

**Supplementary Table 1**

The samples information of 20 batches of YGP.

| <b>Serial number</b> | <b>Manufacturer</b>                  | <b>Batch number</b> |
|----------------------|--------------------------------------|---------------------|
| S1                   | Tong Ren Tang Technologies Co., Ltd. | 4013131             |
| S2                   | Tong Ren Tang Technologies Co., Ltd. | 4013345             |
| S3                   | Henan Wanxi pharmaceutical Co., Ltd. | 140702              |
| S4                   | Henan Wanxi pharmaceutical Co., Ltd. | 140801              |
| S5                   | Tong Ren Tang Technologies Co., Ltd. | 4013591             |
| S6                   | Henan Wanxi pharmaceutical Co., Ltd. | 130106              |
| S7                   | Henan Wanxi pharmaceutical Co., Ltd. | 150107              |
| S8                   | Tong Ren Tang Technologies Co., Ltd. | 4013673             |
| S9                   | Henan Wanxi pharmaceutical Co., Ltd. | 140309              |
| S0                   | Tong Ren Tang Technologies Co., Ltd. | 4013827             |
| S11                  | Tong Ren Tang Technologies Co., Ltd. | 4013593             |
| S12                  | Henan Wanxi pharmaceutical Co., Ltd. | 131214              |
| S13                  | Tong Ren Tang Technologies Co., Ltd. | 4013823             |
| S14                  | Henan Wanxi pharmaceutical Co., Ltd. | 140506              |
| S15                  | Tong Ren Tang Technologies Co., Ltd. | 4013502             |
| S16                  | Henan Wanxi pharmaceutical Co., Ltd. | 140703              |
| S17                  | Tong Ren Tang Technologies Co., Ltd. | 4013590             |
| S18                  | Henan Wanxi pharmaceutical Co., Ltd. | 140807              |
| S19                  | Henan Wanxi pharmaceutical Co., Ltd. | 140808              |
| S20                  | Tong Ren Tang Technologies Co., Ltd. | 4013596             |

**Table 2** The identification of 83 compounds in extractive of YGPs.

| N.O. | t <sub>R</sub> | Precursor ion<br>( <i>m/z</i> ) | Elem.<br>Comp.                                     | Diff.<br>(ppm) | Fragment<br>ions ( <i>m/z</i> ) | Fragmentation pathway                                                                                                                                                               | Identification                  | Source                 |
|------|----------------|---------------------------------|----------------------------------------------------|----------------|---------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|---------------------------------|------------------------|
| 1    | 4.59           | [M+Na] <sup>+</sup>             | C <sub>30</sub> H <sub>52</sub> O <sub>26</sub> Na | -0.625         | -                               | -                                                                                                                                                                                   | maltopentaose                   | SZY/GQ<br>Z/TSZ/R<br>G |
|      |                | 851.2664                        |                                                    |                | -                               | -                                                                                                                                                                                   |                                 |                        |
|      | 4.48           | [M-H] <sup>-</sup>              | C <sub>30</sub> H <sub>51</sub> O <sub>26</sub>    | -1.714         | 647.2021<br>(17)                | [M-H-C <sub>6</sub> H <sub>12</sub> O <sub>6</sub> ] <sup>-</sup>                                                                                                                   |                                 |                        |
|      |                | 827.2649                        |                                                    |                | <b>545.1718</b><br>(100)        | [M-H-C <sub>6</sub> H <sub>12</sub> O <sub>6</sub> -C <sub>4</sub> H <sub>6</sub> O <sub>3</sub> ] <sup>-</sup>                                                                     |                                 |                        |
|      |                |                                 |                                                    |                | 383.1186<br>(44)                | [M-H-C <sub>6</sub> H <sub>12</sub> O <sub>6</sub> -C <sub>4</sub> H <sub>6</sub> O <sub>3</sub> -C <sub>6</sub> H <sub>10</sub> O <sub>5</sub> ] <sup>-</sup>                      |                                 |                        |
|      |                |                                 |                                                    |                | 341.1079<br>(14)                | [M-H-C <sub>6</sub> H <sub>12</sub> O <sub>6</sub> -C <sub>4</sub> H <sub>6</sub> O <sub>3</sub> -C <sub>6</sub> H <sub>10</sub> O <sub>5</sub> -<br>H <sub>2</sub> O] <sup>-</sup> |                                 |                        |
| 2    | 4.80           | [M+Na] <sup>+</sup>             | C <sub>12</sub> H <sub>22</sub> O <sub>11</sub> Na | 0.842          | <b>203.0529</b><br>(100)        | [M+Na -C <sub>6</sub> H <sub>10</sub> O <sub>5</sub> ] <sup>+</sup>                                                                                                                 | maltose                         | DH/SZY/<br>RG          |
|      |                | 365.1057                        |                                                    |                | 185.0423<br>(65)                | [M+Na -C <sub>6</sub> H <sub>10</sub> O <sub>5</sub> -H <sub>2</sub> O] <sup>+</sup>                                                                                                |                                 |                        |
|      | 4.78           | [M+HCOOH-H] <sup>-</sup>        | C <sub>13</sub> H <sub>23</sub> O <sub>13</sub>    | 2.203          | <b>341.1086</b><br>(100)        | [M-H] <sup>-</sup>                                                                                                                                                                  |                                 |                        |
|      |                | 387.1142                        |                                                    |                |                                 |                                                                                                                                                                                     |                                 |                        |
| 3    | 5.10           | [M+H] <sup>+</sup>              | C <sub>6</sub> H <sub>8</sub> NO <sub>2</sub>      | -0.754         | <b>108.0444</b><br>(100)        | [M+H-H <sub>2</sub> O] <sup>+</sup>                                                                                                                                                 | 6-hydroxymethyl-3-<br>pyridinol | DH/SZY/<br>GQZ         |
|      |                | 126.0549                        |                                                    |                |                                 |                                                                                                                                                                                     |                                 |                        |
| 4    | 7.51           | [M+H] <sup>+</sup>              | C <sub>10</sub> H <sub>14</sub> NO <sub>2</sub>    | 0.748          | <b>163.0755</b>                 | [M+H-NH <sub>3</sub> ] <sup>+</sup>                                                                                                                                                 | salsolinol                      | DH                     |

|   |      |                     |                                                               |       |                 |                                                                                                                                                               |                                                                                                                            |         |
|---|------|---------------------|---------------------------------------------------------------|-------|-----------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------|---------|
|   |      |                     |                                                               |       | (100)           |                                                                                                                                                               |                                                                                                                            |         |
|   |      | 180.1020            |                                                               |       | 137.0600        |                                                                                                                                                               |                                                                                                                            |         |
|   |      |                     |                                                               |       | (21)            |                                                                                                                                                               |                                                                                                                            |         |
| 5 | 7.62 | [M+H] <sup>+</sup>  | C <sub>10</sub> H <sub>14</sub> N <sub>5</sub> O <sub>4</sub> | 0.931 | <b>136.0619</b> | [M+H-NH <sub>3</sub> -C <sub>2</sub> H <sub>2</sub> ] <sup>+</sup>                                                                                            |                                                                                                                            | DG/DH/  |
|   |      | 268.1043            |                                                               |       | (100)           | [M+H-C <sub>5</sub> H <sub>8</sub> O <sub>4</sub> ] <sup>+</sup>                                                                                              | adenosine                                                                                                                  | TSZ/SY  |
| 6 | 8.50 | [M+Na] <sup>+</sup> | C <sub>30</sub> H <sub>46</sub> O <sub>22</sub> Na            | 0.712 | <b>671.2007</b> | [M+Na-C <sub>6</sub> H <sub>6</sub> O <sub>2</sub> ] <sup>+</sup>                                                                                             | 6- {[3-O-(α-D-Galactopyranosyl)-β-D-galactopyranosyl]oxy}-2,4-hexadiyn-1-yl 3-O-α-D-galactopyranosyl-β-D-galactopyranoside | TSZ     |
|   |      |                     |                                                               |       | (100)           |                                                                                                                                                               |                                                                                                                            |         |
|   |      | 781.2379            |                                                               |       | 619.1848        | [M+Na-C <sub>6</sub> H <sub>10</sub> O <sub>5</sub> ] <sup>+</sup>                                                                                            |                                                                                                                            |         |
|   |      |                     |                                                               |       | (64)            |                                                                                                                                                               |                                                                                                                            |         |
|   |      |                     |                                                               |       | 509.1479        | [M+Na-C <sub>6</sub> H <sub>6</sub> O <sub>2</sub> -C <sub>6</sub> H <sub>10</sub> O <sub>5</sub> ] <sup>+</sup>                                              |                                                                                                                            |         |
|   |      |                     |                                                               |       | (23)            |                                                                                                                                                               |                                                                                                                            |         |
|   | 8.46 | [M-H] <sup>-</sup>  | C <sub>30</sub> H <sub>45</sub> O <sub>22</sub>               | 0.463 | 647.2047        | [M-H-C <sub>6</sub> H <sub>6</sub> O <sub>2</sub> ] <sup>-</sup>                                                                                              |                                                                                                                            |         |
|   |      |                     |                                                               |       | (19)            |                                                                                                                                                               |                                                                                                                            |         |
|   |      | 757.2401            |                                                               |       | 545.1719        | [M-H-C <sub>6</sub> H <sub>6</sub> O <sub>2</sub> -C <sub>4</sub> H <sub>6</sub> O <sub>3</sub> ] <sup>-</sup>                                                |                                                                                                                            |         |
|   |      |                     |                                                               |       | (27)            |                                                                                                                                                               |                                                                                                                            |         |
|   |      |                     |                                                               |       | <b>383.1194</b> | [M-H-C <sub>6</sub> H <sub>6</sub> O <sub>2</sub> -C <sub>4</sub> H <sub>6</sub> O <sub>3</sub> -C <sub>6</sub> H <sub>10</sub> O <sub>5</sub> ] <sup>-</sup> |                                                                                                                            |         |
|   |      |                     |                                                               |       | (100)           |                                                                                                                                                               |                                                                                                                            |         |
| 7 | 9.13 | [M+Na] <sup>+</sup> | C <sub>18</sub> H <sub>26</sub> O <sub>13</sub> Na            | 0.757 | 347.0953        | [M+Na-C <sub>6</sub> H <sub>6</sub> O <sub>3</sub> ] <sup>+</sup>                                                                                             | nuzhenidic acid                                                                                                            | DH/SZY/ |
|   |      |                     |                                                               |       | (48)            |                                                                                                                                                               |                                                                                                                            | TSZ     |
|   |      | 473.1269            |                                                               |       | <b>311.0742</b> | [M+Na-C <sub>6</sub> H <sub>10</sub> O <sub>5</sub> ] <sup>+</sup>                                                                                            |                                                                                                                            |         |
|   |      |                     |                                                               |       | (100)           |                                                                                                                                                               |                                                                                                                            |         |

|    |       |                          |                                                    |        |                          |                                                                                                                   |                             |       |
|----|-------|--------------------------|----------------------------------------------------|--------|--------------------------|-------------------------------------------------------------------------------------------------------------------|-----------------------------|-------|
|    |       |                          |                                                    |        | 185.0421<br>(7)          | [M+Na-C <sub>6</sub> H <sub>6</sub> O <sub>3</sub> -C <sub>6</sub> H <sub>10</sub> O <sub>5</sub> ] <sup>+</sup>  |                             |       |
|    | 9.07  | [M+HCOOH-H] <sup>-</sup> | C <sub>19</sub> H <sub>27</sub> O <sub>15</sub>    | 0.896  | <b>449.1294</b><br>(100) | [M-H] <sup>-</sup>                                                                                                |                             |       |
|    |       | 495.1349                 |                                                    |        |                          |                                                                                                                   |                             |       |
| 8  | 10.44 | [M+Na] <sup>+</sup>      | C <sub>14</sub> H <sub>18</sub> O <sub>11</sub> Na | 0.539  | 367.0641<br>(93)         | [M+Na-H <sub>2</sub> O] <sup>+</sup>                                                                              | catapol <sup>a</sup>        | DH    |
|    |       | 385.1103                 |                                                    |        | <b>295.0428</b><br>(100) | [M+Na-H <sub>2</sub> O-C <sub>3</sub> H <sub>4</sub> O <sub>2</sub> ] <sup>+</sup>                                |                             |       |
|    | 10.43 | [M-H] <sup>-</sup>       | C <sub>14</sub> H <sub>17</sub> O <sub>11</sub>    | 1.779  | <b>271.0456</b><br>(100) | [M-H-C <sub>3</sub> H <sub>6</sub> O <sub>3</sub> ] <sup>-</sup>                                                  |                             |       |
|    |       | 361.0772                 |                                                    |        |                          |                                                                                                                   |                             |       |
| 9  | 11.21 | [M+Na] <sup>+</sup>      | C <sub>15</sub> H <sub>22</sub> O <sub>10</sub> Na | 0.291  | -                        | -                                                                                                                 | danmelittoside              | DH/DZ |
|    |       | 385.1106                 |                                                    |        |                          |                                                                                                                   |                             |       |
|    | 11.13 | [M-H] <sup>-</sup>       | C <sub>14</sub> H <sub>17</sub> O <sub>11</sub>    | 0.173  | 301.0557<br>(8)          | [M-H-C <sub>2</sub> H <sub>4</sub> O <sub>2</sub> ] <sup>-</sup>                                                  |                             |       |
|    |       | 361.0766                 |                                                    |        | <b>271.0455</b><br>(100) | [M-H-C <sub>3</sub> H <sub>6</sub> O <sub>3</sub> ] <sup>-</sup>                                                  |                             |       |
| 10 | 12.42 | [M+Na] <sup>+</sup>      | C <sub>27</sub> H <sub>42</sub> O <sub>20</sub> Na | -0.486 | 547.1635<br>(1)          | [M+Na-C <sub>6</sub> H <sub>10</sub> O <sub>5</sub> ] <sup>+</sup>                                                | rhmannioside D <sup>a</sup> | DH    |
|    |       | 709.2158                 |                                                    |        | 385.1104<br>(1)          | [M+Na-C <sub>6</sub> H <sub>10</sub> O <sub>5</sub> -C <sub>6</sub> H <sub>10</sub> O <sub>5</sub> ] <sup>+</sup> |                             |       |
|    |       |                          |                                                    |        | <b>365.1056</b><br>(100) | [M+Na-C <sub>15</sub> H <sub>20</sub> O <sub>9</sub> ] <sup>+</sup>                                               |                             |       |
|    | 12.49 | [M+HCOOH-H] <sup>-</sup> | C <sub>28</sub> H <sub>43</sub> O <sub>22</sub>    | 0.015  | <b>685.2193</b><br>(100) | [M-H] <sup>-</sup>                                                                                                |                             |       |

|    |       |                          |                                                    |       |                          |                                                                                     |                             |    |
|----|-------|--------------------------|----------------------------------------------------|-------|--------------------------|-------------------------------------------------------------------------------------|-----------------------------|----|
|    |       | 731.2241                 |                                                    |       | 505.1551<br>(2)          | [M-H-C <sub>6</sub> H <sub>12</sub> O <sub>6</sub> ] <sup>-</sup>                   |                             |    |
| 11 | 13.30 | [M+Na] <sup>+</sup>      | C <sub>21</sub> H <sub>32</sub> O <sub>15</sub> Na | 0.875 | 385.1106<br>(17)         | [M+Na-C <sub>6</sub> H <sub>10</sub> O <sub>5</sub> ] <sup>+</sup>                  | rhmannioside A <sup>a</sup> | DH |
|    |       | 547.1638                 |                                                    |       | <b>367.1002</b><br>(100) | [M+Na-C <sub>6</sub> H <sub>10</sub> O <sub>5</sub> -H <sub>2</sub> O] <sup>+</sup> |                             |    |
|    |       |                          |                                                    |       | 203.0527<br>(23)         | [M+Na-C <sub>15</sub> H <sub>20</sub> O <sub>9</sub> ] <sup>+</sup>                 |                             |    |
|    | 13.26 | [M+HCOOH-H] <sup>-</sup> | C <sub>22</sub> H <sub>33</sub> O <sub>17</sub>    | 0.289 | <b>523.1664</b><br>(100) | [M-H] <sup>-</sup>                                                                  |                             |    |
|    |       | 569.1714                 |                                                    |       | 343.1024<br>(4)          | [M-H-C <sub>6</sub> H <sub>12</sub> O <sub>6</sub> ] <sup>-</sup>                   |                             |    |
| 12 | 14.48 | [M+H] <sup>+</sup>       | C <sub>22</sub> H <sub>36</sub> NO <sub>5</sub>    | 1.447 | <b>376.2488</b><br>(100) | [M+H-H <sub>2</sub> O] <sup>+</sup>                                                 | columbianine                | FZ |
|    |       | 394.2594                 |                                                    |       | 358.2381<br>(3)          | [M+H-2H <sub>2</sub> O] <sup>+</sup>                                                |                             |    |
| 13 | 14.48 | [M+H] <sup>+</sup>       | C <sub>22</sub> H <sub>34</sub> NO <sub>4</sub>    | 0.890 | <b>358.2380</b><br>(100) | [M+H-H <sub>2</sub> O] <sup>+</sup>                                                 | karakanine                  | FZ |
|    |       | 376.2486                 |                                                    |       | 340.2274<br>(2)          | [M+H-2H <sub>2</sub> O] <sup>+</sup>                                                |                             |    |
| 14 | 14.48 | [M+H] <sup>+</sup>       | C <sub>24</sub> H <sub>40</sub> NO <sub>10</sub>   | 1.527 | 470.2386<br>(33)         | [M+H-CH <sub>3</sub> OH] <sup>+</sup>                                               | beiwutinine                 | FZ |
|    |       | 502.2654                 |                                                    |       | <b>452.2281</b><br>(100) | [M+H-CH <sub>3</sub> OH-H <sub>2</sub> O] <sup>+</sup>                              |                             |    |
|    |       |                          |                                                    |       | 420.2019<br>(32)         | [M+H-2CH <sub>3</sub> OH-H <sub>2</sub> O] <sup>+</sup>                             |                             |    |

|    |       |                                            |                                                    |       |                                              |                                                                                                                                    |                                                          |                                  |
|----|-------|--------------------------------------------|----------------------------------------------------|-------|----------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------|----------------------------------|
| 15 | 14.59 | [M+H] <sup>+</sup>                         | C <sub>6</sub> H <sub>7</sub> O <sub>3</sub>       | 1.570 | <b>109.0285</b><br>(100)                     | [M+H-H <sub>2</sub> O] <sup>+</sup>                                                                                                | 5-hydroxymethylfurfural <sup>a</sup>                     | DH/SZY/<br>DZ/DG/<br>GQZ/TS<br>Z |
| 16 | 15.14 | 127.0392<br>[M+H] <sup>+</sup><br>149.0597 | C <sub>9</sub> H <sub>9</sub> O <sub>2</sub>       | 0.026 | -                                            | -                                                                                                                                  | <i>trans</i> -cinnamic acid                              | SZY/DZ                           |
| 17 | 15.14 | [M+Na] <sup>+</sup>                        | C <sub>16</sub> H <sub>22</sub> O <sub>10</sub> Na | 1.415 | 379.1003<br>(43)<br><b>217.0473</b><br>(100) | [M+Na-H <sub>2</sub> O] <sup>+</sup>                                                                                               | geniposidic acid <sup>a</sup>                            | DH/SZY/<br>DZ/RG                 |
|    |       | 397.1111                                   |                                                    |       | 203.0528<br>(50)                             | [M+Na-H <sub>2</sub> O-C <sub>6</sub> H <sub>10</sub> O <sub>5</sub> ] <sup>+</sup>                                                |                                                          |                                  |
|    | 15.10 | [M-H] <sup>-</sup>                         | C <sub>16</sub> H <sub>21</sub> O <sub>10</sub>    | 2.430 | 211.0610<br><b>123.0452</b><br>(100)         | [M+Na-C <sub>10</sub> H <sub>10</sub> O <sub>4</sub> ] <sup>+</sup>                                                                |                                                          |                                  |
|    |       | 373.1138                                   |                                                    |       |                                              | [M-H-C <sub>6</sub> H <sub>10</sub> O <sub>5</sub> ] <sup>-</sup>                                                                  |                                                          |                                  |
|    |       |                                            |                                                    |       |                                              | [M-H-C <sub>6</sub> H <sub>10</sub> O <sub>5</sub> -CO <sub>2</sub> -H <sub>2</sub> O-C <sub>2</sub> H <sub>2</sub> ] <sup>-</sup> |                                                          |                                  |
| 18 | 15.46 | [M+Na] <sup>+</sup>                        | C <sub>22</sub> H <sub>28</sub> O <sub>14</sub> Na | 1.398 | <b>521.1273</b><br>(100)                     | [M+Na-H <sub>2</sub> O] <sup>+</sup>                                                                                               | methyl-3-trihydroxy-6-<br>hexahydrofuro-3-<br>propanoate | DG/GQZ<br>/TSZ                   |
|    |       | 539.1379                                   |                                                    |       | 377.0848<br>(50)                             | [M+Na-C <sub>6</sub> H <sub>10</sub> O <sub>5</sub> ] <sup>+</sup>                                                                 |                                                          |                                  |
|    |       |                                            |                                                    |       | 347.0742<br>(61)                             | [M+Na-2H <sub>2</sub> O-C <sub>7</sub> H <sub>8</sub> O <sub>4</sub> ] <sup>+</sup>                                                |                                                          |                                  |
|    | 15.41 | [M-H] <sup>-</sup>                         | C <sub>22</sub> H <sub>27</sub> O <sub>14</sub>    | 1.530 | <b>353.0876</b><br>(100)                     | [M-H-C <sub>6</sub> H <sub>10</sub> O <sub>5</sub> ] <sup>-</sup>                                                                  |                                                          |                                  |

|    |       |                     |                                                    |        |                          |                                                                                     |                          |     |
|----|-------|---------------------|----------------------------------------------------|--------|--------------------------|-------------------------------------------------------------------------------------|--------------------------|-----|
|    |       | 515.1403            |                                                    |        |                          |                                                                                     |                          |     |
| 19 | 17.98 | [M+H] <sup>+</sup>  | C <sub>24</sub> H <sub>40</sub> NO <sub>9</sub>    | 1.855  | 454.2442<br>(40)         | [M+H-CH <sub>3</sub> OH] <sup>+</sup>                                               | mesaconine <sup>a</sup>  | FZ  |
|    |       | 486.2707            |                                                    |        | <b>436.2337</b><br>(100) | [M+H-CH <sub>3</sub> OH-H <sub>2</sub> O] <sup>+</sup>                              |                          |     |
|    |       |                     |                                                    |        | 404.2075<br>(25)         | [M+H-2CH <sub>3</sub> OH-H <sub>2</sub> O] <sup>+</sup>                             |                          |     |
| 20 | 18.42 | [M+H] <sup>+</sup>  | C <sub>21</sub> H <sub>34</sub> NO <sub>4</sub>    | 0.727  | -                        | -                                                                                   | 16-hydroxycardiopetaline | FZ  |
|    |       | 364.2485            |                                                    |        |                          |                                                                                     |                          |     |
| 21 | 18.86 | [M+Na] <sup>+</sup> | C <sub>16</sub> H <sub>24</sub> O <sub>10</sub> Na | 0.982  | <b>381.1160</b><br>(100) | [M+Na-H <sub>2</sub> O] <sup>+</sup>                                                | loganic acid             | SZY |
|    |       | 399.1266            |                                                    |        | 237.0736<br>(70)         | [M+Na-C <sub>6</sub> H <sub>10</sub> O <sub>5</sub> ] <sup>+</sup>                  |                          |     |
|    |       |                     |                                                    |        | 219.0630<br>(93)         | [M+Na-H <sub>2</sub> O-C <sub>6</sub> H <sub>10</sub> O <sub>5</sub> ] <sup>+</sup> |                          |     |
|    | 18.46 | [M-H] <sup>-</sup>  | C <sub>16</sub> H <sub>23</sub> O <sub>10</sub>    | 1.377  | <b>213.0767</b><br>(100) | [M-H-C <sub>6</sub> H <sub>10</sub> O <sub>5</sub> ] <sup>-</sup>                   |                          |     |
|    |       | 375.1291            |                                                    |        | 169.0870<br>(15)         | [M-H-C <sub>6</sub> H <sub>10</sub> O <sub>5</sub> -CO <sub>2</sub> ] <sup>-</sup>  |                          |     |
| 22 | 20.18 | [M+H] <sup>+</sup>  | C <sub>22</sub> H <sub>36</sub> NO <sub>4</sub>    | -0.410 | <b>360.2539</b><br>(100) | [M+H-H <sub>2</sub> O] <sup>+</sup>                                                 | karacoline <sup>a</sup>  | FZ  |
|    |       | 378.2645            |                                                    |        | 342.2431<br>(5)          | [M+H-2H <sub>2</sub> O] <sup>+</sup>                                                |                          |     |
| 23 | 20.28 | [M+H] <sup>+</sup>  | C <sub>23</sub> H <sub>38</sub> NO <sub>5</sub>    | 1.789  | <b>390.2645</b><br>(100) | [M+H-H <sub>2</sub> O] <sup>+</sup>                                                 | isotalatizidine          | FZ  |

|    |       |                          |                                                    |        |                          |                                                                      |                                             |     |
|----|-------|--------------------------|----------------------------------------------------|--------|--------------------------|----------------------------------------------------------------------|---------------------------------------------|-----|
|    |       | 408.2752                 |                                                    |        | 372.2538<br>(5)          | [M+H-2H <sub>2</sub> O] <sup>+</sup>                                 |                                             |     |
|    |       |                          |                                                    |        | 358.2379<br>(2)          | [M+H-2H <sub>2</sub> O-CH <sub>2</sub> ] <sup>+</sup>                |                                             |     |
| 24 | 20.91 | [M+Na] <sup>+</sup>      | C <sub>17</sub> H <sub>26</sub> O <sub>11</sub> Na | 0.460  | 411.1266<br>(35)         | [M+Na-H <sub>2</sub> O] <sup>+</sup>                                 | morroniside <sup>a</sup>                    | SZY |
|    |       | 429.1369                 |                                                    |        | <b>267.0842</b><br>(100) | [M+Na-C <sub>6</sub> H <sub>10</sub> O <sub>5</sub> ] <sup>+</sup>   |                                             |     |
|    |       |                          |                                                    |        | 185.0421<br>(28)         | [M+Na- C <sub>11</sub> H <sub>16</sub> O <sub>6</sub> ] <sup>+</sup> |                                             |     |
|    | 20.85 | [M+HCOOH-H] <sup>-</sup> | C <sub>18</sub> H <sub>27</sub> O <sub>13</sub>    | 1.846  | <b>405.1399</b><br>(100) | [M-H] <sup>-</sup>                                                   |                                             |     |
|    |       | 451.1454                 |                                                    |        | 243.0872<br>(31)         | [M-H-C <sub>6</sub> H <sub>10</sub> O <sub>5</sub> ] <sup>-</sup>    |                                             |     |
| 25 | 21.01 | [M+H] <sup>+</sup>       | C <sub>11</sub> H <sub>15</sub> O <sub>5</sub>     | 0.616  | <b>195.0654</b><br>(100) | [M+H-CH <sub>3</sub> OH] <sup>+</sup>                                | dehydromorroniaglycone                      | SZY |
|    |       | 227.0915                 |                                                    |        | 183.0653                 | [M+H-C <sub>2</sub> H <sub>2</sub> -H <sub>2</sub> O] <sup>+</sup>   |                                             |     |
| 26 | 21.01 | [M+Na] <sup>+</sup>      | C <sub>27</sub> H <sub>30</sub> O <sub>17</sub> Na | 0.169  | -                        | -                                                                    | quercetin-3-O-galactoside-<br>7-O-glucoside | DZ  |
|    |       | 649.1376                 |                                                    |        | <b>463.0882</b><br>(100) | [M-H-C <sub>6</sub> H <sub>10</sub> O <sub>5</sub> ] <sup>-</sup>    |                                             |     |
|    | 20.75 | [M-H] <sup>-</sup>       | C <sub>27</sub> H <sub>29</sub> O <sub>17</sub>    | -0.841 | 301.0355<br>(24)         | [M-H-2C <sub>6</sub> H <sub>10</sub> O <sub>5</sub> ] <sup>-</sup>   |                                             |     |
|    |       | 625.1394                 |                                                    |        |                          |                                                                      |                                             |     |
| 27 | 21.32 | [M+H] <sup>+</sup>       | C <sub>25</sub> H <sub>42</sub> NO <sub>9</sub>    | 1.503  | 482.2754<br>(17)         | [M+H-H <sub>2</sub> O] <sup>+</sup>                                  | aconitysat                                  | FZ  |



|    |       |                     |                                                   |        |                          |                                                                                     |                                        |                           |
|----|-------|---------------------|---------------------------------------------------|--------|--------------------------|-------------------------------------------------------------------------------------|----------------------------------------|---------------------------|
|    |       | 500.2862            |                                                   |        | 468.2597<br>(41)         | [M+H-CH <sub>3</sub> OH] <sup>+</sup>                                               |                                        |                           |
|    |       |                     |                                                   |        | <b>450.2493</b><br>(100) | [M+H-CH <sub>3</sub> OH-H <sub>2</sub> O] <sup>+</sup>                              |                                        |                           |
| 28 | 22.31 | [M+H] <sup>+</sup>  | C <sub>22</sub> H <sub>32</sub> NO <sub>3</sub>   | 1.534  | <b>340.2275</b><br>(100) | [M+H-H <sub>2</sub> O] <sup>+</sup>                                                 | songorine <sup>a</sup>                 | FZ                        |
|    |       | 358.2382            |                                                   |        |                          |                                                                                     |                                        |                           |
| 29 | 22.42 | [M+Na] <sup>+</sup> | C <sub>16</sub> H <sub>18</sub> O <sub>9</sub> Na | 1.344  | <b>359.0739</b><br>(100) | [M+Na-H <sub>2</sub> O] <sup>+</sup>                                                | chlorogenic Acid                       | SZY/DZ/<br>GQZ/DG<br>/TSZ |
|    |       | 377.0848            |                                                   |        | 215.0527<br>(99)         | [M+Na-C <sub>6</sub> H <sub>10</sub> O <sub>5</sub> ] <sup>+</sup>                  |                                        |                           |
|    |       |                     |                                                   |        | 197.0420<br>(17)         | [M+Na-H <sub>2</sub> O-C <sub>6</sub> H <sub>10</sub> O <sub>5</sub> ] <sup>+</sup> |                                        |                           |
|    | 22.15 | [M-H] <sup>-</sup>  | C <sub>16</sub> H <sub>17</sub> O <sub>9</sub>    | 3.431  | <b>191.0560</b><br>(100) | [M-H-C <sub>6</sub> H <sub>10</sub> O <sub>5</sub> ] <sup>-</sup>                   |                                        |                           |
|    |       | 353.0879            |                                                   |        |                          |                                                                                     |                                        |                           |
| 30 | 23.18 | [M+H] <sup>+</sup>  | C <sub>33</sub> H <sub>46</sub> NO <sub>10</sub>  | 0.920  | -                        | -                                                                                   | hypoconitine                           | FZ                        |
|    |       | 616.3122            |                                                   |        |                          |                                                                                     |                                        |                           |
| 31 | 23.18 | [M+H] <sup>+</sup>  | C <sub>20</sub> H <sub>28</sub> NO <sub>3</sub>   | 1.089  | <b>312.1961</b><br>(100) | [M+H-H <sub>2</sub> O] <sup>+</sup>                                                 | hetisine                               | FZ                        |
|    |       | 330.2067            |                                                   |        | 294.1853<br>(20)         | [M+H-2H <sub>2</sub> O] <sup>+</sup>                                                |                                        |                           |
| 32 | 23.89 | [M+Na] <sup>+</sup> | C <sub>9</sub> H <sub>12</sub> O <sub>3</sub> Na  | -0.709 | -                        | -                                                                                   | 6-hydroxy-2-oxabicyclo-<br>nonen-1-one | DZ                        |
|    |       | 191.0677            |                                                   |        |                          |                                                                                     |                                        |                           |

|    |       |                                      |                                                    |        |                                                                  |                                                                                                                                                                                                               |                                        |        |
|----|-------|--------------------------------------|----------------------------------------------------|--------|------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------|--------|
| 33 | 23.89 | [M+Na] <sup>+</sup><br>683.2152      | C <sub>21</sub> H <sub>32</sub> O <sub>15</sub> Na | -0.821 | -                                                                | -                                                                                                                                                                                                             | rhmannioside B                         | DH     |
| 34 | 25.39 | [M+H] <sup>+</sup><br>454.2807       | C <sub>24</sub> H <sub>40</sub> NO <sub>7</sub>    | 1.763  | <b>436.2698</b><br>(100)<br>418.2590<br>(4)<br>404.2434<br>(7)   | [M+H-H <sub>2</sub> O] <sup>+</sup><br><br>[M+H-2H <sub>2</sub> O] <sup>+</sup><br><br>[M+H-CH <sub>3</sub> OH-H <sub>2</sub> O] <sup>+</sup>                                                                 | fuziline <sup>a</sup>                  | FZ     |
| 35 | 26.04 | [M+Na] <sup>+</sup><br>379.1003      | C <sub>16</sub> H <sub>20</sub> O <sub>9</sub> Na  | 0.941  | <b>217.0471</b><br>(100)<br>185.0420<br>(51)                     | [M+Na-C <sub>6</sub> H <sub>10</sub> O <sub>5</sub> ] <sup>+</sup><br><br>[M+Na-C <sub>10</sub> H <sub>10</sub> O <sub>4</sub> ] <sup>+</sup>                                                                 | <i>trans</i> -feruloyl-4-O-β-glucoside | DG/GQZ |
|    | 25.84 | [M-H] <sup>-</sup><br>355.1027       | C <sub>16</sub> H <sub>19</sub> O <sub>9</sub>     | 0.933  | <b>193.0504</b><br>(100)                                         | [M-H-C <sub>6</sub> H <sub>10</sub> O <sub>5</sub> ] <sup>-</sup>                                                                                                                                             |                                        |        |
| 36 | 26.40 | [M+Na] <sup>+</sup><br>561.1953      | C <sub>26</sub> H <sub>34</sub> O <sub>12</sub> Na | 1.786  | -                                                                | -                                                                                                                                                                                                             | olivil 4'-O-β-D-glucopyranoside        | TSZ    |
|    | 26.18 | [M+HCOOH-H] <sup>-</sup><br>583.2018 | C <sub>27</sub> H <sub>35</sub> O <sub>14</sub>    | -0.501 | -                                                                | -                                                                                                                                                                                                             |                                        |        |
| 37 | 26.85 | [M+Na] <sup>+</sup><br>411.1270      | C <sub>17</sub> H <sub>24</sub> O <sub>10</sub> Na | 1.902  | 379.1003<br>(35)<br>249.0736<br>(76)<br><b>217.0474</b><br>(100) | [M+Na-CH <sub>3</sub> OH] <sup>+</sup><br><br>[M+Na-C <sub>6</sub> H <sub>10</sub> O <sub>5</sub> ] <sup>+</sup><br><br>[M+Na-CH <sub>3</sub> OH-C <sub>6</sub> H <sub>10</sub> O <sub>5</sub> ] <sup>+</sup> | geniposide                             | SZY/DZ |

|    |       |                          |                                                    |       |                                                                  |                                                                                        |                        |     |
|----|-------|--------------------------|----------------------------------------------------|-------|------------------------------------------------------------------|----------------------------------------------------------------------------------------|------------------------|-----|
|    | 26.63 | [M+HCOOH-H] <sup>-</sup> | C <sub>18</sub> H <sub>25</sub> O <sub>12</sub>    | 1.864 | 387.1295<br>(42)<br><b>225.0766</b><br>(100)                     | [M-H] <sup>-</sup>                                                                     |                        |     |
|    |       | 433.1349                 |                                                    |       |                                                                  | [M-H-C <sub>6</sub> H <sub>10</sub> O <sub>5</sub> ] <sup>-</sup>                      |                        |     |
| 38 | 27.06 | [M+Na] <sup>+</sup>      | C <sub>17</sub> H <sub>26</sub> O <sub>10</sub> Na | 1.989 | 395.1317<br>(46)<br>251.0892<br>(73)<br><b>219.0630</b><br>(100) | [M+Na-H <sub>2</sub> O] <sup>+</sup>                                                   | loganin <sup>a</sup>   | SZY |
|    |       | 413.1426                 |                                                    |       |                                                                  | [M+Na-C <sub>6</sub> H <sub>10</sub> O <sub>5</sub> ] <sup>+</sup>                     |                        |     |
|    |       |                          |                                                    |       |                                                                  | [M+Na-CH <sub>3</sub> OH -C <sub>6</sub> H <sub>10</sub> O <sub>5</sub> ] <sup>+</sup> |                        |     |
|    | 26.94 | [M+HCOOH-H] <sup>-</sup> | C <sub>18</sub> H <sub>27</sub> O <sub>12</sub>    | 1.304 | 389.1440<br>(16)<br><b>227.0921</b><br>(100)                     | [M-H] <sup>-</sup>                                                                     |                        |     |
|    |       | 435.1053                 |                                                    |       |                                                                  | [M-H-C <sub>6</sub> H <sub>10</sub> O <sub>5</sub> ] <sup>-</sup>                      |                        |     |
| 39 | 27.25 | [M+Na] <sup>+</sup>      | C <sub>11</sub> H <sub>14</sub> O <sub>5</sub> Na  | 0.061 | -                                                                | -                                                                                      | genipin                | SZY |
|    |       | 249.0734                 |                                                    |       |                                                                  |                                                                                        |                        |     |
| 40 | 27.36 | [M+H] <sup>+</sup>       | C <sub>24</sub> H <sub>40</sub> NO <sub>6</sub>    | 2.066 | <b>420.2751</b><br>(100)                                         | [M+H-H <sub>2</sub> O] <sup>+</sup>                                                    | neoline <sup>a</sup>   | FZ  |
|    |       | 438.2859                 |                                                    |       | 388.2488<br>(34)                                                 | [M+H-H <sub>2</sub> O-CH <sub>3</sub> OH] <sup>+</sup>                                 |                        |     |
|    |       |                          |                                                    |       | 356.2224<br>(6)                                                  | [M+H-H <sub>2</sub> O-2CH <sub>3</sub> OH] <sup>+</sup>                                |                        |     |
| 41 | 28.24 | [M+Na] <sup>+</sup>      | C <sub>16</sub> H <sub>22</sub> O <sub>9</sub> Na  | 1.513 | 255.0842<br>(21)<br><b>219.0630</b><br>(100)                     | [M+Na-C <sub>6</sub> H <sub>6</sub> O <sub>3</sub> ] <sup>+</sup>                      | sweroside <sup>a</sup> | SZY |
|    |       | 381.1162                 |                                                    |       |                                                                  | [M+Na-C <sub>6</sub> H <sub>10</sub> O <sub>5</sub> ] <sup>+</sup>                     |                        |     |

|    |       |                          |                                                    |        |                          |                                                                                                                   |                                                          |               |
|----|-------|--------------------------|----------------------------------------------------|--------|--------------------------|-------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------|---------------|
|    |       |                          |                                                    |        | 149.0210<br>(29)         | [M+Na-C <sub>10</sub> H <sub>16</sub> O <sub>6</sub> ] <sup>+</sup>                                               |                                                          |               |
|    | 28.13 | [M+HCOOH-H] <sup>-</sup> | C <sub>17</sub> H <sub>23</sub> O <sub>11</sub>    | 2.809  | <b>357.1198</b><br>(100) | [M-H] <sup>-</sup>                                                                                                |                                                          |               |
|    |       | 403.1243                 |                                                    |        | 195.0661<br>(42)         | [M-H-C <sub>6</sub> H <sub>10</sub> O <sub>5</sub> ] <sup>-</sup>                                                 |                                                          |               |
| 42 | 28.34 | [M+H] <sup>+</sup>       | C <sub>24</sub> H <sub>38</sub> NO <sub>5</sub>    | 0.643  | -                        | -                                                                                                                 | dolaconine                                               | FZ            |
|    |       | 420.2747                 |                                                    |        |                          |                                                                                                                   |                                                          |               |
| 43 | 28.45 | [M+H] <sup>+</sup>       | C <sub>25</sub> H <sub>40</sub> NO <sub>6</sub>    | 1.323  | -                        | -                                                                                                                 | codelphine                                               | FZ            |
|    |       | 450.2856                 |                                                    |        |                          |                                                                                                                   |                                                          |               |
| 44 | 29.57 | [M+Na] <sup>+</sup>      | C <sub>35</sub> H <sub>46</sub> O <sub>20</sub> Na | 1.094  | <b>663.1898</b><br>(100) | [M+Na-C <sub>6</sub> H <sub>10</sub> O <sub>4</sub> ] <sup>+</sup>                                                | echinacoside <sup>a</sup>                                | DH            |
|    |       | 809.2484                 |                                                    |        | 647.1951<br>(35)         | [M+Na-C <sub>6</sub> H <sub>10</sub> O <sub>5</sub> ] <sup>+</sup>                                                |                                                          |               |
|    |       |                          |                                                    |        | 501.1368<br>(8)          | [M+Na-C <sub>6</sub> H <sub>10</sub> O <sub>4</sub> -C <sub>6</sub> H <sub>10</sub> O <sub>5</sub> ] <sup>+</sup> |                                                          |               |
|    | 29.47 | [M-H] <sup>-</sup>       | C <sub>35</sub> H <sub>45</sub> O <sub>20</sub>    | -0.535 | <b>623.2192</b><br>(100) | [M-H-C <sub>6</sub> H <sub>10</sub> O <sub>5</sub> ] <sup>-</sup>                                                 |                                                          |               |
|    |       | 785.2495                 |                                                    |        |                          |                                                                                                                   |                                                          |               |
| 45 | 30.02 | [M+Na] <sup>+</sup>      | C <sub>32</sub> H <sub>42</sub> O <sub>16</sub> Na | 1.565  | <b>543.1844</b><br>(100) | [M+Na-C <sub>6</sub> H <sub>10</sub> O <sub>5</sub> ] <sup>+</sup>                                                | pinoresinol 4',4''-di-O-β-D-glucopyranoside <sup>a</sup> | DG/DZ/T<br>SZ |
|    |       | 705.2376                 |                                                    |        | 419.1318<br>(10)         | [M+Na-C <sub>6</sub> H <sub>10</sub> O <sub>5</sub> -C <sub>7</sub> H <sub>8</sub> O <sub>2</sub> ] <sup>+</sup>  |                                                          |               |
|    | 29.88 | [M+HCOOH-H] <sup>-</sup> | C <sub>33</sub> H <sub>43</sub> O <sub>18</sub>    | 0.247  | <b>681.2402</b><br>(100) | [M-H] <sup>-</sup>                                                                                                |                                                          |               |
|    |       | 727.2446                 |                                                    |        | 519.1874                 | [M-H-C <sub>6</sub> H <sub>10</sub> O <sub>5</sub> ] <sup>-</sup>                                                 |                                                          |               |

|    |       |                          |                                                    |        |                                              |                                                                     |                                                    |       |
|----|-------|--------------------------|----------------------------------------------------|--------|----------------------------------------------|---------------------------------------------------------------------|----------------------------------------------------|-------|
| 46 | 31.46 | [M+Na] <sup>+</sup>      | C <sub>33</sub> H <sub>44</sub> O <sub>17</sub> Na | 0.992  | (83)<br><b>573.1946</b><br>(100)             | [M+Na-C <sub>6</sub> H <sub>10</sub> O <sub>5</sub> ] <sup>+</sup>  | medioresinol 4'-O-β-D-glucopyranoside              | DZ    |
|    |       | 735.2478                 |                                                    |        |                                              |                                                                     |                                                    |       |
|    | 31.44 | [M+HCOOH-H] <sup>-</sup> | C <sub>34</sub> H <sub>45</sub> O <sub>19</sub>    | -1.143 | 711.2485<br>(36)<br><b>549.1966</b><br>(100) | [M-H] <sup>-</sup>                                                  |                                                    |       |
| 47 |       | 757.2541                 |                                                    |        | 387.1440<br>(6)                              | [M-H-C <sub>6</sub> H <sub>10</sub> O <sub>5</sub> ] <sup>-</sup>   | talatisamine                                       | FZ    |
|    | 31.58 | [M+H] <sup>+</sup>       | C <sub>24</sub> H <sub>40</sub> NO <sub>5</sub>    | 2.250  | <b>390.2644</b><br>(100)                     | [M+H-CH <sub>3</sub> OH] <sup>+</sup>                               |                                                    |       |
|    |       | 422.2910                 |                                                    |        | 372.2537<br>(4)                              | [M+H-CH <sub>3</sub> OH -H <sub>2</sub> O] <sup>+</sup>             |                                                    |       |
| 48 | 32.25 | [M+Na] <sup>+</sup>      | C <sub>23</sub> H <sub>34</sub> O <sub>13</sub> Na | 1.101  | -                                            | -                                                                   | genipinl-O-a-L-rhamnopyranosyl-β-D-glucopyranoside | SZY   |
| 49 | 33.03 | [M+Na] <sup>+</sup>      | C <sub>34</sub> H <sub>46</sub> O <sub>18</sub> Na | 1.430  | <b>603.2057</b><br>(100)                     | [M+Na-C <sub>6</sub> H <sub>10</sub> O <sub>5</sub> ] <sup>+</sup>  | syringaresinol 4',4''-di-O-β-D-glucopyranoside     | DZ/RG |
|    |       | 765.2587                 |                                                    |        | 441.1524<br>(4)                              | [M+Na-2C <sub>6</sub> H <sub>10</sub> O <sub>5</sub> ] <sup>+</sup> |                                                    |       |
|    | 32.98 | [M+HCOOH-H] <sup>-</sup> | C <sub>35</sub> H <sub>47</sub> O <sub>20</sub>    | -1.029 | 741.2589<br>(9)<br><b>579.2081</b><br>(100)  | [M-H] <sup>-</sup>                                                  |                                                    |       |
|    |       | 787.2647                 |                                                    |        |                                              | [M-H-C <sub>6</sub> H <sub>10</sub> O <sub>5</sub> ] <sup>-</sup>   |                                                    |       |

|    |       |                     |                                                    |        |                          |                                                                                                                   |                            |     |
|----|-------|---------------------|----------------------------------------------------|--------|--------------------------|-------------------------------------------------------------------------------------------------------------------|----------------------------|-----|
|    |       |                     |                                                    |        | 417.1545<br>(15)         | [M-H-2C <sub>6</sub> H <sub>10</sub> O <sub>5</sub> ] <sup>-</sup>                                                |                            |     |
| 50 | 34.03 | [M+Na] <sup>+</sup> | C <sub>36</sub> H <sub>48</sub> O <sub>20</sub> Na | -0.066 | 677.2054<br>(9)          | [M+Na-C <sub>6</sub> H <sub>10</sub> O <sub>4</sub> ] <sup>+</sup>                                                | cistanoside A <sup>a</sup> | DH  |
|    |       | 823.2631            |                                                    |        | <b>661.2100</b><br>(100) | [M+Na-C <sub>6</sub> H <sub>10</sub> O <sub>5</sub> ] <sup>+</sup>                                                |                            |     |
|    |       |                     |                                                    |        | 515.1519<br>(36)         | [M+Na-C <sub>6</sub> H <sub>10</sub> O <sub>5</sub> -C <sub>6</sub> H <sub>10</sub> O <sub>4</sub> ] <sup>+</sup> |                            |     |
|    | 33.74 | [M-H] <sup>-</sup>  | C <sub>36</sub> H <sub>47</sub> O <sub>20</sub>    | -1.702 | -                        | -                                                                                                                 |                            |     |
|    |       | 799.2642            |                                                    |        |                          |                                                                                                                   |                            |     |
| 51 | 34.92 | [M+Na] <sup>+</sup> | C <sub>23</sub> H <sub>34</sub> O <sub>13</sub> Na | -0.133 | -                        | -                                                                                                                 | jioglutoside B             | DH  |
|    |       | 541.1891            |                                                    |        |                          |                                                                                                                   |                            |     |
| 52 | 35.60 | [M+Na] <sup>+</sup> | C <sub>26</sub> H <sub>28</sub> O <sub>16</sub> Na | 1.671  | <b>487.0851</b><br>(100) | [M+Na-C <sub>6</sub> H <sub>10</sub> O <sub>5</sub> ] <sup>+</sup>                                                | carlinoside                | TSZ |
|    |       | 619.1280            |                                                    |        |                          |                                                                                                                   |                            |     |
| 53 | 37.38 | [M+Na] <sup>+</sup> | C <sub>27</sub> H <sub>30</sub> O <sub>16</sub> Na | 1.491  | 487.0849<br>(19)         | [M+Na-C <sub>6</sub> H <sub>10</sub> O <sub>4</sub> ] <sup>+</sup>                                                | rutin                      | GQZ |
|    |       | 633.1436            |                                                    |        | <b>331.1001</b><br>(100) | [M+Na-C <sub>6</sub> H <sub>10</sub> O <sub>4</sub> -C <sub>6</sub> H <sub>10</sub> O <sub>5</sub> ] <sup>+</sup> |                            |     |
|    | 37.05 | [M-H] <sup>-</sup>  | C <sub>27</sub> H <sub>29</sub> O <sub>16</sub>    | 2.526  | <b>301.0352</b><br>(100) | [M-H-C <sub>6</sub> H <sub>10</sub> O <sub>4</sub> -C <sub>6</sub> H <sub>10</sub> O <sub>5</sub> ] <sup>-</sup>  |                            |     |
|    |       | 609.1465            |                                                    |        |                          |                                                                                                                   |                            |     |
| 54 | 38.83 | [M+Na] <sup>+</sup> | C <sub>21</sub> H <sub>20</sub> O <sub>12</sub> Na | 1.915  | <b>325.0324</b><br>(100) | [M+Na-C <sub>6</sub> H <sub>10</sub> O <sub>5</sub> ] <sup>+</sup>                                                | hyperoside <sup>a</sup>    | TSZ |
|    |       | 487.0856            |                                                    |        | 185.0423                 | [M+Na-C <sub>15</sub> H <sub>10</sub> O <sub>7</sub> ] <sup>+</sup>                                               |                            |     |

|    |       |                     |                                                    |       |                                  |                                                                     |                                         |                   |
|----|-------|---------------------|----------------------------------------------------|-------|----------------------------------|---------------------------------------------------------------------|-----------------------------------------|-------------------|
|    | 38.40 | [M-H] <sup>-</sup>  | C <sub>21</sub> H <sub>19</sub> O <sub>12</sub>    | 2.305 | (58)<br><b>301.0349</b><br>(100) | [M-H-C <sub>6</sub> H <sub>10</sub> O <sub>5</sub> ] <sup>-</sup>   |                                         |                   |
|    |       | 463.0882            |                                                    |       |                                  |                                                                     |                                         |                   |
| 55 | 40.25 | [M+Na] <sup>+</sup> | C <sub>29</sub> H <sub>36</sub> O <sub>15</sub> Na | 0.662 | <b>501.1374</b><br>(100)         | [M+Na-C <sub>6</sub> H <sub>10</sub> O <sub>4</sub> ] <sup>+</sup>  | acteoside <sup>a</sup>                  | SZY               |
|    |       | 647.1951            |                                                    |       | 467.1528<br>(8)                  | [M+Na-C <sub>9</sub> H <sub>8</sub> O <sub>4</sub> ] <sup>+</sup>   |                                         |                   |
|    | 39.64 | [M-H] <sup>-</sup>  | C <sub>29</sub> H <sub>35</sub> O <sub>15</sub>    | 0.744 | <b>461.1661</b><br>(100)         | [M-H-C <sub>6</sub> H <sub>10</sub> O <sub>5</sub> ] <sup>-</sup>   |                                         |                   |
|    |       | 623.1975            |                                                    |       |                                  |                                                                     |                                         |                   |
| 56 | 40.70 | [M+H] <sup>+</sup>  | C <sub>26</sub> H <sub>42</sub> NO <sub>6</sub>    | 1.110 | <b>432.2752</b><br>(100)         | [M+H-CH <sub>3</sub> OH] <sup>+</sup>                               | 14-acetylaltatisamine                   | FZ                |
|    |       | 464.3012            |                                                    |       |                                  |                                                                     |                                         |                   |
| 57 | 43.39 | [M+Na] <sup>+</sup> | C <sub>26</sub> H <sub>32</sub> O <sub>11</sub> Na | 1.633 | 381.1308<br>(29)                 | [M+Na-C <sub>6</sub> H <sub>10</sub> O <sub>5</sub> ] <sup>+</sup>  | pinoresinol-4-O-glucoside               | SZY/DZ/<br>DG/TSZ |
|    |       | 543.1846            |                                                    |       | <b>309.0945</b><br>(100)         | [M+Na-C <sub>13</sub> H <sub>14</sub> O <sub>4</sub> ] <sup>+</sup> |                                         |                   |
|    |       |                     |                                                    |       | 185.0420<br>(27)                 | [M+Na-C <sub>20</sub> H <sub>22</sub> O <sub>6</sub> ] <sup>+</sup> |                                         |                   |
|    | 42.81 | [M-H] <sup>-</sup>  | C <sub>26</sub> H <sub>31</sub> O <sub>11</sub>    | 2.122 | <b>357.1342</b><br>(100)         | [M-H-C <sub>6</sub> H <sub>10</sub> O <sub>5</sub> ] <sup>-</sup>   |                                         |                   |
|    |       | 519.7872            |                                                    |       |                                  |                                                                     |                                         |                   |
| 58 | 44.25 | [M+Na] <sup>+</sup> | C <sub>28</sub> H <sub>36</sub> O <sub>13</sub> Na | 1.356 | <b>441.1526</b><br>(100)         | [M+Na-C <sub>6</sub> H <sub>10</sub> O <sub>5</sub> ] <sup>+</sup>  | syringaresinol 4'-O-β-D-glucopyranoside | DZ                |

|    |       |                     |                                                    |        |                          |                                                                                                    |                                                 |     |
|----|-------|---------------------|----------------------------------------------------|--------|--------------------------|----------------------------------------------------------------------------------------------------|-------------------------------------------------|-----|
|    |       | 603.2056            |                                                    |        | 309.0948<br>(14)         | [M+Na-C <sub>15</sub> H <sub>18</sub> O <sub>6</sub> ] <sup>+</sup>                                |                                                 |     |
|    | 43.74 | [M-H] <sup>-</sup>  | C <sub>28</sub> H <sub>35</sub> O <sub>13</sub>    | -0.324 | <b>417.1552</b><br>(100) | [M-H-C <sub>6</sub> H <sub>10</sub> O <sub>5</sub> ] <sup>-</sup>                                  |                                                 |     |
|    |       | 579.2070            |                                                    |        |                          |                                                                                                    |                                                 |     |
| 59 | 44.91 | [M+Na] <sup>+</sup> | C <sub>21</sub> H <sub>20</sub> O <sub>11</sub> Na | 1.884  | <b>309.0373</b><br>(100) | [M+Na-C <sub>6</sub> H <sub>10</sub> O <sub>5</sub> ] <sup>+</sup>                                 | kaempferol 7-O-b-D-glucopyranoside <sup>a</sup> | TSZ |
|    |       | 471.0907            |                                                    |        | 185.0422<br>(19)         | [M+Na-C <sub>15</sub> H <sub>10</sub> O <sub>6</sub> ] <sup>+</sup>                                |                                                 |     |
| 60 | 46.00 | [M+Na] <sup>+</sup> | C <sub>22</sub> H <sub>22</sub> O <sub>12</sub> Na | 1.882  | <b>339.0480</b><br>(100) | [M+Na-C <sub>6</sub> H <sub>10</sub> O <sub>5</sub> ] <sup>+</sup>                                 | isorhamnetin 3-O-D-glucoside                    | TSZ |
|    |       | 501.1013            |                                                    |        | 185.0422<br>(13)         | [M+Na-C <sub>16</sub> H <sub>12</sub> O <sub>7</sub> ] <sup>+</sup>                                |                                                 |     |
|    | 45.38 | [M-H] <sup>-</sup>  | C <sub>22</sub> H <sub>21</sub> O <sub>12</sub>    | 2.175  | 357.0611<br>(25)         | [M-H-C <sub>4</sub> H <sub>8</sub> O <sub>4</sub> ] <sup>-</sup>                                   |                                                 |     |
|    |       | 477.1038            |                                                    |        | <b>315.0515</b><br>(100) | [M-H-C <sub>6</sub> H <sub>10</sub> O <sub>5</sub> ] <sup>-</sup>                                  |                                                 |     |
| 61 | 46.21 | [M+Na] <sup>+</sup> | C <sub>11</sub> H <sub>20</sub> O <sub>5</sub> Na  | 0.098  | -                        | -                                                                                                  | jioglutin F                                     | DH  |
|    |       | 255.1203            |                                                    |        |                          |                                                                                                    |                                                 |     |
| 62 | 46.55 | [M+Na] <sup>+</sup> | C <sub>24</sub> H <sub>30</sub> O <sub>14</sub> Na | 1.616  | 403.1003<br>(69)         | [M+Na-C <sub>6</sub> H <sub>10</sub> O <sub>5</sub> ] <sup>+</sup>                                 | cor-nuside I <sup>a</sup>                       | SZY |
|    |       | 565.1537            |                                                    |        | <b>333.0585</b><br>(100) | [M+Na-C <sub>6</sub> H <sub>10</sub> O <sub>5</sub> -C <sub>4</sub> H <sub>6</sub> O] <sup>+</sup> |                                                 |     |
|    | 46.00 | [M-H] <sup>-</sup>  | C <sub>24</sub> H <sub>29</sub> O <sub>14</sub>    | 1.863  | 379.1031<br>(50)         | [M-H-C <sub>6</sub> H <sub>10</sub> O <sub>5</sub> ] <sup>-</sup>                                  |                                                 |     |



|    |       |                                             |                                                    |        |                          |                                                                                                                                    |                                                                                             |       |
|----|-------|---------------------------------------------|----------------------------------------------------|--------|--------------------------|------------------------------------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------|-------|
|    |       | 541.1562                                    |                                                    |        | <b>347.0772</b><br>(100) | [M-H-C <sub>6</sub> H <sub>10</sub> O <sub>5</sub> -CH <sub>3</sub> OH] <sup>-</sup>                                               |                                                                                             |       |
|    |       |                                             |                                                    |        | 277.0714<br>(21)         | [M-H-C <sub>6</sub> H <sub>10</sub> O <sub>5</sub> -CH <sub>3</sub> OH-C <sub>3</sub> H <sub>2</sub> O <sub>2</sub> ] <sup>-</sup> |                                                                                             |       |
| 63 | 48.08 | [M+Na] <sup>+</sup><br>307.1520             | C <sub>15</sub> H <sub>24</sub> O <sub>5</sub> Na  | 1.253  | <b>289.1416</b><br>(100) | [M+Na-H <sub>2</sub> O] <sup>+</sup>                                                                                               | sec-hydroxyaegnetic acid                                                                    | DZ/DG |
| 64 | 48.52 | [M+H] <sup>+</sup>                          | C <sub>25</sub> H <sub>38</sub> NO <sub>6</sub>    | -3.512 | <b>404.2432</b><br>(100) | [M+H-C <sub>2</sub> H <sub>2</sub> -H <sub>2</sub> O] <sup>+</sup>                                                                 | 14-ethyl-4,6,19-trimethoxy-<br>16-methyl-9,11-dioxa-14-<br>azaheptacyclo-docosan-21-<br>one | FZ    |
| 65 | 51.25 | 448.2678<br>[M+Na] <sup>+</sup><br>547.1786 | C <sub>25</sub> H <sub>32</sub> O <sub>12</sub> Na | 0.096  | -                        | -                                                                                                                                  | 6-O-feruloyl ajugol                                                                         | DH    |
|    | 50.79 | [M-H] <sup>-</sup>                          | C <sub>25</sub> H <sub>31</sub> O <sub>12</sub>    | -0.770 | 361.1279<br>(14)         | [M-H-C <sub>6</sub> H <sub>10</sub> O <sub>5</sub> ] <sup>-</sup>                                                                  |                                                                                             |       |
|    |       | 523.1806                                    |                                                    |        | <b>193.0502</b><br>(100) | [M-H-C <sub>6</sub> H <sub>10</sub> O <sub>5</sub> -C <sub>9</sub> H <sub>12</sub> O <sub>3</sub> ] <sup>-</sup>                   |                                                                                             |       |
| 66 | 51.91 | [M+H] <sup>+</sup>                          | C <sub>31</sub> H <sub>44</sub> NO <sub>10</sub>   | 1.537  | <b>540.2601</b><br>(100) | [M+H-CH <sub>3</sub> OH-H <sub>2</sub> O] <sup>+</sup>                                                                             | benzoylmesaconitine <sup>a</sup>                                                            | FZ    |
|    |       | 590.2969                                    |                                                    |        | 508.2337<br>(22)         | [M+H-2CH <sub>3</sub> OH-H <sub>2</sub> O] <sup>+</sup>                                                                            |                                                                                             |       |
| 67 | 54.38 | [M+Na] <sup>+</sup>                         | C <sub>31</sub> H <sub>40</sub> O <sub>15</sub> Na | 1.005  | <b>529.1687</b><br>(100) | [M+Na-C <sub>6</sub> H <sub>10</sub> O <sub>4</sub> ] <sup>+</sup>                                                                 | martynoside                                                                                 | DH    |
|    |       | 675.2266                                    |                                                    |        | 481.1685<br>(8)          | [M+Na-C <sub>10</sub> H <sub>10</sub> O <sub>4</sub> ] <sup>+</sup>                                                                |                                                                                             |       |

|    |       |                     |                                                    |        |                          |                                                                                    |                                  |             |
|----|-------|---------------------|----------------------------------------------------|--------|--------------------------|------------------------------------------------------------------------------------|----------------------------------|-------------|
|    | 54.33 | [M-H] <sup>-</sup>  | C <sub>31</sub> H <sub>39</sub> O <sub>15</sub>    | -0.210 | 505.1702<br>(27)         | [M-H-C <sub>6</sub> H <sub>10</sub> O <sub>4</sub> ] <sup>-</sup>                  |                                  |             |
|    |       | 651.2282            |                                                    |        | <b>475.1812</b><br>(100) | [M-H-C <sub>10</sub> H <sub>8</sub> O <sub>3</sub> ] <sup>-</sup>                  |                                  |             |
|    |       |                     |                                                    |        | 457.1702<br>(23)         | [M-H-C <sub>10</sub> H <sub>8</sub> O <sub>3</sub> -H <sub>2</sub> O] <sup>-</sup> |                                  |             |
| 68 | 55.45 | [M+H] <sup>+</sup>  | C <sub>32</sub> H <sub>46</sub> NO <sub>10</sub>   | 0.740  | 572.2856<br>(44)         | [M+H-CH <sub>3</sub> OH] <sup>+</sup>                                              | benzoylaconitine <sup>a</sup>    | FZ          |
|    |       | 604.3121            |                                                    |        | <b>554.2753</b><br>(100) | [M+H-CH <sub>3</sub> OH-H <sub>2</sub> O] <sup>+</sup>                             |                                  |             |
|    |       |                     |                                                    |        | 522.2489<br>(13)         | [M+H-2CH <sub>3</sub> OH-H <sub>2</sub> O] <sup>+</sup>                            |                                  |             |
| 69 | 57.16 | [M+Na] <sup>+</sup> | C <sub>24</sub> H <sub>30</sub> O <sub>12</sub> Na | 1.299  | -                        | -                                                                                  | 6-O-E-caffeoyl ajugol            | DZ          |
|    |       | 533.1636            |                                                    |        |                          |                                                                                    |                                  |             |
| 70 | 57.27 | [M+H] <sup>+</sup>  | C <sub>31</sub> H <sub>44</sub> NO <sub>9</sub>    | 0.682  | <b>542.2747</b><br>(100) | [M+H-CH <sub>3</sub> OH] <sup>+</sup>                                              | benzoylhypaconitine <sup>a</sup> | FZ          |
|    |       | 574.3015            |                                                    |        | 510.2484<br>(27)         | [M+H-2CH <sub>3</sub> OH] <sup>+</sup>                                             |                                  |             |
| 71 | 58.65 | [M+H] <sup>+</sup>  | C <sub>15</sub> H <sub>11</sub> O <sub>7</sub>     | 1.290  | 285.0396<br>(56)         | [M+H-H <sub>2</sub> O] <sup>+</sup>                                                | quercetin <sup>a</sup>           | GQZ/TS<br>Z |
|    |       | 303.0500            |                                                    |        | <b>257.0448</b><br>(100) | [M+H-H <sub>2</sub> O-CO] <sup>+</sup>                                             |                                  |             |
|    |       |                     |                                                    |        | 229.0497<br>(70)         | [M+H-H <sub>2</sub> O-2CO] <sup>+</sup>                                            |                                  |             |
|    | 58.57 | [M-H] <sup>-</sup>  | C <sub>15</sub> H <sub>9</sub> O <sub>7</sub>      | 3.225  | <b>273.0397</b><br>(100) | [M-H-CO] <sup>-</sup>                                                              |                                  |             |

|    |       |                                 |                                                    |        |                          |                                                                                                                  |                                 |               |
|----|-------|---------------------------------|----------------------------------------------------|--------|--------------------------|------------------------------------------------------------------------------------------------------------------|---------------------------------|---------------|
|    |       | 301.0352                        |                                                    |        | 257.0448<br>(88)         | [M-H-CO <sub>2</sub> ] <sup>-</sup>                                                                              |                                 |               |
|    |       |                                 |                                                    |        | 229.0499<br>(23)         | [M-H-CO <sub>2</sub> -CO] <sup>-</sup>                                                                           |                                 |               |
| 72 | 59.29 | [M+Na] <sup>+</sup><br>559.2518 | C <sub>28</sub> H <sub>40</sub> O <sub>10</sub> Na | 0.718  | -                        | -                                                                                                                | rehmannia terpene C             | DH            |
| 73 | 60.03 | [M+H] <sup>+</sup>              | C <sub>20</sub> H <sub>21</sub> O <sub>5</sub>     | -0.206 | <b>323.1283</b><br>(100) | [M+H-H <sub>2</sub> O] <sup>+</sup>                                                                              | hancinone                       | DZ/TSZ/<br>RG |
|    |       | 341.1387                        |                                                    |        | 271.0969<br>(42)         | [M+H-H <sub>2</sub> O-C <sub>4</sub> H <sub>4</sub> ] <sup>+</sup>                                               |                                 |               |
|    |       |                                 |                                                    |        | 137.0598<br>(19)         | [M+H-H <sub>2</sub> O-C <sub>4</sub> H <sub>4</sub> -C <sub>8</sub> H <sub>6</sub> O <sub>2</sub> ] <sup>+</sup> |                                 |               |
| 74 | 60.35 | [M+Na] <sup>+</sup><br>291.1571 | C <sub>15</sub> H <sub>24</sub> O <sub>4</sub> Na  | 1.578  | -                        | -                                                                                                                | aeginetic acid                  | DZ            |
| 75 | 61.62 | [M+Na] <sup>+</sup>             | C <sub>13</sub> H <sub>22</sub> O <sub>3</sub> Na  | 0.298  | <b>231.1328</b><br>(100) | [M+Na-H <sub>2</sub> O] <sup>+</sup>                                                                             | dihydroxy-β-ionone              | DH            |
|    |       | 249.1462                        |                                                    |        | 161.0960<br>(51)         | [M+Na-H <sub>2</sub> O-C <sub>4</sub> H <sub>6</sub> O] <sup>+</sup>                                             |                                 |               |
|    | 60.53 | [M-H] <sup>-</sup>              | C <sub>12</sub> H <sub>17</sub> O <sub>4</sub>     | 2.596  | <b>207.1025</b><br>(100) | [M-H-H <sub>2</sub> O] <sup>-</sup>                                                                              |                                 |               |
|    |       | 225.1127                        |                                                    |        | 181.1231<br>(29)         | [M-H-CO <sub>2</sub> ] <sup>-</sup>                                                                              |                                 |               |
| 76 | 61.62 | [M+Na] <sup>+</sup>             | C <sub>26</sub> H <sub>28</sub> O <sub>12</sub> Na | 0.077  | -                        | -                                                                                                                | 9-hydroxy-d-sesamin-O-glucoside | TSZ           |
|    |       | 555.1473                        |                                                    |        |                          |                                                                                                                  |                                 |               |
|    | 61.58 | [M+HCOOH-H] <sup>-</sup>        | C <sub>27</sub> H <sub>29</sub> O <sub>14</sub>    | -0.367 | <b>531.1494</b>          | [M-H] <sup>-</sup>                                                                                               |                                 |               |

|    |       |                    |                                                   |       |                 |                                                                                                                 |                                                             |                                        |
|----|-------|--------------------|---------------------------------------------------|-------|-----------------|-----------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------|----------------------------------------|
|    |       |                    |                                                   |       | (100)           |                                                                                                                 |                                                             |                                        |
|    |       | 577.1550           |                                                   |       | 369.0907        | [M-H-C <sub>6</sub> H <sub>10</sub> O <sub>5</sub> ] <sup>-</sup>                                               |                                                             |                                        |
|    |       |                    |                                                   |       | (67)            |                                                                                                                 |                                                             |                                        |
|    |       |                    |                                                   |       | 219.0658        | [M-H-C <sub>6</sub> H <sub>10</sub> O <sub>5</sub> -C <sub>8</sub> H <sub>6</sub> O <sub>3</sub> ] <sup>-</sup> |                                                             |                                        |
|    |       |                    |                                                   |       | (25)            |                                                                                                                 |                                                             |                                        |
| 77 | 64.36 | [M+H] <sup>+</sup> | C <sub>15</sub> H <sub>11</sub> O <sub>6</sub>    | 1.413 | 241.0498        | [M+H-H <sub>2</sub> O-CO] <sup>+</sup>                                                                          | kaempferol                                                  | TSZ                                    |
|    |       |                    |                                                   |       | (98)            |                                                                                                                 |                                                             |                                        |
|    |       | 287.0554           |                                                   |       | 213.0547        | [M+H-H <sub>2</sub> O-2CO] <sup>+</sup>                                                                         |                                                             |                                        |
|    |       |                    |                                                   |       | (73)            |                                                                                                                 |                                                             |                                        |
|    |       |                    |                                                   |       | <b>165.0183</b> | [M+H-C <sub>7</sub> H <sub>6</sub> O <sub>2</sub> ] <sup>+</sup>                                                |                                                             |                                        |
|    |       |                    |                                                   |       | (100)           |                                                                                                                 |                                                             |                                        |
|    | 64.10 | [M-H] <sup>-</sup> | C <sub>15</sub> H <sub>9</sub> O <sub>6</sub>     | 2.896 | <b>257.0447</b> | [M-H-CO] <sup>-</sup>                                                                                           |                                                             |                                        |
|    |       |                    |                                                   |       | (100)           |                                                                                                                 |                                                             |                                        |
|    |       | 285.0402           |                                                   |       | 229.0500        | [M-H-2CO] <sup>-</sup>                                                                                          |                                                             |                                        |
|    |       |                    |                                                   |       | (98)            |                                                                                                                 |                                                             |                                        |
| 78 | 65.19 | [M+H] <sup>+</sup> | C <sub>16</sub> H <sub>13</sub> O <sub>7</sub>    | 0.602 | <b>285.0397</b> | [M+H-CH <sub>3</sub> OH] <sup>+</sup>                                                                           | isorhamnetin                                                | TSZ                                    |
|    |       |                    |                                                   |       | (100)           |                                                                                                                 |                                                             |                                        |
|    |       | 317.0658           |                                                   |       | 261.0759        | [M+H-2CO] <sup>+</sup>                                                                                          |                                                             |                                        |
|    |       |                    |                                                   |       | (25)            |                                                                                                                 |                                                             |                                        |
|    | 65.08 | [M-H] <sup>-</sup> | C <sub>16</sub> H <sub>11</sub> O <sub>7</sub>    | 1.558 | <b>287.0555</b> | [M-H-H <sub>2</sub> O] <sup>-</sup>                                                                             |                                                             |                                        |
|    |       |                    |                                                   |       | (100)           |                                                                                                                 |                                                             |                                        |
|    |       | 315.0504           |                                                   |       |                 |                                                                                                                 |                                                             |                                        |
| 79 | 65.51 | [M+H] <sup>+</sup> | C <sub>18</sub> H <sub>34</sub> O <sub>5</sub> Na | 1.429 | <b>335.2196</b> | [M+H-H <sub>2</sub> O] <sup>+</sup>                                                                             | hexanedioic acid,1-(2-ethylhexyl) 6-(3-methoxypropyl) ester | DH/SZY/<br>DZ/DG/<br>GQZ/TS<br>Z/SY/RG |
|    |       |                    |                                                   |       | (100)           |                                                                                                                 |                                                             |                                        |

|    |       |                          |                                                    |        |                          |                                                                                                                                                                     |                                                                                                                            |     |
|----|-------|--------------------------|----------------------------------------------------|--------|--------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------|-----|
|    |       | 353.2303                 |                                                    |        | 235.1305<br>(28)         | [M+H-H <sub>2</sub> O-C <sub>6</sub> H <sub>12</sub> O] <sup>+</sup>                                                                                                |                                                                                                                            |     |
|    | 65.51 | [M-H] <sup>-</sup>       | C <sub>18</sub> H <sub>33</sub> O <sub>5</sub>     | 2.458  | 311.2226<br>(29)         | [M-H-H <sub>2</sub> O] <sup>-</sup>                                                                                                                                 |                                                                                                                            |     |
|    |       | 329.2331                 |                                                    |        | <b>229.1443</b><br>(100) | [M-H-C <sub>6</sub> H <sub>12</sub> O] <sup>-</sup>                                                                                                                 |                                                                                                                            |     |
|    |       |                          |                                                    |        | 211.1338<br>(67)         | [M-H-H <sub>2</sub> O-C <sub>6</sub> H <sub>12</sub> O] <sup>-</sup>                                                                                                |                                                                                                                            |     |
| 80 | 69.28 | [M+Na] <sup>+</sup>      | C <sub>39</sub> H <sub>68</sub> O <sub>19</sub> Na | 1.319  | <b>745.3627</b><br>(100) | [M+Na-C <sub>5</sub> H <sub>10</sub> O <sub>3</sub> ] <sup>+</sup>                                                                                                  | 6-deoxy- $\alpha$ -L-<br>mannopyranosyl-6-deoxy-<br>4-O-2-O- $\alpha$ -L-<br>mannopyranosyl-6-O-<br>acetyl-D-glucopyranose | TSZ |
|    |       | 863.4258                 |                                                    |        | 701.3728<br>(44)         | [M+Na-C <sub>6</sub> H <sub>10</sub> O <sub>5</sub> ] <sup>+</sup>                                                                                                  |                                                                                                                            |     |
|    |       |                          |                                                    |        | 495.2935<br>(15)         | [M+Na-C <sub>6</sub> H <sub>10</sub> O <sub>5</sub> -C <sub>5</sub> H <sub>10</sub> O <sub>2</sub> -<br>C <sub>3</sub> H <sub>4</sub> O <sub>4</sub> ] <sup>+</sup> |                                                                                                                            |     |
|    | 69.26 | [M+HCOOH-H] <sup>-</sup> | C <sub>40</sub> H <sub>69</sub> O <sub>21</sub>    | -0.029 | 659.3638<br>(37)         | [M-H-C <sub>6</sub> H <sub>10</sub> O <sub>5</sub> -H <sub>2</sub> O] <sup>-</sup>                                                                                  |                                                                                                                            |     |
|    |       | 885.4326                 |                                                    |        | <b>633.3491</b><br>(100) | [M-H-C <sub>6</sub> H <sub>10</sub> O <sub>5</sub> -H <sub>2</sub> O-C <sub>2</sub> H <sub>2</sub> ] <sup>-</sup>                                                   |                                                                                                                            |     |
| 81 | 74.14 | [M+H] <sup>+</sup>       | C <sub>16</sub> H <sub>36</sub> NO <sub>2</sub>    | 1.656  | <b>256.2639</b><br>(100) | [M+H-H <sub>2</sub> O] <sup>+</sup>                                                                                                                                 | 2-propanol,1,1'-<br>(decylimino)bis-                                                                                       | FZ  |
|    |       | 274.2745                 |                                                    |        |                          |                                                                                                                                                                     |                                                                                                                            |     |
| 82 | 74.96 | [M+H] <sup>+</sup>       | C <sub>18</sub> H <sub>40</sub> NO <sub>3</sub>    | 1.789  | 300.2903<br>(11)         | [M+H-H <sub>2</sub> O] <sup>+</sup>                                                                                                                                 | ethanol,2,2'-[2-<br>(dodecyloxy)ethyl]imino]bi                                                                             | FZ  |

|    |       |           |                     |       |                          |                          |             |                                        |
|----|-------|-----------|---------------------|-------|--------------------------|--------------------------|-------------|----------------------------------------|
|    |       |           |                     |       |                          |                          | s-(9Cl)     |                                        |
|    |       | 318.3008  |                     |       | <b>256.2640</b><br>(100) | $[M+H-2H_2O-C_2H_2]^+$   |             |                                        |
| 83 | 86.84 | $[M+H]^+$ | $C_{24}H_{30}O_6Na$ | 1.716 | 407.1833<br>(8)          | $[M+H-C_2H_2O]^+$        | magnoshinin | DH/SZY/<br>DZ/DG/<br>GQZ/TS<br>Z/SY/RG |
|    |       | 437.1942  |                     |       | <b>303.1208</b><br>(100) | $[M+H-C_2H_2O-C_8H_8]^+$ |             |                                        |

<sup>a)</sup> Structures was confirmed by comparing retention time and high-resolution accurate mass with reference standards.

Bold characters: the base peaks in MS/MS spectra.