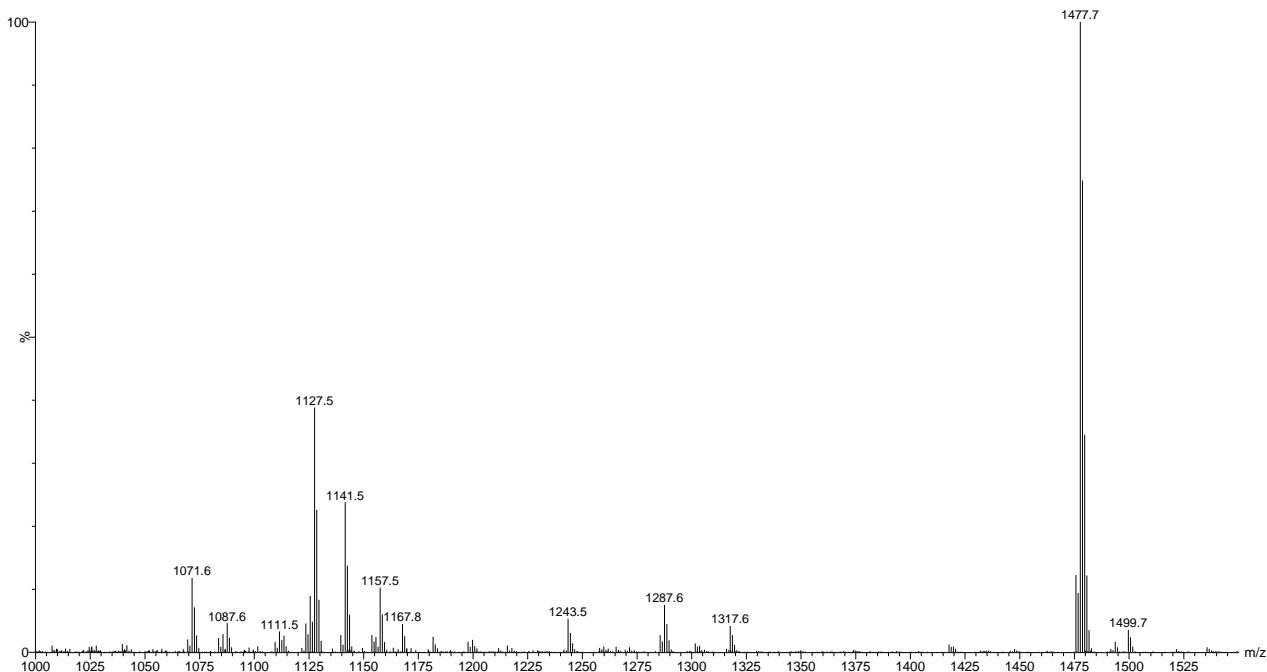
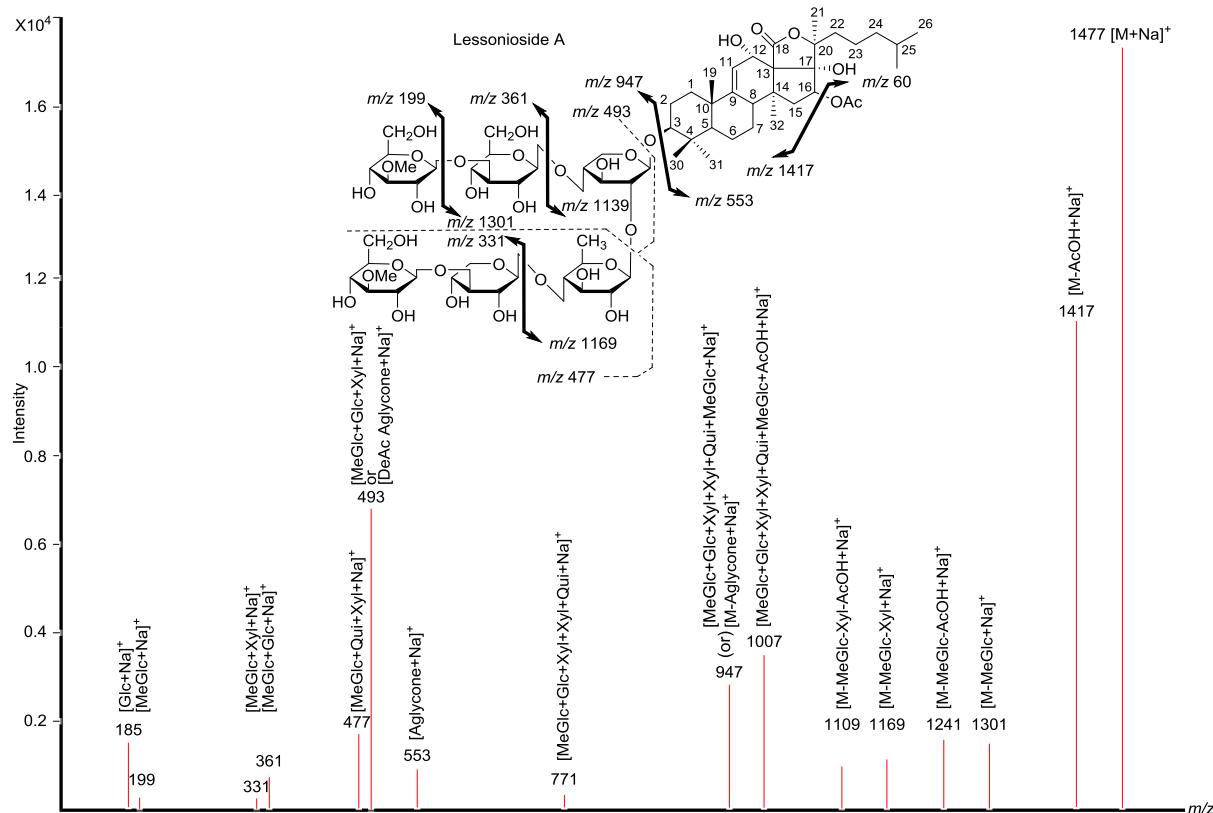


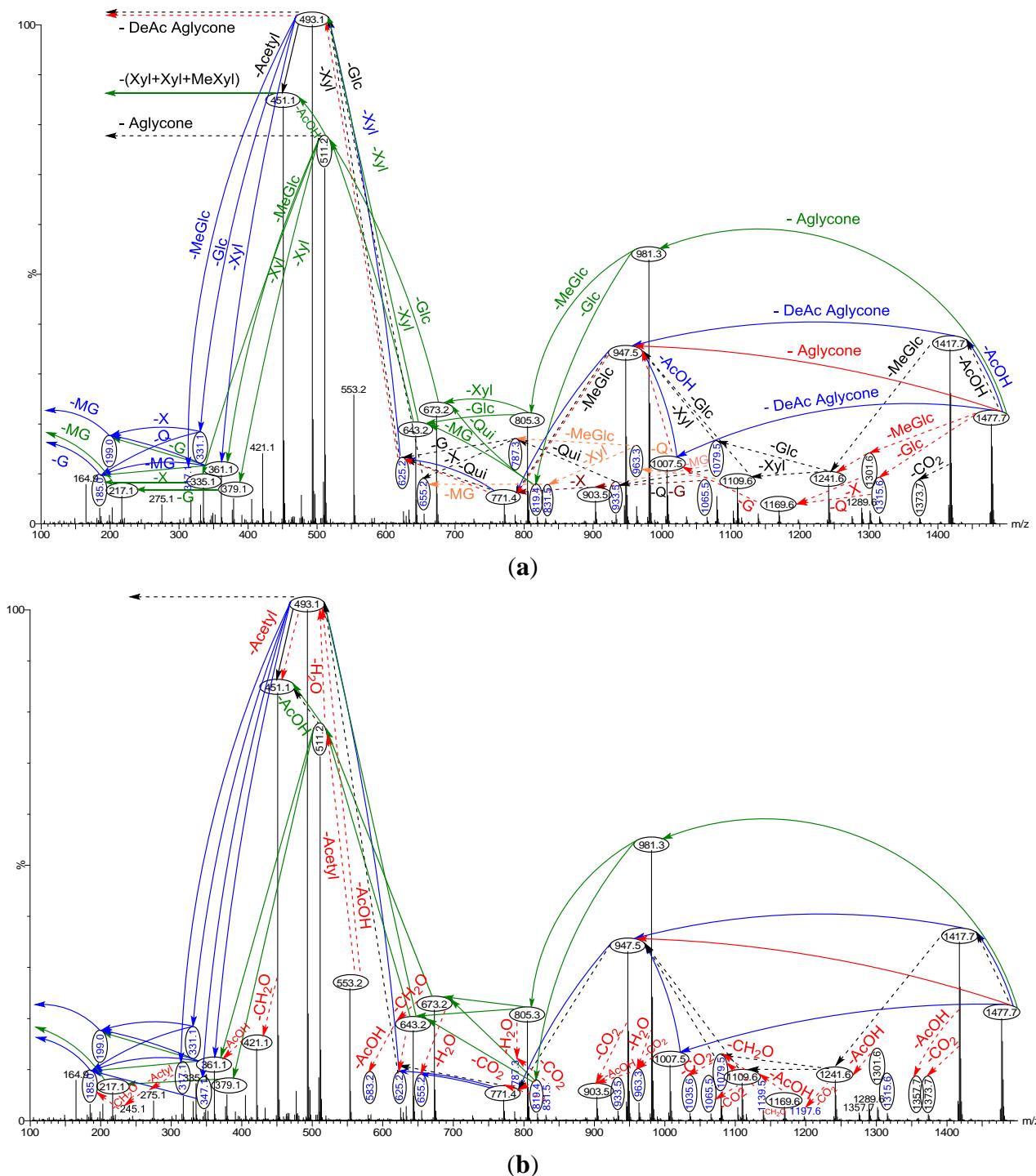
## Supplementary Information



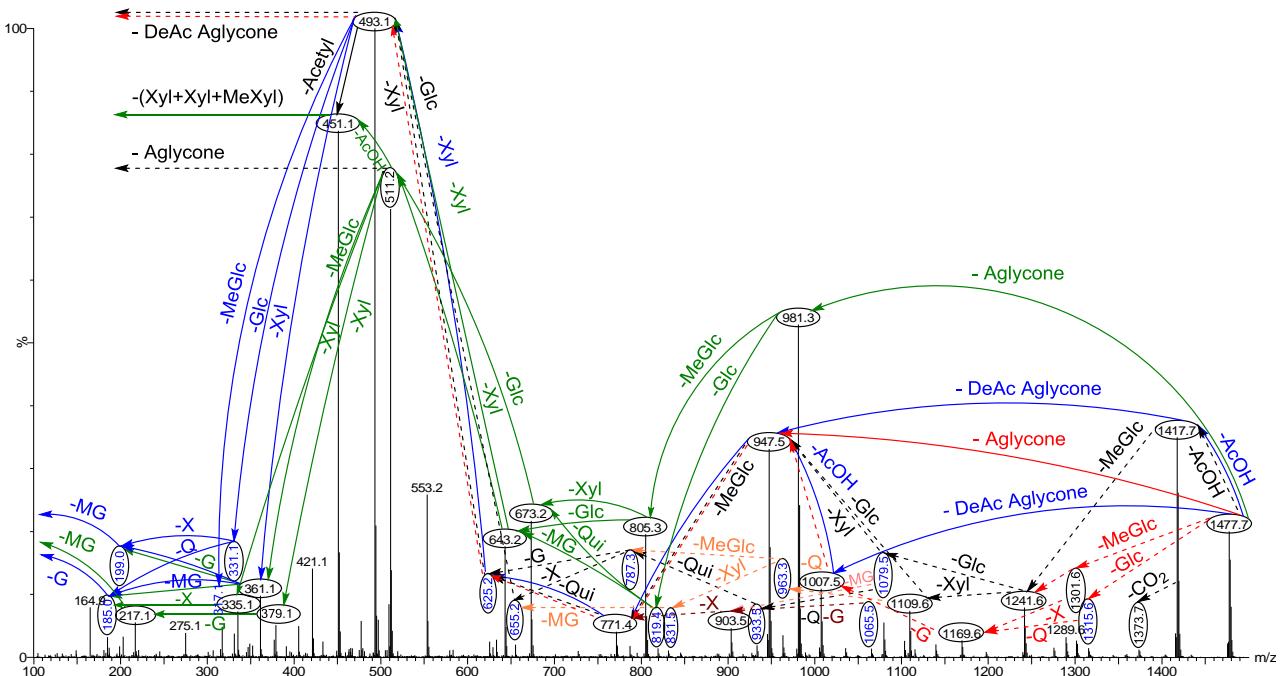
**Figure S1.** The ESI mass spectrum of HPCPC Fraction 18 from the viscera of the *H. lessoni* in the positive ion mode. A mass range of 1000 to 1530 Da is shown here.



**Figure S2.** The MALDI MS<sup>2</sup> schematic fragmentation of Lessonioside A in the positive ion mode as a representative.



**Figure S3.** Ion fragmentation and proposed structures for the isomeric saponins of the precursor ion at  $m/z$  1477.7, the complete ESI-MS/MS fragmentation profile (a); the losses of neutral molecules ( $\text{CO}_2$  and  $\text{H}_2\text{O}$ ) (b). Full and dotted arrows illustrate the three main feasible fragmentation pathways. The blue arrows indicate the fragmentation of the isomeric congeners Lessoniosides A, B and D where the green arrows show the decomposition patterns of Lessoniosides C, E, F and G. Abbreviations; MG = MeGlc, G = Glc, Q = Qui, X = Xyl, Deacetylated Aglycone = DeAc aglycone.



**Figure S4.** This picture shows the feasible ion fragmentations of the non-acetylated isomeric saponins of the precursor ion at  $m/z$  1477.7 from Fraction 18 (green arrows). The losses of Xyl and MeGlc from the ion at  $m/z$  511.2 generated the ions at  $m/z$  379 and 335, respectively.

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