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\(^2\) 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 (CO2 and H2O) (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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