*Supplementary Materials*

# Nucleoside 5′-phosphoramidates control phenylpropanoid pathway in *Vitis vinifera* suspension-cultured cells

**Methods S2: Identification and determination of phenylamides content**

The extracts of freeze dried cells and spent media were subjected to liquid chromatography coupled with tandem mass spectrometry (LC-MS/MS) in the multiple reaction monitoring (MRM) mode for the determination of phenylamide concentrations. Analysis was performed using a Quattro Micro API mass spectrometer (Waters, Milford, MA, USA) connected to an Acquity UPLC system (Waters). The LC conditions were as follows: column: ACQUITY UPLC BEH C18 (2.1 mm ID, 50 mm length, 1.7 μm particle size) (Waters); column temperature: 40°C; solvents: 0.1% formic acid in water (A) and 0.1% formic acid in acetonitrile (B); gradient: 5%-70% B/(A + B) within 10 min; flow rate: 0.2 mL/min. The MRM conditions were optimized using authentic compounds previously synthesized [1]. The ion transition, cone voltage and collision energy are summarized in Table 1. A mixture of authentic compounds in methanol at 10 μg/mL each were used for generation of standard curves.

1. Morimoto, N.; Ueno, K.; Teraishi, M.; Okumoto, Y.; Mori, N.; Ishihara, A. Induced phenylamide accumulation in response to pathogen infection and hormone treatment in rice (*Oryza sativa*). *Biosci. Biotechnol. Biochem.* **2018**, *82*, 407–416, doi:10.1080/09168451.2018.1429889.

**Table.** MRM conditions for the detection of phenylamides in cultured cells and spent media by liquid chromatography coupled with tandem mass spectrometry.

| Compound* | Precursor ion (*m*/*z*) | Product ion (*m*/*z*) | Cone voltage (V) | Collision energy (eV) |
|---|---|---|---|---|
| CinAgm | 261.19 | 130.92 | 25.00 | 32.00 |
| CouAgm | 277.11 | 146.89 | 25.00 | 26.00 |
| CafAgm | 293.09 | 162.83 | 30.00 | 30.00 |
| FerAgm | 307.05 | 176.89 | 34.00 | 24.00 |
| BenAgm | 265.21 | 175.93 | 25.00 | 20.00 |
| CinTyr | 268.12 | 131.00 | 20.00 | 14.00 |
| CouTyr | 284.10 | 146.87 | 25.00 | 22.00 |

| | | | | |
|---|---|---|---|---|
| CafTyr | 300.09 | 162.82 | 20.00 | 22.00 |
| FerTyr | 313.99 | 176.91 | 28.00 | 18.00 |
| BenTyr | 242.20 | 120.98 | 20.00 | 26.00 |
| CinTry | 291.16 | 130.92 | 20.00 | 18.00 |
| CouTry | 307.08 | 146.93 | 20.00 | 22.00 |
| CafTry | 323.13 | 162.96 | 20.00 | 26.00 |
| FerTry | 337.04 | 176.90 | 30.00 | 14.00 |
| BenTry | 265.18 | 143.96 | 20.00 | 18.00 |
| CinSer | 307.14 | 130.91 | 20.00 | 22.00 |
| CouSer | 323.04 | 146.88 | 22.00 | 16.00 |
| CafSer | 338.97 | 176.95 | 22.00 | 12.00 |
| FerSer | 353.03 | 176.89 | 24.00 | 14.00 |
| BenSer | 281.16 | 160.04 | 20.00 | 16.00 |
| FerPut | 265.24 | 176.96 | 20.00 | 18.00 |
| CafPut | 251.19 | 162.97 | 20.00 | 22.00 |
| CouPut | 235.21 | 146.95 | 20.00 | 22.00 |
| CinPut | 219.23 | 102.93 | 20.00 | 34.00 |
| BenPut | 193.20 | 104.90 | 20.00 | 26.00 |

Abbreviations: CinAgm: *N*-cinnamoylagmatine; CouAgm: *N*-*p*-coumaroylagmatine; CafAgm: *N*-caffeoylagmatine; FerAgm: *N*-feruloylagmatine; BenAgm: *N*-benzoylagmatine; CinTyr: *N*-cinnamoyltyramine; CouTyr: *N*-*p*-coumaroyltyramine; CafTyr: *N*-caffeoyltyramine; FerTyr: *N*-feruloyltyramine; BenTyr: *N*-beyzoyltyramine; CinTry: *N*-cinnamoyltryptamine; CouTry: *N*-*p*-coumaroyltryptamine; CafTry: *N*-caffeoyltryptamine; FerTry: *N*-feruloyltryptamine; BenTry: *N*-benzoyltryptamine; CinSer: *N*-cinnamoylserotonin; CouSer: *N*-*p*-coumaroylserotonin; CafSer: *N*-caffeoylserotonin; FerSer: *N*-feruloylserotonin; BenSer: *N*-benzoylserotonin; FerPut: *N*-feruloylputresscine; CafPut: *N*-caffeoylputresscine; CouPut: *N*-*p*-coumaroylputresscine; CinPut: *N*-cinnamoylputresscine; BenPut: *N*-benzoylputresscine