

Supporting Information

Matrix-Assisted ^1H DOSY Applied to Flavonoid Analysis in *Scutellaria baicalensis*

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Mass spectrometry analysis and test conditions

Chromatographic column: Extend-C₁₈ column (150 mm × 4.6 mm i.d., 5 μm; Agela Technologies); connected C₁₈ guard column (4.0 mm × 3.0 mm i.d., 5 μm; Phenomenex). Liquid phase conditions: aqueous solution containing 0.1% formic acid was used as the A phase and acetonitrile was used as the B phase; the gradient elution conditions used were: 0-22 min: 10%-90% B; 22-24 min: 90%-10% B; the flow rate was set to 1 mL/min and the column temperature was set to 25 °C.

Mass spectrometry parameters: Mass spectrometry was performed in positive ion mode, and the instrument was calibrated by external standard method with mass accuracy less than 3 ppm. Ionization voltage was set to 4.0 kV, capillary temperature was set to 320 °C, and nitrogen was used as sheath gas (40 units) and auxiliary gas (5 units). The resolution of primary full scan of the instrument was set to 15000, and the resolution of secondary full scan was set to 7500. The [M + H]⁺ or [M+NH₄]⁺ ions were used as parent ions were dissociated in the high-energy cleavage (HCD) mode at 50% of the normalized collision energy, with a separation width of 3 Da and a reaction time of 30 ms.

Table S1

The results obtained by mass spectrometric analysis of total flavonoid extract of *S. baicalensis* for compound search.

| No. | Name | Formula | Molecular Weight |
|-----|---|---|------------------|
| 1 | (2R,3S,4S,5R,6R)-5-{{(2S,3R,4R)-3,4-dihydroxy-4-(hydroxymethyl) oxolan-2-yl} oxy}-2-(hydroxymethyl)-6-[2-(4-hydroxyphenyl) ethoxy] oxane-3,4-diol | C ₁₉ H ₂₈ O ₁₁ | 449.18974 |
| 2 | (2S,3S,4S,5R,6S)-3,4,5-trihydroxy-6-[(5-hydroxy-8-methoxy-4-oxo-2-phenyl-4H-chromen-7-yl) oxy] oxane-2-carboxylic acid | C ₂₂ H ₂₀ O ₁₁ | 460.1007 |
| 3 | 2-(3,4-Dihydroxyphenyl) ethyl 3-O-(6-deoxy-β-L-mannopyranosyl)-6-O-[(2E)-3-(3,4-dihydroxyphenyl)-2-propenoyl]-β-D-glucopyranoside | C ₂₉ H ₃₆ O ₁₅ | 641.23198 |
| 4 | 3-C-Methylfluteolin 5-rhamnoside | C ₂₂ H ₂₂ O ₁₀ | 446.11965 |
| 5 | 5,2'-Dihydroxy-6,7,8,6'-tetramethoxyflavone | C ₁₉ H ₁₈ O ₈ | 374.10058 |
| 6 | 5,3',4',5'-Tetrahydroxy-6,7-dimethoxyflavone | C ₁₇ H ₁₄ O ₈ | 346.06914 |
| 7 | 5,6,7-trihydroxy-2-(4-methoxyphenyl)-4H-chromen-4-one | C ₁₆ H ₁₂ O ₆ | 300.06352 |
| 8 | 5,7-dihydroxy-2-phenyl-6-[3,4,5-trihydroxy-6-(hydroxymethyl) oxan-2-yl]-8-(3,4,5-trihydroxyoxan-2-yl)-4H-chromen-4-one | C ₂₆ H ₂₈ O ₁₃ | 548.15318 |
| 9 | 5,7-dihydroxy-3-(4-hydroxyphenyl)-6-methoxy-4H-chromen-4-one | C ₁₆ H ₁₂ O ₆ | 300.06352 |
| 10 | 5,7-dihydroxy-3,8-dimethoxy-2-phenyl-4H-chromen-4-one | C ₁₇ H ₁₄ O ₆ | 314.08037 |
| 11 | 5,7-Dihydroxy-4'-methoxy-3-O-acetylflavanone | C ₁₈ H ₁₆ O ₇ | 344.09108 |
| 12 | 5-hydroxy-2-(4-hydroxyphenyl)-6-methoxy-7-{{(2S,3R,4S,5S,6R)-3,4,5-trihydroxy-6-(hydroxymethyl) oxan-2-yl} oxy}-4H-chromen-4-one | C ₂₂ H ₂₂ O ₁₁ | 462.11574 |
| 13 | 6-O-Methylscutellarin | C ₂₂ H ₂₀ O ₁₂ | 476.09508 |
| 14 | Adenosine | C ₁₀ H ₁₃ N ₅ O ₄ | 267.09722 |
| 15 | Apigenin | C ₁₅ H ₁₀ O ₅ | 270.05282 |
| 16 | Apigenin 7-O-glucuronide | C ₂₁ H ₁₈ O ₁₁ | 446.0847 |
| 17 | Aureusin | C ₂₁ H ₂₀ O ₁₁ | 448.10068 |
| 18 | Baicalin | C ₂₁ H ₁₈ O ₁₁ | 446.08476 |
| 19 | Chrysin | C ₁₅ H ₁₀ O ₄ | 254.05831 |
| 20 | Cirsiliol | C ₁₇ H ₁₄ O ₇ | 330.07454 |
| 21 | D - (+)-Maltose | C ₁₂ H ₂₂ O ₁₁ | 364.09786 |
| 22 | DL-Tryptophan | C ₁₁ H ₁₂ N ₂ O ₂ | 204.08978 |
| 23 | Eupatilin | C ₁₈ H ₁₆ O ₇ | 344.08934 |
| 24 | Genistin | C ₂₁ H ₂₀ O ₁₀ | 432.10558 |

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|----|--------------------------------|---|-----------|
| 25 | Genistein | C ₁₅ H ₁₀ O ₅ | 270.05318 |
| 26 | Apigenin | C ₂₁ H ₂₀ O ₁₀ | 432.10558 |
| 27 | Isovitexin 2"-O-rhamnoside | C ₂₇ H ₃₀ O ₁₄ | 578.16326 |
| 28 | L-Tyrosine | C ₉ H ₁₁ NO ₃ | 181.07367 |
| 29 | Luteolin | C ₁₅ H ₁₀ O ₆ | 286.04799 |
| 30 | Palmitic Acid | C ₁₆ H ₃₂ O ₂ | 273.26692 |
| 31 | Pectolinarigenin 7-glucuronide | C ₂₃ H ₂₂ O ₁₂ | 490.11046 |
| 32 | Phytosphingosine | C ₁₈ H ₃₉ NO ₃ | 317.29317 |
| 33 | Puerarin | C ₂₁ H ₂₀ O ₉ | 416.11064 |
| 34 | Puerarin 4'-O-glucoside | C ₂₇ H ₃₀ O ₁₄ | 578.16319 |
| 35 | Scutellarin | C ₂₁ H ₁₈ O ₁₂ | 462.07961 |
| 36 | Vigabatrin | C ₆ H ₁₁ NO ₂ | 129.07884 |
| 37 | Wogonin | C ₁₆ H ₁₂ O ₅ | 284.06905 |
| 38 | α-Lactose | C ₁₂ H ₂₂ O ₁₁ | 359.14327 |

Figure S1

The mass spectra of several compounds in *S. baicalensis* extract

