Electronic Supplementary Material (ESI) for Analytical Methods.

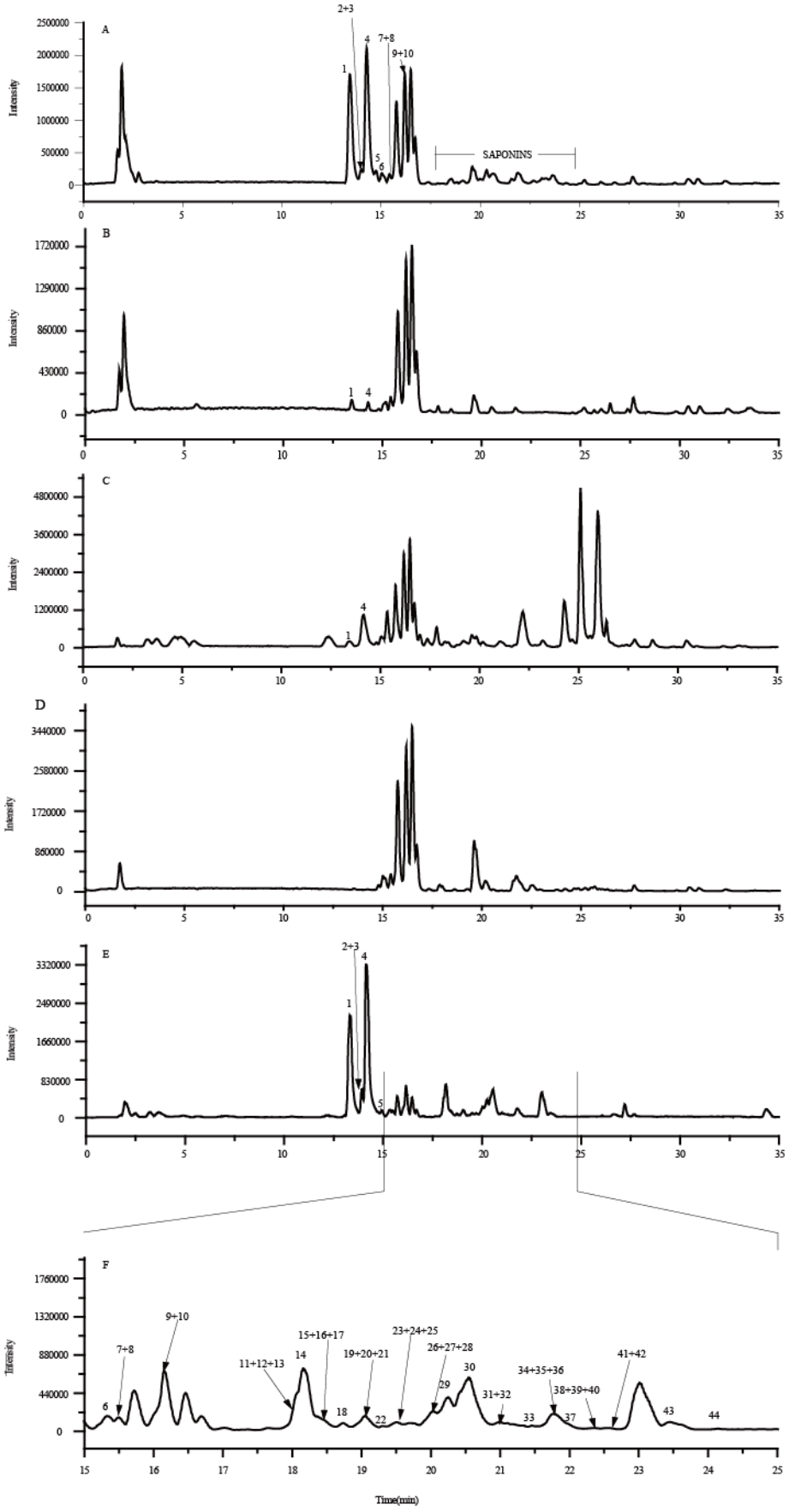




**Fig. S1** Base peak chromatograms of the following fractions: (A) hydro-alcoholic extracts; (B)

Aqueous fraction;(C) Ethyl acetate fraction; (D) Chloroform fraction; (E)Butanolic fraction; (F) Partial enlarged drawing of butanolic fraction.

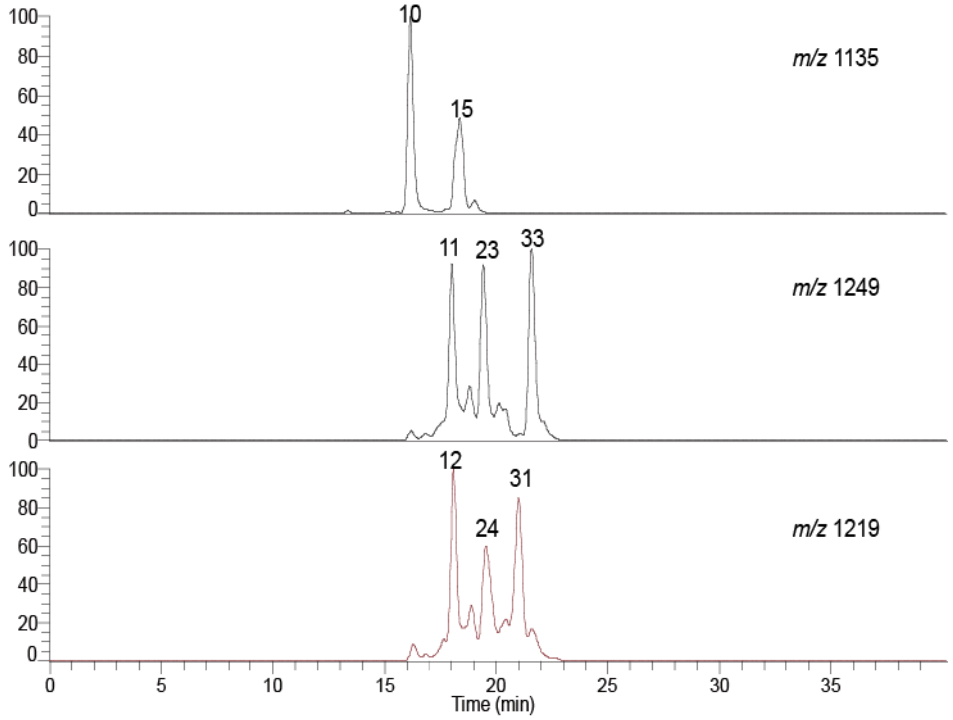



**Fig. S2** Extracted ion chromatograms of the ions at *m/z* 1135, 1249 and 1219 respectively.

**Table S1** Accurate mass measurements for the product ion of $[M-H]^-$ ion at *m/z* 1203 for compound **29** by negative ion high-resolution ESI-$MS^2$.

| Observed mass (Da) | Calculated mass (Da) | Error (ppm) | Formular |
|---|---|---|---|
| 1101.50989 | 1101.51123 | -1.22 | $C_{53}H_{81}O_{24}$ |
| 1071.53516 | 1071.53705 | -1.77 | $C_{53}H_{83}O_{22}$ |
| 1023.51300 | 1023.51592 | -2.85 | $C_{53}H_{83}O_{22}$ |
| 891.47260 | 891.47366 | -1.20 | $C_{47}H_{71}O_{16}$ |
| 667.41962 | 667.42045 | -1.24 | $C_{40}H_{59}O_8$ |
| 553.38806 | 553.38875 | -1.25 | $C_{35}H_{53}O_5$ |
| 451.10828 | 451.10823 | 0.10 | $C_{17}H_{23}O_{14}$ |

**Table S2** Accurate mass measurements for the product ion of *m/z* 1071ion from $[M-H]^-$ ion at *m/z* 1203 by negative ion high-resolution ESI-$MS^3$.

| Observed mass (Da) | Calculated mass (Da) | Error (ppm) | Formular |
|---|---|---|---|
| 909.48248 | 909.48423 | -1.92 | $C_{47}H_{73}O_{17}$ |
| 891.47015 | 891.47366 | -3.94 | $C_{47}H_{71}O_{16}$ |

**Table S3** Accurate mass measurements for the product ion of *m/z* 1023 ion from $[M-H]^-$ ion at *m/z* 1203 ion by negative ion high-resolution ESI-$MS^3$.

| Observed mass (Da) | Calculated mass (Da) | Error (ppm) | Formular |
|---|---|---|---|
| 451.10822 | 451.10823 | -0.04 | $C_{17}H_{23}O_{14}$ |

**Table S4** Accurate mass measurements for the product ion of *m/z* 891 ion from $[M-H]^-$ ion at *m/z* 1203 by negative ion high-resolution ESI-$MS^3$

| Observed mass (Da) | Calculated mass (Da) | Error (ppm) | Formular |
|---|---|---|---|
| 553.38782 | 553.38875 | -1.69 | $C_{35}H_{53}O_5$ |
| 571.39825 | 571.39932 | -1.86 | $C_{35}H_{55}O_6$ |

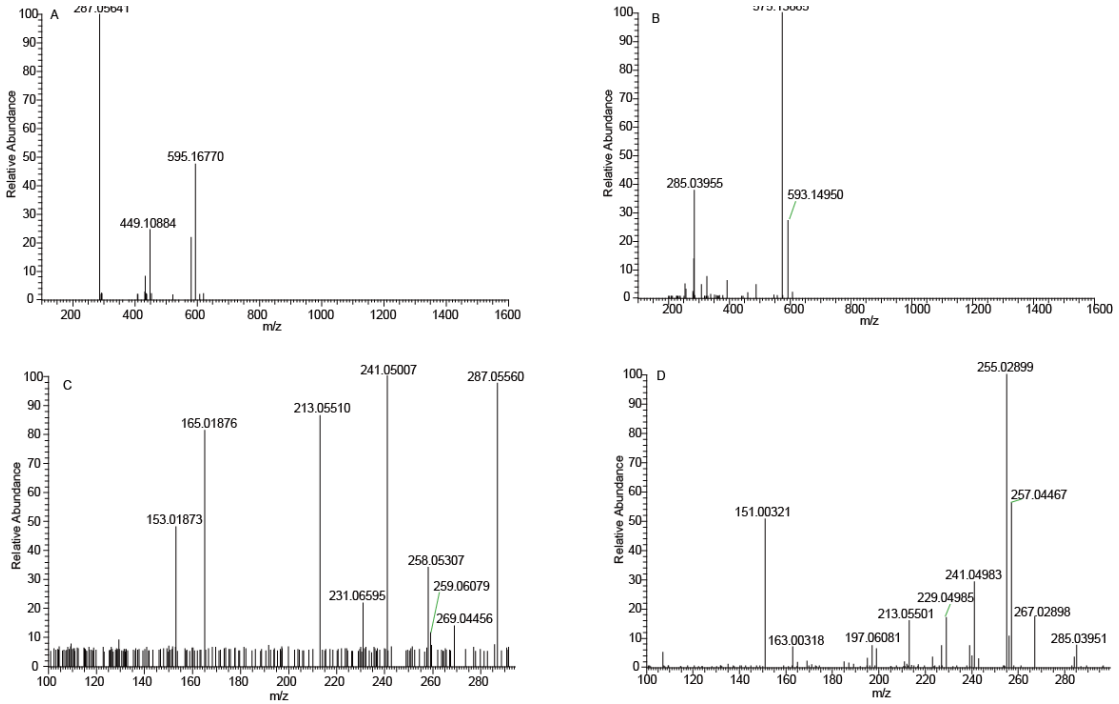



**Fig. S3** The $MS^2$ and $MS^3$ spectra of Camelliaside A (compound **1**). (A) The positive $MS^2$ spectra （B） The negative $MS^2$ spectra (C) The positive $MS^3$ spectra (D) The negative $MS^3$ spectra

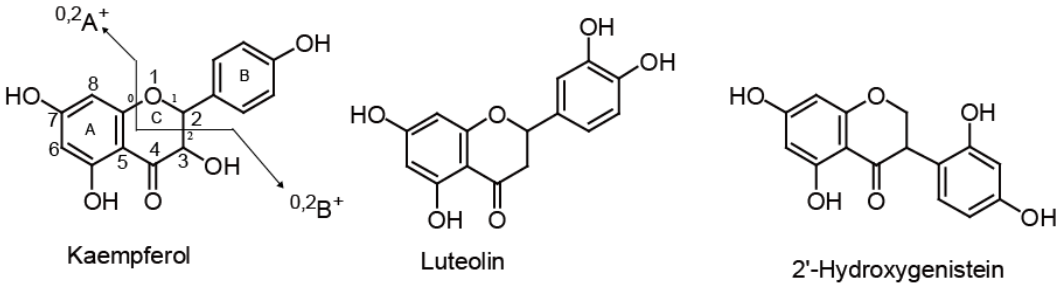
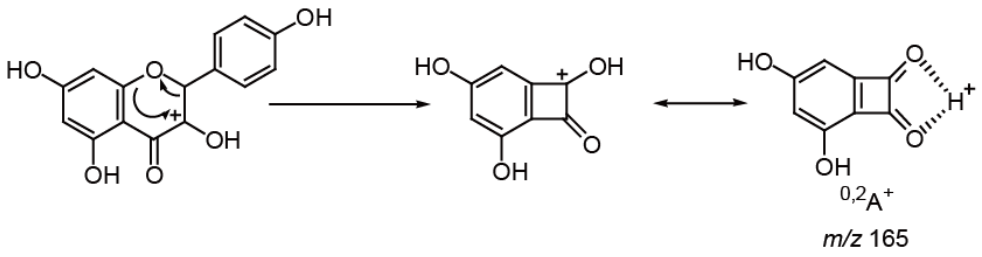



**Fig. S4.** Structures of kaempferol and its isomers.




**Scheme S1.** Proposed mechanism for the formation of *m/z* 165 ion.

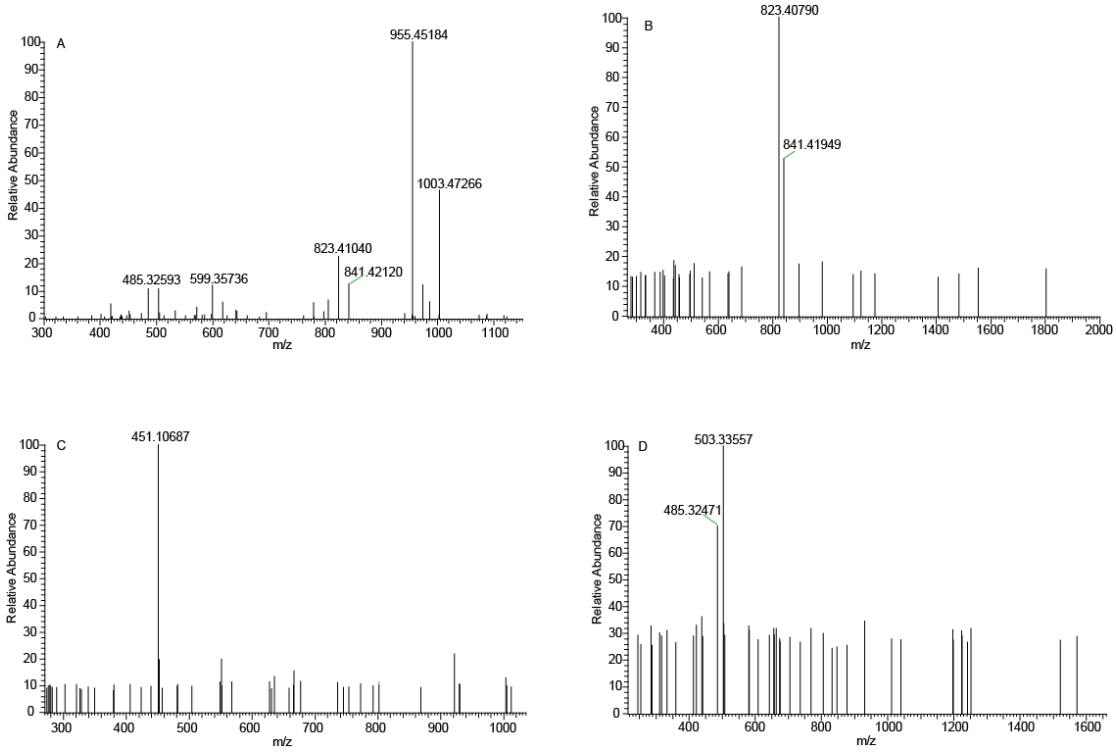
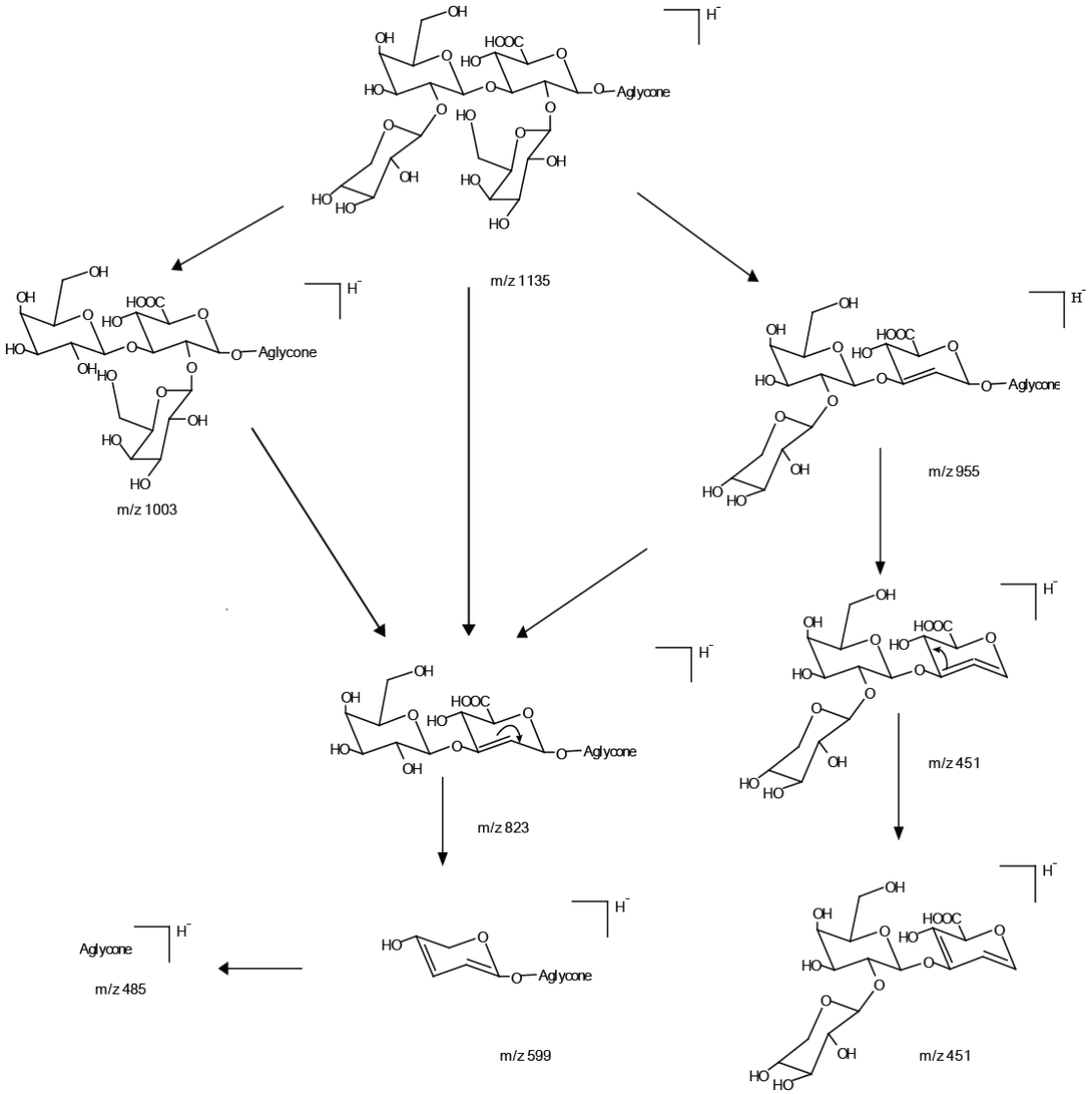



**Fig. S5** The $MS^2$ and $MS^3$ spectra of compound **10** in negative ion mode**.** (A) The $MS^2$ spectra. (B) The product ion of *m/z* 1003 ion. (C) The product ion of *m/z* 955 ion. (D) The product ion of *m/z* 823 ion.




**Scheme S2** The proposal fragmentation pathway of compound **10**.

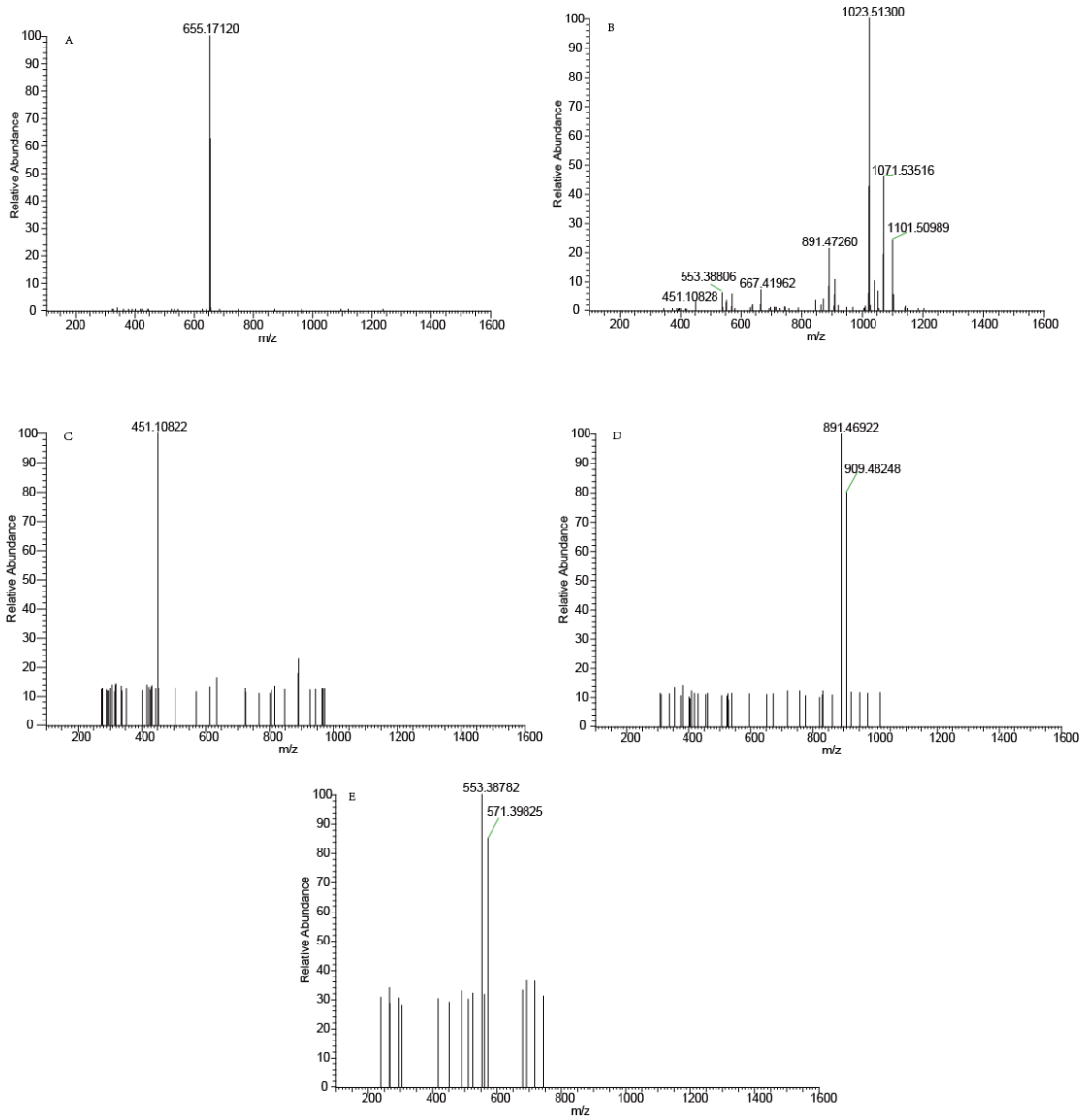



**Fig.S6** The $MS^2$ and $MS^3$ spectra of compound **29**. (A) The product ion of $[M+Na]^+$ ion at *m/z* 1227 in positive ion mode. (B) The $MS^2$ spectra of *m/z* 1203 ion in negative ion mode. (C) The product ion of *m/z* 1023 ion in $MS^3$ spectra . (D) The product ion of *m/z* 1071 ion in $MS^3$ spectra. (D) The product ion of *m/z* 891 ion in $MS^3$ spectra.