SUPPLEMENTARY INFORMATION

Legends of the figures

Figure S1: Biosynthetic pathways to aromatic amino acids and malonyl-CoA from glucose. Abbreviations used: DAHP, 2-keto-3-deoxy-D-arabino-heptulosonate-7-phosphate; ACC, acetyl-CoA carboxylase complex, CM1, chorismate mutase 1; PPA-AT, prephenate aminotransferase; ADT, arogenate dehydratase; ADH, arogenate dehydrogenase

Figure S2: Putative relationships between 8-8' dimeric naturally-occurring stilbenes (according to Stephenson's group[29])

Figure S3: Examples of stilbene tetramers resulting from the 3-8' condensation of e-viniferin. The two tetramers, vitisin A and vitisin B isolated from grapevine root extracts result from the 3-8' coupling of two oxidized molecules of (-)-ε-viniferin (according to Stephenson's group[29])

Figure S4: Hypothetical mechanism for the formation of a stilbene heptamer. The stilbene heptamer pauciflorol D is formed by condensation between the resveratrol 8-10' tetramer, vaticaphenol A, and an 8-8' quinone trimer formed by the coupling of three resveratrol hydroxyphenyl radicals C (according to Stephenson's group[29])

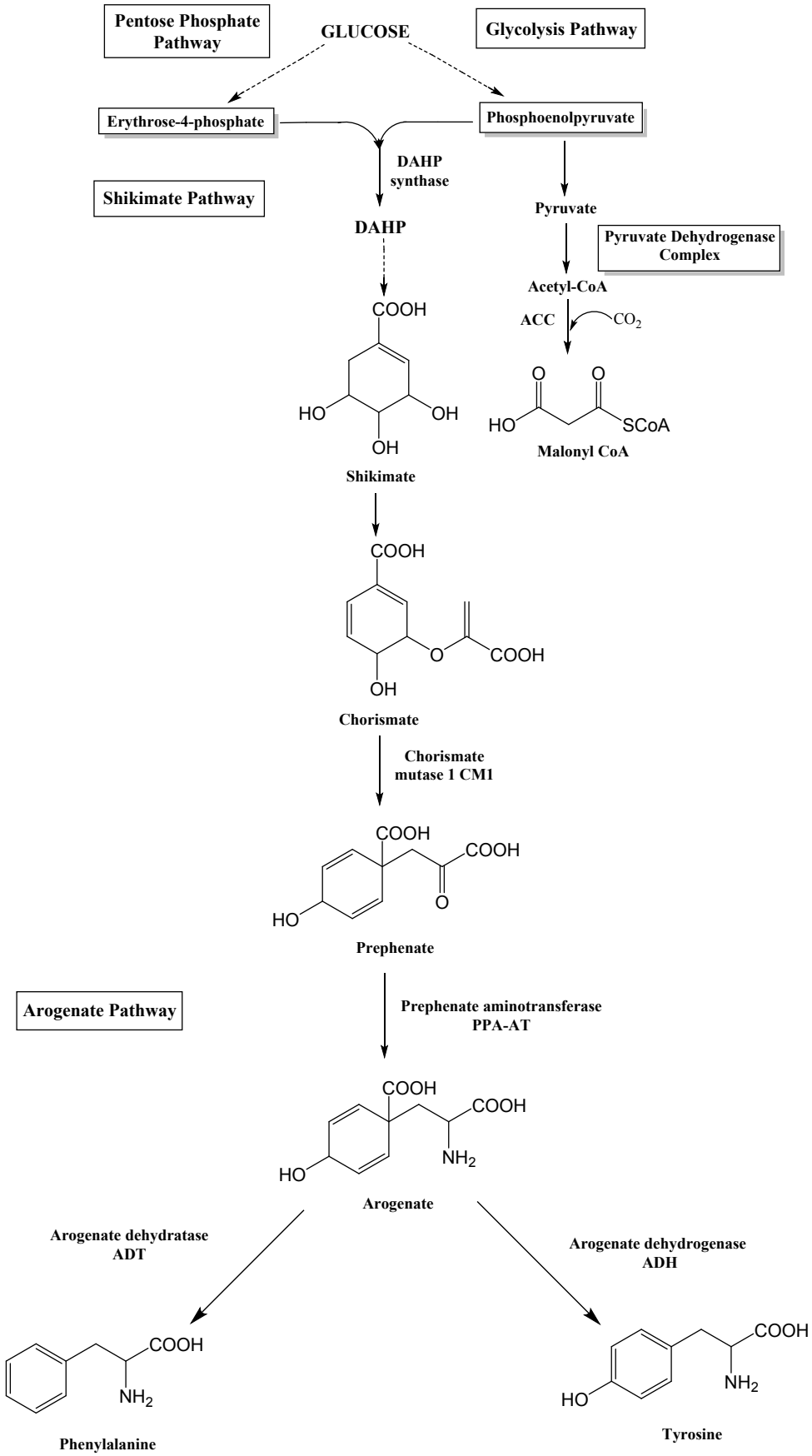
Pentose Phosphate Pathway
GLUCOSE
Glycolysis Pathway
Erythrose-4-phosphate
Phosphoenolpyruvate
DAHP synthase
Shikimate Pathway
DAHP
Pyruvate
Pyruvate Dehydrogenase Complex
Acetyl-CoA
ACC
CO_2
COOH
HO
OH
OH
Shikimate
O
O
HO
SCoA
Malonyl CoA
COOH
O
COOH
OH
Chorismate
Chorismate mutase 1 CM1
COOH
COOH
O
HO
Prephenate
Arogenate Pathway
Prephenate aminotransferase PPA-AT
COOH
COOH
HO
NH_2
Arogenate
Arogenate dehydratase ADT
Arogenate dehydrogenase ADH
COOH
NH_2
Phenylalanine
COOH
NH_2
HO
Tyrosine

Figure S1

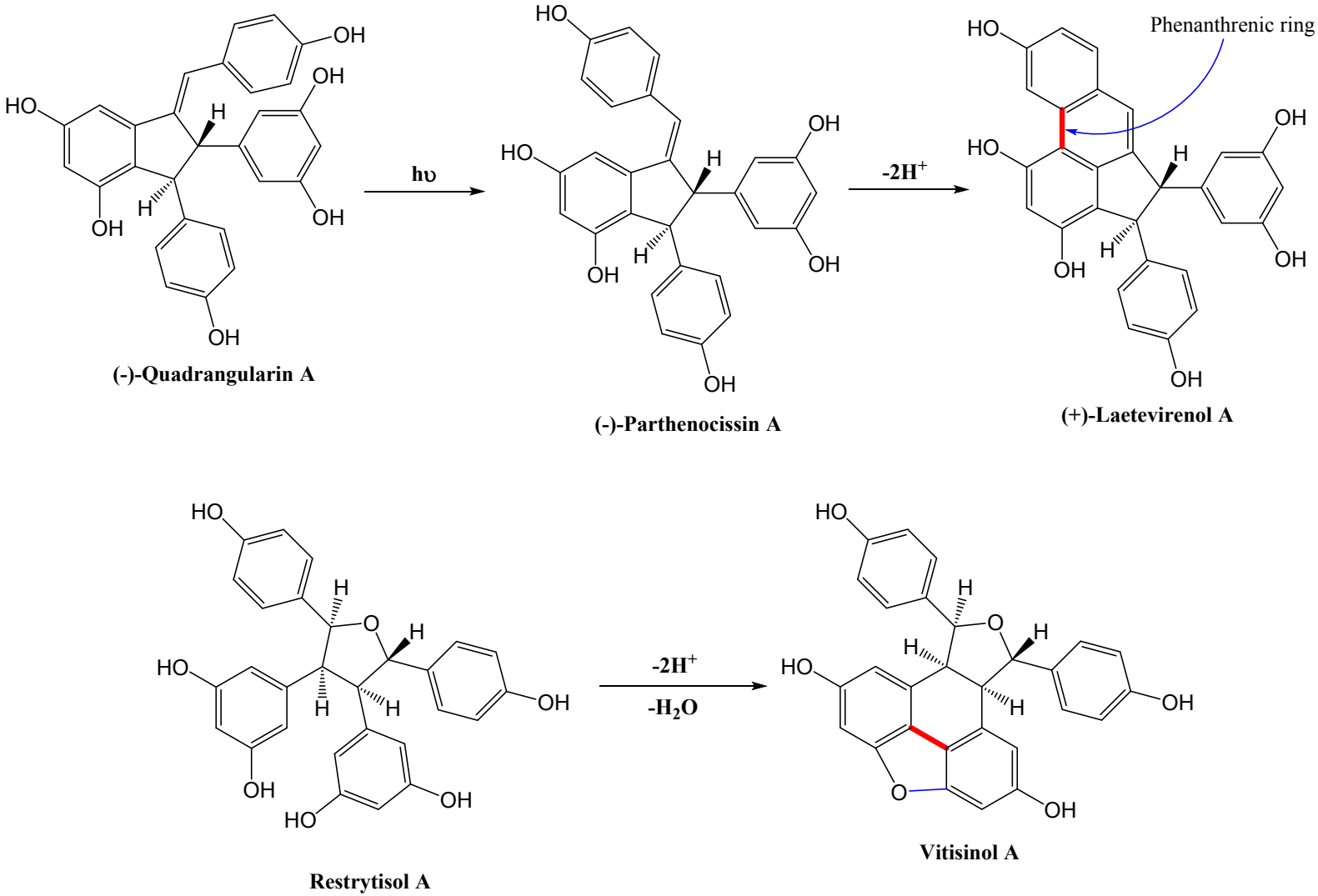
(-)-Quadrangularin A
hυ
(-)-Parthenocissin A
-2H+
Phenanthrenic ring
(+)-Laetevirenol A
Restrytisol A
-2H+
-H2O
Vitisinol A

Figure S2

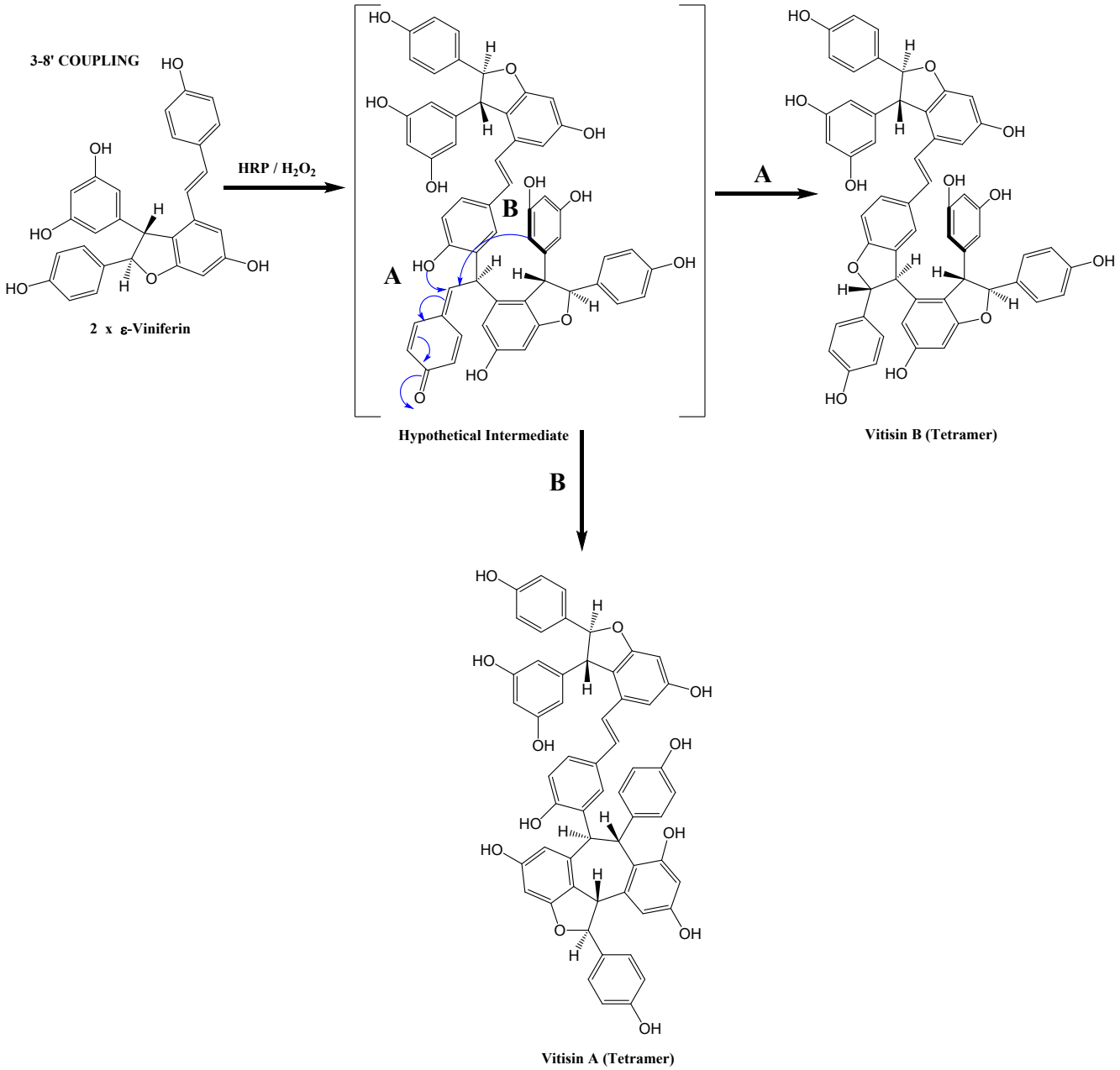
3-8' COUPLING
HRP / H2O2
2 x ε-Viniferin
A
B
Hypothetical Intermediate
Vitisin B (Tetramer)
B
Vitisin A (Tetramer)

Figure S3

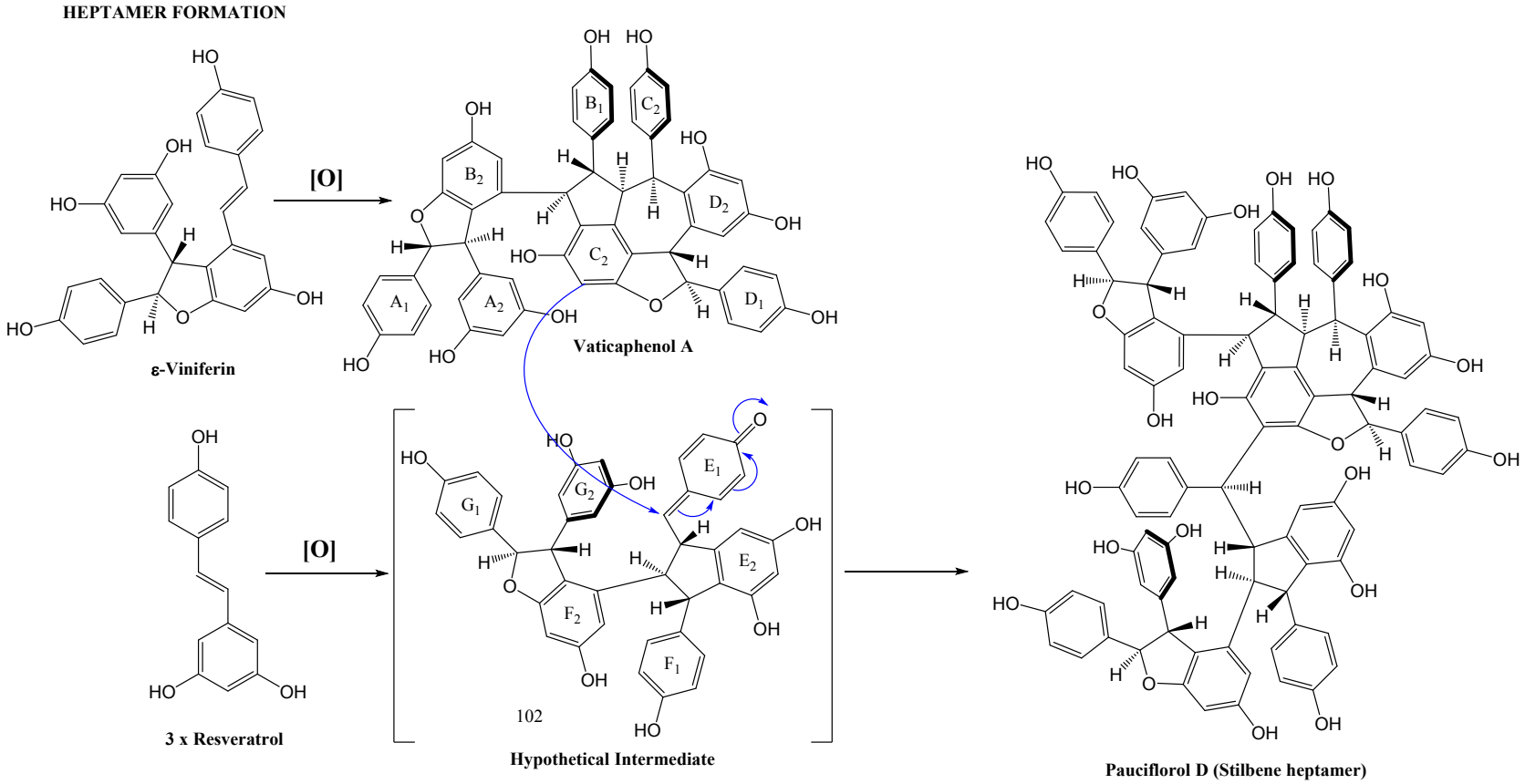
HEPTAMER FORMATION
ε-Viniferin
[O]
Vaticaphenol A
3 x Resveratrol
[O]
102
Hypothetical Intermediate
Pauciflorol D (Stilbene heptamer)

Figure S4

Table S1 Antifungal activity of stilbene monomers and oligomers towards various microorganisms

Tested stilbenes	Microorganisms/structures	Inhibiting activity	References
Resveratrol	*Cladosporium cuccumerinum* (spores) *Botrytis cinerea* (spores) *Pyricularia oryzae* (spores) *Plasmopara viticola* (zoospore motility)	ED_{50} > 870 μM	**17**
Resveratrol	*B. cinerea* (mycelium) *P. oryzae* (mycelium) *Fusarium oxysporum* (mycelium)	ED_{50} : 438 μM ED_{50} : 276 μM ED_{50} : 88 μM	**17**
Resveratrol	*B. cinerea* (spores)	ED_{50} : 390 μM	**117**
Resveratrol	*Stereum hirsutum* *Fomitiporia punctata* *Libertella blepharis* *Phaeomoniella chlamydospora* *Phaeoacremonium aleophilum*	Fungal growth inhibition at 490 μM Ineffective or stimulator on fungal growth at 490 μM	**283**
Resveratrol	Yeast *Penicillium expansum* *Aspergillus niger*	57.2% growth decrease at 48 μM 16.1% growth decrease at 48 μM 36.4% growth decrease at 48 μM	**284**

Table S1 Antifungal activity of stilbene monomers and oligomers towards various microorganisms (continued)			
Resveratrol	*P. viticola* (zoospore motility) *P. viticola* (disease development)	ED_{50} : 192 μM ED_{50} : 145 μM	**282**
Resveratrol	*B. cinerea* (spores)	ED_{50} : 438 μM	**280**
Resveratrol	*P. viticola* (zoospore motility)	ED_{100} : 500 μM	**286**
Resveratrol	*P. viticola* (sporulation)	ED_{50} : 484 μM	**287**
Resveratrol	*B. cinerea* (spores)	ED_{50} : 1153 μM	**281**
Pterostilbene	*B. cinerea* (spores) *P. oryzae* (spores)	ED_{50} : 70 μM ED_{50} : 35 μM	**112**
Pterostilbene	*P. viticola* (sporangia release) *P. viticola* (zoospore motility)	ED_{50} : 17.6 μM ED_{50} : 9 μM	**288**
Pterostilbene	*B. cinerea* (spores)	ED_{50} : 70 μM	**289**
Pterostilbene	*B. cinerea* (spores)	ED_{50} : 78 μM	**117**
Pterostilbene	Esca disease-associated fungi	Inhibition of fungal growth (39 to 390 μM)	**283**

Table S1 Antifungal activity of stilbene monomers and oligomers towards various microorganisms (continued)			
Pterostilbene	*P. viticola* (zoospore motility)	ED_{50} : 14.6 μM	**282**
Piceatannol Isorhapontigenin Astringin Isorhapontin	Development of downy mildew	ED_{50} : 254 μM ED_{50} : 116 μM ED_{50} : 705 μM ED_{50} : 272 μM	**290**
ε-viniferin ε-viniferin	*B. cinerea* (spores) *B. cinerea* (mycelium growth)	ED_{50} : 220 μM ED_{50} : 230 μM	**288**
ε-viniferin ε-viniferin	*P. viticola* (sporulation) *P. viticola* (sporulation)	ED_{50} : 12.7 μM ED_{50} : 70 μM	**282,287**
Glucosylated dimers Piceasides I-L Ampelopsin A	Development of downy mildew	ED_{50} : 96-147 μM ED_{50} : 934 μM	**290**
Stilbene tetramers Hopeaphenol Miyabenol C Vitisin A Vitisin B	Development of downy mildew	ED_{50} : 18 μM ED_{50} : 40 μM ED_{50} : 20 μM ED_{50} : 12 μM	**287**

Table S2 Metabolic engineering of stilbene pathways in yeast

Strain used for transformation	Incorporated genes	Substrate	Stilbenes produced	References
Saccharomyces cerevisiae FY23	*4CL* from *Populus trichocarpa* X *Populus deltoides*, *STS* from *Vitis vinifera*	*p*-coumarate	Resveratrol (1.45 µg/L)	**394**
S.cerevisiae CEN.PK113-3b	*4CL* from *Nicotiana tabacum*, *STS* from *V. vinifera*	*p*-coumarate	Resveratrol (5.8 mg/L)	**395**
S.cerevisiae WAT11	*TAL* from *Rhodobacter sphaeroides*, 4CL::STS-*4CL* from *Arabidopsis thaliana* and *STS* from *V. vinifera*	*p*-coumarate	Resveratrol (5.25 mg/L)	**398**
Yarrowia lipolytica	*TAL* from *Rhodotorula glutinis*, *4CL* from *Streptomyces coelicolor*, *STS* from *V. vinifera*	Tyrosine	Resveratrol (1.46 mg/L)	**408**
S. cerevisiae YPH499	*PAL* and *CPR* from *P. trichocarpia* x *P. deltoides*, *C4H* and *4CL* from *Glycine max*, *STS* from *V. vinifera*	Phenylalanine	Resveratrol (0.31 mg/L)	**403**
S. cerevisiae CEN.PK2–1	*4CL* from *A. thaliana*, *STS* from *V. vinifera*	*p*-coumarate	Resveratrol (391 mg/L)	**397**
S. cerevisiae W303-1A	*4CL* from *A. thaliana*, *STS* from *A. hypogea*, ΔPAD1 in *S. cerevisiae*	*p*-coumarate	Resveratrol (3.1 mg/L)	**396**
S. cerevisiae WAT11	*TAL* from *R. sphaeroides*, 4CL::STS, *4CL* from *A. thaliana* and *STS* from *V. vinifera*, *araE* from *E. coli*	Tyrosine	Resveratrol (3.1 mg/L)	**406**

Table S2 Metabolic engineering of stilbene pathways in yeast (continued)				
S. cerevisiae WAT11	4CL::STS, *4CL* from *A. thaliana* and *STS* from *V. vinifera*	Tyrosine	Resveratrol (14.4 mg/L)	**402**
S. cerevisiae W303-1A	*PAL* from *Rhodosporidium toruloides*, *C4H* and *4CL* from *A. thaliana*, *STS* from *A. hypogea*, *ACC1* from *S. cerevisiae*	Tyrosine	Resveratrol (5.8 mg/L)	**407**
S. cerevisiae CEN.PK102-5B	*TAL* from *Herpetosiphon aurianticus*, *4CL* from *Arabidopsis thaliana* and *STS* from *V. vinifera*, ScARO4^{K229L}, ScARO7^{G141S}, ACC$^{S659A, S1157A}$	Glucose/ Ethanol	Resveratrol (415.65 with glucose/531.41 mg/L with ethanol)	**386**
S. cerevisiae CEN.PK102-5B	*PAL*, *C4H*, *ATR2* and *4CL* from *A. thaliana*, *STS* from *V. vinifera*, *ACS* from *Salmonella enterica*, *AroL* from *E. coli*, *CYB5* from *S. cerevisiae* *SbROMT* from *Sorghum bicolor*/*VvROMT* from *V. vinifera*, ΔARO10 in *S. cerevisiae*	Glucose	Resveratrol (800 mg/L) Pinostilbene (5.5 mg/L) Pterostilbene (34.93 mg/L)	**387**

Abbreviations used: *PAL*, phenylalanine ammonia lyase, *TAL*, tyrosine ammonia lyase, *C4H*, cinnamate-4-hydroxylase; *4CL*, *p*-coumaroyl-CoA ligase; *STS*, stilbene synthase; *ACC*, acetyl-CoA carboxylase complex; *ROMT*, resveratrol-*O*-methyltransferase; *ARO10*, gene encoding the phenylpyruvate decarboxylase; Sc*ARO4*^{K229L} and Sc*ARO7*^{G141S} genes encoding feedback-inhibition resistant versions of DAHP synthase and chorismate mutase, respectively; *araE*, arabinose-H^+-transporter; *PAD1* gene encoding the phenyl acrylic acid decarboxylase; *CPR*, cytochrome P450 reductases; *aroL,* shikimate kinase 2.