

**a**



**b**



**c**



**d**



**e**

Fig.S1. TIC of five representative saponins absorbed in L929 cells in negative ion mode;

（a: Cauloside G; b: Cauloside C; c: Cauloside D; d: Cauloside H; e：Leonticin D）

**red**: the experimental group; **blue**: the control group; **black**: the blank group.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| ***m/z* 1235.6065** | ***m/z* 765.4419** | ***m/z* 1073.5527** | ***m/z*1251.6012** | ***m/z* 1089.5487** |
| ***m/z* 603.3902** | ***m/z* 619.3851** | ***m/z* 471.3479** | ***m/z* 487.3429** | **C2H2O**  ***m/z* 529.3534** |
| **-O**  **2H2**  **SO3**  ***m/z* 1349.6042** | **-O**  **H2**  **HPO3**  ***m/z* 1271.5831** | **-2H**  ***m/z* 423.3268** | **-O**  **2H2**  **SO3**  ***m/z* 671.3823** | **-O**  **H2**  **HPO3**  ***m/z* 801.4915** |
| **-O**  **2H2**  **SO3**  ***m/z* 833.4351** | **C2H2O**  ***m/z* 1277.6171** | **-2O**  **H2**  **HPO3**  ***m/z* 1109.5302** | **-O**  **2H2**  **SO3**  ***m/z* 1187.5477** | **-2O**  **H2**  **HPO3**  ***m/z* 1125.5252** |
| **-O**  **2H2**  **SO3**  ***m/z* 1203.5462** | ***m/z* 573.3821** | ***m/z* 439.3218** | **-O**  **H2**  ***m/z* 825.4306** | **4O**  ***m/z* 875.4306** |

Fig. S2. Identification of prototype and metabolic components structures of Cauloside G (a), Cauloside C (b), Cauloside D (c), Cauloside H(d), Leonticin D (e)

CLG-M0



CLG-M5



CLG-M1



CLG-M2



CLG-M3



CLG-M4



CLG-M6

CLG-M7



CLG-M8

**a**

CLC-M0



CLC-M1



CLC-M2

CLC-M3



CLC-M4



CLC-M5



CLC-M6



CLC-M7

**b**



CLD-M0

CLD-M2



CLD-M1



CLD-M3



CLD-M4

**c**



CLH-M0



CLH-M1



CLH-M2



CLH-M3

CLH-M4



CLH-M5



CLH-M6

**d**



LD-M0



LD-M2



LD-M3



LD-M1

LD-M4



**e**

Fig. S3.MS/MS spectrum of the metabolites of Cauloside G (a), Cauloside C (b), Cauloside D (c), Cauloside H(d), Leonticin D (e) in the negative ion mode.

Tab. S1 Identification of prototype and metabolic components of five representative saponins in simulate an inflammatory FLS.

|  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| NO | Observed  RT (min ) | Identification | Formula | Experimental Molecular Weight | | Theoretical Molecular Weight | Diff (ppm) | Adducts | MS/MS Fragment ions (m/z) | Status |
| M0  M1  M2  M3  M4  M5  M6  M7  M8  M0  M1  M2  M3  M4  M5  M6  M7  M0  M1  M2  M3  M4  M0  M1  M2  M3  M4  M1  M2  M3  M4 | Cauloside G  9.04  11.94  12.71  14.67  20.72  8.95  9.05  20.60  9.75  Cauloside C  11.98  12.70  14.69  20.74  11.96  11.50  11.27  10.99  Cauloside D  9.32  12.73  9.30  12.74  9.30  Cauloside H  9.17  8.80  11.48  8.78  8.80  Leonticin D  8.78  11.48  8.78  8.81 | Cauloside G  CLG-Rha-Glc-Glc  CLG-Rha-Glc  -Glc-Glc  CLG-Rha-Glc  -Glc-Glc-Ara  CLG-Rha-Glc-Glc  -Glc-Ara  HCOOH-2H  CLG+SO3-O+2H2  CLG-CH2O+HPO3  -O+H2  CLG-Rha-Glc-Glc  -Glc-Ara-CH2OH  CLG+C2H2O  Cauloside C  CLC-Glc  CLC-Glc-Ara  CLC-Glc-Ara  - HCOOH-2H  CLC+SO3-O+2H2  CLC-CH2O+HPO3  -O+H2  CLC-O+H2  CLC+4O  Cauloside D  CLD-Rha-Glc-Glc  CLD+SO3-O+2H2  CLD+SO3-O+2H2  -Rha-Glc-Glc  CLD-CH2+HPO3  -2O+H2  Cauloside H  CLH-Glc  CLH-Glc-Rha-Glc  -Glc  CLH-Glc+SO3-O+2H2  CLH-Glc-CH2 +HPO3-2O+H2  Leonticin D  LD-Glc-Rha-Glc  -Glc  LD+SO3-O+2H2  LD-CH2+HPO3-2O+H2 | C59H96O27  C41H66O13  C35H56O8  C30H48O4  C29H44O2  C60H102O31S  C58H97O28P  C29H44O3  C61H98O28  C41H66O13  C35H56O8  C30H48O4  C29H44O2  C41H70O15S  C40H67O14P  C42H66O16  C42H68O19  C53H86O22  C35H56O8   |  | | --- | | C54H92O26S |   C35H60O10S  C52H87O23P  C59H96O28   |  | | --- | | C53H86O23  C35H56O9 |   C54H92O27S  C52H87O24P  C53H86O23   |  | | --- | | C35H56O9 |   C54H92O27S  C52H87O24P | | 1235.6043  765.4418  603.3910  471.3485  423.3279  1349.5994  1271.5846  439.3224  1277.6166  765.4417  603.3910  471.3490  423.3277  833.4318  801.4216  825.4300  875.4283  1073.5507  603.3912  1187.5476  671.3821  1109.5319  1251.6038  1089.5468  619.3865  1203.5426  1125.5270  1089.5493  619.3866  1203.5443  1125.5276 | 1235.6065  765.4419  603.3902  471.3479  423.3268  1349.6042  1271.5831  439.3218  1277.6171  765.4419  603.3902  471.3479  423.3268  833.4351  801.4195  825.4278  875.4282  1073.5537  603.3902  1187.5513  671.3823  1109.5302  1251.6015  1089.5487  619.3851    1203.5462  1125.5241  1089.5487  619.3851  1203.5462  1125.5241 | -1.78  -0.13  1.33  1.27  2.6  -3.56  1.18  1.37  -0.39  -0.26  1.33  2.34  2.13  -3.96  2.62  2.67  0.11  -0.28  1.66  -3.12  -0.29  1.53  1.54  -1.74  2.26  -2.99  2.58  0.55  2.42  -1.58  3.11 | -H  -H  -H  -H  -H    +HCOO  -H  -H  -H  -H  -H  -H  -H  -H  -H  +HCOO  +HCOO  -H  -H  +HCOO  +HCOO  -H  -H  -H  -H  +HCOO  -H  -H  -H  +HCOO  -H | 765.4418、603.3910、471.3485  765.4418、603.3910、471.3485  603.3910  471.3485  423.3279  1349.5994、603.3922、471.3487  1271.5846、603.3910、471.3485  439.3224  1277.6166  765.4417、603.3910、471.3490  603.3910  471.3490  423.3277  833.4311、603.3912、471.3485  801.4219、603.3912、471.3485  825.4300  875.4283  1119.5613、1073.5508、603.3912  603.3912  1187.5476、671.3823、603.3912  671.3821  1109.5319、603.3922  1251.6038、1135.5554、619.3865  1135.554、1089.5468、619.3865  619.3865  1203.5426、619.3868  1125.5270、619.3874  1135.5562、1089.5493、619.3872  619.3866  1203.5443  1125.5276 | Prototype  Metabolites  Metabolites  Metabolites  Metabolites  Metabolites  Metabolites  Metabolites  Metabolites  Prototype  Metabolites  Metabolites  Metabolites  Metabolites  Metabolites  Metabolites  Metabolites  Prototype  Metabolites  Metabolites  Metabolites  Metabolites  Prototype  Metabolites  Metabolites  Metabolites  Metabolite  Prototype  Metabolites  Metabolites  Metabolites |



CLG-M7



CLG-M6

CLG-M4



CLG-M2

CLG-M5



CLG-M8

**a**



CLG-M3



CLG-M1

CLC-M4



CLC-M2



CLC-M1



**b**

CLC-M3

CLC-M5

CLC-M6

CLC-M7

**c**



CLD-M0



CLD-M1



CLD-M3



CLD-M4



CLD-M2



CLH-M0



CLH-M2



CLH-M4



CLH-M3

CLH-M1



**d**



LD-M0



LD-M1

LD-M2



LD-M3



**e**

Fig. S4 MS/MS spectrum of the metabolites of Cauloside G (a), Cauloside C (b), Cauloside D (c), Cauloside H(d), Leonticin D (e) in simulate an inflammatory FLS.