

**Table S1.** Changes in potato sprouts' metabolome in response to *Rhizoctonia solani* 72 h post infection. Metabolites with the largest variation in their relative content between control and infected sprouts and essential components of plant defence are displayed. Compound identification (ID) is provided according to the PubChem database (<http://pubchem.ncbi.nlm.nih.gov/>).

| Metabolites                    | Relative content<br>change in infected<br>sprouts (%) <sup>a</sup> | Relative content<br>of infected sprouts<br>(%) <sup>a</sup> | Analytical<br>platform <sup>b</sup> | Molecular<br>form                                | Monoisotopic mass<br>(Da) | P-values   | ID   |
|--------------------------------|--|---|-------------------------------------|--|---------------------------|------------|--|
| <i>Alkaloids</i>               |  |   |                                     |  |                           |            |  |
| <i>Sesquiterpene alkaloids</i> |  |   |                                     |  |                           |            |  |
| Phytuberin                     | <i>n/a</i> <sup>c</sup>  | 0.20  | FT+                                 | C <sub>17</sub> H <sub>26</sub> O <sub>4</sub>   | 294.1831                  | <i>n/a</i> | 10379702, 315114                                 |
| Rishitin                       | <i>n/a</i> <sup>c</sup>  | 0.16  | FT+                                 | C <sub>14</sub> H <sub>22</sub> O <sub>2</sub>   | 222.1619                  | <i>n/a</i> | 108064, 534260                                   |
| Solavetivone                   | <i>n/a</i> <sup>c</sup>  | 1.52  | FT-                                 | C <sub>15</sub> H <sub>22</sub> O                | 218.1671                  | <i>n/a</i> | 10104810, 442399,<br>521550, 185777,<br>11085279 |
| <i>Steroid alkaloids</i>       |  |   |                                     |  |                           |            |  |
| $\alpha$ -Chaconine            | -36.82   | 4.78  | FT+                                 | C <sub>45</sub> H <sub>73</sub> NO <sub>14</sub> | 851.5031                  | <0.0001    | 104750, 442971                                   |
| $\alpha$ -Solanine             | -27.81   | 2.02  | FT+                                 | C <sub>45</sub> H <sub>73</sub> NO <sub>15</sub> | 867.4980                  | 0.0022     | 30185, 51020424,<br>9549171, 262500,<br>6537493  |
| $\beta$ -Chaconine             | 88.91  | 0.95  | FT+                                 | C <sub>39</sub> H <sub>63</sub> NO <sub>10</sub> | 705.4452                  | <0.0001    | 119393   |
| $\beta$ -Solanine              | <i>n/a</i> <sup>c</sup>  | 0.33  | FT+                                 | C <sub>39</sub> H <sub>63</sub> NO <sub>11</sub> | 721.4401                  | <i>n/a</i> | 45479590   |

|   |                         |       |     |  |          |            |   |
|---|-------------------------|-------|-----|--|----------|------------|---|
| $\gamma$ -Chaconine/ $\gamma$ -Solanine | 57.07                   | 7.64  | FT+ | C <sub>33</sub> H <sub>53</sub> NO <sub>6</sub>              | 559.3873 | <0.0001    | 160496/25245074   |
| Solanaviol                              | <i>n/a</i> <sup>c</sup> | 0.30  | FT+ | C <sub>27</sub> H <sub>43</sub> NO <sub>3</sub>              | 429.3243 | <i>n/a</i> | -   |
| Solanidine                              | 53.86                   | 30.59 | FT+ | C <sub>27</sub> H <sub>43</sub> NO                           | 397.3345 |            | 65727   |
| Solasodenone                            | <i>n/a</i> <sup>c</sup> | 0.65  | FT+ | C <sub>27</sub> H <sub>41</sub> NO <sub>2</sub>              | 411.3137 | <i>n/a</i> | 331777  |
| Solasodiene                             | <i>n/a</i> <sup>c</sup> | 1.17  | FT+ | C <sub>27</sub> H <sub>41</sub> NO                           | 395.3188 | <i>n/a</i> | 495009  |
| Solasodine                              | 88.81                   | 3.89  | FT+ | C <sub>27</sub> H <sub>43</sub> NO <sub>2</sub>              | 413.3294 | <0.0001    | 5250, 31342, 442985,<br>5200420, 44584207,<br>6432036, 5701987    |
| Solasonine                              | <i>n/a</i> <sup>c</sup> | 0.06  | FT+ | C <sub>45</sub> H <sub>73</sub> NO <sub>16</sub>             | 883.4929 | <i>n/a</i> | 73410, 119247,<br>255983, 537159,<br>9876101, 9942086,<br>6326050 |
| Solaspinalidine                         | <i>n/a</i> <sup>c</sup> | 0.11  | FT+ | C <sub>27</sub> H <sub>41</sub> NO <sub>3</sub>              | 427.3086 | <i>n/a</i> | -   |
| <i>Nortropane alkaloids</i>             |                         |       |     |  |          |            |   |
| Calystegine A3                          | -49.34                  | 0.05  | FT+ | C <sub>7</sub> H <sub>13</sub> NO <sub>3</sub>               | 159.0895 | <0.0001    | 442999, 183073,<br>45109777                                       |
| Calystegine B2                          | -23.45                  | 0.05  | FT+ | C <sub>7</sub> H <sub>13</sub> NO <sub>4</sub>               | 175.0845 | 0.0009     | 124434, 443000  |
| <i>Amino acids</i>                      |                         |       |     |  |          |            |   |
| <i>Protein amino acids</i>              |                         |       |     |  |          |            |   |
| 5-Oxo-L-proline                         | 40.18                   | 1.07  | GC  | C <sub>5</sub> H <sub>7</sub> NO <sub>3</sub>                | 129.0426 | 0.043      | 7405  |
| (Pyroglutamic acid)                     |                         |       |     |  |          |            |   |
| <i>L</i> -asparagine <sup>d</sup>       | -32.32                  | 3.21  | GC  | C <sub>4</sub> H <sub>8</sub> N <sub>2</sub> O <sub>3</sub>  | 132.0535 | <0.0001    | 6267  |
| <i>L</i> -glutamine <sup>d</sup>        | -57.23                  | 0.62  | GC  | C <sub>5</sub> H <sub>10</sub> N <sub>2</sub> O <sub>3</sub> | 146.0691 | 0.0005     | 5961  |
| <i>L</i> -histidine                     | -89.74                  | 0.09  | FT- | C <sub>6</sub> H <sub>9</sub> N <sub>3</sub> O <sub>2</sub>  | 155.0695 | <0.0001    | 6274  |

|  |        |      |     |   |          |         |             |
|--|--------|------|-----|---|----------|---------|-------------|
| <i>L</i> -isoleucine <sup>d</sup>        | -43.52 | 0.46 | GC  | C <sub>6</sub> H <sub>13</sub> NO <sub>2</sub>                | 131.0946 | <0.0001 | 6306        |
| <i>L</i> -leucine <sup>d</sup>           | -59.25 | 0.15 | GC  | C <sub>6</sub> H <sub>13</sub> NO <sub>2</sub>                | 131.0946 | <0.0001 | 6106        |
| <i>L</i> -proline <sup>d</sup>           | -42.87 | 6.53 | GC  | C <sub>5</sub> H <sub>9</sub> NO <sub>2</sub>                 | 115.0633 | <0.0001 | 145742      |
|  | -79.17 | 0.18 | FT+ |   |          | 0.0118  |             |
| <i>L</i> -serine <sup>d</sup>            | -34.43 | 0.68 | GC  | C <sub>3</sub> H <sub>7</sub> NO <sub>3</sub>                 | 105.0426 | <0.0001 | 5951        |
| <i>L</i> -threonine <sup>d</sup>         | -48.43 | 0.58 | GC  | C <sub>4</sub> H <sub>9</sub> NO <sub>3</sub>                 | 119.0582 | <0.0001 | 6288        |
| <i>L</i> -valine                         | -68.56 | 0.07 | FT+ | C <sub>5</sub> H <sub>11</sub> NO <sub>2</sub>                | 117.0790 | <0.0001 | 6287        |
|  | -15.80 | 1.92 | GC  |   |          | 0.0154  |             |
| <i>Nonprotein amino acids</i>            |        |      |     |   |          |         |             |
| $\beta$ -Alanine <sup>d</sup>            | 20.05  | 0.05 | GC  | C <sub>3</sub> H <sub>7</sub> NO <sub>2</sub>                 | 89.0477  | 0.0246  | 239         |
| 4-aminobutanoic acid (GABA) <sup>d</sup> | 20.87  | 3.67 | GC  | C <sub>4</sub> H <sub>9</sub> NO <sub>2</sub>                 | 103.0633 | 0.0205  | 119         |
| Piperidine-2-carboxylic acid             | 33.18  | 0.02 | GC  | C <sub>6</sub> H <sub>11</sub> NO <sub>2</sub>                | 129.0789 | 0.0058  | 849, 439227 |
| (Pipelic acid)                           |        |      |     |   |          |         |             |
| <i>CARBOHYDRATES</i>                     |        |      |     |   |          |         |             |
| <i>D</i> -Fructose <sup>d</sup>          | -28.01 | 6.41 | GC  | C <sub>6</sub> H <sub>12</sub> O <sub>6</sub>                 | 180.0634 | 0.0216  | 5984        |
| Myo-inositol <sup>d</sup>                | -22.47 | 4.40 | GC  | C <sub>6</sub> H <sub>12</sub> O <sub>6</sub>                 | 180.0634 | 0.0050  | 892         |
| <i>Carboxylic acids and</i>              |        |      |     |   |          |         |             |
| <i>phenolics</i>                         |        |      |     |   |          |         |             |
| 2-Hydroxybutanedioic acid                | -71.13 | 0.10 | FT- | C <sub>4</sub> H <sub>6</sub> O <sub>5</sub>                  | 134.0215 | 0.0039  | 222656      |
| (Malic acid)                             |        |      |     |   |          |         |             |
|  | -21.52 | 6.64 | GC  |   |          | <0.0001 |             |
| 2-Hydroxyundecanoic acid                 | -62.67 | 0.36 | GC  | C <sub>11</sub> H <sub>22</sub> O <sub>3</sub>                | 202.1569 |         | 5282899     |
| 2-Thiobarbituric acid                    | 20.9   | 5.96 | GC  | C <sub>4</sub> H <sub>4</sub> N <sub>2</sub> O <sub>2</sub> S | 143.9993 | 0.0490  | 2723628     |
| Citramalic acid                          | 92.75  | 0.25 | FT- | C <sub>5</sub> H <sub>8</sub> O <sub>5</sub>                  | 148.0372 | <0.0001 | 1081        |
| Chlorogenic acid                         | -95.03 | 0.01 | FT- | C <sub>16</sub> H <sub>18</sub> O <sub>9</sub>                | 354.0950 | <0.0001 | 1794427     |
| <i>D</i> -galacturonic acid              | -21.58 | 0.06 | GC  | C <sub>6</sub> H <sub>10</sub> O <sub>7</sub>                 | 194.0427 | 0.0356  | 3627        |
| <i>D</i> -gluconic acid                  | 56.35  | 2.69 | GC  | C <sub>6</sub> H <sub>12</sub> O <sub>7</sub>                 | 196.0583 | 0.0209  | 10690       |

|  |        |       |     |   |          |         |  |
|--|--------|-------|-----|---|----------|---------|--|
| <i>D</i> -glucuronic acid                                    | -41.46 | 0.02  | GC  | C <sub>6</sub> H <sub>10</sub> O <sub>7</sub>                 | 194.0427 | 0.0039  | 444791   |
| Ferulic acid   | 22.34  | 0.41  | FT- | C <sub>10</sub> H <sub>10</sub> O <sub>4</sub>                | 194.0579 | 0.0437  | 445858, 1548883  |
| <i>N</i> -feruloylputrescine                                 | -7.59  | 3.36  | FT+ | C <sub>14</sub> H <sub>20</sub> N <sub>2</sub> O <sub>3</sub> | 264.1473 | 0.0487  | 5281796  |
| <i>N</i> -feruloyltyramine                                   | 48.08  | 0.09  | FT+ | C <sub>18</sub> H <sub>19</sub> NO <sub>4</sub>               | 313.1314 | 0.0172  | 5280537  |
| Nonanedioic acid <sup>d</sup> (Azelaic acid)                 | 41.55  | 0.08  | GC  | C <sub>9</sub> H <sub>16</sub> O <sub>4</sub>                 | 188.1049 | 0.0009  | 2266   |
|  | 24.36  | 0.02  | FT- |   |          | 0.0451  |  |
| Pentanedioic acid (Glutaric acid)                            | -14.56 | 0.16  | FT- | C <sub>5</sub> H <sub>8</sub> O <sub>4</sub>                  | 132.0423 | 0.0205  | 743  |
|  | -49.39 | 1.24  | GC  |   |          | <0.0001 |  |
| Succinic acid <sup>d</sup>                                   | 65.36  | 1.54  | GC  | C <sub>4</sub> H <sub>6</sub> O <sub>4</sub>                  | 118.0266 | <0.0001 | 1110   |
| <i>Fatty acids and peroxides</i>                             |        |       |     |   |          |         |  |
| ( <i>Z</i> )-Octadec-9-enoic acid (Oleate)                   | -24.61 | 7.61  | FT- | C <sub>18</sub> H <sub>34</sub> O <sub>2</sub>                | 282.2558 | 0.0487  | 445639   |
|  | -31.40 | 0.06  | GC  |   |          | 0.0057  |  |
| Colneleic acid   | 84.79  | 4.26  | FT- | C <sub>18</sub> H <sub>30</sub> O <sub>3</sub>                | 294.2194 | 0.0012  | 6441681  |
| Colnelenic acid  | 20.68  | 1.51  | FT- | C <sub>18</sub> H <sub>28</sub> O <sub>3</sub>                | 292.2038 | 0.0457  | 6441679  |
| Hydroperoxyoctadecatrienoic acid (Hydroperoxylinolenic acid) | -51.54 | 1.16  | FT- | C <sub>18</sub> H <sub>30</sub> O <sub>4</sub>                | 310.2144 | 0.0378  | 5497123, 6440263, 5282866  |
| Hydroxyoctadecadienoic acid (Hydroxylinoleic acid)           | 26.93  | 0.09  | FT+ | C <sub>18</sub> H <sub>32</sub> O <sub>3</sub>                | 296.2351 | 0.0346  | 5282948, 6443013, 5282945, 5312833 5281117, 5312830 6433819, 6440705 |
|  | 70.96  | 6.23  | FT- |   |          |         |  |
| Octadecadienoic acid (Linolate)                              | 44.34  | 18.84 | FT- | C <sub>18</sub> H <sub>32</sub> O <sub>2</sub>                | 280.2402 | 0.0001  | 5280450  |
|  | 26.32  | 0.30  | GC  |   |          | 0.0167  |  |
| Trihydroxyoctadecanoic acid (Trihydroxystearic acid)         | -49.03 | 1.21  | FT- | C <sub>18</sub> H <sub>36</sub> O <sub>5</sub>                | 332.2563 | 0.0015  | 147011   |
| <i>Several groups</i>  |        |       |     |   |          |         |  |
| $\alpha$ -Tocotrienol  | 58.95  | 2.39  | FT- | C <sub>29</sub> H <sub>44</sub> O <sub>2</sub>                | 424.3341 | 0.0300  | 5282347, 92161, 11464420   |
| 7H-Purin-6-amine (Adenine)                                   | 69.82  | 1.01  | GC  | C <sub>5</sub> H <sub>5</sub> N <sub>5</sub>                  | 135.0545 | 0.0015  | 190  |

|                                |        |      |     |   |          |         |      |
|--------------------------------|--------|------|-----|---|----------|---------|------|
|                                | 42.88  | 0.12 | FT- |   |          | <0.0001 |      |
| 4-(1H-indol-3-yl)butanoic acid | -62.75 | 1.16 | FT+ | C <sub>12</sub> H <sub>13</sub> NO <sub>2</sub> | 203.0946 | 0.0206  | 8617 |
| (Indolebutyric acid)           |        |      |     |   |          |         |      |

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<sup>a</sup> Values refer to the relative (%) peak area or amplitude of total peak area or amplitude and represent the mean of eight biological replications

<sup>b</sup> FT+; Fourier transform-ion cyclotron resonance-mass spectrometry (FT-ICR/MS)-positive mode, FT-; FT-ICR/MS-negative mode, GC; gas chromatography MS

<sup>c</sup> not detected in controls

<sup>d</sup> Metabolites that were definitely identified based on matching their mass spectra and retention times to those of the authentic chemical standards analyzed on the same system with the same analytical method.