

Table S1 <sup>1</sup>H chemical shift assignments of the metabolites observed in the NMR spectra of apple samples using one dimensional (1D) NOESY, two-dimensional COSY, HSQC spectra and comparing standard NMR spectrum of individual metabolites taken from human metabolites database (HMDB).

| Metabolites     | Assignments                                                                                    | $\delta$ <sup>1</sup> H (ppm) | $\delta$ <sup>13</sup> C | Methods                 |
|-----------------|------------------------------------------------------------------------------------------------|-------------------------------|--------------------------|-------------------------|
| 1-Butanol       | $\delta$ CH <sub>3</sub>                                                                       | 0.89(t)                       | -                        | NOESY                   |
| Isoleucine      | $\alpha$ CH, $\gamma$ CH <sub>2</sub> ,<br>$\gamma$ CH <sub>3</sub> , $\delta$ CH <sub>3</sub> | 0.94(t)                       | -                        | NOESY,<br>COSY          |
| Valine          | $\alpha$ CH, $\beta$ CH,<br>$\gamma$ CH <sub>3</sub>                                           | 0.98(d), 1.03(d),<br>2.26(m)  | -                        | NOESY,<br>HSQC          |
| Leucine         | $\alpha$ CH, $\gamma$ CH,<br>$\delta$ CH <sub>3</sub>                                          | 0.95(d), 1.71(m),<br>3.72(dd) | -                        | NOESY,<br>COSY          |
| L-Rhamnitrol    | CH <sub>3</sub>                                                                                | 1.26(d)                       | 69.44                    | NOESY,<br>HSQC          |
| Lactate         | $\alpha$ CH, $\beta$ CH <sub>3</sub>                                                           | 1.32(d), 4.11(q)              | -                        | NOESY,<br>COSY,         |
| Alanine         | $\beta$ CH <sub>3</sub>                                                                        | 1.47(d)                       | 18.90                    | NOESY,<br>COSY,<br>HSQC |
| Acetate         | $\beta$ CH <sub>3</sub>                                                                        | 1.91(s)                       | -                        | NOESY                   |
| Quinic acid     | CH <sub>2</sub> CH                                                                             | 1.86(m), 1.95(m)              | 43.41,<br>40.16          | NOESY,<br>COSY,<br>HSQC |
| Glutamine       | $\beta$ CH <sub>2</sub> , $\gamma$ CH <sub>2</sub>                                             | 2.13(m), 2.44(m)              | -                        | NOESY,<br>COSY          |
| Glutamate       | $\beta$ CH <sub>2</sub> , $\gamma$ CH                                                          | 2.05(m), 2.34(m)              | 36.35                    | NOESY,<br>COSY          |
| 4-Aminobutyrate | $\gamma$ CH <sub>2</sub>                                                                       | 3.01(t)                       | -                        | NOESY,<br>COSY          |
| Malate          | $\beta$ CH <sub>2</sub>                                                                        | 2.69(dd),<br>2.84(dd)         | 45.23,<br>45.30          | NOESY,<br>HSQC          |
| Succinate       | CH <sub>2</sub>                                                                                | 2.41(s)                       | -                        | NOESY,<br>HSQC,<br>JRES |
| Aspartate       | $\alpha$ CH <sub>2</sub>                                                                       | 2.80(dd)                      | 39.47                    | NOESY,<br>JRES          |
| Asparagine      | CH <sub>2</sub>                                                                                | 2.85 2.96                     | 37.23                    | NOESY                   |
| Choline         | CH <sub>3</sub>                                                                                | 3.19(s)                       | -                        | NOESY,<br>HSQC          |
| Methanol        | CH <sub>3</sub>                                                                                | 3.34(t)                       | -                        | NOESY                   |
| Glucose         | $\beta$ CH                                                                                     | 4.65(d)                       | 98.71                    | NOESY,<br>HSQC          |
| Xylitol         | $\gamma$ CH                                                                                    | 3.65(m)                       | -                        | NOESY                   |
| Raffinose       | $\beta$ CH                                                                                     | 4.2 (d)                       | -                        | NOESY                   |
| Fructose        | $\gamma$ CH (3)                                                                                | 4.1(d)                        | 77.42.78.20              | NOESY,<br>HSQC          |

|                      |                           |                  |       |                |
|----------------------|---------------------------|------------------|-------|----------------|
| Sucrose              | $\gamma$ CH (3)           | 4.2(d)           | 79.21 | NOESY,<br>HSQC |
| Galactarate          | $\alpha$ CH               | 4.26(s)          | -     |                |
| Tartrate             | CH                        | 4.33 (s)         | -     |                |
| Arabinose            | $\alpha$ CH               | 4.5(d)           | 99.59 | NOESY,<br>HSQC |
| Xylose               | $\alpha$ CH               | 4.57(d)          | 99.42 | NOESY,<br>HSQC |
| Galactose            | $\alpha$ CH               | 4.58(d)          | -     | NOESY          |
| Rhamnose             | $\alpha$ CH               | 5.11 (s)         | -     | NOESY          |
| Uridine              | CH                        | 7.86(d)          |       | NOESY          |
| Unknown              | -                         | 6.03(s)          | -     | NOESY          |
| Fumarate             | CH                        | 6.51(s)          | -     | NOESY          |
| Phenylalanine        | C2,6H,Ring;C3,<br>5H,Ring | 7.33(d), 7.43(m) | -     | NOESY          |
| Condensed polyphenol | H, Ring                   | 7.72(b)          | -     | NOESY          |
| Formate              | HCOO-                     | 8.48(s)          | -     | NOESY          |
| Trigonelline         | C2,1H,Ring                | 9.10(s), 8.80(d) | -     | NOESY          |

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s = singlet; d = doublet; dd = double doublet; t = triplet; q = quartet; m = multiplet; br = broad peak