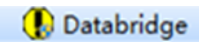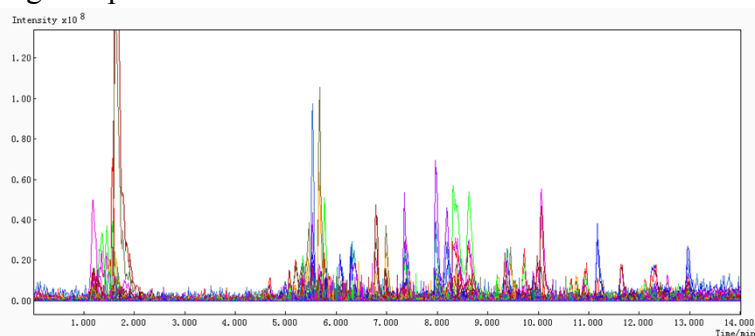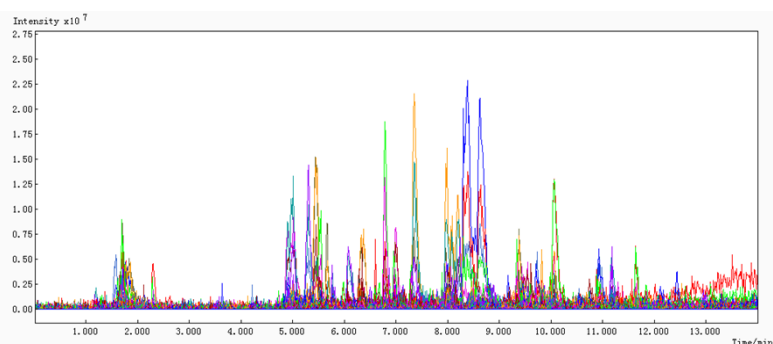# 1 Supplementary information 1

2

3 1. Firstly, the UPLC-MS data was converted to NetCDF or ASCII format using databridge

4 , then, the files with Matlab format were obtained using our software, in which

5 different ion curves could be observed, similarly to GC-MS data. Certainly, other methods were
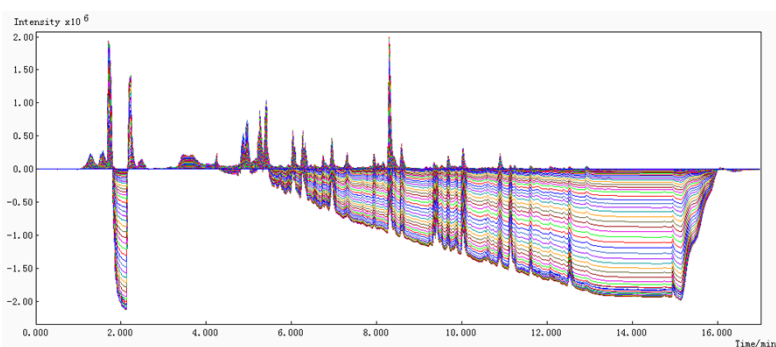
6 also feasible.

7 Fig 1-a: positive modes

8
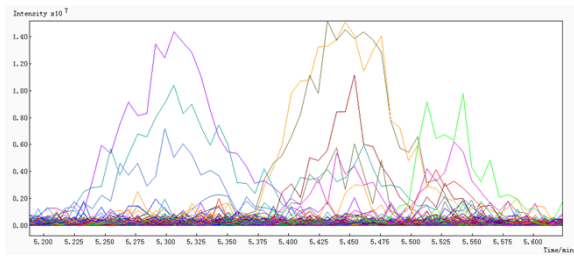
9 Fig 1-b: negative modes
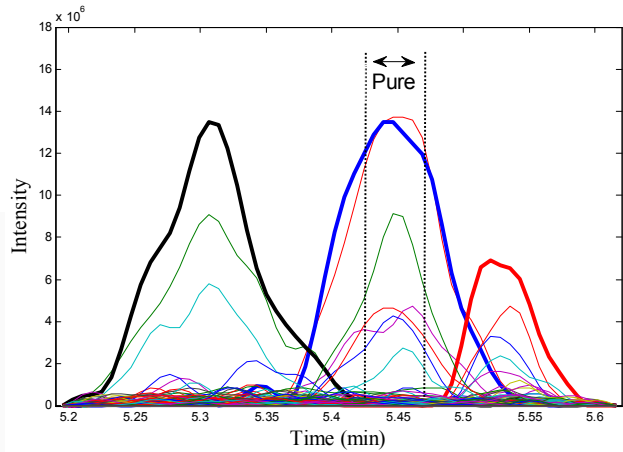

10

11 Fig 1-c: PDA

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13

14 2. Secondly, the background was deducted and smoothing was conducted using the ordinary

15 linear deduction. Certainly, other software could be used, including MZ mine 2 (free).

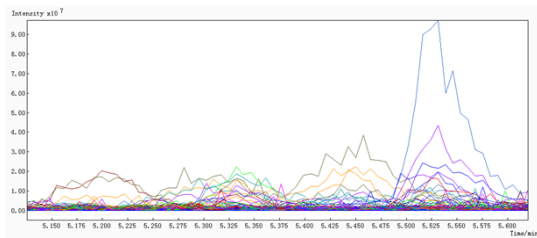16 The figure (left) before treatment and the figure (right) after treatment can be seen below.
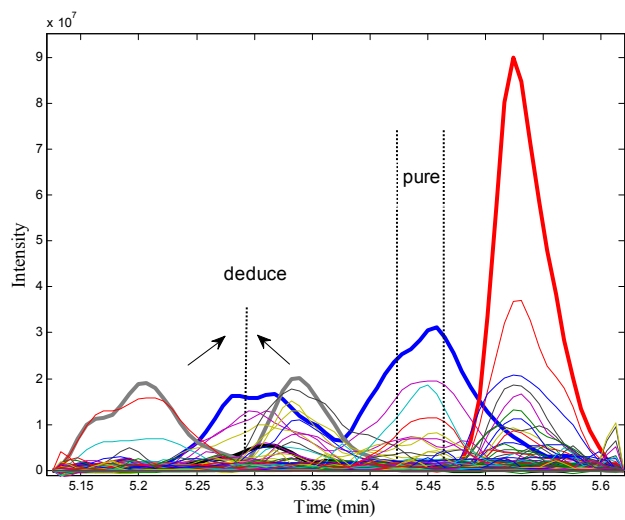
17

18 Fig 2a

1

Fig 2b

3. Now, an example is shown, which is the segment in the range of 5.16-5.62 min taken from the negative ion mode. The rankmap on the basis of the eigenstructure tracking analysis, which can be seen below, and the selective regions (pure component) marked with 1, 2 and 3 could be clearly observed. The zero component region of each component was also determined, being the detailed steps described in the references.[11,12]

Fig 3
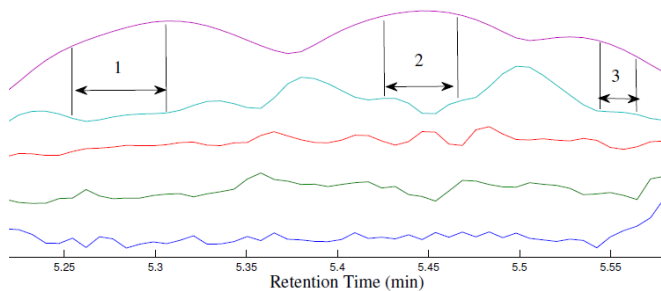
4. Maybe the program about the rankmap can't be written, a simple method can be introduced. As

31 a precondition, the visualization of all ions should be conducted in Matlab or other suitable
32 software. The "pure" zone can be observed in figure below, and the corresponding mass spectrum
33 can be obtained, that is vertical column in the matrix. For some zones with interferences (grey),
34 the ion ascription can be evaluated according to the simple inference, such as "deduce" zone
35 (5.31 min), interfered by two grey peaks.
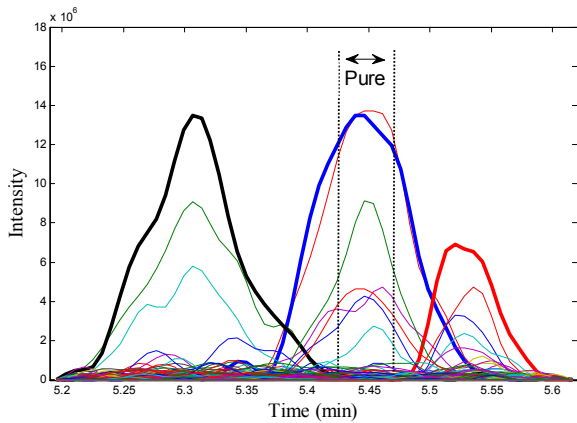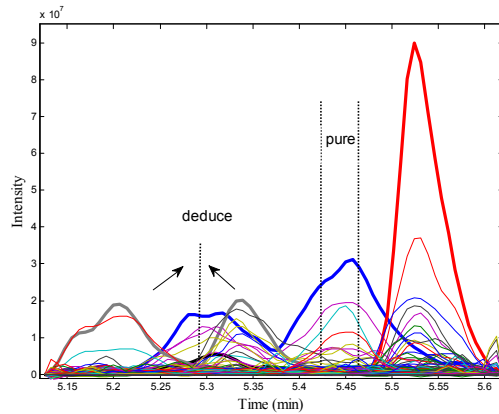
36 Fig 4-a negative ion mode   Fig 4-b positive ion mode

37

38 5. Finally, pure mass spectrum could be obtained in the corresponding selective regions of the
39 positive and negative mode, which are shown below. Nevertheless, pure mass spectrum is the
40 guarantees and premise before qualitative analysis.
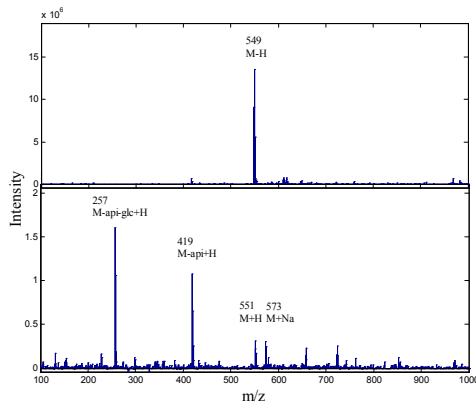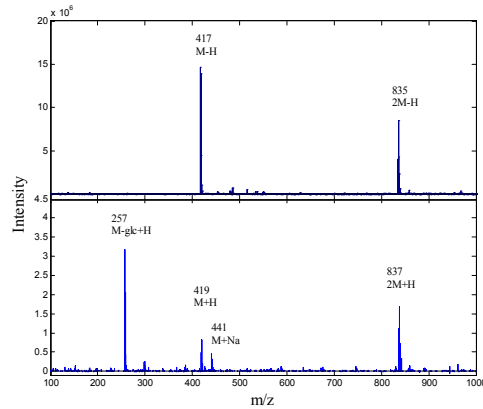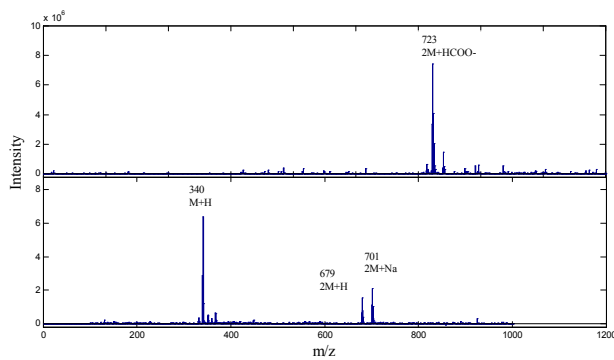
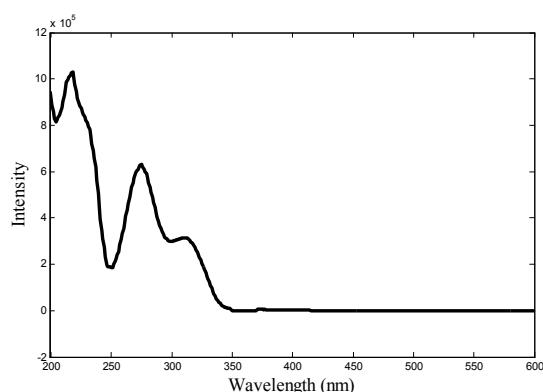41 Fig 5a (black peak, 5.31min)   Fig 5b (blue peak, 5.45 min)

42

43 Fig 5b (red peak, 5.45min)

44

3

45 6. The corresponding UV spectrum (liquiritin, 5.45 min) could also be obtained. For some
46 complicated data, we should use HELP, AMWFA, EFA and other classic chemometrics methods.
47 Fig 6

48
49

50 7. Pure spectrum is the guarantees and premise before qualitative analysis. Moreover, we should
51 mine some useful information from pure spectrum. For example, some programs based on
52 isotope program, such as Massworks, MZmine 2, have been widely used to improve low-
53 resolution data under "Continum" or "Profile" mode, followed by determination of molecular
54 formulas. Additionaly, there are simple methods to process the GC-MS data using Origin
55 software. Based on the reliable mass information, the main components could be
56 identified by comparison with an in-house database.
57 For isotopic profile improvement of the data came from licorice (Fig 7-a), which analyzed by AB
58 MS. We can use Gaussian fitting and simple external calibration methods to obtain accurate mass.
59 More details regarding the calibration process using Origin 8.6 can be found in the study by He *et*
60 *al*.[16]" That is to say, a mixture of several external calibration standards (or the known compounds
61 in Licorice) were measured, their molecular ions were extracted and isotopic profiles were fitted.
62 The errors were calculated by subtracting the measured value (accurate mass) from the true value
63 (exact mass). The obtained statistical standard calibration curve of the known masses against the
64 calculated errors was linearly fitted, and the parameters were used for the calibration step of
65 unknown compounds. And the results were precise.
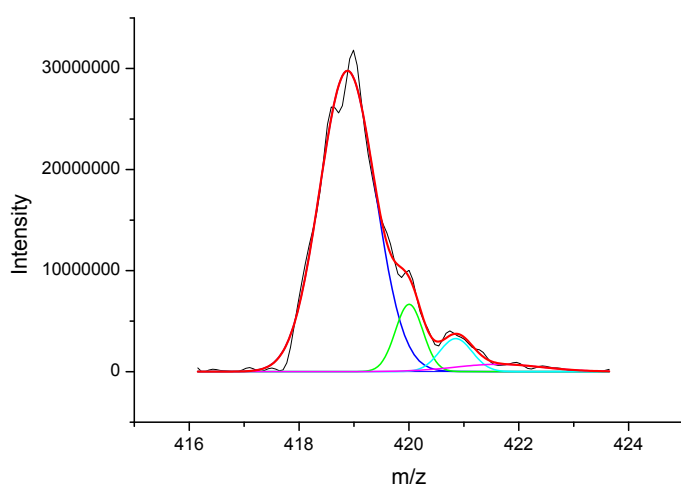66 Fig 7-a
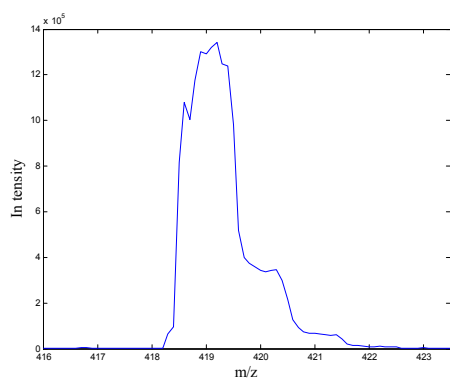
67

68 Here, we have gotten some vague profiles, such as m/z 419 from Liquiritin (5.45 min) in licorice
69 (Fig 7-b). The corrected data (Fig 7-c) could not provide enough precision when compared with
70 high resolution MS, on the other hand it provides a reference for the qualitative analysis to a
71 certain extent.

72 Fig 7-b
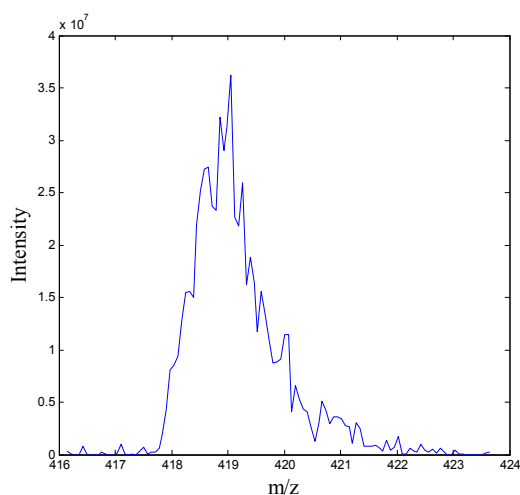
73

74 Fig 7-c

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76 8. As result, the precursor ions of different compounds also produce their characteristic fragment
77 ions, for instance, the different cleavage rules occurred among flavonoid glycoside, chalcone,
78 flavanones, triterpenoid saponins and coumarins. Although MS^n fragment ions of these
79 compounds are very complex, the structures and compound name could be readily inferred
80 according to the existing references, such as liquiritin in licorice (5.45 min), the cleavage rule was
81 shown in Fig 8, and that of liquiritin apioside (5.31min) is similar.
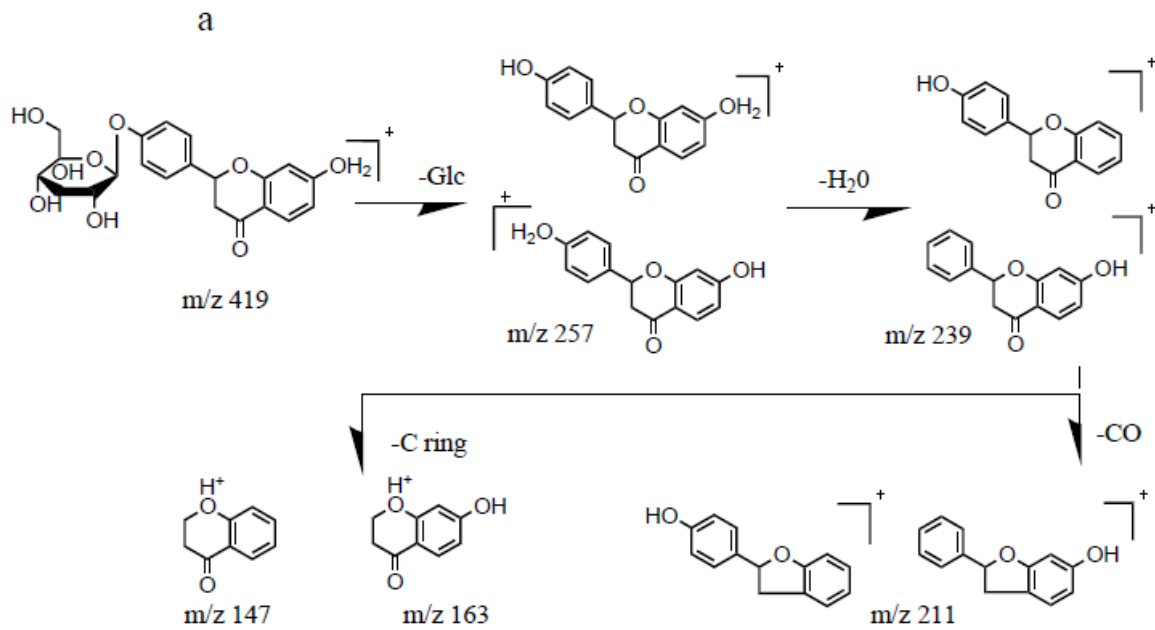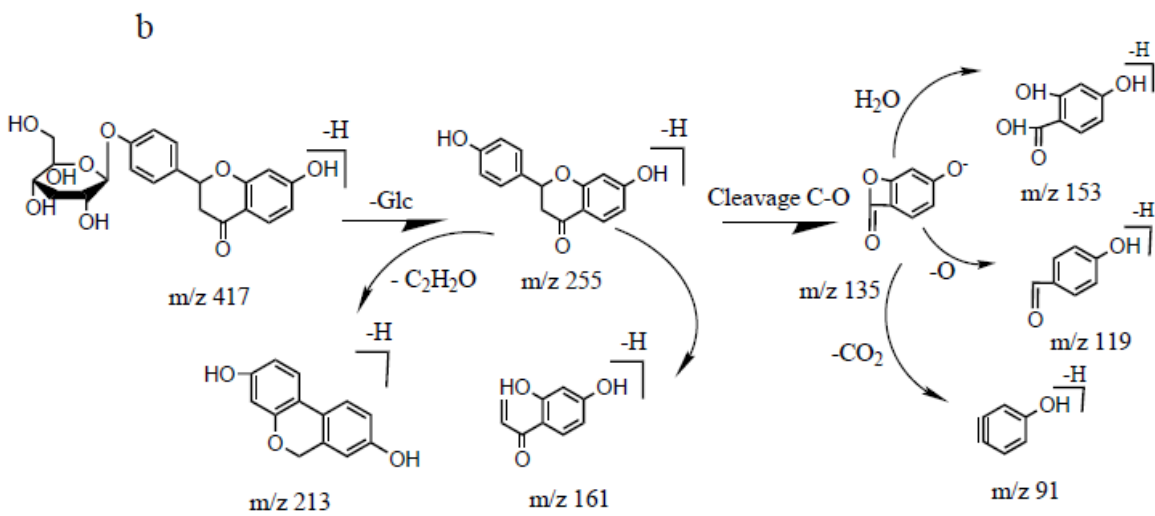
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84

85　Fig 8

86

a

b

87

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92　For some isomers, the qualitative analysis should be accomplished in accordance to the retention

93　time provided by the known reference, or references substances.