

**Table S1. Chromatographic conditions for amino acids, astragalosides and flavonoids**

|   | Detection of amino acids   | Detection of astragalosides   | Detection of flavonoids                       |
|---|--|---|---|
| Distance from lower edge of plate           | 8.0 mm   | 8.0 mm  | 8.0 mm  |
| Distance from left and right edges of plate | 20 mm  | 23 mm   | 25 mm   |
| Space between bands                         | 15 mm  | 13.5 mm   | 16.6 mm                                       |
| Track number per plate                      | 5  | 5   | 4   |
| Development distance                        | 50 mm  | 70 mm   | 70 mm   |
| Development temperature                     | 27.2 C   | 27.8°C  | 22.7°C  |
| Development relative humidity               | 36.5%  | 35.5%   | 36.5%   |
| Mobile phase                                | Butanol/ acetone/ acetic acid/ water (7/7/2/1) with 50.2 mg of ninhydrin | Ethyl acetate/methanol/water (50/6.75/5)  | Ethyl acetate/toluene/formic acid (15/35/0.5) |
| Derivatization                              | Through heating to 100°C for 5 min                                       | Through heating to 105°C for 3 min on a TLC plate heater and dipping (speed: 5, time: 0) in NP reagent then PEG reagent | No derivatization                             |
| Visualization                               | Under white light  | Under UV light at 366 nm  | Under UV light at 366 nm                      |

NP: natural product; PEG: polyethylene glycol; TLC: thin layer chromatography; UV: ultraviolet

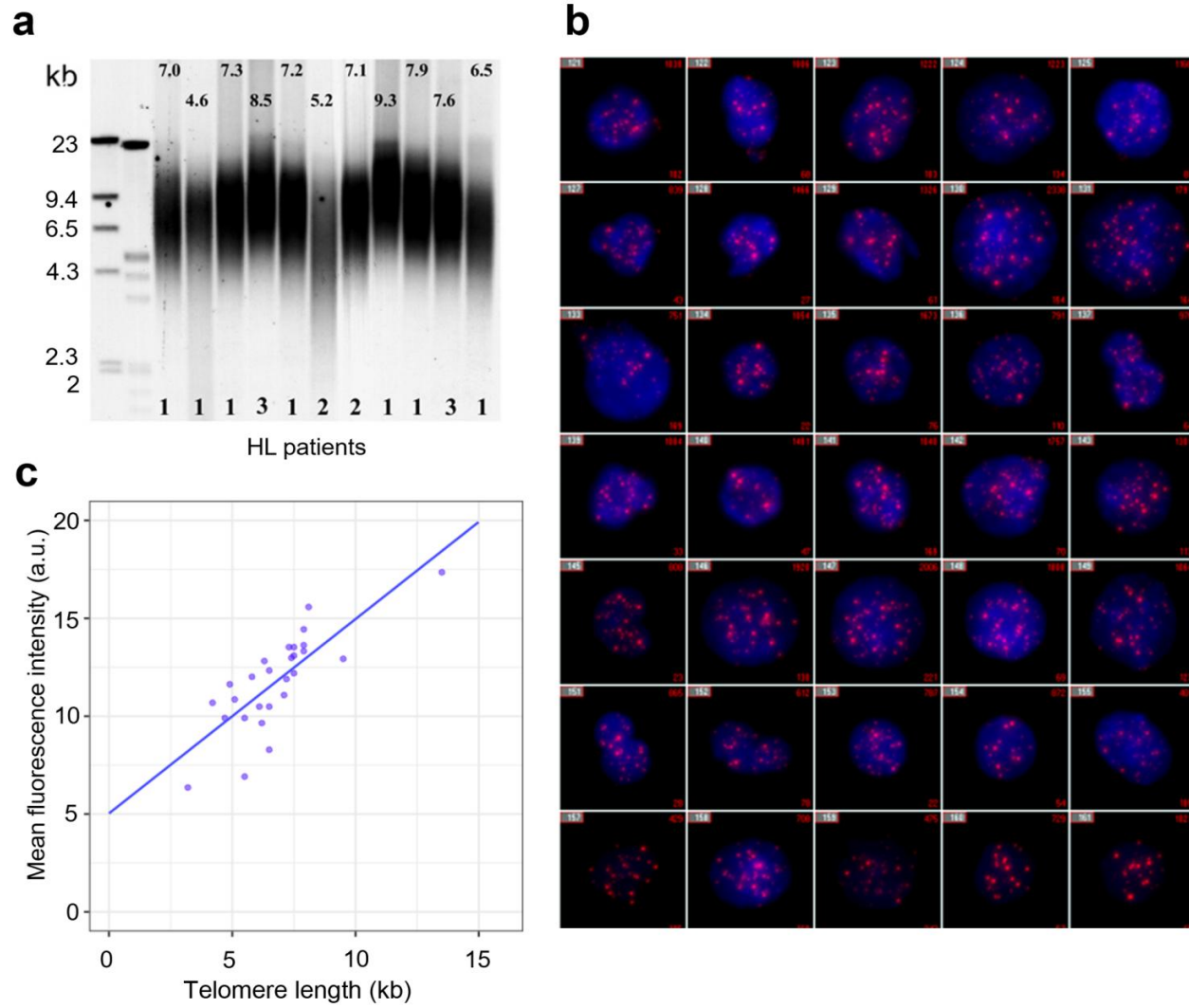
**Table S2: Compounds identified using liquid chromatography with mass spectrometry (LC-MS) in the positive ion mode**

| No. | t <sub>R</sub>  | Compound                    | Formula  | Mass     | Ion m/z<br>M+H<br>theoretical | M+H<br>(MS) | M+H (MS/MS)            | Ref.     | M+H standard or<br>reference<br>(MS/MS) |
|-----|-----------------|-----------------------------|--|----------|-------------------------------|-------------|------------------------|----------|---|
| 1   | 2.76            | L-canavanine                | C <sub>5</sub> H <sub>12</sub> N <sub>4</sub> O <sub>3</sub> | 176.0909 | 177.0982                      | 177.0979    | (177)76/160/118/72/102 | [49][50] | 76<br>76/118/190/102/72                 |
| 2   | 2.99            | asparagine                  | C <sub>4</sub> H <sub>8</sub> N <sub>2</sub> O <sub>3</sub>  | 132.0535 | 133.0608                      | 133.0606    | (133)74/87/116         | [49][51] | 116<br>74/87                            |
| 3   | 3.04            | aspartic acid               | C <sub>4</sub> H <sub>7</sub> NO <sub>4</sub>                | 133.0375 | 134.0448                      | 134.0446    | 88                     | [49]     | 88                                      |
| 4   | 3.26            | glutamic acid               | C <sub>5</sub> H <sub>9</sub> NO <sub>4</sub>                | 147.0532 | 148.0604                      | 148.0602    | (148)84/102/130        | [49,52]  | 102<br>84/102/130                       |
| 5   | 6.57<br>ou 6.71 | leucine                     | C <sub>6</sub> H <sub>13</sub> NO <sub>2</sub>               | 131.0947 | 132.1019                      | 132.1018    | 86                     | [49]     | 86                                      |
| 6   | 6.57<br>ou 6.71 | isoleucine                  | C <sub>6</sub> H <sub>13</sub> NO <sub>2</sub>               | 131.0947 | 132.1019                      | 132.1018    | 86                     | [49]     | 86                                      |
| 7   | 11.19           | calycosin-7-o-β-D-glucoside | C <sub>22</sub> H <sub>22</sub> O <sub>10</sub>              | 446.1213 | 447.1286                      | 447.1280    | See negative ion mode  |          |   |
| 8   | 13.47           | ononine                     | C <sub>22</sub> H <sub>22</sub> O <sub>9</sub>               | 430.1264 | 431.1337                      | 431.1329    | See negative ion mode  |          |   |
| 9   | 14.95           | calycosine                  | C <sub>16</sub> H <sub>12</sub> O <sub>5</sub>               | 284.0685 | 285.0757                      | 285.0751    | See negative ion mode  |          |   |
| 10  | 16.06           | astragaloside IV            | C <sub>41</sub> H <sub>68</sub> O <sub>14</sub>              | 784.4609 | 785.4682                      | 785.4668    | See negative ion mode  |          |   |
| 11  | 16.31           | astragaloside III           | C <sub>41</sub> H <sub>68</sub> O <sub>14</sub>              | 784.4609 | 785.4682                      | 785.4677    | See negative ion mode  |          |   |
| 12  | 17.27           | astragaloside II            | C <sub>43</sub> H <sub>70</sub> O <sub>15</sub>              | 826.4715 | 827.4787                      | 827.4775    | See negative ion mode  |          |   |
| 13  | 17.92           | formononetin                | C <sub>16</sub> H <sub>12</sub> O <sub>4</sub>               | 268.0736 | 269.0808                      | 269.0803    | See negative ion mode  |          |   |

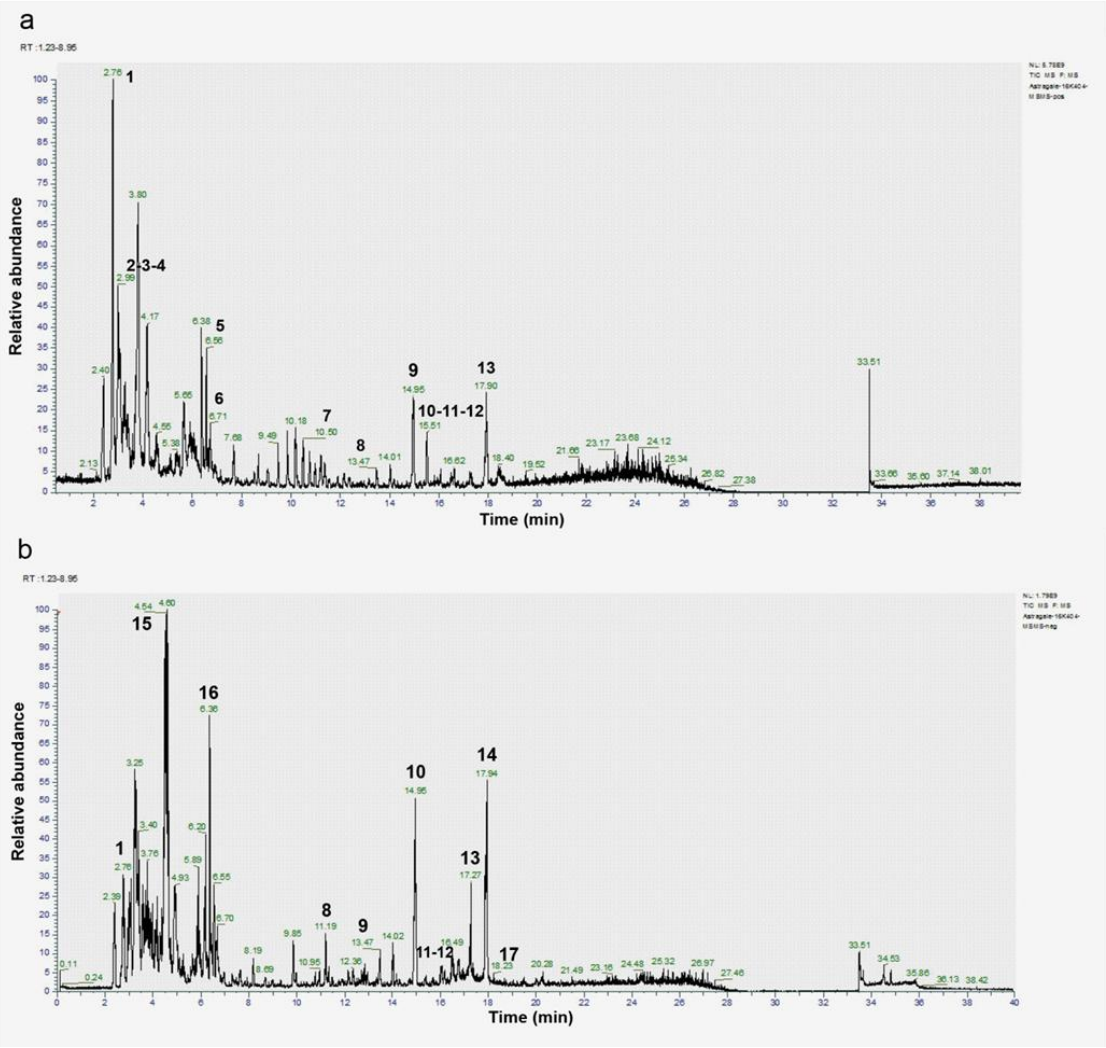
**Table S3: Compounds identified using liquid chromatography with mass spectrometry (LC-MS) in the negative ion mode**\*M+HCOO<sup>-</sup>; STD: standard

| No. | t <sub>R</sub> | Compound                    | Formula  | Mass     | Ion m/z [M-H] <sup>-</sup><br>(theoretical) | Ion m/z [M-H] <sup>-</sup><br>(experimental) | Ion m/z [M-H] <sup>-</sup><br>(MS/MS) | Ref  | Ion m/z [M-H] <sup>-</sup><br>standard or ref<br>(MS/MS) |
|-----|----------------|-----------------------------|--|----------|---|--|---------------------------------------|------|--|
| 1   | 2.76           | L-canavanine                | C <sub>5</sub> H <sub>12</sub> N <sub>4</sub> O <sub>3</sub> | 176.0909 | 175.0837                                    | 175.0830                                     | See positive ion mode                 |      |  |
| 15  | 4.54           | Saccharose                  | C <sub>12</sub> H <sub>22</sub> O <sub>11</sub>              | 342.1162 | 341.1089                                    | 341.1088                                     | (341)89/59/71/179/119/101/113         | [53] | (341)71/89/101/179/59/113/119                            |
| 16  | 6.36           | citric acid                 | C <sub>6</sub> H <sub>8</sub> O <sub>7</sub>                 | 192.0270 | 191.0197                                    | 191.0189                                     | (191)111/87/85                        | STD  | (191)111/87/85   |
| 8   | 11.19          | calycosin-7-O-β-D-glucoside | C <sub>22</sub> H <sub>22</sub> O <sub>10</sub>              | 446.1213 | 445.1140                                    | 491.1199*                                    | 283/268                               | [54] | 283  |
| 9   | 13.44          | Ononine                     | C <sub>22</sub> H <sub>22</sub> O <sub>9</sub>               | 430.1264 | 429.1191                                    | 475.1246*                                    | 267/252                               | [54] | 267  |
| 10  | 14.95          | Calycosine                  | C <sub>16</sub> H <sub>12</sub> O <sub>5</sub>               | 284.0685 | 283.0612                                    | 283.0612                                     | (283)268                              | [54] | 268  |
| 11  | 16.06          | astragaloside IV            | C <sub>41</sub> H <sub>68</sub> O <sub>14</sub>              | 784.4609 | 783.4536                                    | 829.4601*                                    | (829)783/59/89/101/119/71/179/113/161 | STD  | (829)783/89/101/59/71/119/179/161/113                    |
| 12  | 16.31          | astragaloside III           | C <sub>41</sub> H <sub>68</sub> O <sub>14</sub>              | 784.4609 | 783.4536                                    | 829.4600*                                    | 873/71/101/113/85/161/59/489          | [54] | 161/101/489  |
| 13  | 17.27          | astragaloside II            | C <sub>43</sub> H <sub>70</sub> O <sub>15</sub>              | 826.4715 | 825.4642                                    | 871.4705*                                    | (871/825)59/89/101/179/71/161/766     | [54] | 766/59/179   |
| 14  | 17.94          | Formononetin                | C <sub>16</sub> H <sub>12</sub> O <sub>4</sub>               | 268.0736 | 267.0663                                    | 267.0664                                     | (267)252                              | STD  | 252  |
| 17  | 18.51          | astragaloside I             | C <sub>45</sub> H <sub>72</sub> O <sub>16</sub>              | 868.4820 | 867.4748                                    | 867.4750                                     | 59                                    | [54] | 807/59   |

FigS1.



FigS2.



FigS3.

