Reference | [43] |

| | |
|---|---|
| Gene | *tyrB* |
| Enzyme | tyrosine aminotransferase |
| Reaction |  |
| Coenzyme | unnecessary |
| Kinetics<br>$V_{\mathrm{max}}$ and $K_{\mathrm{m}}$ | L-phenylalanine, 9.1 μmol·min$^{-1}$·nmol protein$^{-1}$ and 333 μM<br>L-tyrosine, 20.0 μmol·min$^{-1}$·nmol protein$^{-1}$ and 625 μM |
| Reference | [44] |

| | |
|---|---|
| Gene | *UGT72E1* |
| Enzyme | coniferaldehyde UDP-glucosyl transferase |
| Reaction |  |
| Coenzyme | unnecessary |
| Kinetics<br>$k_{\text{cat}}$ and $K_{\text{m}}$ | coniferaldehyde, 1.22 sec$^{-1}$ and 270 μM<br>sinapaldehyde, 1.43 sec$^{-1}$ and 460 μM |
| Reference | [45] |

| | |
|---|---|
| Gene | *UGT84A2* |
| Enzyme | sinapic acid-1-glucosyltransferase |
| Reaction |  |
| Coenzyme | unnecessary |
| Kinetics<br>$V_{\text{max}}$ and $K_{\text{m}}$ | sinapic acid, 13.44 nkat·mg$^{-1}$ and 250 μM |
| Reference | [46] |

| | |
|---|---|
| Gene | *VpVAN* |
| Enzyme | vanillin synthase |
| Reaction |  |
| Coenzyme | unnecessary |
| Substrate range | ferulic acid and ferulic acid glucoside |
| Reference | [47] |

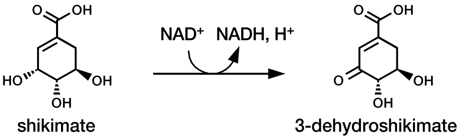
| | |
|---|---|
| Gene | *ydiB* |
| Enzyme | quinic acid/shikimic acid 5-dehydrogenase |
| Reaction |  |
| Coenzyme | NAD$^{+}$ |
| Kinetics<br>$k_{\text{cat}}$ and $K_{\text{m}}$ | shikimic acid, 91000 sec$^{-1}$ and 2.9 μM<br>quinic acid, 113000 sec$^{-1}$ and 9.1 μM |
| Reference | [48] |

**Table S3.** List of plants generated and mixed Agrobacterium strains harboring different gene constructs used for seven independent inoculation procedures.

| Gene set | | Gene | Number of plants | Efficiency (%) |
|---|---|---|---|---|
| 1 | Single-gene introduction | *CASHT* | 9 | 18.4 |
| | | *pdc* | 7 | 14.3 |
| | | *CCMT1* | 7 | 14.3 |
| | | *tyrB* | 6 | 12.2 |
| | | *THT10* | 5 | 10.2 |
| | | *FDC1* | 4 | 8.2 |
| | | *couA* | 2 | 4.1 |
| | | *Atu1417* | 0 | 0 |
| | Multiple-genes introduction | | 9 | - |
| | Subtotal | | 49 | - |
| 2 | Single-gene introduction | *rpaI* | 11 | 26.2 |
| | | *STS2* | 7 | 16.7 |
| | | *C2H* | 6 | 14.3 |
| | | *CURS3* | 2 | 4.8 |
| | | *PKS1* | 2 | 4.8 |
| | | *AT208* | 2 | 4.8 |
| | | *CHS5* | 1 | 2.4 |
| | Multiple-genes introduction | | 11 | - |
| | Subtotal | | 42 | - |
| 3 | Single-gene introduction | *3AT2* | 11 | 22.4 |
| | | *HCBT* | 8 | 16.3 |
| | | *ACT* | 6 | 12.2 |
| | | *HCT2* | 5 | 10.2 |
| | | *OsHCT4* | 5 | 10.2 |
| | | *RAS* | 2 | 4.1 |
| | | *SDT* | 2 | 4.1 |
| | | *CYP84A4* | 2 | 4.1 |
| | Multiple-genes introduction | | 8 | - |
| | Subtotal | | 49 | - |
| 4 | Single-gene introduction | *CALipB* | 8 | 16.3 |
| | | *SPC4* | 8 | 16.3 |
| | | *UGT84A2* | 6 | 12.2 |
| | | *BrRCD* | 4 | 8.2 |
| | | *F5H* | 4 | 8.2 |
| | | *PFOMT* | 3 | 6.1 |
| | | *slr0095* | 2 | 4.1 |
| | | *VpVAN* | 2 | 4.1 |
| | Multiple-genes introduction | | 12 | - |
| | Subtotal | | 49 | - |

**Table S3.** ***continued***

| Gene set | Gene | | Number of Plants | Efficiency (%) |
|---|---|---|---|---|
| 5 | Single-gene introduction | *Balat_0669* | 8 | 16.3 |
| | | *calB* | 8 | 16.3 |
| | | *HHT1* | 5 | 10.2 |
| | | *HCALDH* | 5 | 10.2 |
| | | *CGT* | 4 | 8.2 |
| | | *F6H1* | 4 | 8.2 |
| | | *UGT72E1* | 4 | 8.2 |
| | | *padC* | 0 | 0 |
| | Multiple-genes introduction | | 11 | - |
| | Subtotal | | 49 | - |
| 6 | Single-gene introduction | *CYP98A22* | 7 | 16.3 |
| | | *CA9OMT* | 6 | 14 |
| | | *CADH* | 3 | 9.3 |
| | | *calA* | 4 | 9.3 |
| | | *ligL* | 2 | 4.7 |
| | | *ydiB* | 2 | 4.7 |
| | | *SNG1* | 2 | 4.7 |
| | Multiple-genes introduction | | 16 | - |
| | Subtotal | | 43 | - |
| 7 | Single-gene introduction | *pcaG2 + pcaH2* | 8 | 53.3 |
| | | *pcaG + pcaH* | 7 | 46.7 |
| | Multiple-genes introduction | | 0 | - |
| | Subtotal | | 15 | - |

The number of transgenic plants generated with a single gene and with multiple transgenes are indicated in the third column. Efficiency refers to the relative proportions of plants harboring a particular gene among all of the plants generated with the same mixture of Agrobacterium strains.

**Table S4.** Relative abundance of pyrolysis products within AIR-sample from wild-type and transgenic inflorescence stem

| No. | Products | Stractural feature | Wild type | _PkC4Hpro:: F5H_ | _PkC4Hpro:: calB_ | _PkC4Hpro:: couA_ | _PkC4Hpro:: F6H1_ |
|---|---|---|---|---|---|---|---|
| 1 | Phenol | H, unsub | 0.8 (0.36) | 0.49 (0.26) | 0.65 (0.21) | _1.36 (0.24)*_ | 0.81 (0.3) |
| 2 | 2-methylphenol | H, unsub | 0.19 (0.06) | _0.08 (0.05)*_ | 0.16 (0.05) | 0.23 (0.04) | 0.15 (0.07) |
| 3 | 4-Methylphenol | H, unsub | 0.41 (0.14) | _0.21 (0.12)*_ | 0.36 (0.07) | _0.65 (0.1)*_ | 0.42 (0.15) |
| 4 | Guaiacol | G, unsub | 2.87 (0.56) | _0.56 (0.49)***_ | 2.73 (0.2) | 2.79 (0.31) | 2.56 (0.38) |
| 5 | hydroquinone | H, misc | 1.4 (0.44) | 0.85 (0.52) | 1.4 (0.36) | 1.98 (0.48) | 1.55 (0.5) |
| 6 | 4-ethylphenol | H, ethyl | ND | ND | ND | 0.01 (0.01) | 0.01 (0.02) |
| 7 | 2,4-dimethylphenol | H, methyl | 1.12 (0.14) | _0.22 (0.25)***_ | 1.13 (0.15) | 1.1 (0.17) | 1.26 (0.22) |
| 8 | 4-methylguaiacol | G, methyl | 1.36 (0.14) | _0.25 (0.3)***_ | 1.35 (0.16) | 1.29 (0.18) | 1.52 (0.27) |
| 9 | 4-Ethylguaiacol | G, ethyl | 0.15 (0.08) | ND | 0.15 (0.09) | _0.31 (0.05)**_ | 0.15 (0.09) |
| 10 | 4-Vinylguaiacol | G, vinyl | 12.13 (2.15) | _2.34 (2.26)***_ | 11.79 (0.74) | _15.45 (1.71)*_ | 11.43 (1.74) |
| 11 | 4-vinylphenol | H, vinyl | 8.09 (1.43) | _1.56 (1.51)***_ | 7.86 (0.49) | _10.3 (1.14)*_ | 7.62 (1.16) |
| 12 | 3-methoxy-5-methylphenol | G, methyl | 0.02 (0.02) | 0.03 (0.02) | 0.04 (0.02) | _0.08 (0.05)*_ | 0.03 (0.03) |
| 13 | 4-propenylphenol | H, methyl | 0.02 (0.01) | 0.02 (0.01) | 0.01 (0.01) | 0.03 (0.01) | 0.02 (0.02) |
| 14 | syringol | S, unsub | 1.38 (0.26) | _3.51 (0.7)***_ | _1.96 (0.32)**_ | _1.99 (0.39)**_ | _1.79 (0.35)*_ |
| 15 | Eugenol | G, misc | 0.61 (0.08) | _0.13 (0.14)***_ | 0.59 (0.07) | _0.41 (0.07)**_ | 0.64 (0.12) |
| 16 | 4-hydroxybenzaldehyde | H, Cα-O | 0.03 (0.01) | 0.02 (0.01) | 0.02 (0.02) | 0.06 (0.04) | 0.03 (0.03) |
| 17 | 4-Propylguaiacol | G, misc | 0.27 (0.05) | _0.05 (0.07)***_ | 0.27 (0.05) | _0.33 (0.04)*_ | 0.28 (0.05) |
| 18 | Vanillin | G, Cα-O | 1.01 (0.11) | _0.21 (0.17)***_ | 0.93 (0.12) | 0.88 (0.07) | 0.98 (0.13) |
| 19 | cis-isoeugenol | G, misc | 0.49 (0.1) | _0.11 (0.11)***_ | 0.47 (0.07) | 0.38 (0.05) | 0.5 (0.1) |
| 20 | 4-methylsyringol | S, methyl | 0.71 (0.13) | _1.46 (0.29)***_ | _1.01 (0.15)**_ | _1.08 (0.12)***_ | _1.11 (0.14)***_ |
| 21 | trans-Isoeugenol | G, misc | 3.4 (0.64) | _0.76 (0.76)***_ | 3.32 (0.37) | _2.6 (0.31)*_ | 3.5 (0.67) |
| 22 | 4-propyneguaiacol | G, misc | 0.35 (0.06) | _0.16 (0.05)***_ | 0.31 (0.06) | 0.29 (0.06) | 0.32 (0.08) |
| 23 | 4-alleneguaiacol | G, misc | 0.31 (0.06) | _0.14 (0.04)**_ | 0.27 (0.06) | 0.25 (0.05) | 0.28 (0.06) |
| 24 | acetovanilone | G, Cα-O | 1.08 (0.03) | _0.25 (0.2)***_ | _0.99 (0.05)**_ | _1.34 (0.15)**_ | 1.06 (0.13) |
| 25 | 4-ethylsyringol | S, ethyl | 0.05 (0.01) | _0.12 (0.04)**_ | _0.08 (0.02)*_ | _0.11 (0.02)***_ | _0.07 (0.02)*_ |
| 26 | Guaiacylaceton | G, Cβ-O | 1.21 (0.11) | _0.25 (0.27)***_ | 1.19 (0.04) | 1.1 (0.06) | 1.34 (0.21) |
| 27 | 4-vinlysyringol | S, vinyl | 5.29 (0.73) | _13.16 (2.94)***_ | _7.22 (1.28)**_ | _9.26 (0.82)***_ | _6.87 (1.05)**_ |
| 28 | 4-allylsyringol | S, misc | 0.42 (0.06) | _1.2 (0.35)***_ | _0.6 (0.1)**_ | _0.65 (0.09)***_ | _0.62 (0.08)***_ |
| 29 | homosyringaldehyde | S, Cβ-O | 0.08 (0.01) | _0.18 (0.05)***_ | _0.11 (0.02)*_ | _0.13 (0.02)***_ | _0.11 (0.02)**_ |
| 30 | cis-4-propenylsyringol | S, misc | 0.29 (0.05) | _0.8 (0.25)***_ | _0.41 (0.08)**_ | _0.49 (0.07)***_ | _0.42 (0.07)**_ |
| 31 | Syringaldehyde | S, Cα-O | 0.9 (0.13) | _2.8 (0.34)***_ | _1.29 (0.15)***_ | 1.05 (0.22) | _1.29 (0.18)***_ |
| 32 | cis-Coniferyl-alcohol | G, Cc-O | 3.45 (0.18) | _0.69 (0.8)***_ | _3.14 (0.27)*_ | _2.45 (0.24)***_ | _3.15 (0.27)*_ |
| 33 | 4-propynesyringol | S, misc | 0.22 (0.03) | _0.76 (0.27)***_ | _0.31 (0.05)***_ | _0.34 (0.05)***_ | _0.29 (0.05)**_ |
| 34 | 4-allenesyringol | S, misc | 0.16 (0.02) | _0.52 (0.18)***_ | _0.22 (0.04)**_ | _0.24 (0.04)***_ | _0.2 (0.03)*_ |
| 35 | trans-4-propenylsyringol | S, misc | 2 (0.35) | _5.55 (1.71)***_ | _2.85 (0.53)**_ | _3.36 (0.47)***_ | _2.89 (0.44)**_ |
| 36 | acetosyringone | S, Cα-O | 0.11 (0.15) | _1.06 (0.32)***_ | 0.25 (0.19) | _0.36 (0.23)*_ | _0.35 (0.15)*_ |
| 37 | Coniferylaldehyde | G, Cγ-O | 1.12 (0.88) | ND | 0.54 (0.78) | 0.16 (0.3) | 1.27 (0.74) |
| 38 | trans-coniferyl-alcohol | G, Cγ-O | 30.77 (2.46) | _7.07 (5.66)***_ | _26.41 (3.03)*_ | _19.46 (1.83)***_ | _24.87 (3.24)**_ |
| 39 | Syringylacetone | S, Cβ-O | 0.17 (0.02) | _0.54 (0.12)***_ | _0.24 (0.04)***_ | _0.32 (0.04)***_ | _0.25 (0.05)***_ |
| 41 | Coniferylacetate | S, Cγ-O | 0.01 (0) | ND | 0.01 (0) | _0.01 (0.01)*_ | _0.02 (0)*_ |
| 42 | cis-Sinapyl alcohol | S, Cγ-O | 1.22 (0.19) | _3.72 (0.49)***_ | _1.54 (0.11)*_ | 1.45 (0.25) | _1.6 (0.25)**_ |
| 43 | trans-sinapalaldehyde | S, Cγ-O | 0.08 (0.09) | _0.65 (0.49)*_ | 0.08 (0.12) | 0.02 (0.03) | 0.13 (0.09) |
| 44 | trans-sinapyl-alcohol | S, Cγ-O | 14.26 (3.74) | _47.49 (11.44)***_ | 15.73 (1.78) | 13.81 (2.95) | 15.61 (4.53) |

Peak molar areas were calculated for the lignin degradation products with relative responce factor reporte by van Erven (2017).

The summed areas were normalized, and the amount of each compound is expressed as percentages.

Numbers in parentheses are 95% confidential intervals.

**Table S5.** carbohydrates composition in transgenic lines supporting Fig.6

| Lines | Carbohydrates (µg/mgAIR) | | | | | | | | | | Total carbohydrates (µg/mgAIR) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | Glc | Xyl | GalA | Rha | Man | Gal | Ara | GlcA | mGlcA | Fuc | |
| Wild-type | 377 (16) | 145 (7) | 119 (9) | 44.9 (2.9) | 30.5 (1.1) | 22.1 (2) | 12.7 (2.2) | 5.92 (0.43) | 2.03 (0.27) | 1.07 (0.11) | 685 (26) |
| _PkC4Hpro::F5H_ | 381 (9) | _154 (6)_* | 120 (11) | 46 (3.7) | 31.8 (1.4) | 23.4 (1.9) | 14.5 (1.7) | 6.48 (0.78) | 2.09 (0.86) | 1.08 (0.21) | 702 (41) |
| _PkC4Hpro::calB_ | 377 (10) | 151 (5) | 130 (9) | 48 (2.9) | 31 (1.4) | _24.2 (1.3)_* | 15.1 (1.6) | 5.91 (0.52) | _5.92 (2.28)_*** | 1.11 (0.19) | 710 (34) |
| _PkC4Hpro::couA_ | _326 (10)_*** | 143 (6) | _140 (6)_** | _63.9 (5.1)_*** | 31.2 (1.1) | _36 (3.7)_*** | _31.8 (6.3)_*** | _6.8 (0.55)_** | _7.53 (2.75)_*** | 1.21 (0.09)* | 708 (23) |
| _PkC4Hpro::F6H1_ | _352 (18)_* | _133 (8)_* | 128 (7) | 46.5 (2.2) | _28.3 (1.4)_* | 23.5 (1.2) | 14.2 (1.2) | 5.71 (0.55) | 1.87 (1.15) | 1.23 (0.11)** | 661 (50) |

Numbers in parentheses are 95% confidential intervals.

**Table S6.** sugar yield by enzymatic saccharification supporting to Fig.7

| Line | Glucose yield (μg/mgAIR) |  | Xylose yield (μg/mgAIR) |  |
|---|---|---|---|---|
|  | Without pretreatment | Pretreatment with 100 mM NaOH | Without pretreatment | Pretreatment with 100 mM NaOH |
| Wild-type | 126.2 (16) | 136 (11) | 3.9 (2) | 87 (5) |
| _PkC4Hpro::F5H_ | 126.1 (12) | _178 (32)_* | _0.9 (1)_* | _127 (16)_*** |
| _PkC4Hpro::calB_ | 133.5 (17) | 164 (25) | 4.5 (2) | _108 (12)_** |
| _PkC4Hpro::couA_ | 144.7 (13) | _210 (17)_*** | _17.9 (7)_** | _134 (16)_*** |
| _PkC4Hpro::F6H1_ | 118.8 (7) | 140 (13) | _0.8 (1)_* | 91 (10) |

Numbers in parentheses are 95% confidential intervals.

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