

**Table S1. Levels of endogenous and deuterium (D) -labelled SGA.**

The SGA metabolites indicated in the table were analysed in upper and lower leaves of potato shoots (cv. King Edward) that had been fed 200 µg D-labelled sterols solubilised in Tween-80 or in methyl- $\beta$ -cyclodextrin (MBD) for three or five weeks, and compared to water control samples (blanks). Each data point is based on one analysis of an extract made from two or three pooled shoots from independent plants. Levels of D-labelled SGA are corrected for the natural abundance of  $^{13}\text{C}$  where needed. ND, not detected.

| Solubiliser | Sterol fed         | Shoot part   | 3 weeks                          |                                   |   |  | 5 weeks                          |                                   |   |  |
|-------------|--------------------|--------------|----------------------------------|-----------------------------------|---|--|----------------------------------|-----------------------------------|---|--|
|             |                    |              | (mg/kg FW)                       |                                   |   |  | (mg/kg FW)                       |                                   |   |  |
|             |                    |              | $\alpha$ -solanine<br>endogenous | $\alpha$ -chaconine<br>endogenous | $\alpha$ -<br>solanine<br>$D_5$ - $D_7$ | $\alpha$ -<br>chaconine<br>$D_5$ - $D_7$ | $\alpha$ -solanine<br>endogenous | $\alpha$ -chaconine<br>endogenous | $\alpha$ -<br>solanine<br>$D_5$ - $D_7$ | $\alpha$ -<br>chaconine<br>$D_5$ - $D_7$ |
| Tween-80    | Control (Blank)    | upper leaves | 1088                             | 2024                              | ND                                      | ND                                       | 901                              | 2343                              | ND                                      | ND                                       |
|             |                    | lower leaves | 425                              | 636                               | ND                                      | ND                                       | 477                              | 779                               | ND                                      | ND                                       |
|             | $D_6$ -cholesterol | upper leaves | 1109                             | 2372                              | ND                                      | 0,02                                     | 1227                             | 2952                              | 0,01                                    | 0,03                                     |
|             |                    | lower leaves | 495                              | 842                               | ND                                      | 0,02                                     | 701                              | 1277                              | 0,02                                    | 0,22                                     |
|             | $D_7$ -cholesterol | upper leaves | 1250                             | 2618                              | ND                                      | ND                                       | 1023                             | 2638                              | ND                                      | ND                                       |
|             |                    | lower leaves | 388                              | 656                               | ND                                      | ND                                       | 1143                             | 1873                              | ND                                      | 0,06                                     |
| MBD         | $D_6$ -sitosterol  | upper leaves | 838                              | 1898                              | ND                                      | ND                                       | 1440                             | 3290                              | ND                                      | ND                                       |
|             |                    | lower leaves | 489                              | 863                               | ND                                      | ND                                       | 780                              | 1382                              | ND                                      | ND                                       |
|             | Control (Blank)    | upper leaves | 1088                             | 2024                              | ND                                      | ND                                       | 901                              | 2343                              | ND                                      | ND                                       |
|             |                    | lower leaves | 425                              | 636                               | ND                                      | ND                                       | 477                              | 779                               | ND                                      | ND                                       |
|             | $D_6$ -cholesterol | upper leaves | 952                              | 1848                              | 0,69                                    | 4,68                                     | 1018                             | 2385                              | 0,28                                    | 2,85                                     |
|             |                    | lower leaves | 518                              | 825                               | 0,04                                    | 0,32                                     | 832                              | 1407                              | 0,31                                    | 2,06                                     |
|             | $D_7$ -cholesterol | upper leaves | 903                              | 1959                              | 0,34                                    | 2,26                                     | 946                              | 2437                              | 0,11                                    | 0,51                                     |
|             |                    | lower leaves | 379                              | 729                               | 0,08                                    | 0,51                                     | 1193                             | 1948                              | 0,32                                    | 1,71                                     |
|             | $D_7$ -sitosterol  | upper leaves | 1122                             | 1743                              | ND                                      | ND                                       | 1373                             | 3153                              | ND                                      | ND                                       |
|             |                    | lower leaves | 448                              | 733                               | ND                                      | ND                                       | 1279                             | 2345                              | ND                                      | ND                                       |