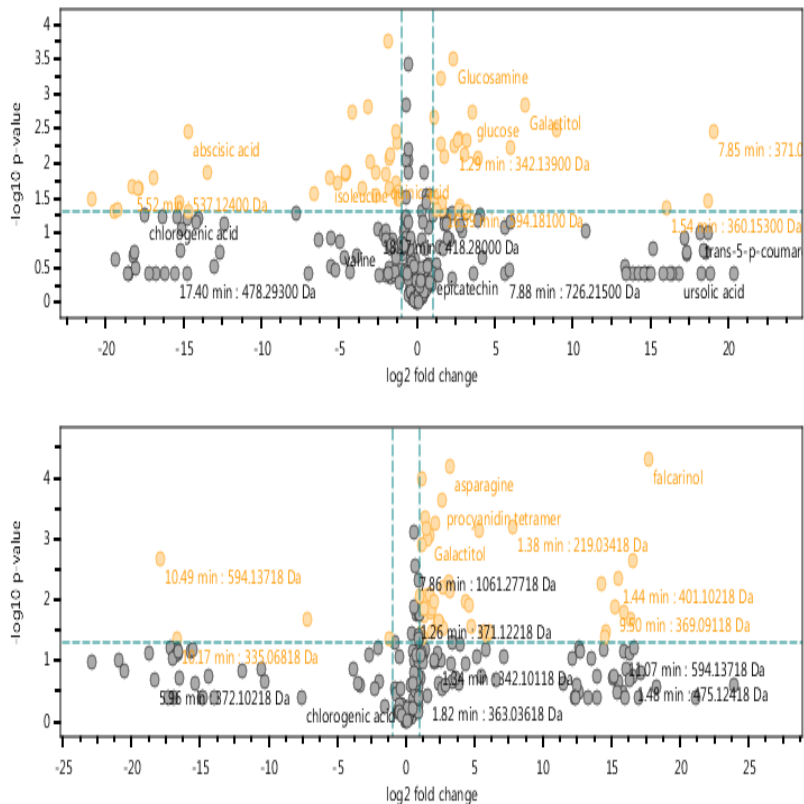


(a)



(b)

| Metabolite                     | Adduct            | Formula         | Annotation                      | ID confidence† | Classification      | Comment  | p-value      | log2 fold change <br>'Abscission'/'Normal' | ion detection mode |
|--------------------------------|-------------------|-----------------|---------------------------------|----------------|---------------------|--|--------------|--|--------------------|
| 17.04 min : 487.35 m/z         | [2M-H]-           | C12H24N2O3      | (Iso)Leucyl-leucine             | 3              | Dipeptide           | Protein catabolism   | 0.000        | 17.71                                      | neg                |
| <b>15.49 min : 247.133 m/z</b> | <b>[M+H-H2O]+</b> | <b>C15H20O4</b> | <b>Absciscic acid</b>           | <b>2</b>       | <b>Terpene</b>      | <b>ABA biosynthesis, metabolism abscission, cold stress response</b> | <b>0.003</b> | <b>14.71</b>                               | <b>pos</b>         |
| 1.26 min : 183.086 m/z         | [M+H]+            | C6H14O6         | Sorbitol                        | 2              | Sugar alcohol       | Product of sugar (galactose) breakdown                               | 0.001        | 6.91                                       | pos                |
| 3.07 min : 268.104 m/z         | [M+H]+            | C10H13N5O4      | Adenosine                       | 2              | Nucleic acid        | DNA, RNA metabolism  | 0.006        | 5.99                                       | pos                |
| 2.81 min : 132.102 m/z         | [M+H]+            | C6H13NO2        | (Iso)Leucine                    | 2              | Amino acid          | Glucose homeostasis, amino acid metabolism                           | 0.016        | 5.61                                       | pos                |
| 1.45 min : 198.097 m/z         | [M+NH4]+          | C6H12O6         | Hexose                          | 2              | Sugar               | Starch degradation   | 0.002        | 3.46                                       | pos                |
| 1.26 min : 133.060 m/z         | [M+H]+            | C4H8N2O3        | Asparagine                      | 3              | Amino acid          | Interconversion of aspartate and asparagine                          | 0.007        | 2.87                                       | pos                |
| 1.30 min : 118.086 m/z         | [M+H]+            | C5H11NO2        | Valine                          |                | Amino acid          | Amino acid metabolism  | 0.007        | 2.87                                       | pos                |
| 14.76 min : 871.267 m/z        | [2M-H]-           | C21H24O10       | Phloridzin                      | 2              | Polyphenol          | Oxidative stress   | 0.006        | 2.51                                       | neg                |
| 1.27 min : 148.060 m/z         | [M+H]+            | C5H9NO4         | Glutamic acid                   | 2              | Amino acid          | NAD biosynthesis, oxidative stress                                   | 0.005        | 2.41                                       | pos                |
| 10.48 min : 1153.261 m/z       | [M-H]-            | C60H50O24       | Procyanidin tetramer            | 3              | Polyphenol          | Oxidative stress   | 0.000        | 2.39                                       | neg                |
| 1.64 min : 180.086 m/z         | [M+H]+            | C6H13NO5        | Glucosamine                     | 3              | Sugar               | -  | 0.000        | 2.04                                       | pos                |
| <b>1.44 min : 193.070 m/z</b>  | <b>[M+H]+</b>     | <b>C7H12O6</b>  | <b>Quinic acid</b>              | <b>2</b>       | <b>Organic acid</b> | <b>Lignin biosynthesis, cell wall component</b>                      | <b>0.014</b> | <b>1.60</b>                                | <b>pos</b>         |
| 8.24 min : 305.065 m/z         | [M+H]+            | C15H12O7        | Dihydroquercetin                | 2              | Flavonoid           | Oxidative stress   | 0.000        | 1.42                                       | pos                |
| <b>9.02 min : 195.065 m/z</b>  | <b>[M+H]+</b>     | <b>C10H10O4</b> | <b>Ferulic acid</b>             | <b>2</b>       | <b>Phenol</b>       | <b>Lignin component</b>  | <b>0.022</b> | <b>1.28</b>                                | <b>pos</b>         |
| 16.03 min : 230.248 m/z        | [M+NH4]+          | C14H28O         | Tetradecanal                    | 3              | Aldehyde            | -  | 0.008        | 1.24                                       | pos                |
| 10.83 min : 867.213 m/z        | [M+H]+            | C45H38O18       | Procyanidin trimer              | 2              | Polyphenol          | Oxidative stress   | 0.007        | 1.23                                       | pos                |
| 17.04 min : 487.342 m/z        | [M-H]-            | C30H48O5        | Trihydroxyurs-12-en-28-oic acid | 2              | Terpene             | Triterpene   | 0.001        | -1.01                                      | neg                |
| 11.46 min : 1729.388 m/z       | [M-H]-            | C90H74O36       | Procyanidin hexamer             | 3              | Polyphenol          | Oxidative stress   | 0.014        | -1.08                                      | neg                |
| 14.34 min : 447.093 m/z        | [M-H]-            | C21H20O11       | Quercetin 3-rhamnoside          | 2              | Flavonoid           | Oxidative stress   | 0.040        | -1.09                                      | neg                |
| 1.39 min : 133.014 m/z         | [M-H]-            | C4H6O5          | Malic acid                      | 2              | Organic acid        | -  | 0.018        | -2.24                                      | neg                |
| 14.02 min : 433.077 m/z        | [M-H]-            | C20H18O11       | Quercetin 3-xyloside            | 2              | Flavonoid           | Oxidative stress   | 0.014        | -2.28                                      | neg                |
| 10.09 min : 865.198 m/z        | [M-H]-            | C45H38O18       | Procyanidin trimer              | 2              | Polyphenol          | Oxidative stress   | 0.013        | -3.80                                      | neg                |
| 14.94 min : 417.082 m/z        | [M-H]-            | C20H18O10       | Kaempferol 3-arabinoside        | 2              | Flavonoid           | Oxidative stress   | 0.038        | -4.72                                      | neg                |
| 8.57 min : 577.134 m/z         | [M-H]-            | C30H26O12       | Procyanidin B2                  | 2              | Polyphenol          | Oxidative stress   | 0.017        | -6.14                                      | neg                |

† Metabolites are annotated with three confidence levels (1 = compared to standard; 2 = exact mass/formula + ms/ms or retention time; 3 = exact mass/formula).