

# Supplementary Materials

**Table S1.** MS/MS data and proposed fragmentation pathways of reference compounds.

| Peak No. | Compounds                              | t <sub>R</sub> (min) | Precursor Ion (m/z)             | Error (ppm) | Formula                                         | Fragments (m/z) | Elem. comp.                                                     | Pathways                                                      |
|----------|----------------------------------------|----------------------|---------------------------------|-------------|-------------------------------------------------|-----------------|-----------------------------------------------------------------|---------------------------------------------------------------|
| 1        | nortrachelogenin<br>5'-C-β-D-glucoside | 20.090               | 559.1801<br>[M+Na] <sup>+</sup> | 1.79        | C <sub>26</sub> H <sub>32</sub> O <sub>12</sub> | 483.1670        | C <sub>26</sub> H <sub>27</sub> O <sub>9</sub> <sup>+</sup>     | [M+H-3H <sub>2</sub> O] <sup>+</sup>                          |
|          |                                        |                      |                                 |             |                                                 | 441.1555        | C <sub>24</sub> H <sub>25</sub> O <sub>8</sub> <sup>+</sup>     | [M+H-2H <sub>2</sub> O-(CHO-CH <sub>2</sub> OH)] <sup>+</sup> |
|          |                                        |                      |                                 |             |                                                 | 465.1556        | C <sub>26</sub> H <sub>25</sub> O <sub>8</sub> <sup>+</sup>     | [M+H-4H <sub>2</sub> O] <sup>+</sup>                          |
|          |                                        |                      |                                 |             |                                                 | 423.1459        | C <sub>24</sub> H <sub>23</sub> O <sub>7</sub> <sup>+</sup>     | [M+H-3H <sub>2</sub> O-(CHO-CH <sub>2</sub> OH)] <sup>+</sup> |
|          |                                        |                      |                                 |             |                                                 | 203.0711        | C <sub>12</sub> H <sub>11</sub> O <sub>3</sub> <sup>+</sup>     | [C+H-HCOH] <sup>+</sup>                                       |
|          |                                        |                      |                                 |             |                                                 | 137.0607        | C <sub>8</sub> H <sub>9</sub> O <sub>2</sub> <sup>+</sup>       | [A'] <sup>+</sup>                                             |
| 2        | nortracheloside                        | 24.370               | 559.1769<br>[M+Na] <sup>+</sup> | -3.93       | C <sub>26</sub> H <sub>32</sub> O <sub>12</sub> | 397.1255        | C <sub>20</sub> H <sub>22</sub> O <sub>7</sub> Na <sup>+</sup>  | [M+Na-Glc] <sup>+</sup>                                       |
|          |                                        |                      |                                 |             |                                                 | 375.1438        | C <sub>20</sub> H <sub>23</sub> O <sub>7</sub> <sup>+</sup>     | [M+H-Glc] <sup>+</sup>                                        |
|          |                                        |                      |                                 |             |                                                 | 357.1332        | C <sub>20</sub> H <sub>21</sub> O <sub>6</sub> <sup>+</sup>     | [M+H-Glc-H <sub>2</sub> O] <sup>+</sup>                       |
|          |                                        |                      |                                 |             |                                                 | 329.1388        | C <sub>19</sub> H <sub>21</sub> O <sub>5</sub> <sup>+</sup>     | [M+H-Glc-H <sub>2</sub> O-CO] <sup>+</sup>                    |
|          |                                        |                      |                                 |             |                                                 | 311.1281        | C <sub>19</sub> H <sub>19</sub> O <sub>4</sub> <sup>+</sup>     | [M+H-Glc-2H <sub>2</sub> O-CO] <sup>+</sup>                   |
|          |                                        |                      |                                 |             |                                                 | 233.0816        | C <sub>13</sub> H <sub>13</sub> O <sub>4</sub> <sup>+</sup>     | [C+H] <sup>+</sup>                                            |
|          |                                        |                      |                                 |             |                                                 | 189.0924        | C <sub>12</sub> H <sub>13</sub> O <sub>2</sub> <sup>+</sup>     | [C+H-CO <sub>2</sub> ] <sup>+</sup>                           |
| 3        | nortrachelogenin<br>8'-O-β-D-glucoside | 25.227               | 559.1805<br>[M+Na] <sup>+</sup> | 2.50        | C <sub>26</sub> H <sub>32</sub> O <sub>12</sub> | 137.0610        | C <sub>8</sub> H <sub>9</sub> O <sub>2</sub> <sup>+</sup>       | [A] <sup>+</sup> /[A'] <sup>+</sup>                           |
|          |                                        |                      |                                 |             |                                                 | 375.1446        | C <sub>20</sub> H <sub>23</sub> O <sub>7</sub> <sup>+</sup>     | [M+H-Glc] <sup>+</sup>                                        |
|          |                                        |                      |                                 |             |                                                 | 357.1342        | C <sub>20</sub> H <sub>21</sub> O <sub>6</sub> <sup>+</sup>     | [M+H-Glc-H <sub>2</sub> O] <sup>+</sup>                       |
|          |                                        |                      |                                 |             |                                                 | 329.1390        | C <sub>19</sub> H <sub>21</sub> O <sub>5</sub> <sup>+</sup>     | [M+H-Glc-H <sub>2</sub> O-CO] <sup>+</sup>                    |
|          |                                        |                      |                                 |             |                                                 | 311.1281        | C <sub>19</sub> H <sub>19</sub> O <sub>4</sub> <sup>+</sup>     | [M+H-Glc-2H <sub>2</sub> O-CO] <sup>+</sup>                   |
|          |                                        |                      |                                 |             |                                                 | 233.0812        | C <sub>13</sub> H <sub>13</sub> O <sub>4</sub> <sup>+</sup>     | [C+H] <sup>+</sup>                                            |
|          |                                        |                      |                                 |             |                                                 | 189.0915        | C <sub>12</sub> H <sub>13</sub> O <sub>2</sub> <sup>+</sup>     | [C+H-CO <sub>2</sub> ] <sup>+</sup>                           |
| 4        | matairesinol<br>4'-O-β-gentiobioside   | 26.719               | 705.2364<br>[M+Na] <sup>+</sup> | -0.99       | C <sub>32</sub> H <sub>42</sub> O <sub>16</sub> | 137.0602        | C <sub>8</sub> H <sub>9</sub> O <sub>2</sub> <sup>+</sup>       | [A] <sup>+</sup> /[A'] <sup>+</sup>                           |
|          |                                        |                      |                                 |             |                                                 | 543.1831        | C <sub>26</sub> H <sub>32</sub> O <sub>11</sub> Na <sup>+</sup> | [M+Na-Glc] <sup>+</sup>                                       |
|          |                                        |                      |                                 |             |                                                 | 381.1292        | C <sub>20</sub> H <sub>22</sub> O <sub>6</sub> Na <sup>+</sup>  | [M+Na-2Glc] <sup>+</sup>                                      |
|          |                                        |                      |                                 |             |                                                 | 159.0422        | C <sub>8</sub> H <sub>8</sub> O <sub>2</sub> Na <sup>+</sup>    | [A+Na] <sup>+</sup> /[A'+Na] <sup>+</sup>                     |
|          |                                        |                      |                                 |             |                                                 | 137.0603        | C <sub>8</sub> H <sub>9</sub> O <sub>2</sub> <sup>+</sup>       | [A] <sup>+</sup> /[A'] <sup>+</sup>                           |

Table S1. *Cont.*

| Peak No. | Compounds                             | t <sub>R</sub> (min) | Precursor Ion (m/z)                           | Error (ppm) | Formula                                         | Fragments (m/z) | Elem. comp.                                                  | Pathways                                     |
|----------|---------------------------------------|----------------------|-----------------------------------------------|-------------|-------------------------------------------------|-----------------|--------------------------------------------------------------|----------------------------------------------|
| 5        | trachelogenin<br>4'-O-β-gentiobioside | 29.039               | 730.2925<br>[M+NH <sub>4</sub> ] <sup>+</sup> | 0.41        | C <sub>33</sub> H <sub>44</sub> O <sub>17</sub> | 551.2136        | C <sub>27</sub> H <sub>35</sub> O <sub>12</sub> <sup>+</sup> | [M+H-Glc] <sup>+</sup>                       |
|          |                                       |                      |                                               |             |                                                 | 389.1615        | C <sub>21</sub> H <sub>25</sub> O <sub>7</sub> <sup>+</sup>  | [M+H-2Glc] <sup>+</sup>                      |
|          |                                       |                      |                                               |             |                                                 | 371.1508        | C <sub>21</sub> H <sub>23</sub> O <sub>6</sub> <sup>+</sup>  | [M+H-2Glc-H <sub>2</sub> O] <sup>+</sup>     |
|          |                                       |                      |                                               |             |                                                 | 343.1562        | C <sub>20</sub> H <sub>23</sub> O <sub>5</sub> <sup>+</sup>  | [M+H-2Glc-H <sub>2</sub> O-CO] <sup>+</sup>  |
|          |                                       |                      |                                               |             |                                                 | 325.1445        | C <sub>20</sub> H <sub>21</sub> O <sub>4</sub> <sup>+</sup>  | [M+H-2Glc-2H <sub>2</sub> O-CO] <sup>+</sup> |
|          |                                       |                      |                                               |             |                                                 | 247.0982        | C <sub>14</sub> H <sub>15</sub> O <sub>4</sub> <sup>+</sup>  | [C+H] <sup>+</sup>                           |
|          |                                       |                      |                                               |             |                                                 | 203.1082        | C <sub>13</sub> H <sub>15</sub> O <sub>2</sub> <sup>+</sup>  | [C+H-CO <sub>2</sub> ] <sup>+</sup>          |
|          |                                       |                      |                                               |             |                                                 | 151.0775        | C <sub>9</sub> H <sub>11</sub> O <sub>2</sub> <sup>+</sup>   | [A'] <sup>+</sup>                            |
|          |                                       |                      |                                               |             |                                                 | 137.0619        | C <sub>8</sub> H <sub>9</sub> O <sub>2</sub> <sup>+</sup>    | [A] <sup>+</sup>                             |
| 6        | matairesinoside                       | 32.188               | 543.1857<br>[M+Na] <sup>+</sup>               | 2.76        | C <sub>26</sub> H <sub>32</sub> O <sub>11</sub> | 359.1500        | C <sub>20</sub> H <sub>23</sub> O <sub>6</sub> <sup>+</sup>  | [M+H-Glc] <sup>+</sup>                       |
|          |                                       |                      |                                               |             |                                                 | 341.1393        | C <sub>20</sub> H <sub>21</sub> O <sub>5</sub> <sup>+</sup>  | [M+H-Glc-H <sub>2</sub> O] <sup>+</sup>      |
|          |                                       |                      |                                               |             |                                                 | 323.1289        | C <sub>20</sub> H <sub>19</sub> O <sub>4</sub> <sup>+</sup>  | [M+H-Glc-2H <sub>2</sub> O] <sup>+</sup>     |
|          |                                       |                      |                                               |             |                                                 | 223.0973        | C <sub>12</sub> H <sub>15</sub> O <sub>4</sub> <sup>+</sup>  | [M+H-Glc-A] <sup>+</sup>                     |
|          |                                       |                      |                                               |             |                                                 | 163.0755        | C <sub>10</sub> H <sub>11</sub> O <sub>2</sub> <sup>+</sup>  | [B] <sup>+</sup>                             |
|          |                                       |                      |                                               |             |                                                 | 137.0599        | C <sub>8</sub> H <sub>9</sub> O <sub>2</sub> <sup>+</sup>    | [A] <sup>+</sup> /[A'] <sup>+</sup>          |
| 7        | tracheloside                          | 33.679               | 573.1951<br>[M+Na] <sup>+</sup>               | 0.52        | C <sub>27</sub> H <sub>34</sub> O <sub>12</sub> | 389.1603        | C <sub>21</sub> H <sub>25</sub> O <sub>7</sub> <sup>+</sup>  | [M+H-Glc] <sup>+</sup>                       |
|          |                                       |                      |                                               |             |                                                 | 371.1501        | C <sub>21</sub> H <sub>23</sub> O <sub>6</sub> <sup>+</sup>  | [M+H-Glc-H <sub>2</sub> O] <sup>+</sup>      |
|          |                                       |                      |                                               |             |                                                 | 343.1548        | C <sub>20</sub> H <sub>23</sub> O <sub>5</sub> <sup>+</sup>  | [M+H-Glc-H <sub>2</sub> O-CO] <sup>+</sup>   |
|          |                                       |                      |                                               |             |                                                 | 325.1444        | C <sub>20</sub> H <sub>21</sub> O <sub>4</sub> <sup>+</sup>  | [M+H-Glc-2H <sub>2</sub> O-CO] <sup>+</sup>  |
|          |                                       |                      |                                               |             |                                                 | 247.0973        | C <sub>14</sub> H <sub>15</sub> O <sub>4</sub> <sup>+</sup>  | [C+H] <sup>+</sup>                           |
|          |                                       |                      |                                               |             |                                                 | 203.1075        | C <sub>13</sub> H <sub>15</sub> O <sub>2</sub> <sup>+</sup>  | [C+H-CO <sub>2</sub> ] <sup>+</sup>          |
|          |                                       |                      |                                               |             |                                                 | 151.0763        | C <sub>9</sub> H <sub>11</sub> O <sub>2</sub> <sup>+</sup>   | [A'] <sup>+</sup>                            |
|          |                                       |                      |                                               |             |                                                 | 137.0605        | C <sub>8</sub> H <sub>9</sub> O <sub>2</sub> <sup>+</sup>    | [A] <sup>+</sup>                             |

Table S1. *Cont.*

| Peak No. | Compounds                          | t <sub>R</sub> (min) | Precursor Ion (m/z)                           | Error (ppm) | Formula                                         | Fragments (m/z) | Elem. comp.                                                 | Pathways                                                    |
|----------|------------------------------------|----------------------|-----------------------------------------------|-------------|-------------------------------------------------|-----------------|-------------------------------------------------------------|-------------------------------------------------------------|
| 8        | arctigenin<br>4'-O-β-gentiobioside | 34.517               | 714.2961<br>[M+NH <sub>4</sub> ] <sup>+</sup> | −1.68       | C <sub>33</sub> H <sub>44</sub> O <sub>16</sub> | 373.1645        | C <sub>21</sub> H <sub>25</sub> O <sub>6</sub> <sup>+</sup> | [M+H−2Glc] <sup>+</sup>                                     |
|          |                                    |                      |                                               |             |                                                 | 355.1540        | C <sub>21</sub> H <sub>23</sub> O <sub>5</sub> <sup>+</sup> | [M+H−2Glc−H <sub>2</sub> O] <sup>+</sup>                    |
|          |                                    |                      |                                               |             |                                                 | 237.1117        | C <sub>13</sub> H <sub>17</sub> O <sub>4</sub> <sup>+</sup> | [M+H−2Glc−A] <sup>+</sup>                                   |
|          |                                    |                      |                                               |             |                                                 | 137.0601        | C <sub>8</sub> H <sub>9</sub> O <sub>2</sub> <sup>+</sup>   | [A] <sup>+</sup>                                            |
| 9        | nortrachelogenin                   | 37.508               | 397.1262<br>[M+Na] <sup>+</sup>               | −0.25       | C <sub>20</sub> H <sub>22</sub> O <sub>7</sub>  | 357.1342        | C <sub>20</sub> H <sub>21</sub> O <sub>6</sub> <sup>+</sup> | [M+H−H <sub>2</sub> O] <sup>+</sup>                         |
|          |                                    |                      |                                               |             |                                                 | 329.1392        | C <sub>19</sub> H <sub>21</sub> O <sub>5</sub> <sup>+</sup> | [M+H−H <sub>2</sub> O−CO] <sup>+</sup>                      |
|          |                                    |                      |                                               |             |                                                 | 311.1288        | C <sub>19</sub> H <sub>19</sub> O <sub>4</sub> <sup>+</sup> | [M+H−2H <sub>2</sub> O−CO] <sup>+</sup>                     |
|          |                                    |                      |                                               |             |                                                 | 233.0822        | C <sub>13</sub> H <sub>13</sub> O <sub>4</sub> <sup>+</sup> | [C+H] <sup>+</sup>                                          |
|          |                                    |                      |                                               |             |                                                 | 189.0925        | C <sub>12</sub> H <sub>13</sub> O <sub>2</sub> <sup>+</sup> | [C+H−CO <sub>2</sub> ] <sup>+</sup>                         |
|          |                                    |                      |                                               |             |                                                 | 175.0766        | C <sub>11</sub> H <sub>11</sub> O <sub>2</sub> <sup>+</sup> | [C+H−CO−HCOH] <sup>+</sup>                                  |
| 10       | arctiin                            | 40.640               | 557.1993<br>[M+Na] <sup>+</sup>               | −1.08       | C <sub>27</sub> H <sub>34</sub> O <sub>11</sub> | 137.0614        | C <sub>8</sub> H <sub>9</sub> O <sub>2</sub> <sup>+</sup>   | [A] <sup>+</sup> /[A'] <sup>+</sup>                         |
|          |                                    |                      |                                               |             |                                                 | 373.1649        | C <sub>21</sub> H <sub>25</sub> O <sub>6</sub> <sup>+</sup> | [M+H−Glc] <sup>+</sup>                                      |
|          |                                    |                      |                                               |             |                                                 | 355.1544        | C <sub>21</sub> H <sub>23</sub> O <sub>5</sub> <sup>+</sup> | [M+H−Glc−H <sub>2</sub> O] <sup>+</sup>                     |
|          |                                    |                      |                                               |             |                                                 | 337.1439        | C <sub>21</sub> H <sub>21</sub> O <sub>4</sub> <sup>+</sup> | [M+H−Glc−2H <sub>2</sub> O] <sup>+</sup>                    |
|          |                                    |                      |                                               |             |                                                 | 295.1338        | C <sub>19</sub> H <sub>19</sub> O <sub>3</sub> <sup>+</sup> | [M+H−Glc−H <sub>2</sub> O−2HCOH] <sup>+</sup>               |
|          |                                    |                      |                                               |             |                                                 | 237.1127        | C <sub>13</sub> H <sub>17</sub> O <sub>4</sub> <sup>+</sup> | [M+H−Glc−A] <sup>+</sup>                                    |
|          |                                    |                      |                                               |             |                                                 | 177.0923        | C <sub>11</sub> H <sub>13</sub> O <sub>2</sub> <sup>+</sup> | [B] <sup>+</sup>                                            |
|          |                                    |                      |                                               |             |                                                 | 151.0759        | C <sub>9</sub> H <sub>11</sub> O <sub>2</sub> <sup>+</sup>  | [A'] <sup>+</sup>                                           |
| 11       | matairesinol                       | 46.937               | 359.1493<br>[M+H] <sup>+</sup>                | −0.56       | C <sub>20</sub> H <sub>22</sub> O <sub>6</sub>  | 137.0604        | C <sub>8</sub> H <sub>9</sub> O <sub>2</sub> <sup>+</sup>   | [A] <sup>+</sup>                                            |
|          |                                    |                      |                                               |             |                                                 | 341.1392        | C <sub>20</sub> H <sub>21</sub> O <sub>5</sub> <sup>+</sup> | [M+H−H <sub>2</sub> O] <sup>+</sup>                         |
|          |                                    |                      |                                               |             |                                                 | 323.1286        | C <sub>20</sub> H <sub>19</sub> O <sub>4</sub> <sup>+</sup> | [M+H−2H <sub>2</sub> O] <sup>+</sup>                        |
|          |                                    |                      |                                               |             |                                                 | 305.1178        | C <sub>20</sub> H <sub>17</sub> O <sub>3</sub> <sup>+</sup> | [M+H−3H <sub>2</sub> O] <sup>+</sup>                        |
|          |                                    |                      |                                               |             |                                                 | 291.1019        | C <sub>19</sub> H <sub>15</sub> O <sub>3</sub> <sup>+</sup> | [M+H−2H <sub>2</sub> O−CH <sub>3</sub> OH] <sup>+</sup>     |
|          |                                    |                      |                                               |             |                                                 | 231.0810        | C <sub>17</sub> H <sub>11</sub> O <sup>+</sup>              | [M+H−2H <sub>2</sub> O−2CH <sub>3</sub> OH−CO] <sup>+</sup> |
|          |                                    |                      |                                               |             |                                                 | 223.0968        | C <sub>12</sub> H <sub>15</sub> O <sub>4</sub> <sup>+</sup> | [M+H−A] <sup>+</sup>                                        |
|          |                                    |                      |                                               |             |                                                 | 163.0762        | C <sub>10</sub> H <sub>11</sub> O <sub>2</sub> <sup>+</sup> | [B] <sup>+</sup>                                            |
|          |                                    |                      |                                               |             |                                                 | 137.0607        | C <sub>8</sub> H <sub>9</sub> O <sub>2</sub> <sup>+</sup>   | [A] <sup>+</sup> /[A'] <sup>+</sup>                         |
|          |                                    |                      |                                               |             |                                                 | 131.0503        | C <sub>9</sub> H <sub>7</sub> O <sup>+</sup>                | [B−CH <sub>3</sub> OH] <sup>+</sup>                         |

Table S1. *Cont.*

| Peak No. | Compounds              | t <sub>R</sub> (min) | Precursor Ion (m/z)             | Error (ppm) | Formula                                        | Fragments (m/z) | Elem. comp.                                                  | Pathways                                |
|----------|------------------------|----------------------|---------------------------------|-------------|------------------------------------------------|-----------------|--------------------------------------------------------------|-----------------------------------------|
| 12       | trachelogenin          | 48.366               | 411.1422<br>[M+Na] <sup>+</sup> | 0.49        | C <sub>21</sub> H <sub>24</sub> O <sub>7</sub> | 371.1496        | C <sub>21</sub> H <sub>23</sub> O <sub>6</sub> <sup>+</sup>  | [M+H-H <sub>2</sub> O] <sup>+</sup>     |
|          |                        |                      |                                 |             |                                                | 343.1548        | C <sub>20</sub> H <sub>23</sub> O <sub>5</sub> <sup>+</sup>  | [M+H-H <sub>2</sub> O-CO] <sup>+</sup>  |
|          |                        |                      |                                 |             |                                                | 325.1443        | C <sub>20</sub> H <sub>21</sub> O <sub>4</sub> <sup>+</sup>  | [M+H-2H <sub>2</sub> O-CO] <sup>+</sup> |
|          |                        |                      |                                 |             |                                                | 247.0977        | C <sub>14</sub> H <sub>15</sub> O <sub>4</sub> <sup>+</sup>  | [C+H] <sup>+</sup>                      |
|          |                        |                      |                                 |             |                                                | 203.1082        | C <sub>13</sub> H <sub>15</sub> O <sub>2</sub> <sup>+</sup>  | [C+H-CO <sub>2</sub> ] <sup>+</sup>     |
|          |                        |                      |                                 |             |                                                | 189.0918        | C <sub>12</sub> H <sub>13</sub> O <sub>2</sub> <sup>+</sup>  | [C'+H-CO <sub>2</sub> ] <sup>+</sup>    |
|          |                        |                      |                                 |             |                                                | 151.0770        | C <sub>9</sub> H <sub>11</sub> O <sub>2</sub> <sup>+</sup>   | [A'] <sup>+</sup>                       |
|          |                        |                      |                                 |             |                                                | 137.0613        | C <sub>8</sub> H <sub>9</sub> O <sub>2</sub> <sup>+</sup>    | [A] <sup>+</sup>                        |
| 13       | 5-methoxytrachelogenin | 49.403               | 441.1527<br>[M+Na] <sup>+</sup> | 0.45        | C <sub>22</sub> H <sub>26</sub> O <sub>8</sub> | 181.0861        | C <sub>10</sub> H <sub>13</sub> O <sub>3</sub> <sup>+</sup>  | [A'] <sup>+</sup>                       |
|          |                        |                      |                                 |             |                                                | 159.0433        | C <sub>8</sub> H <sub>8</sub> O <sub>2</sub> Na <sup>+</sup> | [A+Na] <sup>+</sup>                     |
|          |                        |                      |                                 |             |                                                | 137.0613        | C <sub>8</sub> H <sub>9</sub> O <sub>2</sub> <sup>+</sup>    | [A] <sup>+</sup>                        |
| 14       | arctigenin             | 53.235               | 395.1488<br>[M+Na] <sup>+</sup> | 4.30        | C <sub>21</sub> H <sub>24</sub> O <sub>6</sub> | 137.0599        | C <sub>8</sub> H <sub>9</sub> O <sub>2</sub> <sup>+</sup>    | [A] <sup>+</sup>                        |
|          |                        |                      |                                 |             |                                                | 159.0405        | C <sub>8</sub> H <sub>8</sub> O <sub>2</sub> Na <sup>+</sup> | [A+Na] <sup>+</sup>                     |

Table S2. Constituents comparing with reference compounds detected in the sample extraced from Caulis Trachelospermi.

| Peak No. | t <sub>R</sub> (min) | Precursor Ion (m/z)             | Error (ppm) | Formula                                         | Fragments (m/z) | Elem. comp.                                                  | Pathways                                                                                           | Identity                            |
|----------|----------------------|---------------------------------|-------------|-------------------------------------------------|-----------------|--------------------------------------------------------------|----------------------------------------------------------------------------------------------------|-------------------------------------|
| 1        | 20.090               | 559.1797<br>[M+Na] <sup>+</sup> | 1.07        | C <sub>26</sub> H <sub>32</sub> O <sub>12</sub> | 501.1779        | C <sub>26</sub> H <sub>29</sub> O <sub>10</sub> <sup>+</sup> | [M+H-2H <sub>2</sub> O] <sup>+</sup>                                                               | nortrachelogenin 5'-C-β-D-glucoside |
|          |                      |                                 |             |                                                 | 483.1664        | C <sub>26</sub> H <sub>27</sub> O <sub>9</sub> <sup>+</sup>  | [M+H-3H <sub>2</sub> O] <sup>+</sup>                                                               |                                     |
|          |                      |                                 |             |                                                 | 465.1555        | C <sub>26</sub> H <sub>27</sub> O <sub>9</sub> <sup>+</sup>  | [M+H-4H <sub>2</sub> O] <sup>+</sup>                                                               |                                     |
|          |                      |                                 |             |                                                 | 441.1555        | C <sub>24</sub> H <sub>25</sub> O <sub>8</sub> <sup>+</sup>  | [M+H-2H <sub>2</sub> O-(CHO-CH <sub>2</sub> OH)] <sup>+</sup>                                      |                                     |
|          |                      |                                 |             |                                                 | 423.1448        | C <sub>24</sub> H <sub>23</sub> O <sub>7</sub> <sup>+</sup>  | [M+H-3H <sub>2</sub> O-(CHO-CH <sub>2</sub> OH)] <sup>+</sup>                                      |                                     |
|          |                      |                                 |             |                                                 | 399.1450        | C <sub>22</sub> H <sub>23</sub> O <sub>7</sub> <sup>+</sup>  | [M+H-H <sub>2</sub> O-C <sub>4</sub> H <sub>6</sub> O <sub>3</sub> -H <sub>2</sub> O] <sup>+</sup> |                                     |
|          |                      |                                 |             |                                                 | 203.0725        | C <sub>12</sub> H <sub>11</sub> O <sub>3</sub> <sup>+</sup>  | [C+H-HCOH] <sup>+</sup>                                                                            |                                     |
|          |                      |                                 |             |                                                 | 137.0614        | C <sub>8</sub> H <sub>9</sub> O <sub>2</sub> <sup>+</sup>    | [A'] <sup>+</sup>                                                                                  |                                     |

Table S2. *Cont.*

| Peak No. | t <sub>R</sub> (min) | Precursor Ion ( <i>m/z</i> )                  | Error (ppm) | Formula                                         | Fragments ( <i>m/z</i> ) | Elem. comp.                                                     | Pathways                                     | Identity                                     |
|----------|----------------------|-----------------------------------------------|-------------|-------------------------------------------------|--------------------------|-----------------------------------------------------------------|----------------------------------------------|----------------------------------------------|
| 2        | 24.416               | 559.1776<br>[M+Na] <sup>+</sup>               | −2.68       | C <sub>26</sub> H <sub>32</sub> O <sub>12</sub> | 375.1443                 | C <sub>20</sub> H <sub>23</sub> O <sub>7</sub> <sup>+</sup>     | [M+H−Glc] <sup>+</sup>                       | nortracheloside                              |
|          |                      |                                               |             |                                                 | 357.1341                 | C <sub>20</sub> H <sub>21</sub> O <sub>6</sub> <sup>+</sup>     | [M+H−Glc−H <sub>2</sub> O] <sup>+</sup>      |                                              |
|          |                      |                                               |             |                                                 | 329.1397                 | C <sub>19</sub> H <sub>21</sub> O <sub>5</sub> <sup>+</sup>     | [M+H−Glc−H <sub>2</sub> O−CO] <sup>+</sup>   |                                              |
|          |                      |                                               |             |                                                 | 311.1290                 | C <sub>19</sub> H <sub>19</sub> O <sub>4</sub> <sup>+</sup>     | [M+H−Glc−2H <sub>2</sub> O−CO] <sup>+</sup>  |                                              |
|          |                      |                                               |             |                                                 | 233.0822                 | C <sub>13</sub> H <sub>13</sub> O <sub>4</sub> <sup>+</sup>     | [C+H] <sup>+</sup>                           |                                              |
|          |                      |                                               |             |                                                 | 189.0927                 | C <sub>12</sub> H <sub>13</sub> O <sub>2</sub> <sup>+</sup>     | [C+H−CO <sub>2</sub> ] <sup>+</sup>          |                                              |
|          |                      |                                               |             |                                                 | 137.0620                 | C <sub>8</sub> H <sub>9</sub> O <sub>2</sub> <sup>+</sup>       | [A] <sup>+</sup> /[A'] <sup>+</sup>          |                                              |
|          |                      |                                               |             |                                                 | 375.1459                 | C <sub>20</sub> H <sub>23</sub> O <sub>7</sub> <sup>+</sup>     | [M+H−Glc] <sup>+</sup>                       |                                              |
|          |                      |                                               |             |                                                 | 357.1356                 | C <sub>20</sub> H <sub>21</sub> O <sub>6</sub> <sup>+</sup>     | [M+H−Glc−H <sub>2</sub> O] <sup>+</sup>      |                                              |
| 3        | 25.296               | 559.1802<br>[M+Na] <sup>+</sup>               | 1.97        | C <sub>26</sub> H <sub>32</sub> O <sub>12</sub> | 329.1408                 | C <sub>19</sub> H <sub>21</sub> O <sub>5</sub> <sup>+</sup>     | [M+H−Glc−H <sub>2</sub> O−CO] <sup>+</sup>   | nortrachelogenin 8'- <i>O</i> -β-D-glucoside |
|          |                      |                                               |             |                                                 | 311.1293                 | C <sub>19</sub> H <sub>19</sub> O <sub>4</sub> <sup>+</sup>     | [M+H−Glc−2H <sub>2</sub> O−CO] <sup>+</sup>  |                                              |
|          |                      |                                               |             |                                                 | 233.0830                 | C <sub>13</sub> H <sub>13</sub> O <sub>4</sub> <sup>+</sup>     | [C+H] <sup>+</sup>                           |                                              |
|          |                      |                                               |             |                                                 | 189.0930                 | C <sub>12</sub> H <sub>13</sub> O <sub>2</sub> <sup>+</sup>     | [C+H−CO <sub>2</sub> ] <sup>+</sup>          |                                              |
|          |                      |                                               |             |                                                 | 137.0612                 | C <sub>8</sub> H <sub>9</sub> O <sub>2</sub> <sup>+</sup>       | [A] <sup>+</sup> /[A'] <sup>+</sup>          |                                              |
|          |                      |                                               |             |                                                 | 543.1852                 | C <sub>26</sub> H <sub>32</sub> O <sub>11</sub> Na <sup>+</sup> | [M+Na−Glc] <sup>+</sup>                      |                                              |
|          |                      |                                               |             |                                                 | 381.1320                 | C <sub>20</sub> H <sub>22</sub> O <sub>6</sub> Na <sup>+</sup>  | [M+Na−2Glc] <sup>+</sup>                     |                                              |
| 4        | 26.719               | 705.2364<br>[M+Na] <sup>+</sup>               | −0.99       | C <sub>32</sub> H <sub>42</sub> O <sub>16</sub> | 159.0423                 | C <sub>8</sub> H <sub>8</sub> O <sub>2</sub> Na <sup>+</sup>    | [A+Na] <sup>+</sup> /[A'+Na] <sup>+</sup>    | matairesinol 4'- <i>O</i> -β-gentiobioside   |
|          |                      |                                               |             |                                                 | 137.0620                 | C <sub>8</sub> H <sub>9</sub> O <sub>2</sub> <sup>+</sup>       | [A] <sup>+</sup> /[A'] <sup>+</sup>          |                                              |
|          |                      |                                               |             |                                                 | 551.2149                 | C <sub>27</sub> H <sub>35</sub> O <sub>12</sub> <sup>+</sup>    | [M+H−Glc] <sup>+</sup>                       |                                              |
|          |                      |                                               |             |                                                 | 389.1616                 | C <sub>21</sub> H <sub>25</sub> O <sub>7</sub> <sup>+</sup>     | [M+H−2Glc] <sup>+</sup>                      |                                              |
|          |                      |                                               |             |                                                 | 371.1515                 | C <sub>21</sub> H <sub>23</sub> O <sub>6</sub> <sup>+</sup>     | [M+H−2Glc−H <sub>2</sub> O] <sup>+</sup>     |                                              |
|          |                      |                                               |             |                                                 | 343.1567                 | C <sub>20</sub> H <sub>23</sub> O <sub>5</sub> <sup>+</sup>     | [M+H−2Glc−H <sub>2</sub> O−CO] <sup>+</sup>  |                                              |
|          |                      |                                               |             |                                                 | 325.1446                 | C <sub>20</sub> H <sub>21</sub> O <sub>4</sub> <sup>+</sup>     | [M+H−2Glc−2H <sub>2</sub> O−CO] <sup>+</sup> |                                              |
| 5        | 29.039               | 730.2937<br>[M+NH <sub>4</sub> ] <sup>+</sup> | 2.05        | C <sub>33</sub> H <sub>44</sub> O <sub>17</sub> | 247.0984                 | C <sub>14</sub> H <sub>15</sub> O <sub>4</sub> <sup>+</sup>     | [C+H] <sup>+</sup>                           | trachelogenin 4'- <i>O</i> -β-gentiobioside  |
|          |                      |                                               |             |                                                 | 203.1091                 | C <sub>13</sub> H <sub>15</sub> O <sub>2</sub> <sup>+</sup>     | [C+H−CO <sub>2</sub> ] <sup>+</sup>          |                                              |
|          |                      |                                               |             |                                                 | 151.0773                 | C <sub>9</sub> H <sub>11</sub> O <sub>2</sub> <sup>+</sup>      | [A] <sup>+</sup>                             |                                              |
|          |                      |                                               |             |                                                 | 137.0615                 | C <sub>8</sub> H <sub>9</sub> O <sub>2</sub> <sup>+</sup>       | [A] <sup>+</sup>                             |                                              |
|          |                      |                                               |             |                                                 |                          |                                                                 |                                              |                                              |

Table S1. *Cont.*

| Peak No. | t <sub>R</sub> (min) | Precursor Ion (m/z)                           | Error (ppm) | Formula                                         | Fragments (m/z) | Elem. comp.                                                 | Pathways                                    | Identity                        |
|----------|----------------------|-----------------------------------------------|-------------|-------------------------------------------------|-----------------|-------------------------------------------------------------|---------------------------------------------|---------------------------------|
| 6        | 32.188               | 543.1849<br>[M+Na] <sup>+</sup>               | 1.29        | C <sub>26</sub> H <sub>32</sub> O <sub>11</sub> | 359.1506        | C <sub>20</sub> H <sub>23</sub> O <sub>6</sub> <sup>+</sup> | [M+H-Glc] <sup>+</sup>                      | matairesinoside                 |
|          |                      |                                               |             |                                                 | 341.1404        | C <sub>20</sub> H <sub>21</sub> O <sub>5</sub> <sup>+</sup> | [M+H-Glc-H <sub>2</sub> O] <sup>+</sup>     |                                 |
|          |                      |                                               |             |                                                 | 323.1299        | C <sub>20</sub> H <sub>19</sub> O <sub>4</sub> <sup>+</sup> | [M+H-Glc-2H <sub>2</sub> O] <sup>+</sup>    |                                 |
|          |                      |                                               |             |                                                 | 223.0980        | C <sub>12</sub> H <sub>15</sub> O <sub>4</sub> <sup>+</sup> | [M+H-Glc-A] <sup>+</sup>                    |                                 |
|          |                      |                                               |             |                                                 | 163.0770        | C <sub>10</sub> H <sub>11</sub> O <sub>2</sub> <sup>+</sup> | [B] <sup>+</sup>                            |                                 |
|          |                      |                                               |             |                                                 | 137.0615        | C <sub>8</sub> H <sub>9</sub> O <sub>2</sub> <sup>+</sup>   | [A] <sup>+</sup> /[A'] <sup>+</sup>         |                                 |
|          |                      |                                               |             |                                                 | 389.1601        | C <sub>21</sub> H <sub>25</sub> O <sub>7</sub> <sup>+</sup> | [M+H-Glc] <sup>+</sup>                      |                                 |
|          |                      |                                               |             |                                                 | 371.1499        | C <sub>21</sub> H <sub>23</sub> O <sub>6</sub> <sup>+</sup> | [M+H-Glc-H <sub>2</sub> O] <sup>+</sup>     |                                 |
|          |                      |                                               |             |                                                 | 343.1549        | C <sub>20</sub> H <sub>23</sub> O <sub>5</sub> <sup>+</sup> | [M+H-Glc-H <sub>2</sub> O-CO] <sup>+</sup>  |                                 |
| 7        | 33.679               | 573.1940<br>[M+Na] <sup>+</sup>               | -1.40       | C <sub>27</sub> H <sub>34</sub> O <sub>12</sub> | 325.1445        | C <sub>20</sub> H <sub>21</sub> O <sub>4</sub> <sup>+</sup> | [M+H-Glc-2H <sub>2</sub> O-CO] <sup>+</sup> | tracheloside                    |
|          |                      |                                               |             |                                                 | 247.0975        | C <sub>14</sub> H <sub>15</sub> O <sub>4</sub> <sup>+</sup> | [C+H] <sup>+</sup>                          |                                 |
|          |                      |                                               |             |                                                 | 203.1078        | C <sub>13</sub> H <sub>15</sub> O <sub>2</sub> <sup>+</sup> | [C+H-CO <sub>2</sub> ] <sup>+</sup>         |                                 |
|          |                      |                                               |             |                                                 | 151.0768        | C <sub>9</sub> H <sub>11</sub> O <sub>2</sub> <sup>+</sup>  | [A'] <sup>+</sup>                           |                                 |
|          |                      |                                               |             |                                                 | 137.0610        | C <sub>8</sub> H <sub>9</sub> O <sub>2</sub> <sup>+</sup>   | [A] <sup>+</sup>                            |                                 |
|          |                      |                                               |             |                                                 | 373.1658        | C <sub>21</sub> H <sub>25</sub> O <sub>6</sub> <sup>+</sup> | [M+H-2Glc] <sup>+</sup>                     |                                 |
|          |                      |                                               |             |                                                 | 355.1570        | C <sub>21</sub> H <sub>23</sub> O <sub>5</sub> <sup>+</sup> | [M+H-2Glc-H <sub>2</sub> O] <sup>+</sup>    |                                 |
| 8        | 34.517               | 714.2968<br>[M+NH <sub>4</sub> ] <sup>+</sup> | -0.70       | C <sub>33</sub> H <sub>44</sub> O <sub>16</sub> | 237.1138        | C <sub>13</sub> H <sub>17</sub> O <sub>4</sub> <sup>+</sup> | [M+H-2Glc-A] <sup>+</sup>                   | arctigenin 4'-O-β-gentiobioside |
|          |                      |                                               |             |                                                 | 137.0598        | C <sub>8</sub> H <sub>9</sub> O <sub>2</sub> <sup>+</sup>   | [A] <sup>+</sup>                            |                                 |
|          |                      |                                               |             |                                                 | 357.1343        | C <sub>20</sub> H <sub>21</sub> O <sub>6</sub> <sup>+</sup> | [M+H-H <sub>2</sub> O] <sup>+</sup>         |                                 |
|          |                      |                                               |             |                                                 | 329.1394        | C <sub>19</sub> H <sub>21</sub> O <sub>5</sub> <sup>+</sup> | [M+H-H <sub>2</sub> O-CO] <sup>+</sup>      |                                 |
|          |                      |                                               |             |                                                 | 311.1288        | C <sub>19</sub> H <sub>19</sub> O <sub>4</sub> <sup>+</sup> | [M+H-2H <sub>2</sub> O-CO] <sup>+</sup>     |                                 |
|          |                      |                                               |             |                                                 | 233.0819        | C <sub>13</sub> H <sub>13</sub> O <sub>4</sub> <sup>+</sup> | [C+H] <sup>+</sup> /[C'+H] <sup>+</sup>     |                                 |
| 9        | 37.657               | 397.1275<br>[M+Na] <sup>+</sup>               | 3.02        | C <sub>20</sub> H <sub>22</sub> O <sub>7</sub>  | 189.0923        | C <sub>12</sub> H <sub>13</sub> O <sub>2</sub> <sup>+</sup> | [C+H-CO <sub>2</sub> ] <sup>+</sup>         | nortrachelogenin                |
|          |                      |                                               |             |                                                 | 175.0764        | C <sub>11</sub> H <sub>11</sub> O <sub>2</sub> <sup>+</sup> | [C+H-CO-HCOH] <sup>+</sup>                  |                                 |
|          |                      |                                               |             |                                                 | 137.0609        | C <sub>8</sub> H <sub>9</sub> O <sub>2</sub> <sup>+</sup>   | [A] <sup>+</sup> /[A'] <sup>+</sup>         |                                 |
|          |                      |                                               |             |                                                 |                 |                                                             |                                             |                                 |

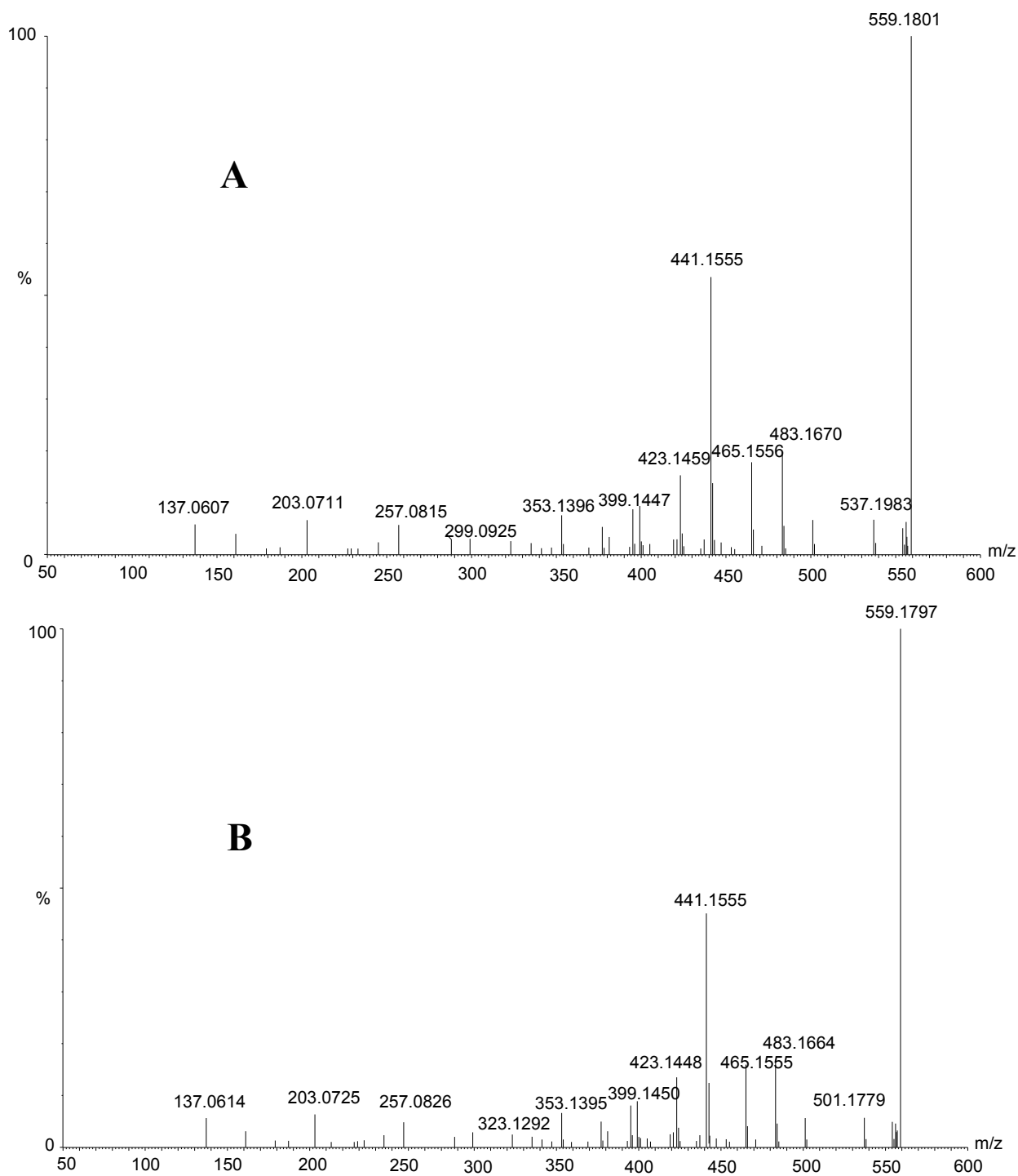
Table S2. *Cont.*

| Peak No. | t <sub>R</sub> (min) | Precursor Ion (m/z)             | Error (ppm) | Formula                                         | Fragments (m/z) | Elem. comp.                                                 | Pathways                                                    | Identity      |
|----------|----------------------|---------------------------------|-------------|-------------------------------------------------|-----------------|-------------------------------------------------------------|-------------------------------------------------------------|---------------|
| 10       | 40.708               | 557.1996<br>[M+Na] <sup>+</sup> | -0.54       | C <sub>27</sub> H <sub>34</sub> O <sub>11</sub> | 373.1651        | C <sub>21</sub> H <sub>25</sub> O <sub>6</sub> <sup>+</sup> | [M+H-Glc] <sup>+</sup>                                      | arctiin       |
|          |                      |                                 |             |                                                 | 355.1548        | C <sub>21</sub> H <sub>23</sub> O <sub>5</sub> <sup>+</sup> | [M+H-Glc-H <sub>2</sub> O] <sup>+</sup>                     |               |
|          |                      |                                 |             |                                                 | 337.1438        | C <sub>21</sub> H <sub>21</sub> O <sub>4</sub> <sup>+</sup> | [M+H-Glc-2H <sub>2</sub> O] <sup>+</sup>                    |               |
|          |                      |                                 |             |                                                 | 295.1339        | C <sub>19</sub> H <sub>19</sub> O <sub>3</sub> <sup>+</sup> | [M+H-Glc-H <sub>2</sub> O-2HCOH] <sup>+</sup>               |               |
|          |                      |                                 |             |                                                 | 237.1130        | C <sub>13</sub> H <sub>17</sub> O <sub>4</sub> <sup>+</sup> | [M+H-Glc-A] <sup>+</sup>                                    |               |
|          |                      |                                 |             |                                                 | 177.0911        | C <sub>11</sub> H <sub>13</sub> O <sub>2</sub> <sup>+</sup> | [B] <sup>+</sup>                                            |               |
|          |                      |                                 |             |                                                 | 151.0765        | C <sub>9</sub> H <sub>11</sub> O <sub>2</sub> <sup>+</sup>  | [A'] <sup>+</sup>                                           |               |
|          |                      |                                 |             |                                                 | 137.0603        | C <sub>8</sub> H <sub>9</sub> O <sub>2</sub> <sup>+</sup>   | [A] <sup>+</sup>                                            |               |
|          |                      |                                 |             |                                                 | 341.1396        | C <sub>20</sub> H <sub>21</sub> O <sub>5</sub> <sup>+</sup> | [M+H-H <sub>2</sub> O] <sup>+</sup>                         |               |
|          |                      |                                 |             |                                                 | 323.1295        | C <sub>20</sub> H <sub>19</sub> O <sub>4</sub> <sup>+</sup> | [M+H-2H <sub>2</sub> O] <sup>+</sup>                        |               |
|          |                      |                                 |             |                                                 | 305.1178        | C <sub>20</sub> H <sub>17</sub> O <sub>3</sub> <sup>+</sup> | [M+H-3H <sub>2</sub> O] <sup>+</sup>                        |               |
|          |                      |                                 |             |                                                 | 291.1021        | C <sub>19</sub> H <sub>15</sub> O <sub>3</sub> <sup>+</sup> | [M+H-2H <sub>2</sub> O-CH <sub>3</sub> OH] <sup>+</sup>     |               |
|          |                      |                                 |             |                                                 | 263.1074        | C <sub>18</sub> H <sub>15</sub> O <sub>2</sub> <sup>+</sup> | [M+H-2H <sub>2</sub> O-CO-CH <sub>3</sub> OH] <sup>+</sup>  |               |
| 11       | 47.006               | 359.1510<br>[M+H] <sup>+</sup>  | 4.18        | C <sub>20</sub> H <sub>22</sub> O <sub>6</sub>  | 231.0814        | C <sub>17</sub> H <sub>11</sub> O <sup>+</sup>              | [M+H-2H <sub>2</sub> O-2CH <sub>3</sub> OH-CO] <sup>+</sup> | matairesinol  |
|          |                      |                                 |             |                                                 | 223.0968        | C <sub>12</sub> H <sub>15</sub> O <sub>4</sub> <sup>+</sup> | [M+H-A] <sup>+</sup>                                        |               |
|          |                      |                                 |             |                                                 | 163.0758        | C <sub>10</sub> H <sub>11</sub> O <sub>2</sub> <sup>+</sup> | [B] <sup>+</sup>                                            |               |
|          |                      |                                 |             |                                                 | 137.0603        | C <sub>8</sub> H <sub>9</sub> O <sub>2</sub> <sup>+</sup>   | [A] <sup>+</sup> /[A'] <sup>+</sup>                         |               |
|          |                      |                                 |             |                                                 | 131.0495        | C <sub>9</sub> H <sub>7</sub> O <sup>+</sup>                | [B-CH <sub>3</sub> OH] <sup>+</sup>                         |               |
|          |                      |                                 |             |                                                 | 371.1496        | C <sub>21</sub> H <sub>23</sub> O <sub>6</sub> <sup>+</sup> | [M+H-H <sub>2</sub> O] <sup>+</sup>                         |               |
|          |                      |                                 |             |                                                 | 343.1549        | C <sub>20</sub> H <sub>23</sub> O <sub>5</sub> <sup>+</sup> | [M+H-H <sub>2</sub> O-CO] <sup>+</sup>                      |               |
|          |                      |                                 |             |                                                 | 325.1443        | C <sub>20</sub> H <sub>21</sub> O <sub>4</sub> <sup>+</sup> | [M+H-2H <sub>2</sub> O-CO] <sup>+</sup>                     |               |
|          |                      |                                 |             |                                                 | 247.0970        | C <sub>14</sub> H <sub>15</sub> O <sub>4</sub> <sup>+</sup> | [C+H] <sup>+</sup>                                          |               |
|          |                      |                                 |             |                                                 | 233.0820        | C <sub>13</sub> H <sub>13</sub> O <sub>4</sub> <sup>+</sup> | [C'+H] <sup>+</sup>                                         |               |
| 12       | 48.446               | 411.1426<br>[M+Na] <sup>+</sup> | 1.46        | C <sub>21</sub> H <sub>24</sub> O <sub>7</sub>  | 203.1073        | C <sub>13</sub> H <sub>15</sub> O <sub>2</sub> <sup>+</sup> | [C+H-CO <sub>2</sub> ] <sup>+</sup>                         | trachelogenin |
|          |                      |                                 |             |                                                 | 189.0912        | C <sub>12</sub> H <sub>13</sub> O <sub>2</sub> <sup>+</sup> | [C'+H-CO <sub>2</sub> ] <sup>+</sup>                        |               |
|          |                      |                                 |             |                                                 | 151.0760        | C <sub>9</sub> H <sub>11</sub> O <sub>2</sub> <sup>+</sup>  | [A'] <sup>+</sup>                                           |               |
|          |                      |                                 |             |                                                 | 137.0604        | C <sub>8</sub> H <sub>9</sub> O <sub>2</sub> <sup>+</sup>   | [A] <sup>+</sup>                                            |               |
|          |                      |                                 |             |                                                 |                 |                                                             |                                                             |               |

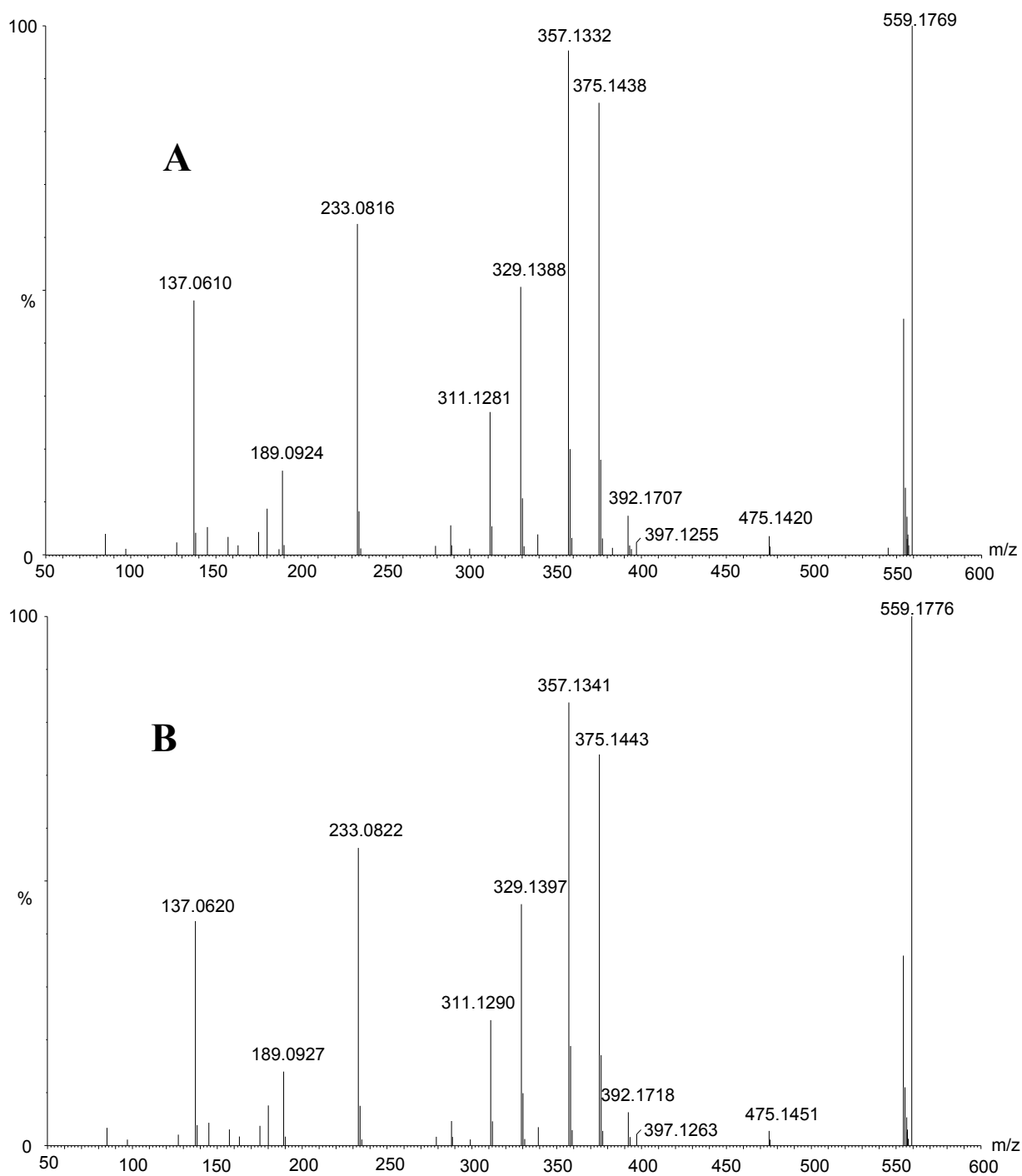
Table S2. *Cont.*

| Peak No. | t <sub>R</sub> (min) | Precursor Ion ( <i>m/z</i> )    | Error (ppm) | Formula                                        | Fragments ( <i>m/z</i> ) | Elem. comp.                                                  | Pathways            | Identity               |
|----------|----------------------|---------------------------------|-------------|------------------------------------------------|--------------------------|--------------------------------------------------------------|---------------------|------------------------|
| 13       | 48.855               | 441.1526<br>[M+Na] <sup>+</sup> | 0.23        | C <sub>22</sub> H <sub>26</sub> O <sub>8</sub> |                          |                                                              |                     | 5-methoxytrachelogenin |
| 14       | 52.955               | 395.1463<br>[M+Na] <sup>+</sup> | −1.01       | C <sub>21</sub> H <sub>24</sub> O <sub>6</sub> | 159.0408                 | C <sub>8</sub> H <sub>8</sub> O <sub>2</sub> Na <sup>+</sup> | [A+Na] <sup>+</sup> | arctigenin             |

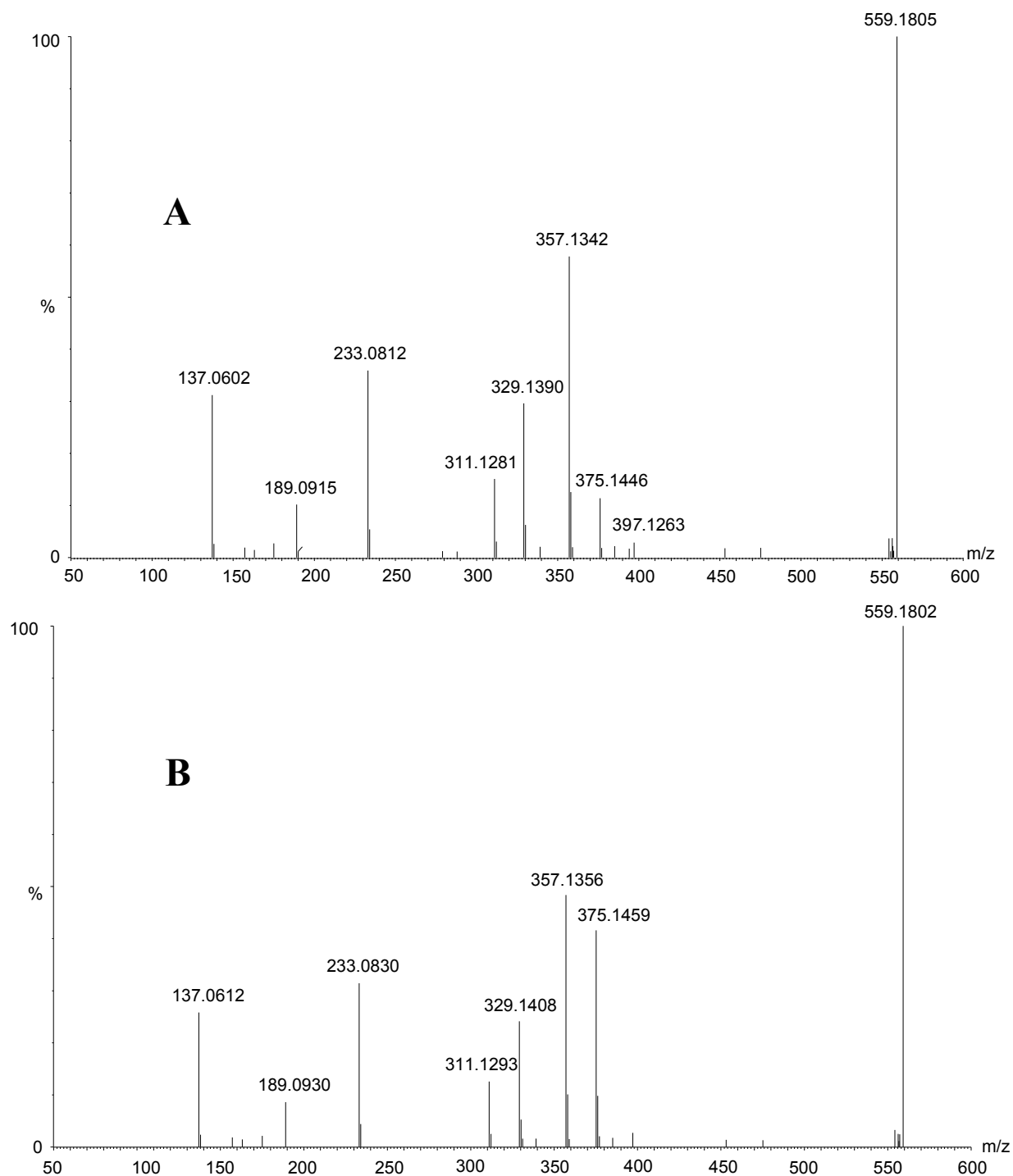




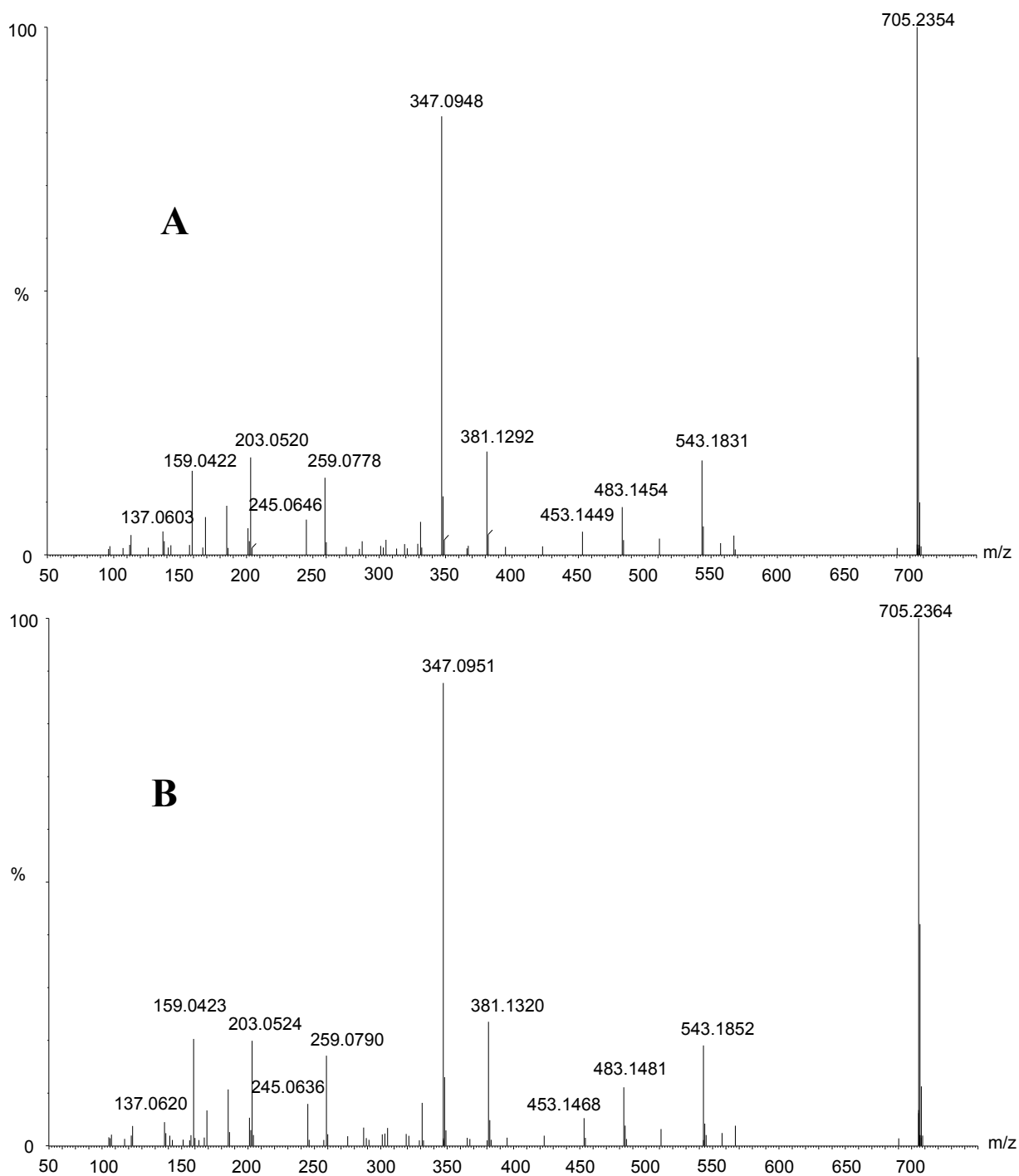
**Figure S1.** MS/MS spectrum of nortrachelogenin 5'-C- $\beta$ -D-glucoside (**1**) in the standard sample (**A**) and in the sample extracted from *Caulis Trachelospermi* (**B**), respectively.



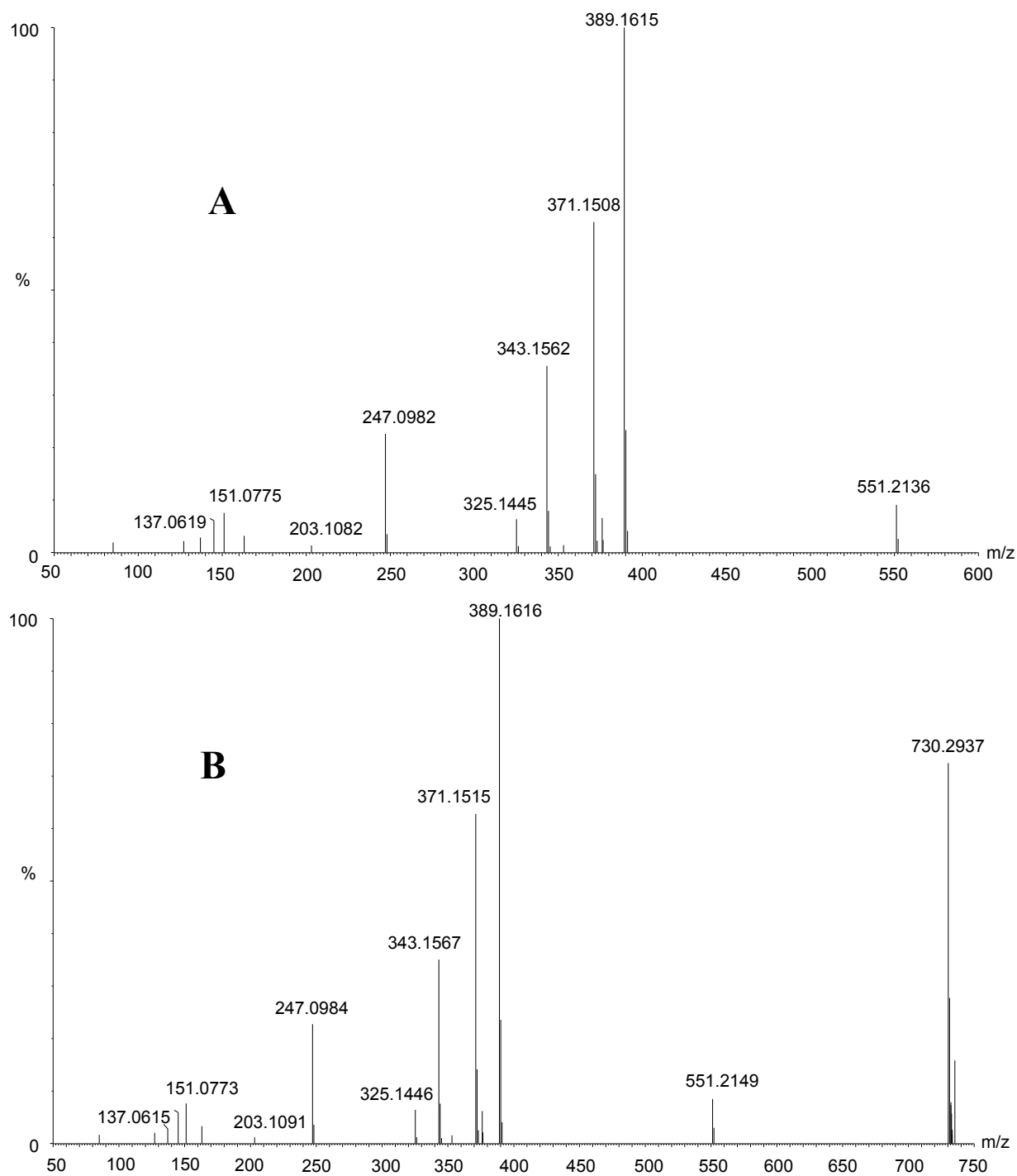
**Figure S2.** MS/MS spectrum of nortracheloside (**2**) in the standard sample (**A**) and in the sample extracted from *Caulis Trachelospermi* (**B**), respectively.



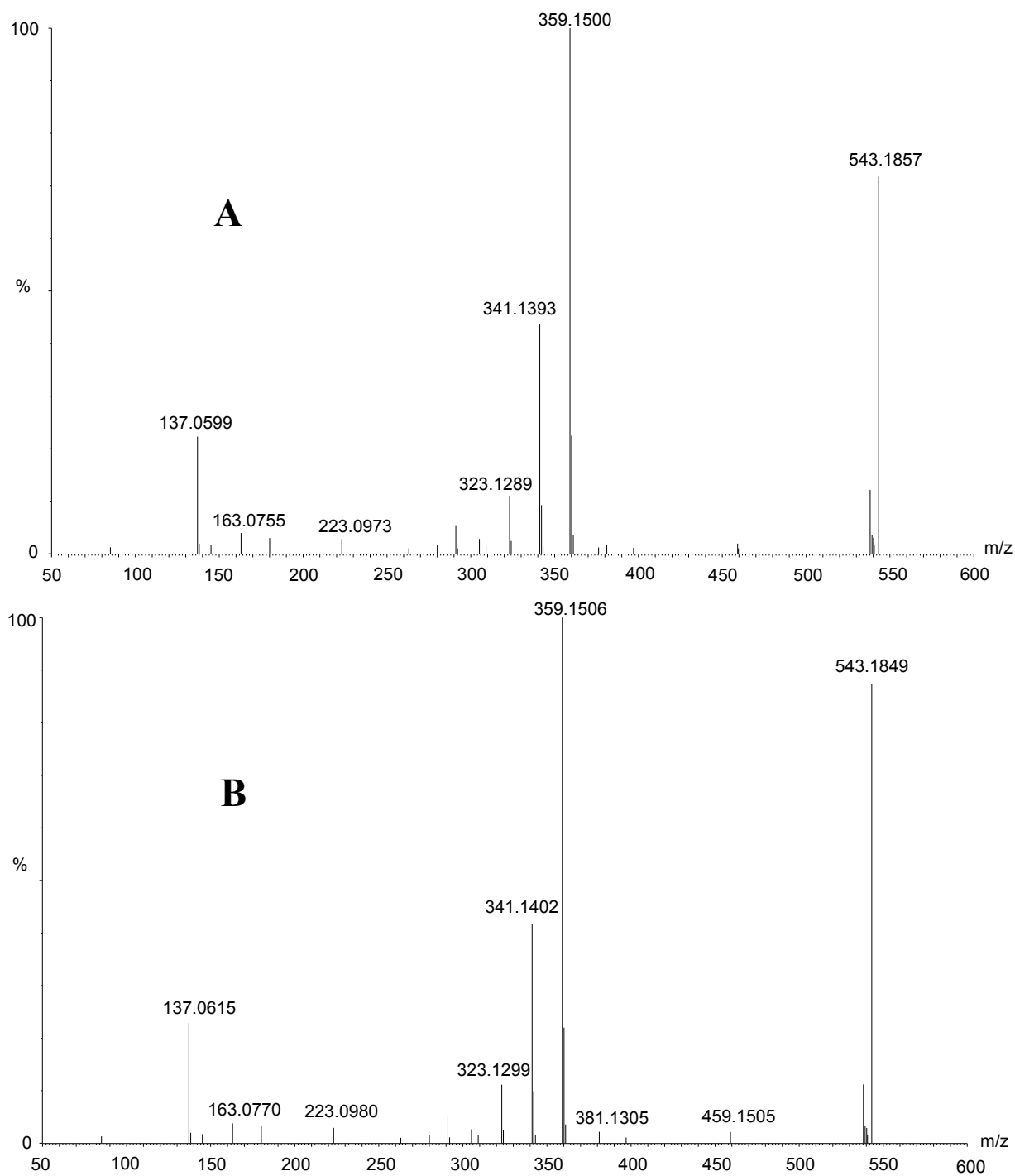
**Figure S3.** MS/MS spectrum of nortrachelogenin 8'-*O*- $\beta$ -D-glucoside (**3**) in the standard sample (**A**) and in the sample extracted from *Caulis Trachelospermi* (**B**), respectively.



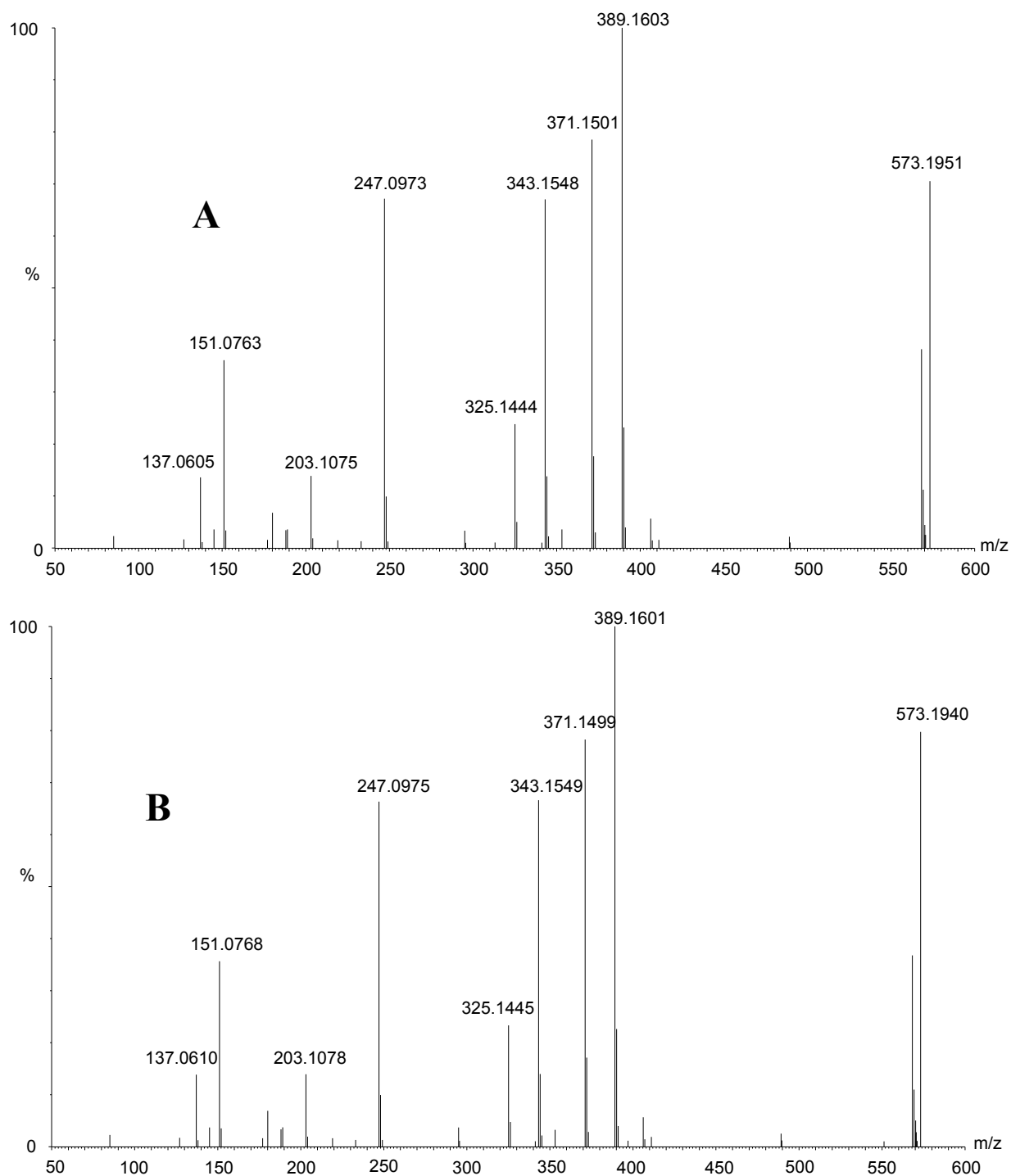
**Figure S4.** MS/MS spectrum of matairesinol 4'-*O*- $\beta$ -gentiobioside (**4**) in the standard sample (**A**) and in the sample extracted from *Caulis Trachelospermi* (**B**), respectively.



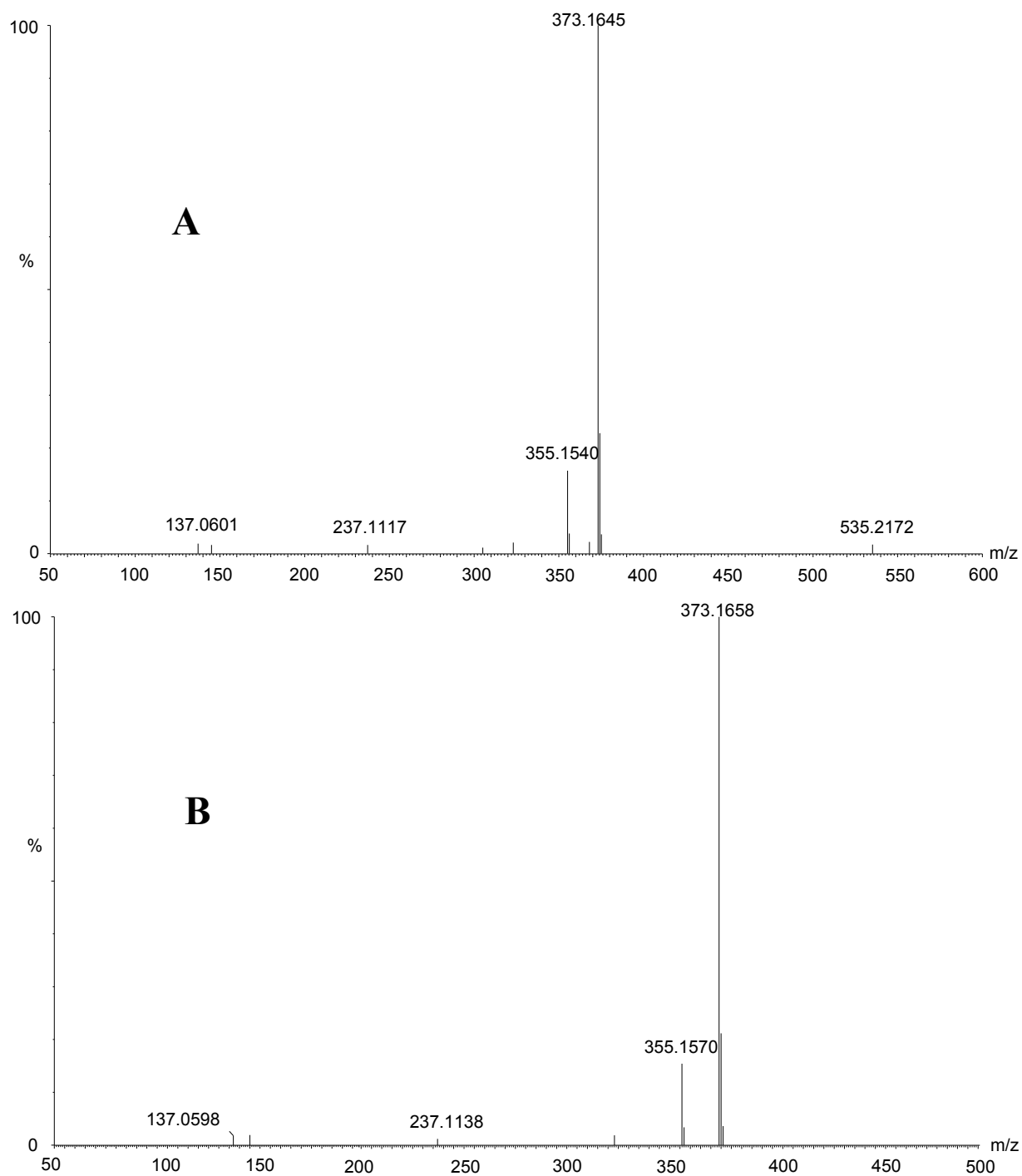
**Figure S5.** MS/MS spectrum of trachelogenin 4'-*O*- $\beta$ -gentiobioside (**5**) in the standard sample (**A**) and in the sample extracted from *Caulis Trachelospermi* (**B**), respectively.



**Figure S6.** MS/MS spectrum of matairesinoside (**6**) in the standard sample (**A**) and in the sample extracted from *Caulis Trachelospermi* (**B**), respectively.

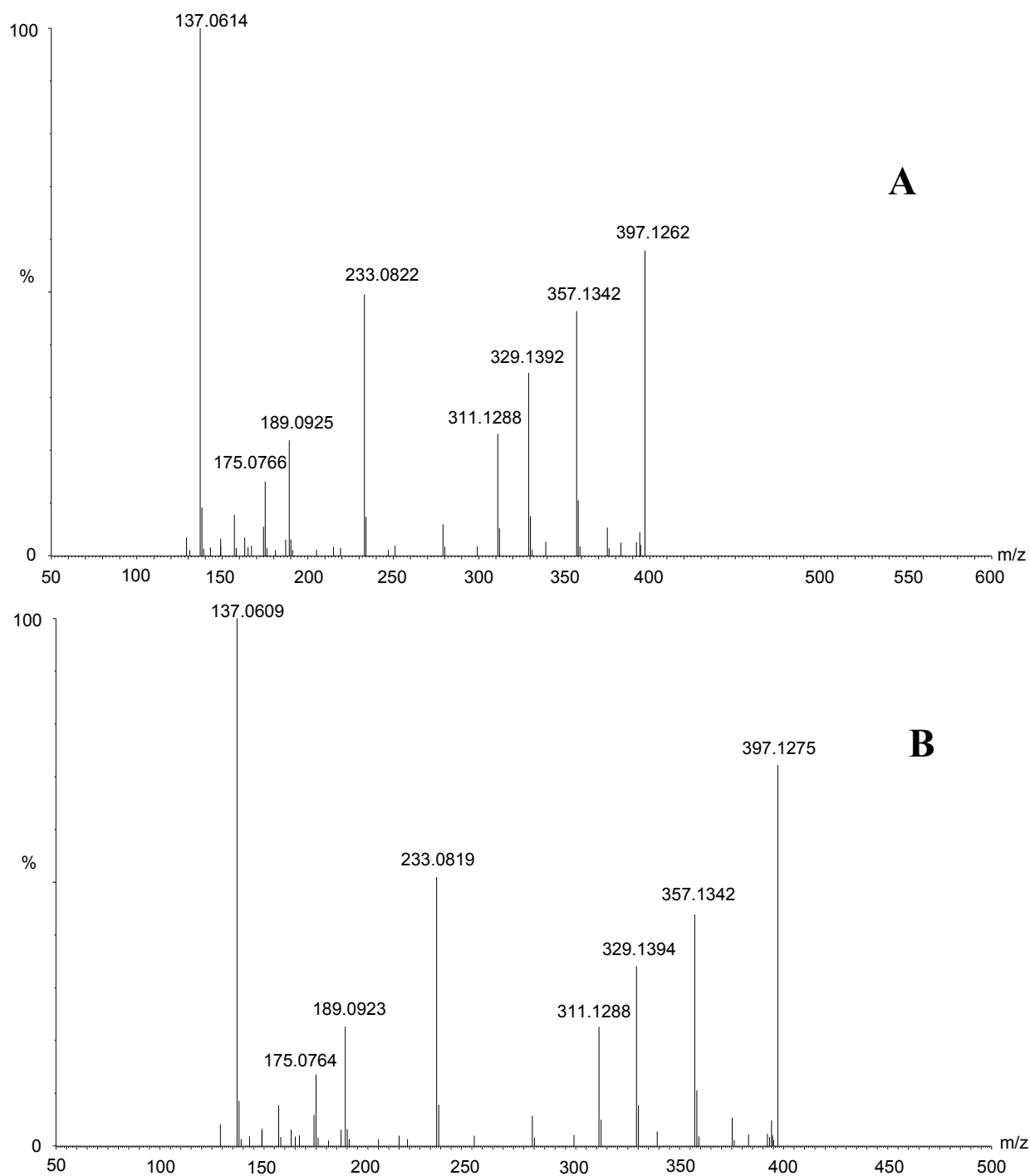


**Figure S7.** MS/MS spectrum of tracheloside (**7**) in the standard sample (**A**) and in the sample extracted from *Caulis Trachelospermi* (**B**), respectively.

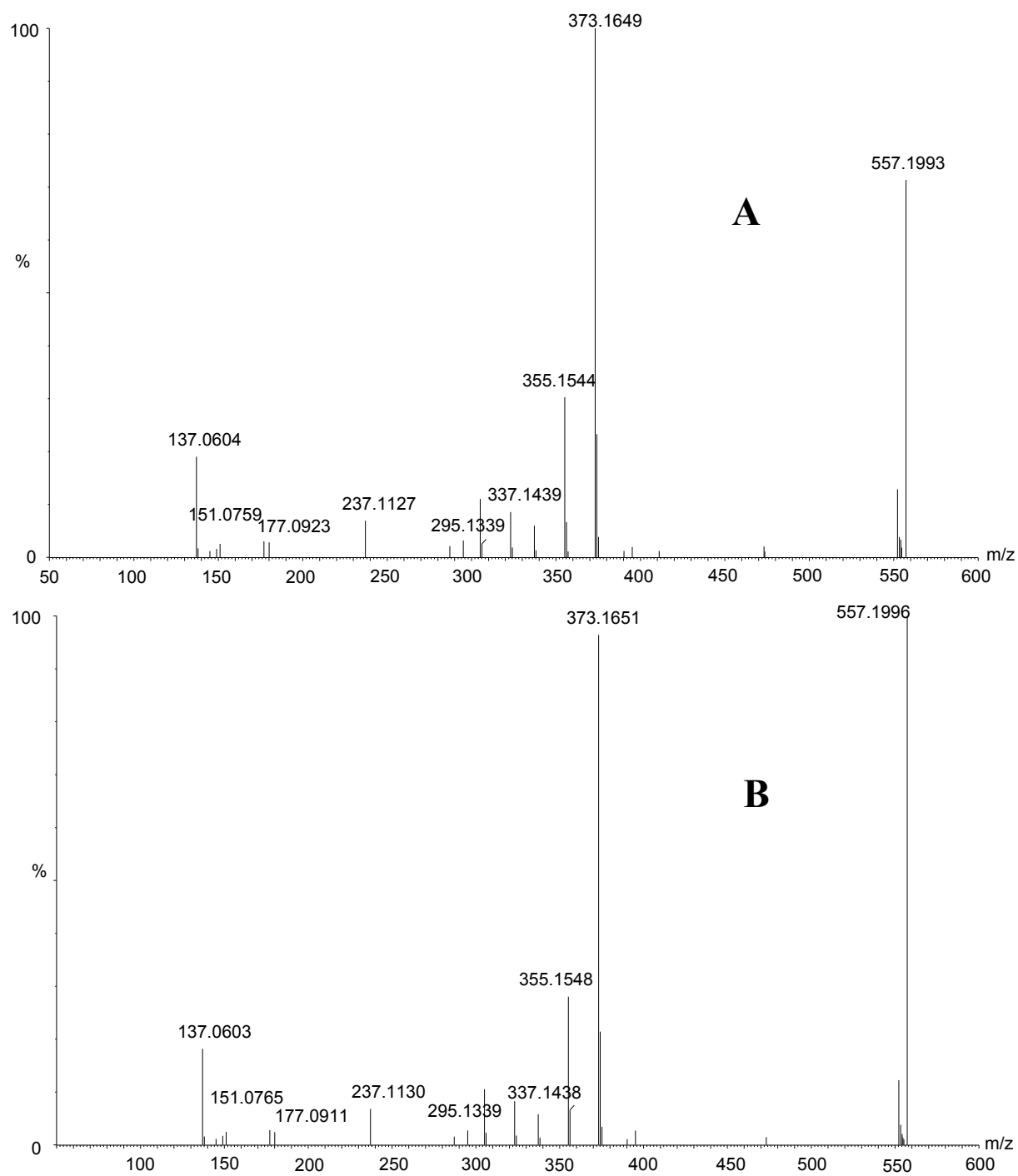


**Figure S8.** MS/MS spectrum of arctigenin 4'-*O*- $\beta$ -gentiobioside (**8**) in the standard sample (**A**) and in the sample extracted from *Caulis Trachelospermi* (**B**), respectively.

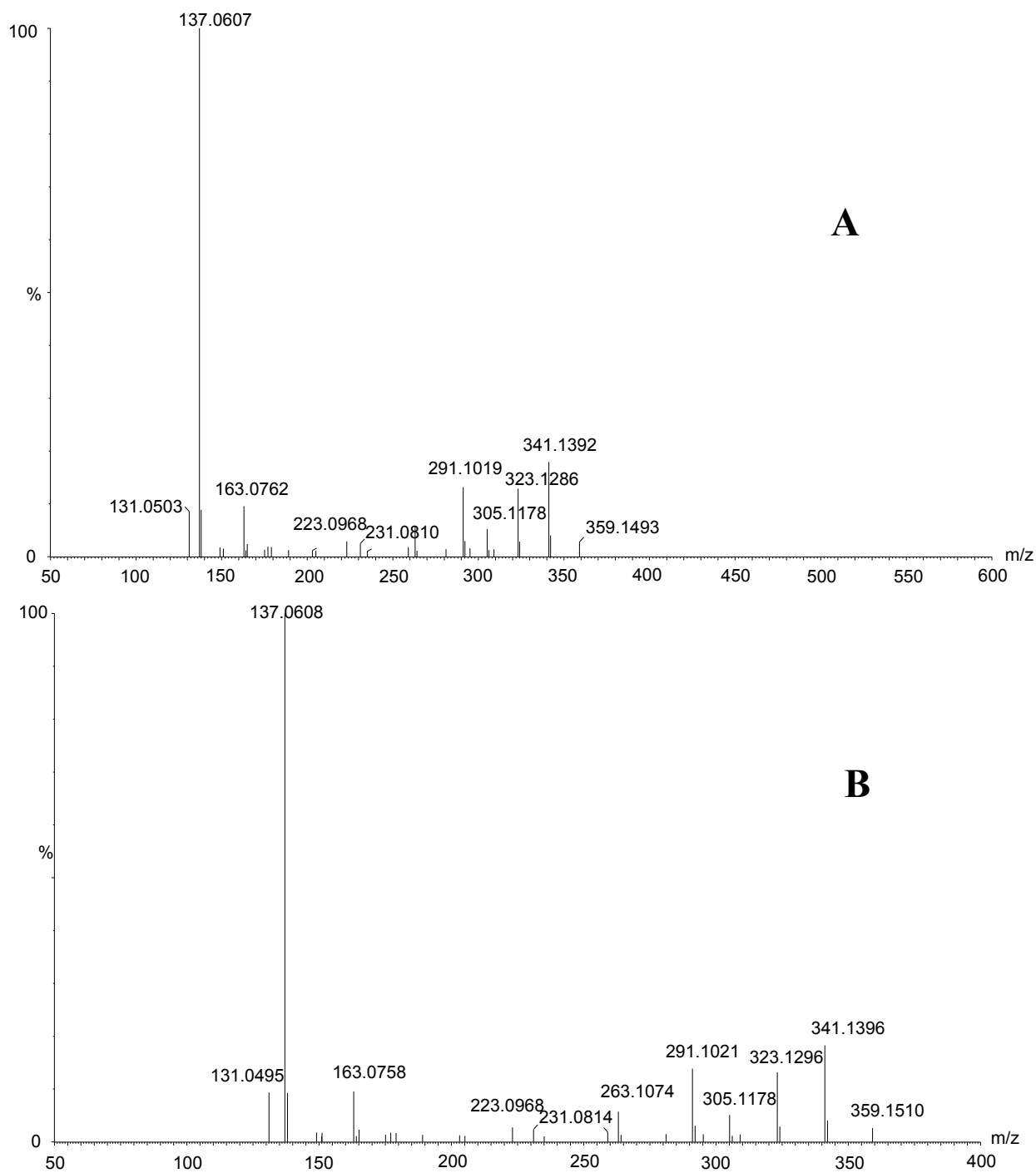




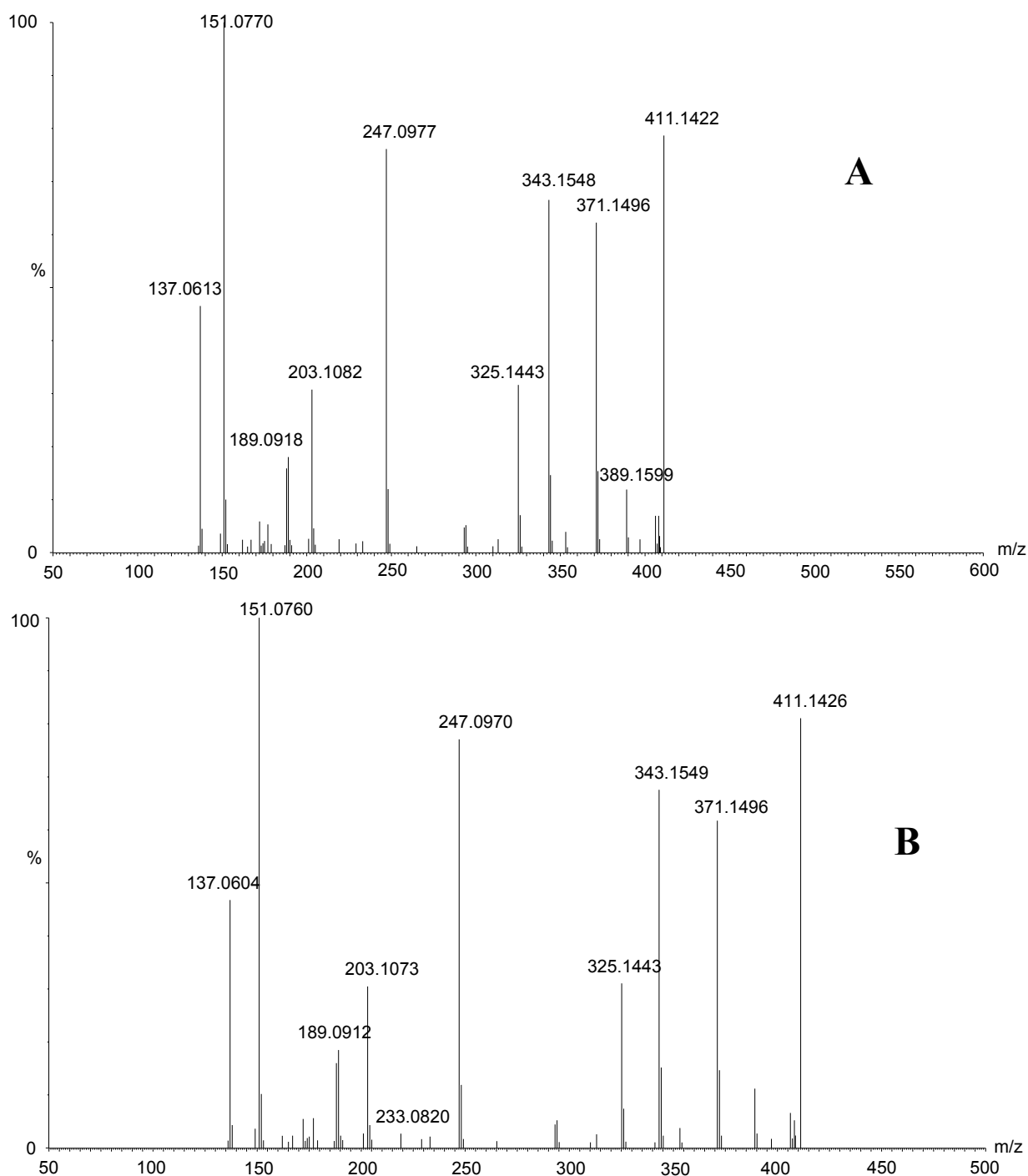
**Figure S9.** MS/MS spectrum of nortrachelogenin (**9**) in the standard sample (**A**) and in the sample extracted from *Caulis Trachelospermi* (**B**), respectively.



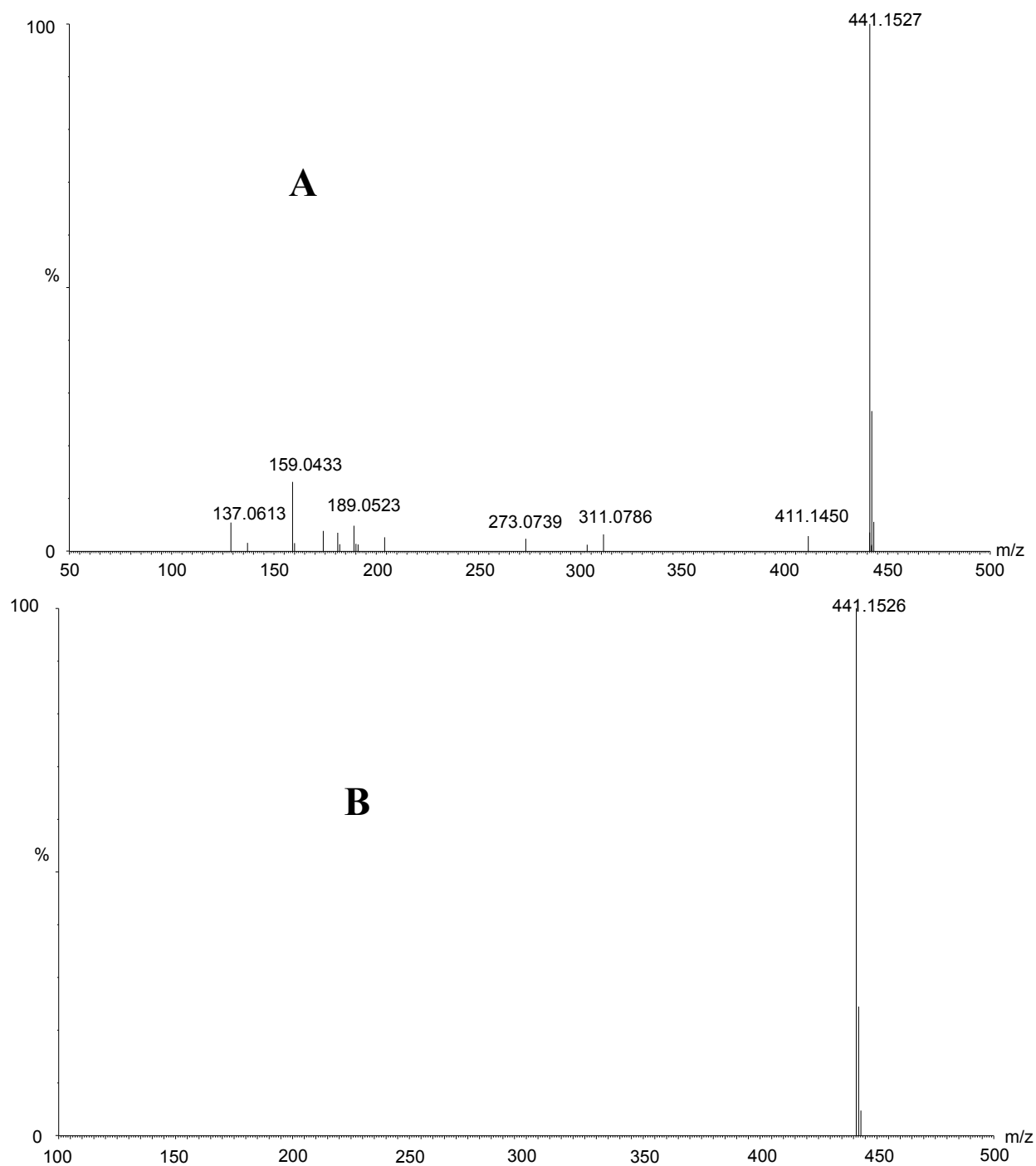
**Figure S10.** MS/MS spectrum of arctiin (**10**) in the standard sample (**A**) and in the sample extracted from *Caulis Trachelospermi* (**B**), respectively.



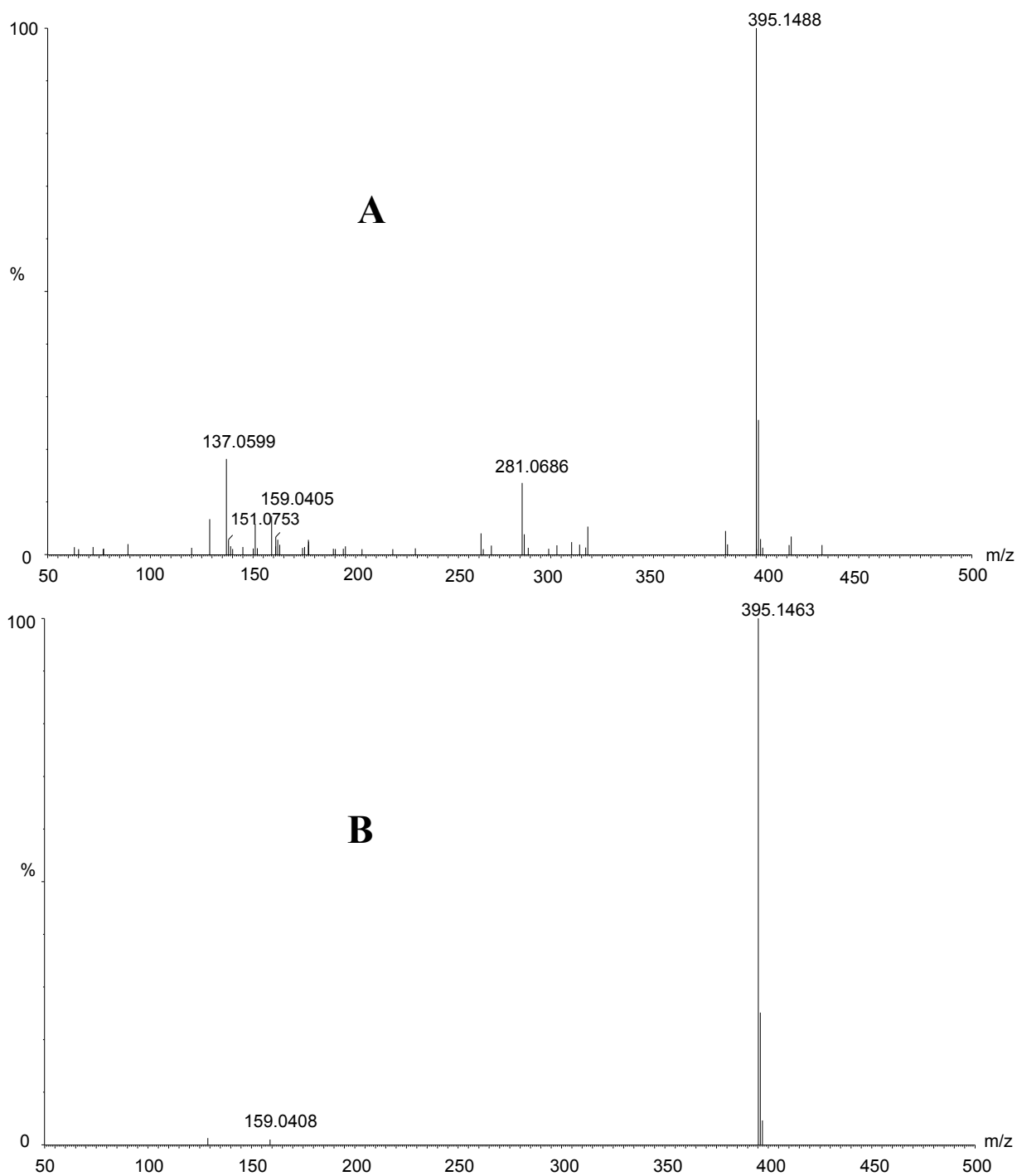
**Figure S11.** MS/MS spectrum of matairesinol (**11**) in the standard sample (**A**) and in the sample extracted from *Caulis Trachelospermi* (**B**), respectively.



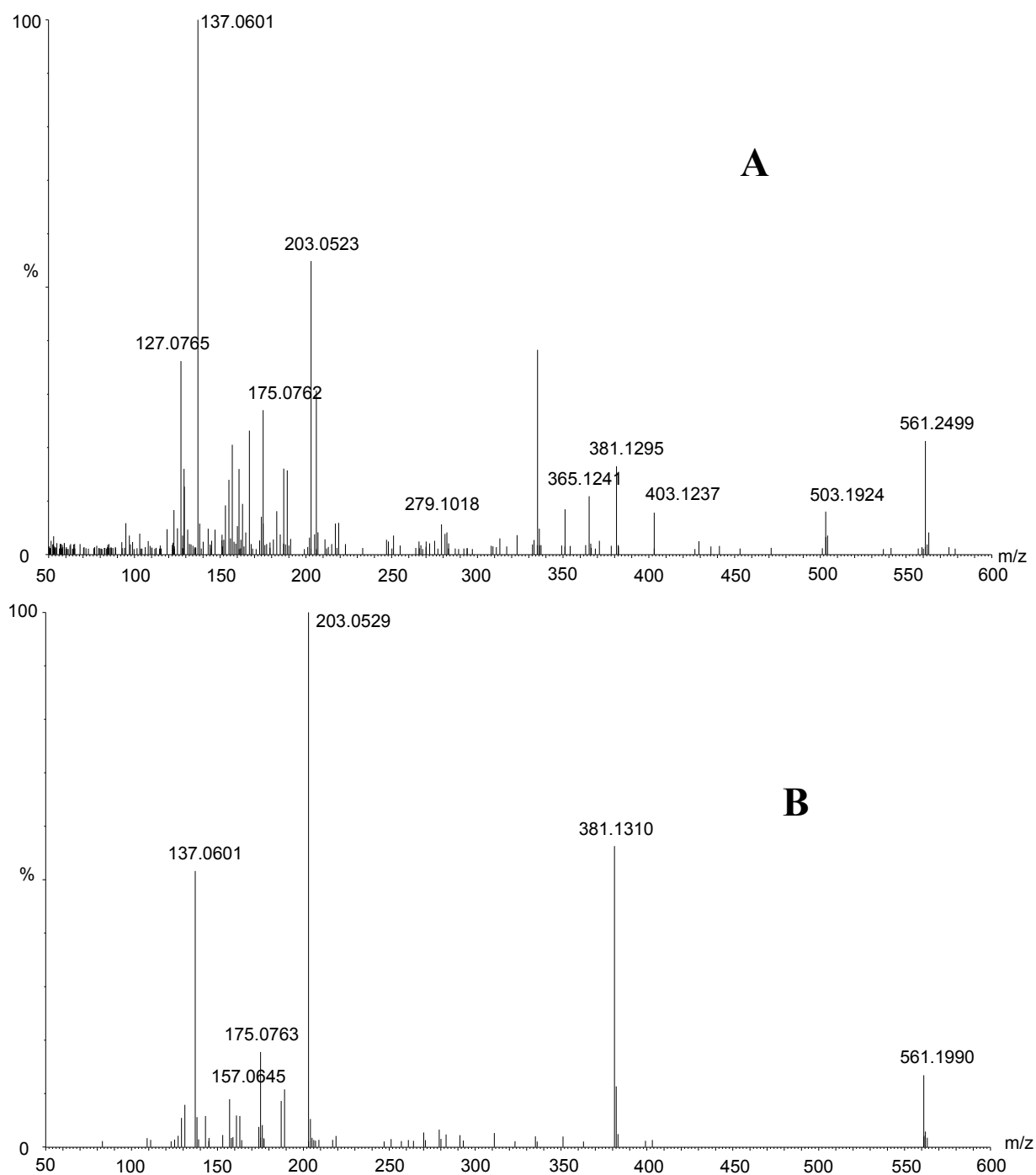
**Figure S12.** MS/MS spectrum of trachelogenin (**12**) in the standard sample (**A**) and in the sample extracted from *Caulis Trachelospermi* (**B**), respectively.



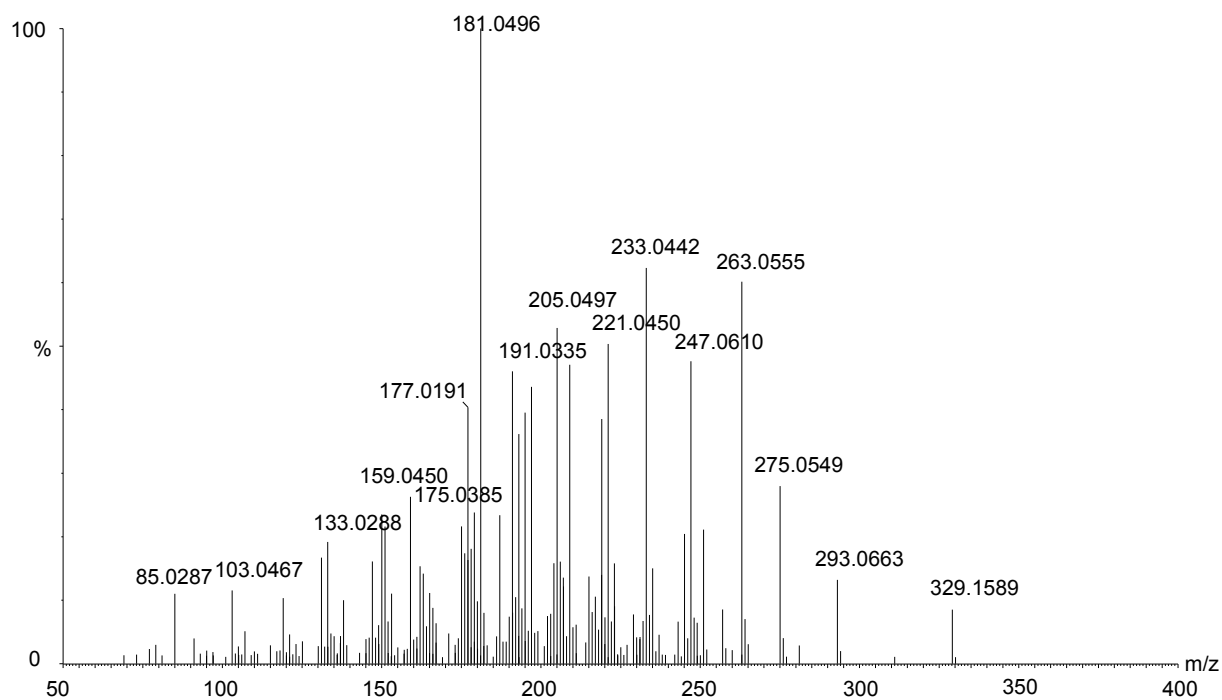
**Figure S13.** MS/MS spectrum of 5-methoxytrachelogenin (**13**) in the standard sample (**A**) and in the sample extracted from *Caulis Trachelospermi* (**B**), respectively.



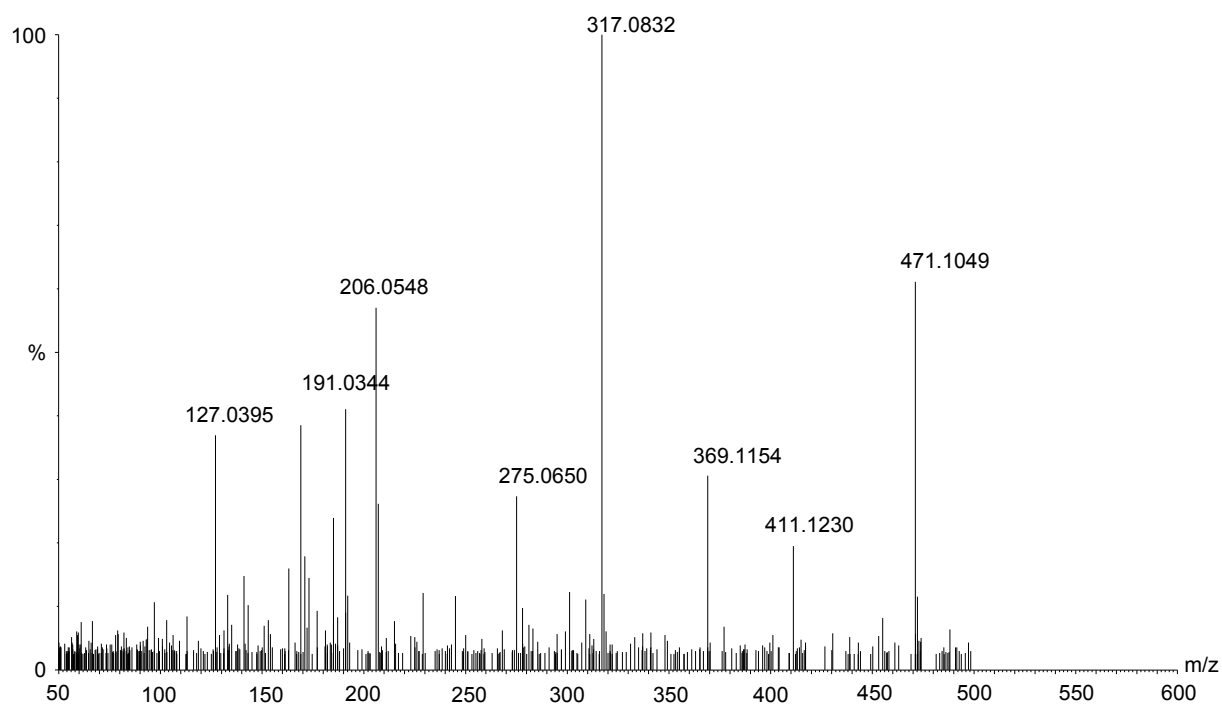
**Figure S14.** MS/MS spectrum of arctigenin (**14**) in the standard sample (**A**) and in the sample extracted from *Caulis Trachelospermi* (**B**), respectively.



**Figure S15.** MS/MS spectrum of tanegoside A (**17**) in the standard sample (**A**) and in the sample extracted from *Caulis Trachelospermi* (**B**), respectively.

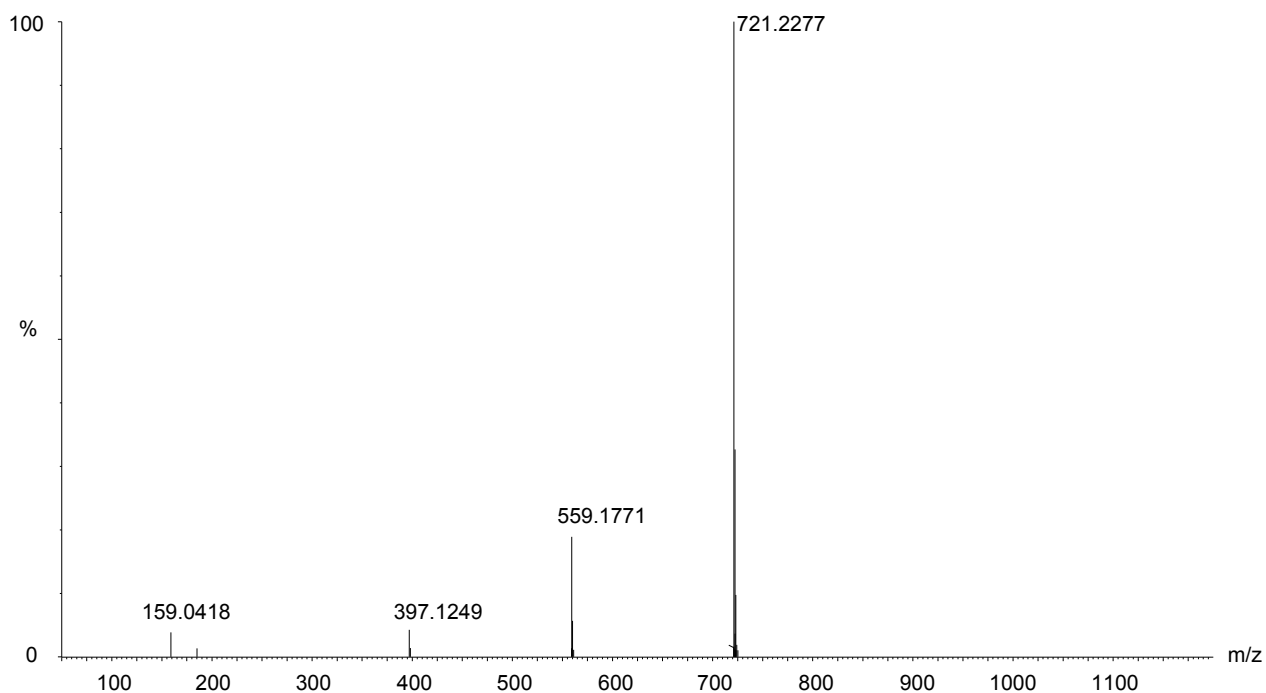


**Figure S16.** MS/MS spectrum of bergenin (15) in the sample extracted from *Caulis Trachelospermi*.

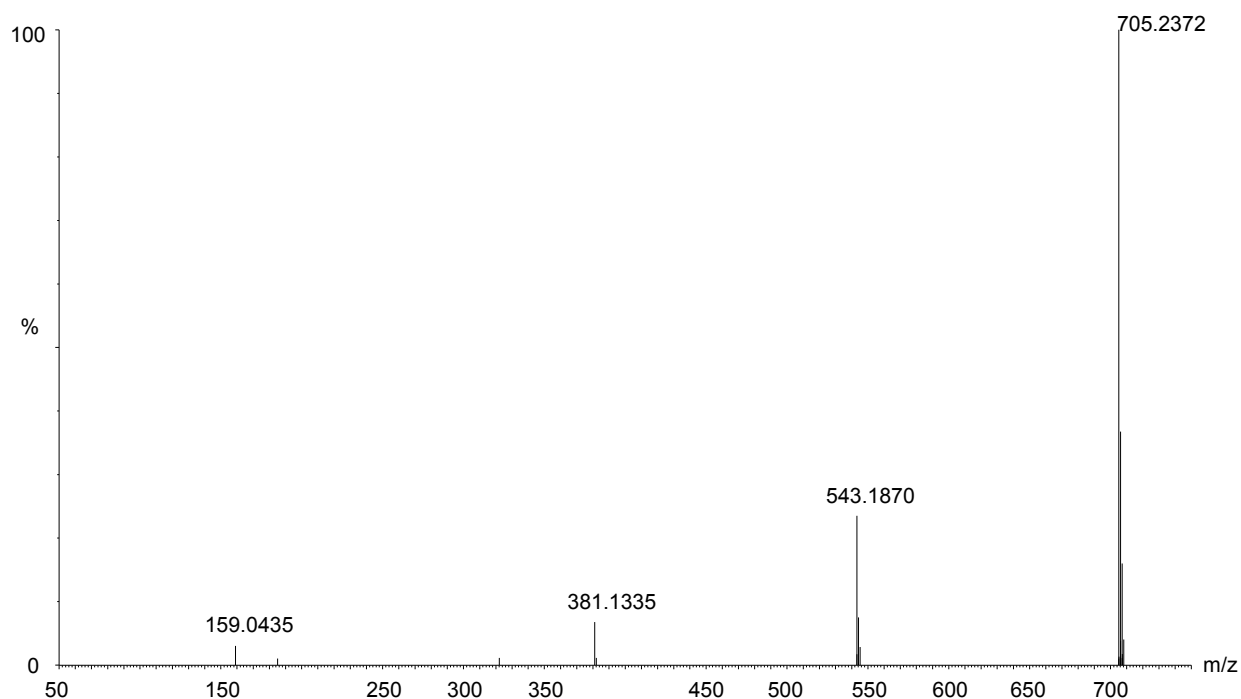


**Figure S17.** MS/MS spectrum of kelampayoside A (16) in the sample extracted from *Caulis Trachelospermi*.

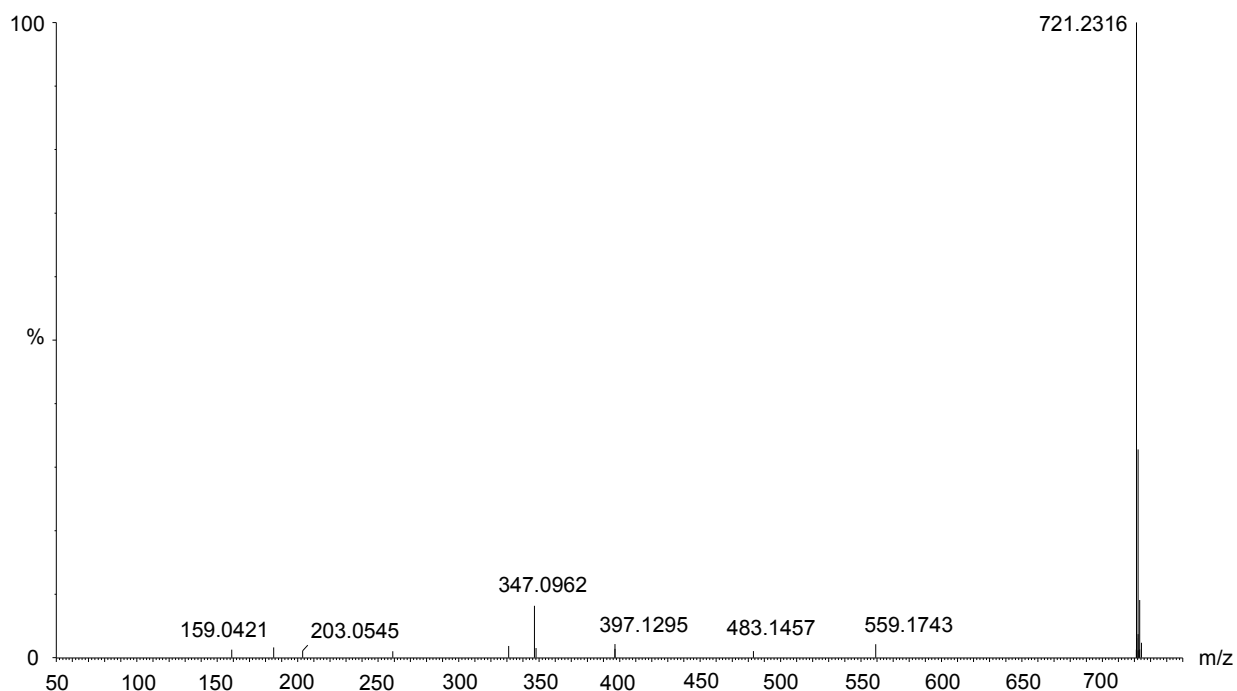




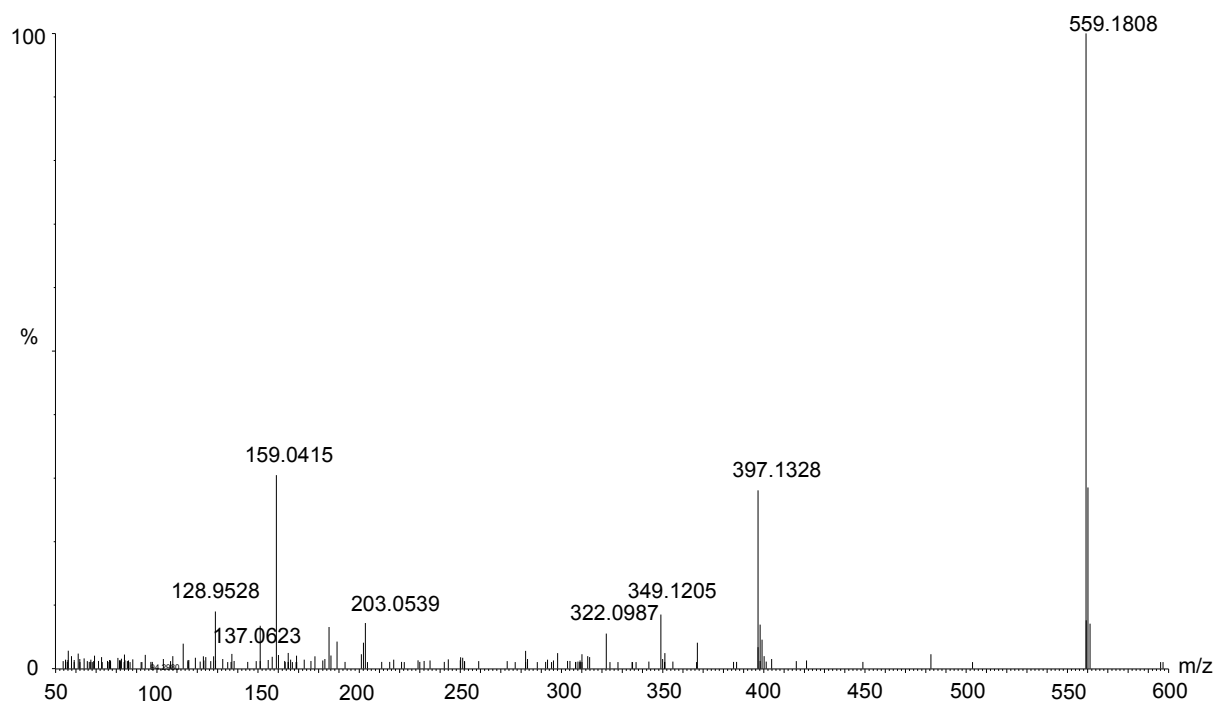
**Figure S18.** MS/MS spectrum of nortrachelogenin 4, 4'-di- $O$ - $\beta$ -D-glucoside (**18**) in the sample extracted from *Caulis Trachelospermi*.



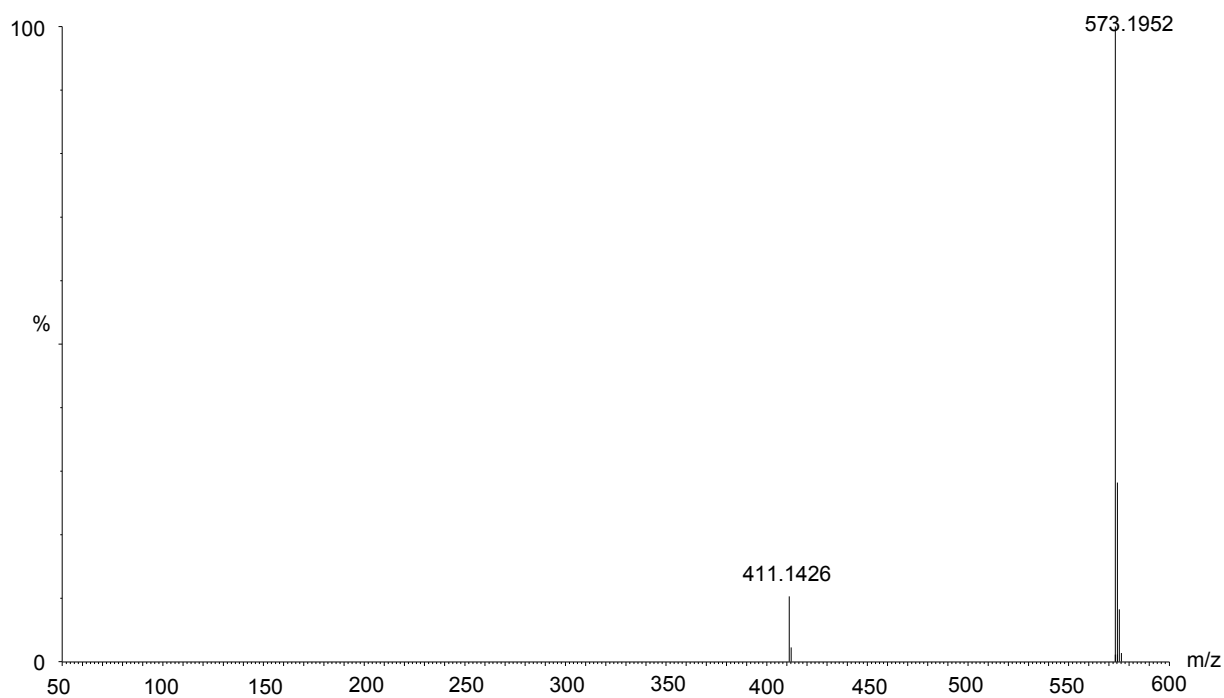
**Figure S19.** MS/MS spectrum of matairesinol 4, 4'-di- $O$ - $\beta$ -D-glucoside (**19**) in the sample extracted from *Caulis Trachelospermi*.



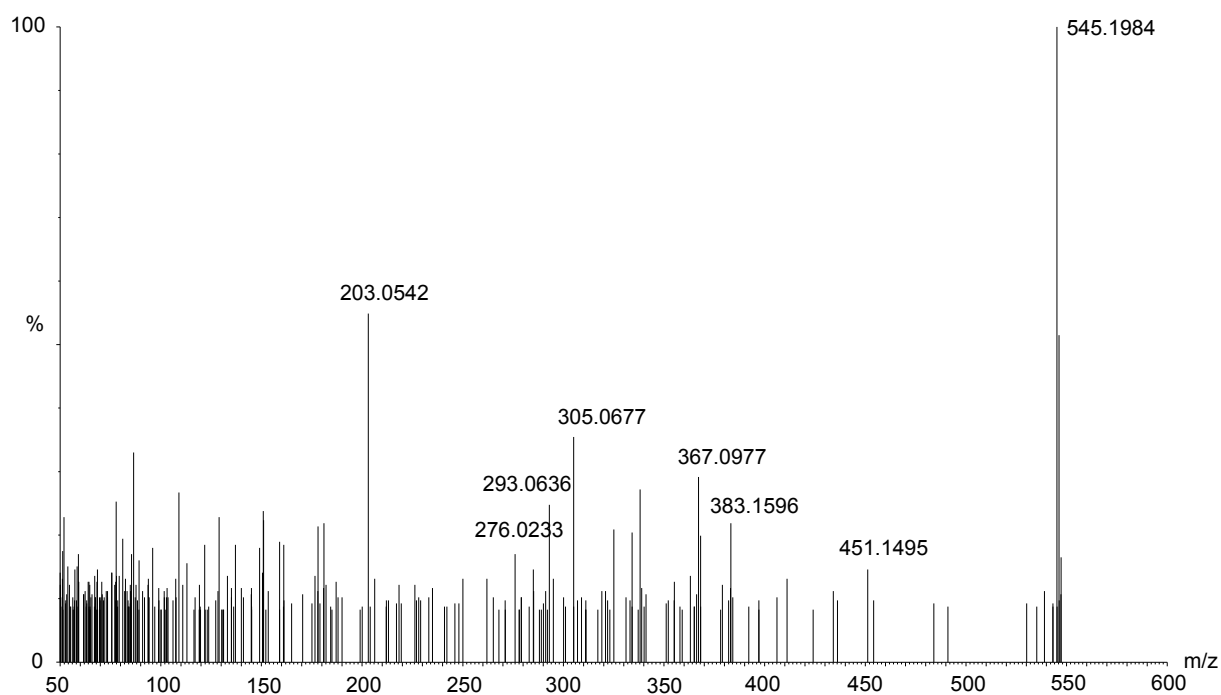
**Figure S20.** MS/MS spectrum of nortrachelogenin 4'-O- $\beta$ -gentiobioside (**20**) in the sample extracted from Caulis Trachelospermi.



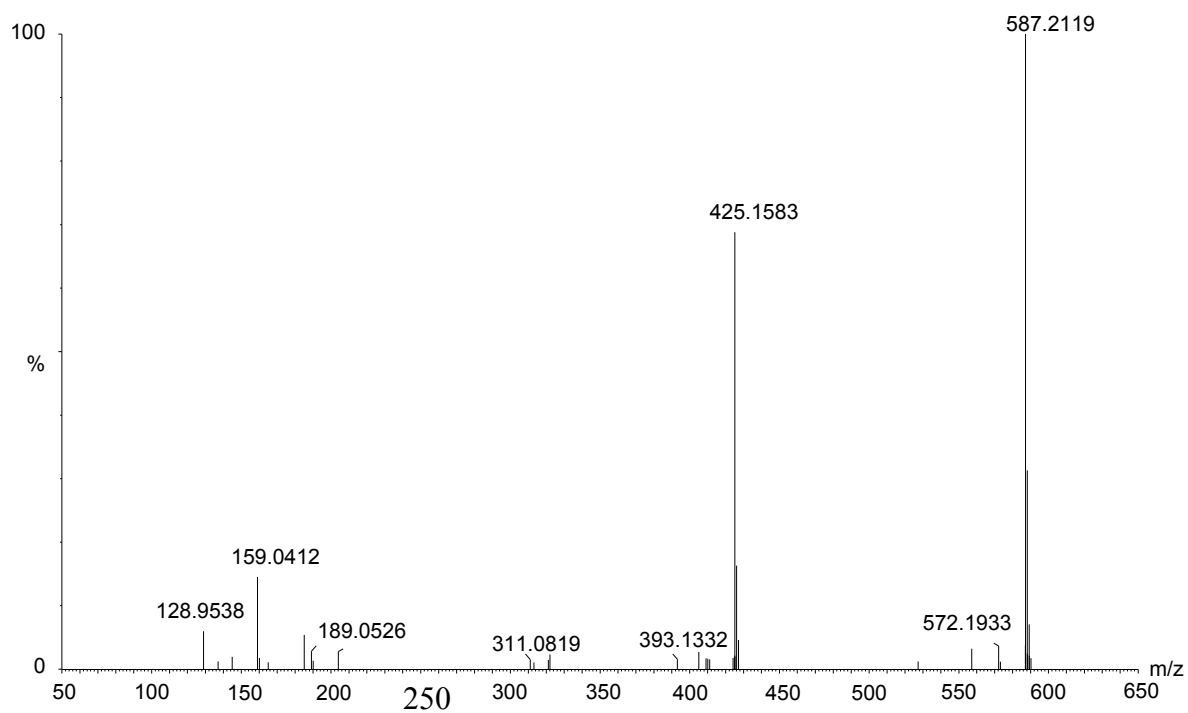
**Figure S21.** MS/MS spectrum of nortrachelogenin 4-O- $\beta$ -D-glucoside (**21**) in the sample extracted from Caulis Trachelospermi.



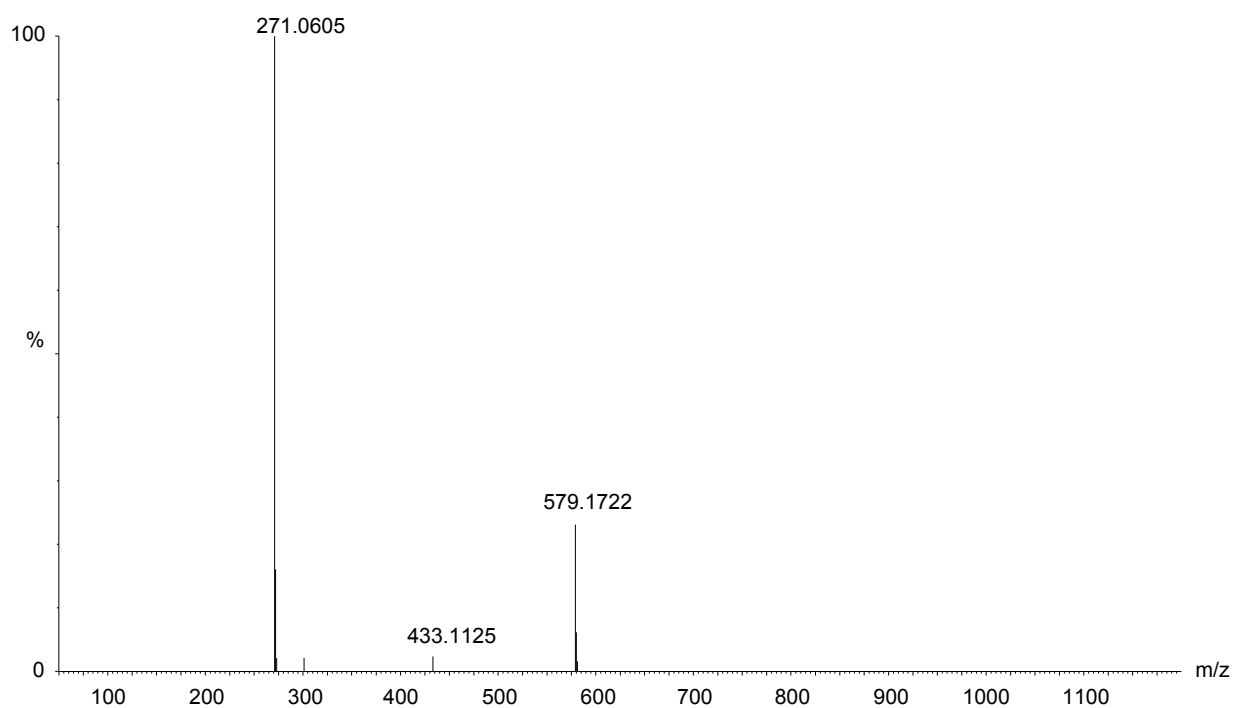
**Figure S22.** MS/MS spectrum of 4-demethyltraxillaside (**22**) in the sample extracted from *Caulis Trachelospermi*.



**Figure S23.** MS/MS spectrum of dihydrodehydrodiconiferyl alcohol-9-*O*- $\beta$ -D-glucoside (**23**) in the sample extracted from *Caulis Trachelospermi*.



**Figure S24.** MS/MS spectrum of traxillageside (**24**) in the sample extracted from *Caulis Trachelospermi*.



**Figure S25.** MS/MS spectrum of apigenin 7-*O*- $\beta$ -neospheroside (**25**) in the sample extracted from *Caulis Trachelospermi*.