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*Supplementary information*

# Characterization of Metabolic Changes under Low Mineral Supply (N, K, or Mg) and Supplemental LED Lighting (Red, Blue, or Red–Blue Combination) in *Perilla frutescens* Using a Metabolomics Approach

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**Table S1.** Significantly different primary metabolites of perilla grown under different mineral nutrient supply conditions and supplemental LED lighting conditions analyzed by GC–TOF-MS.

| RT [a] | Metabolites | TMS [b] | Unique Mass | Mass Fragments |
|---|---|---|---|---|
| | | **Amino Acids** | | |
| 6.76 | Valine *,# | 2TMS | 144 | 73,100,144,218 |
| 7.31 | Leucine * | 2TMS | 158 | 59,73,86,102,116,158,218,232,260 |
| 7.53 | Isoleucine * | 2TMS | 158 | 73,100,158,218 |
| 7.58 | Proline * | 2TMS | 142 | 73,100,142,216 |
| 7.66 | Glycine *,# | 3TMS | 174 | 59,73,86,100,117,133,147,158,174,248,276 |
| 8.15 | Serine # | 3TMS | 204 | 59,73,100,116,133,147,174,188,204,218,278 |
| 8.4 | Threonine * | 3TMS | 117 | 57,73,86,101,117,147,203,219,291 |
| 9.54 | Aspartic acid *,# | 3TMS | 232 | 73,100,147,188,202,200,000 |
| 9.59 | 5-Oxoproline * | 2TMS | 156 | 59,73,84,100,133,147,156,230,258 |
| 9.83 | Cysteine *,# | 3TMS | 220 | 59,73,100,116,132,147,163,204,220,294 |
| 10.32 | Glutamic acid # | 3TMS | 128 | 56,73,84,100,114,128,147,204,230,246,258,348 |
| 10.42 | Phenylalanine * | 2TMS | 218 | 59,73,100,117,130,147,160,177,192,204,218,266 |
| 11.8 | Ornithine *,# | 4TMS | 174 | 59,73,86,100,130,142,174 |
| 12.03 | Lysine *,# | 4TMS | 174 | 59,73,86,100,156,174,200 |
| 12.64 | Tyrosine # | 4TMS | 218 | 59,73,100,117,133,147,179,218,280 |
| | | **Carbohydrates** | | |
| 7.34 | Glycerol | 3TMS | 103 | 59,73,89,103,117,133,147,205,218 |
| 12.47 | Glucose * | 5TMS | 205 | 59,73,89,103,117,147,189,205,229,319 |
| 12.58 | Glucose *,# | 5TMS | 205 | 59,73,89,103,129,147,160,205,319 |
| 12.71 | Adonitol * | 5TMS | 103 | 59,73,89,103,117,129,147,189,217,319 |
| 13.69 | Myo-inositol * | 6TMS | 217 | 59,73,81,103,129,147,191,217,265,305 |
| 16.95 | Lactose * | 8TMS | 204 | 59,73,103,129,147,169,191,204,217,243,271,305,331,361 |
| 17.3 | Maltose * | 8TMS | 204 | 59,73,103,129,147,169,191,204,217,243,271,305,331,361 |
| | | **Organic Acids** | | |
| 7.68 | Succinic acid *,# | 2TMS | 129 | 55,73,86,117,129,147,218,247,262 |
| 7.88 | Propanoic acid * | 3TMS | 189 | 59,73,103,117,133,147,175,189,205,292,307 |
| 7.97 | Fumaric acid * | 2TMS | 245 | 73,147,217,245 |
| 9.27 | Malic acid *,# | 3TMS | 233 | 55,73,101,117,133,147,189,217,233,265,307,335 |
| 9.96 | Pentanedioic acid * | 3TMS | 129 | 73,129,147,231,247,300 |
| | | **Purines & Pyrimidines** | | |
| 7.96 | Uracil | 2TMS | 241 | 73,99,113,126,147,169,185,241,255 |
| 12.19 | Adenine * | 2TMS | 264 | 73,84,192,206,264,279 |
| 16.35 | Inosine * | 4TMS | 217 | 59,73,103,129,147,169,193,217,245,281 |
| | | **Fatty Acids** | | |
| 13.21 | Palmitic acid | 1TMS | 117 | 73,117,129,185,313 |
| 14.26 | Linoleic acid | 1TMS | 117 | 67,103,117,129,147,200,000 |
| 14.4 | Stearic acid * | 1TMS | 117 | 55,73,117,129,145,185,201,341 |
| | | **Etc.** | | |
| 12.95 | Pantothenic acid *,# | 3TMS | 103 | 73,103,117,129,147,200,000,000 |

a Retention time.

b Trimethylsilyl.

* Significantly altered metabolites under different mineral deficient conditions (VIP >1.0 and p value < 0.05).

# Significantly altered metabolites under different supplemental LED lighting conditions (VIP >1.0 and $p$ value < 0.05).

**Table S2.** Significantly different secondary metabolites of perilla grown under different mineral nutrient supply conditions and supplemental LED lighting conditions analyzed by UHPLC–LTQ-MS/MS and UPLC–Q-TOF-MS.

| | | | UHPLC-LTQ-MS/MS | | | | UPLC-Q-TOF-MS | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **RT** [a] | **Mass** | **Tentative Metabolites** | **Adduct** | **Mass Fragments** | **λ max** | ***m/z*** | **Elemental Composition** | **mDa** | **PPM** | **DBE** | **i-FIT** |
| | | | | **Cinnamic Acids** | | | | | | | |
| 0.98 | 163 | Coumaric acid *,# | $[M-H]^-$ | 163/145/117/62 | 218 | 163.0382 | C9H7O3 | −1.3 | 8 | 6.5 | 0.1 |
| 4.99 | 179 | Caffeic acid *,# | $[M-H]^-$ | 179/135 | 323/244 | 179.0348 | C9H7O4 | 0.4 | 2.2 | 6.5 | 0.8 |
| 8.58 | 359 | Rosmarinic acid *,# | $[M-H]^-$ | 359/341/223/197/179/161 | 326/292 | 359.0762 | C18H15O8 | −0.5 | −1.4 | 11.5 | 0.3 |
| 9.38 | 355 | Ferulic acid-4-glucoside *,# | $[M-H]^-$ | 355/337/311/219/193 | 328 | | | | | | |
| 10.14 | 207 | 3,4-Dimethoxycinnamic acid *,# | $[M-H]^-$ | 207/179/161/135 | 328 | 207.0657 | C11H11O4 | −0.6 | −2.9 | 6.5 | 0 |
| 10.47 | 491 | Salvianolic acid C *,# | $[M-H]^-$ | 491/447/311/267 | 205/326 | 491.0986 | C26H19O20 | 0.8 | 1.6 | 17.5 | 3.2 |
| 10.66 | 313 | Salvianolic acid F *,# | $[M-H]^-$ | 313/269/203/161 | 326 | | | | | | |
| 11.04 | 315 | Isopulegone caffeate# | $[M-H]^-$ | 315/300/271/195/119 | 215/325 | | | | | | |
| | | | | **Flavonoids** | | | | | | | |
| 6.61 | 637 | Luteolin-7-*O*-diglucuronide *,# | $[M-H]^-$ | 637/351/285/193 | 366/330/269 | 637.103 | C27H25O18 | −1.1 | −1.7 | 15.5 | 2.3 |
| 7.97 | 447 | Luteolin-7-*O*-glucoside | $[M-H]^-$ | 447/403/285/181 | 366/319/283 | 447.0917 | C21H19O11 | −1 | −2.2 | 12.5 | 0.7 |
| 7.26 | 621 | Apigenin-7-*O*-diglucuronide *,# | $[M-H]^-$ | 621/487/351/269 | 365/326/285/269 | 621.1097 | C27H25O17 | 0.5 | 0.8 | 15.5 | 3.5 |
| 8.33 | 445 | Apigenin-7-*O*-glucuronide * | $[M-H]^-$ | 445/401/365/307/269/175 | 328 | 445.0778 | C21H17O11 | 0.7 | 1.6 | 13.5 | 0.7 |
| 7.73 | 461 | Scutellarein-7-*O*-glucuronide * | $[M-H]^-$ | 461/425/415/381/357/327/285/263/175 | 366/316/287 | 461.0708 | C21H17O12 | −1.2 | −2.6 | 13.5 | 3 |
| 12.59 | 253 | Chrysin * | $[M-H]^-$ | 253/225/209 | 220/291 | 253.0499 | C15H9O4 | −0.2 | −0.8 | 11.5 | 0.4 |
| 12.7 | 255 | Liquiritigenin * | $[M-H]^-$ | 213/187/151/145 | 366/325/300/292 | 255.0651 | C15H11O4 | −0.7 | −2.7 | 10.5 | 1 |
| | | | | **Lipids and Derivatives** | | | | | | | |
| 10.37 | 327 | oxo-Dihydroxy-octadecenoic acid * | $[M-H]^-$ | 327/309/291/229/221 | 323/297 | | | | | | |
| 10.82 | 329 | Trihydroxy-octadecenoic acid * | $[M-H]^-$ | 311/293/229/211/171 | 326 | 329.2312 | C18H33O5 | −1.6 | −4.9 | 2.5 | 0.2 |
| 13.13 | 721 | Gingerglycolipid A *,# | $[M+FA-H]^-$ | 721/675/415/397 | 221/326 | | | | | | |
| 14.12 | 311 | Tanshinone II-B * | $[M-H]^-$ | 311/293/283/275/171 | 222 | | | | | | |
| 15.53 | 295 | Tanshinone IIA * | $[M-H]^-$ | 295/277/251/195/171 | 223 | | | | | | |
| 14.48 | 699 | Palmitic-oleic glucoside *,# | $[M-H]^-$ | 699/653/397 | 222 | | | | | | |
| | | | | **Etc.** | | | | | | | |
| 1.07 | 191 | Citric acid *,# | $[M-H]^-$ | 191/173/129/111/85 | 247/273 | 191.0192 | C6H7O7 | −1.4 | −7.3 | 3.5 | 0 |
| 6.82 | 239 | Syringic acid acetate | $[M-H]^-$ | 239/221/195/177 | 366/328/280 | | | | | | |
| 8.57 | 719 | Sagerinic acid * | $[M-H]^-$ | 719/556/522/359/285 | 326 | 719.1641 | C36H31O16 | 2.9 | 4 | 21.5 | 3.5 |

| | | | | | |
|---|---|---|---|---|---|
| 8.83 | 467 | N-Octanoylsucrose *,# | $[M-H]^-$ | 467/421/286 | 323/291 |
| | | | | **N.I** | |
| 7.63 | 449 | N.I 1 * | | 449/403/269 | 285/328 |
| 10.46 | 527 | N.I 2 * | | 527/491 | 326 |
| 11.45 | 667 | N.I 3 * | | 667/505/311 | 302/326 |
| 12.11 | 625 | N.I 4 *,# | | 625/463/311 | 292/326 |
| 12.51 | 325 | N.I 5 * | | 325/307/263 | 219/323 |
| 13.81 | 723 | N.I 6 *,# | | 723/677/397 | 222/328 |
| 14.57 | 559 | N.I 7 * | | 559/513/277 | 225 |
| 15.53 | 561 | N.I 8 * | | 561/515/279 | 223 |
| 15.57 | 529 | N.I 9 *,# | | 529/511/279 | 223 |

a Retention time.

* Significantly altered metabolites under different mineral deficient conditions (VIP >1.0 and $p$ value < 0.05).

# Significantly altered metabolites under different supplemental LED lighting conditions (VIP >1.0 and $p$ value < 0.05).