

Structural Characterization and Profiles of Saponins from Two Algerian Sea Cucumbers

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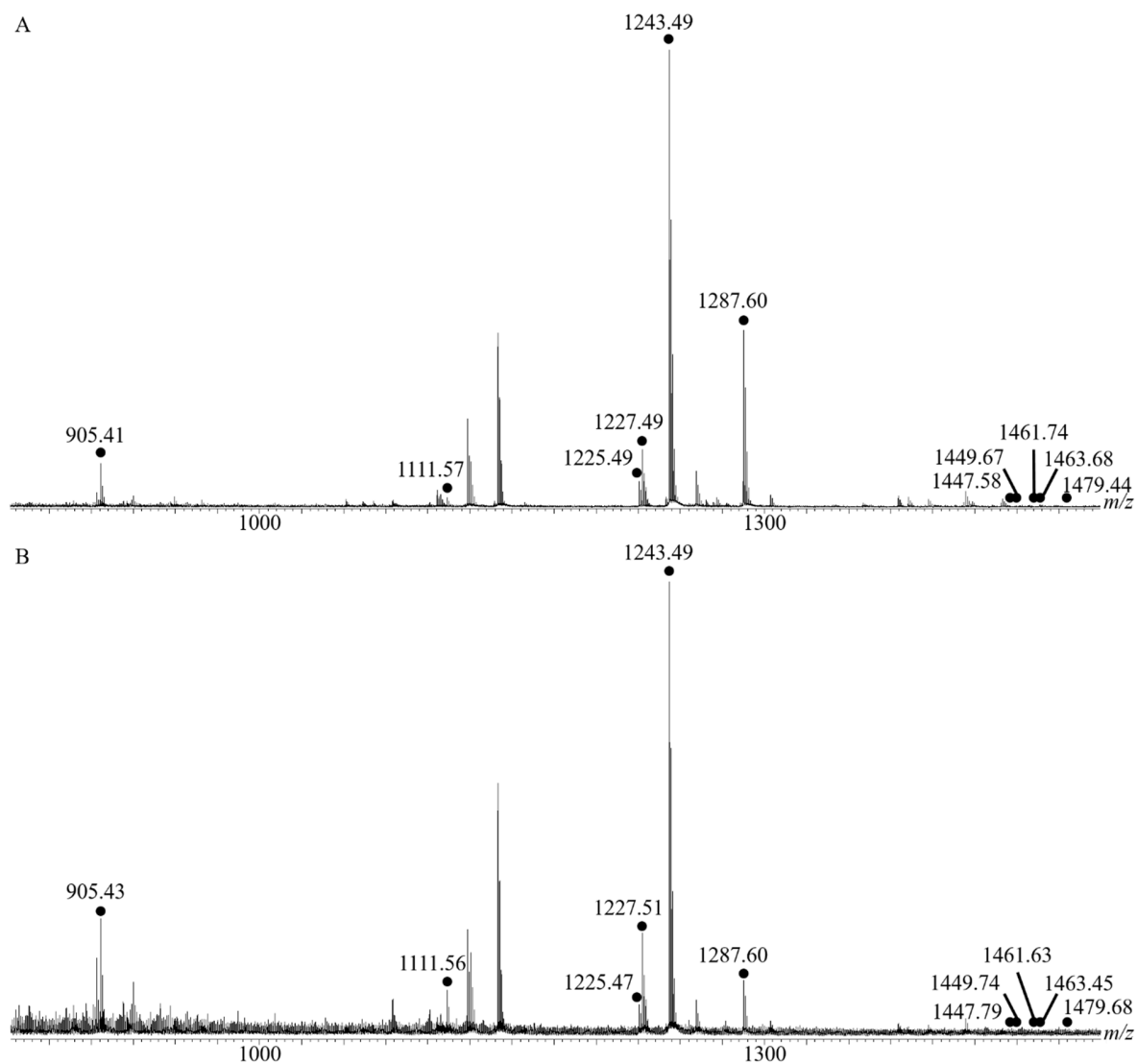


Figure S1. (A) Matrix-assisted Laser Desorption/Ionization mass spectrum [MALDI-MS (+)] of the total saponin mixture of the second individual of *Holothuria (H.) algeriensis* integument extracts. **(B)** MALDI-MS (+) mass spectrum of the total saponin mixture of the third individual of *Holothuria (H.) algeriensis* integument extracts. Saponins signals are highlighted by black dots on which the $[M+Na]^+$ values are noted.

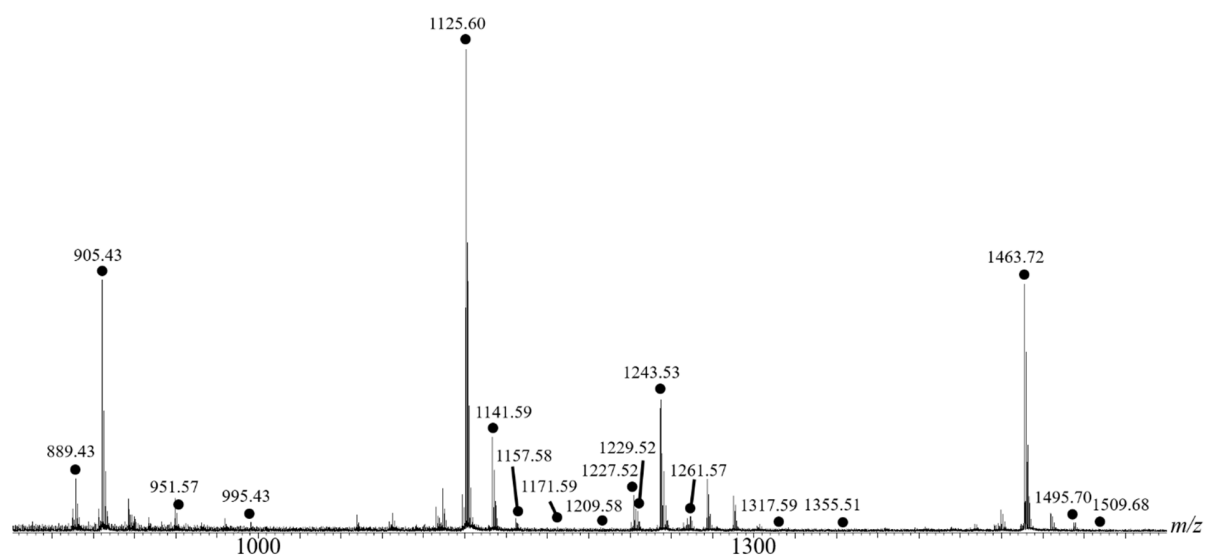
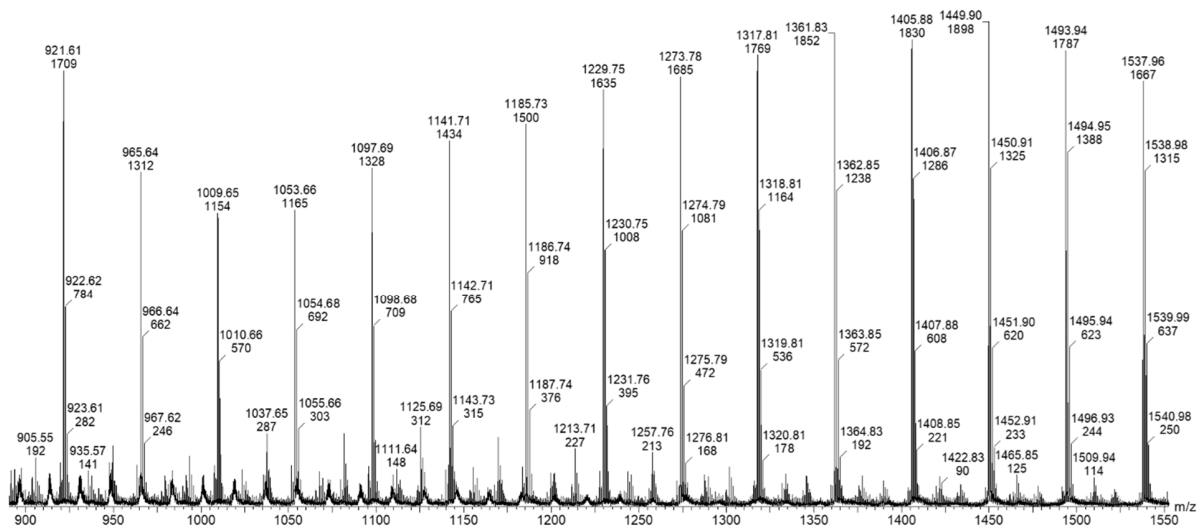
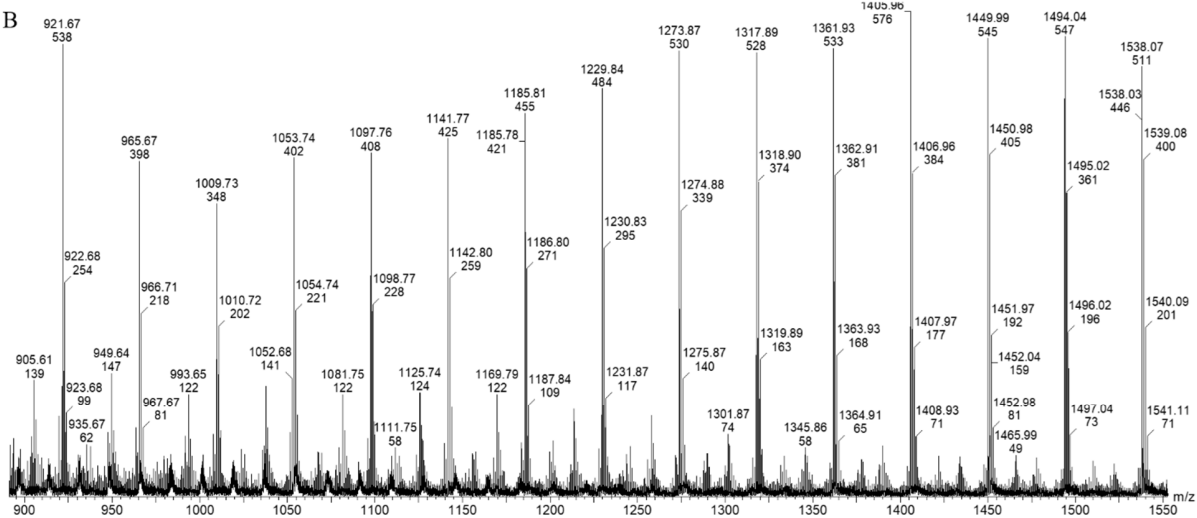


Figure S2. Matrix-assisted Laser Desorption/Ionization mass spectrum [MALDI-MS (+)] of the total saponin mixture of the second individual of *Holothuria (R.) arguinensis* integument extracts. Saponin signals are highlighted by black dots on which the m/z values for $[M+Na]^+$ ions are noted.

A



B



C

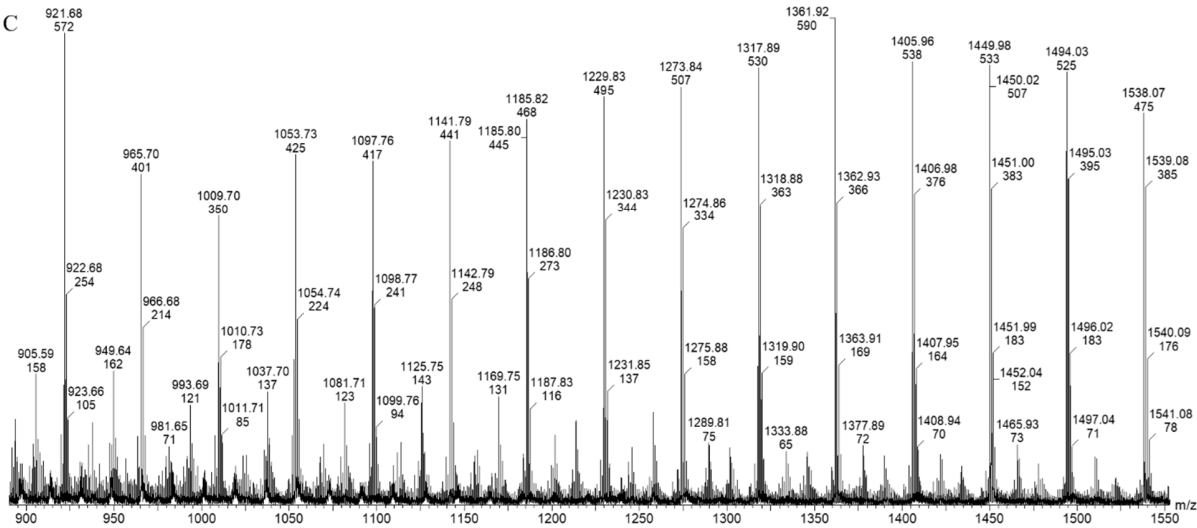


Figure S3. (A) MALDI-HRMS(+) mass spectrum of the first individual of *Holothuria (H.) algeriensis*. **(B)** MALDI-HRMS(+) mass spectrum of the second individual of *Holothuria (H.) algeriensis*. **(C)** MALDI-HRMS(+) mass spectrum of the third individual of *Holothuria (H.) algeriensis*. Note that PEG (polyethylene glycol) was used as the internal reference (lock mass).

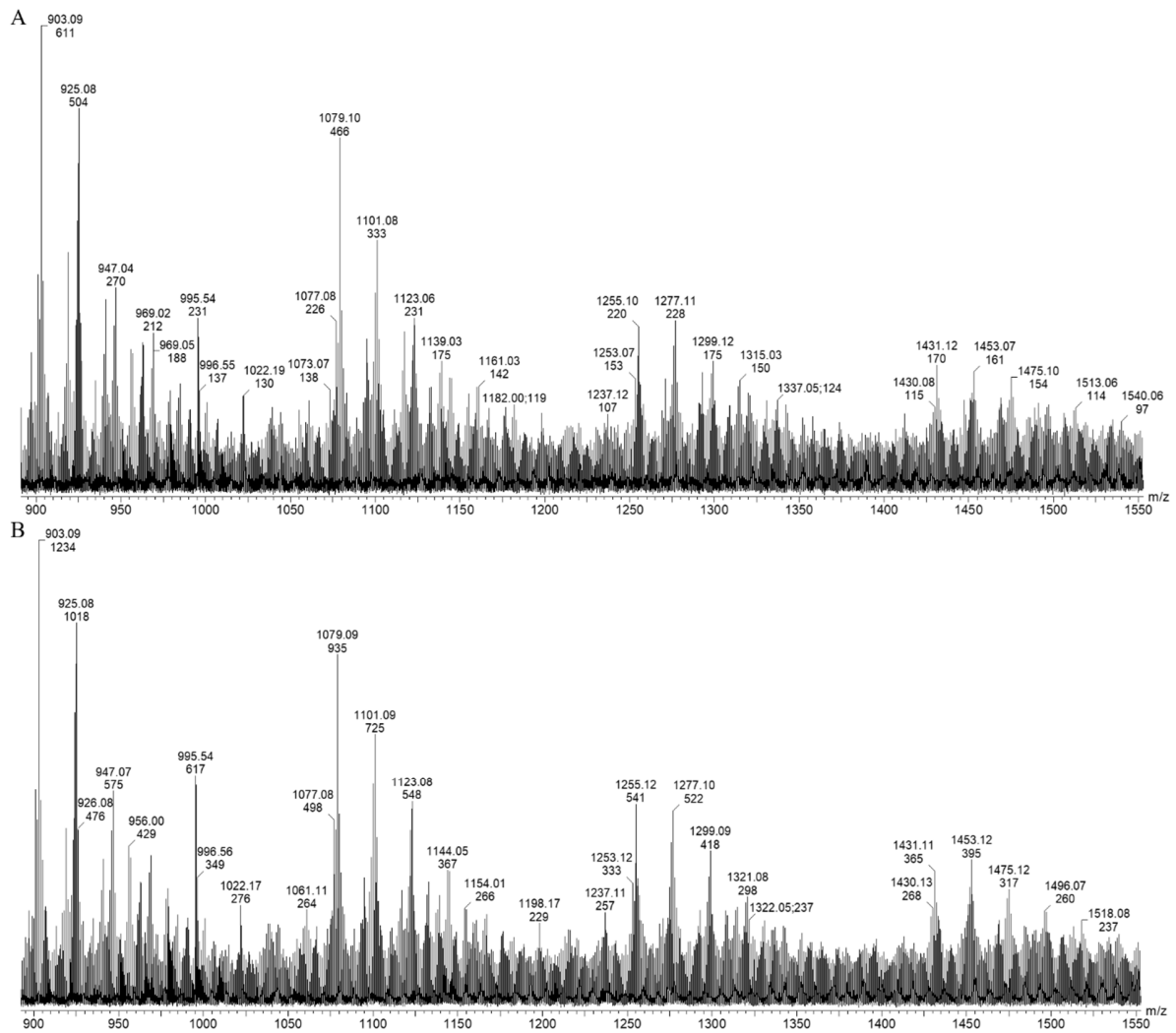


Figure S4. (A) MALDI-HRMS(+) mass spectrum of the first individual of *Holothuria (R.) arguinensis*. **(B)** MALDI-HRMS(+) mass spectrum of the second individual of *Holothuria (R.) arguinensis*. Note that PEG (polyethylene glycol) was used as the standard reference.



Figure S5. LC-MS analysis of the *Holothuria (H.) algeriensis* saponin extract: EIC (Extracted Ion Current Chromatogram) of the m/z 1425 $[M+H]^+$ ions.

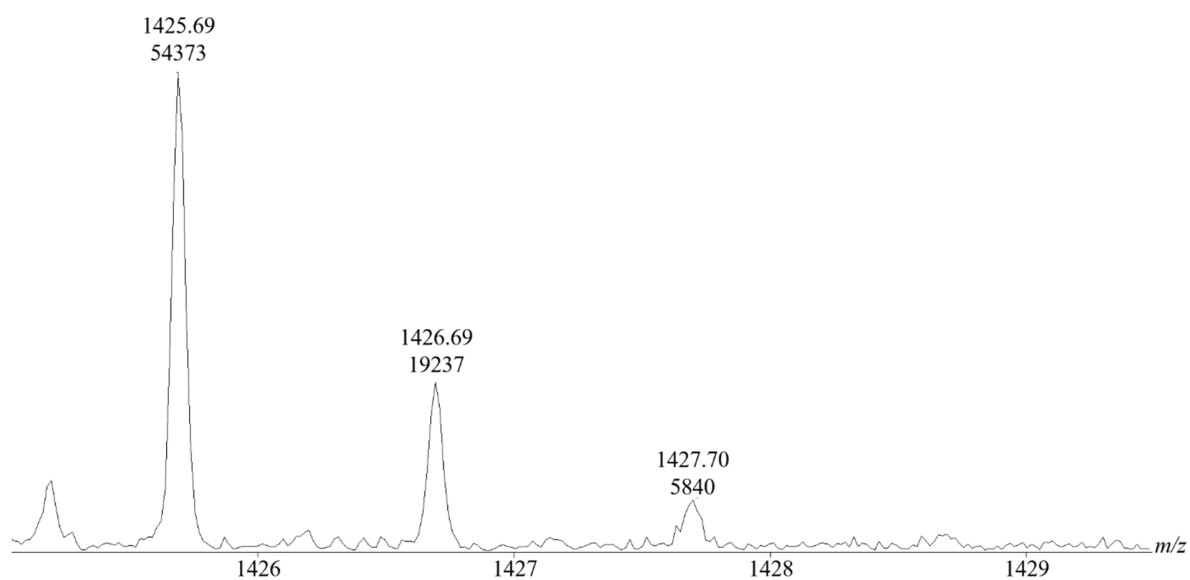


Figure S6. LC-MS analysis of a *Holothuria (H.) algeriensis* saponin extract : mass spectrum at 7.6 min retention time.

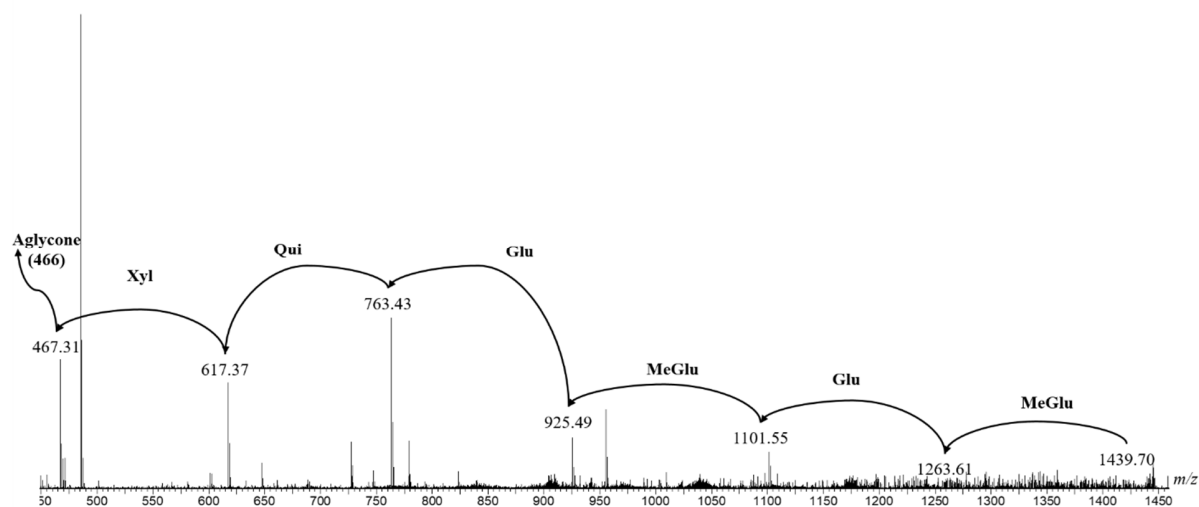


Figure S7. LC-MS/MS(+) analysis of *H. (H.) algeriensis* saponin extract: CID spectrum recorded for the m/z 1439 precursor ions $[M+H]^+$ at 7.3 min retention time (Saponin B).

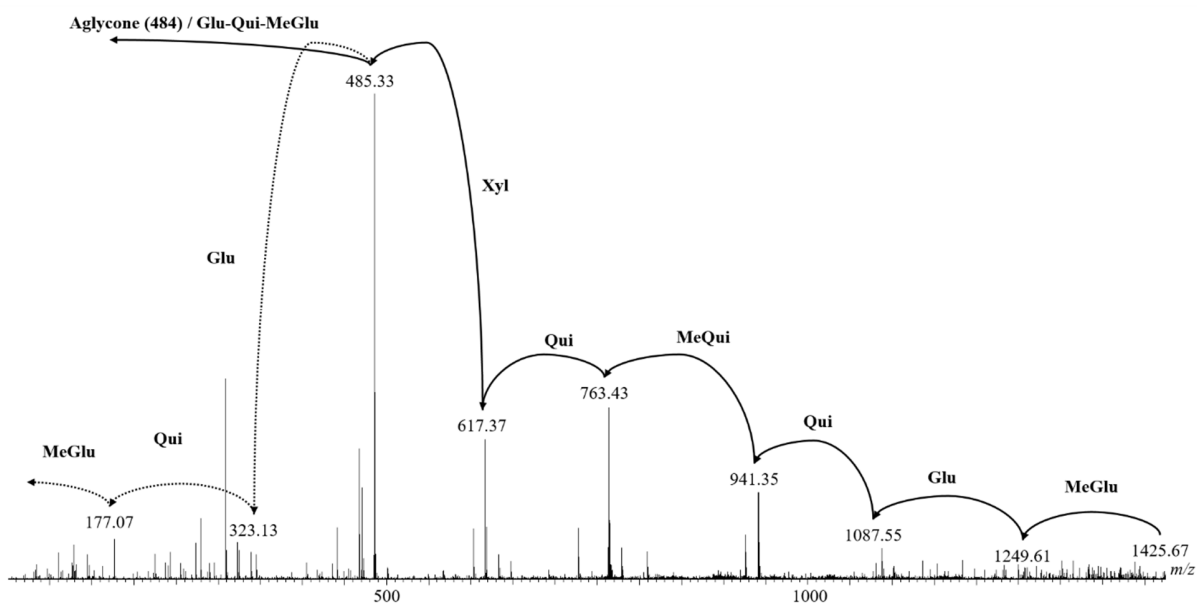


Figure S8. LC-MS/MS(+) analysis of *H. (H.) algeriensis* saponin extract: CID spectrum recorded for the m/z 1425 precursor ions $[M+H]^+$ at 7.1 min retention time (Saponin C).

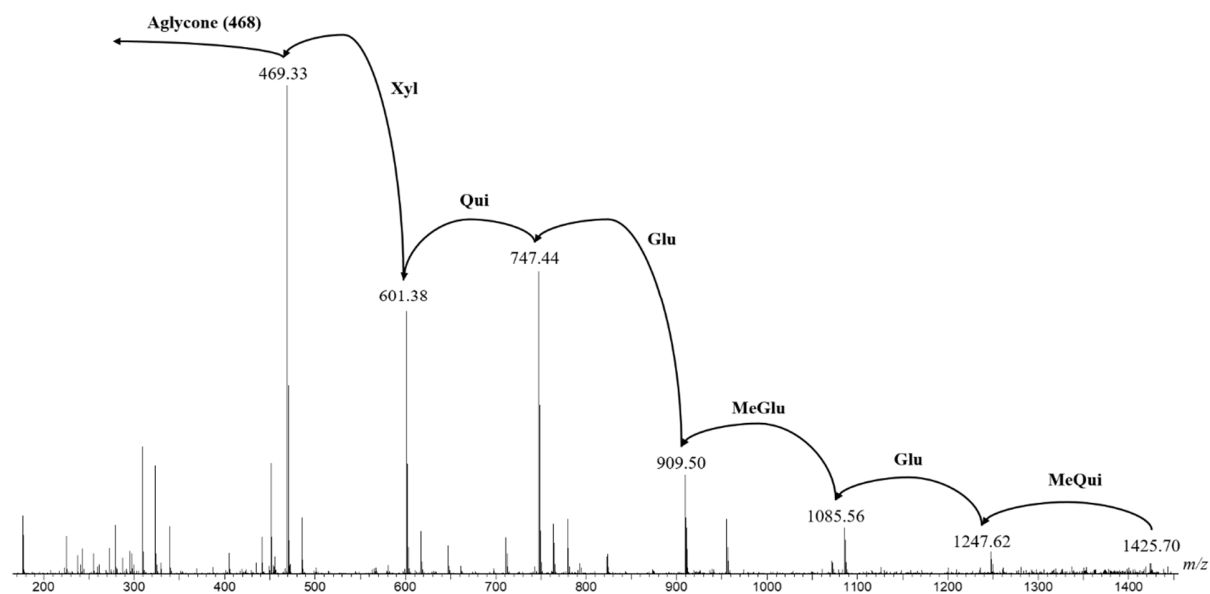


Figure S9. LC-MS/MS(+) analysis of *H. (H.) algeriensis* saponin extract: CID spectrum recorded for the m/z 1425 precursor ions $[M+H]^+$ at 7.6 min retention time (Saponin D).

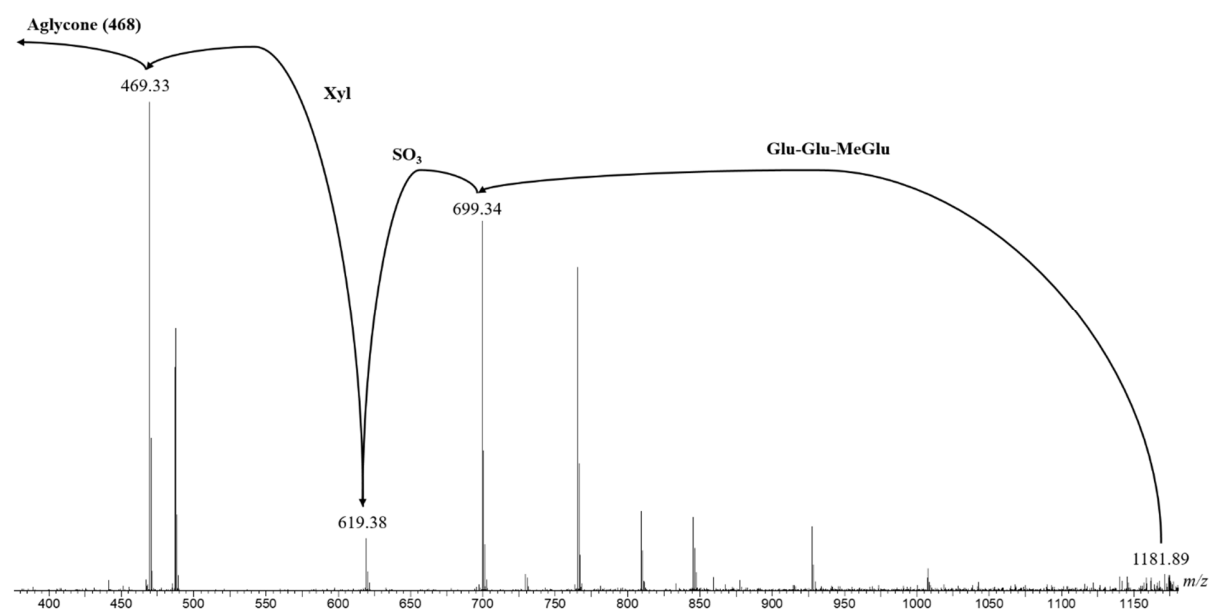


Figure S10. LC-MS/MS(+) analysis of *H. (H.) algeriensis* saponin extract: CID spectrum recorded for the m/z 1181 precursor ions $[M+H]^+$ at 8.7 min retention time (Saponin E).

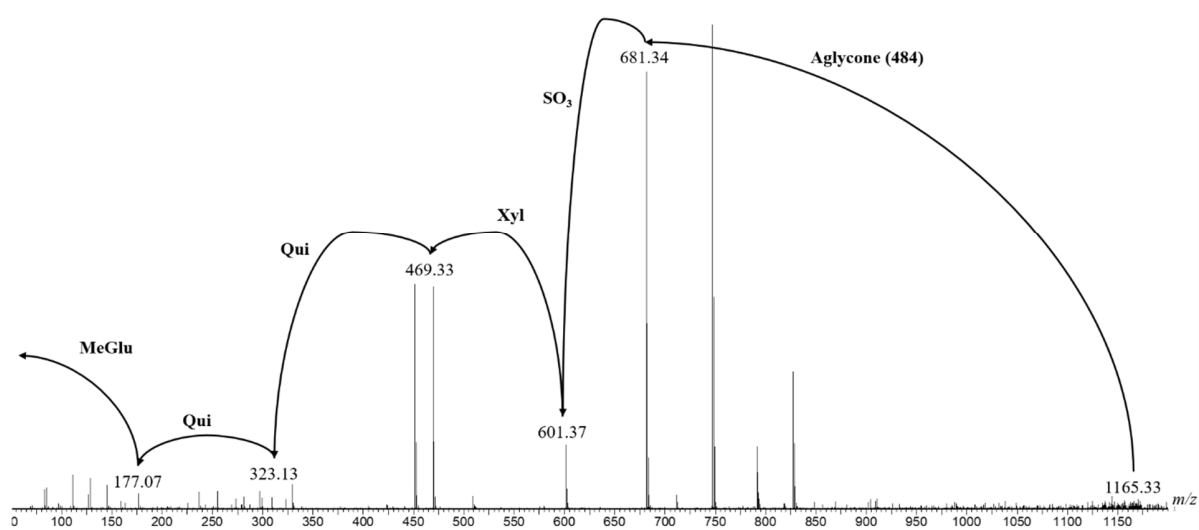


Figure S11. LC-MS/MS(+) analysis of *H. (H.) algeriensis* saponin extract: CID spectrum recorded for the m/z 1165 precursor ions $[M+H]^+$ at 7.9 min retention time (Saponin F).

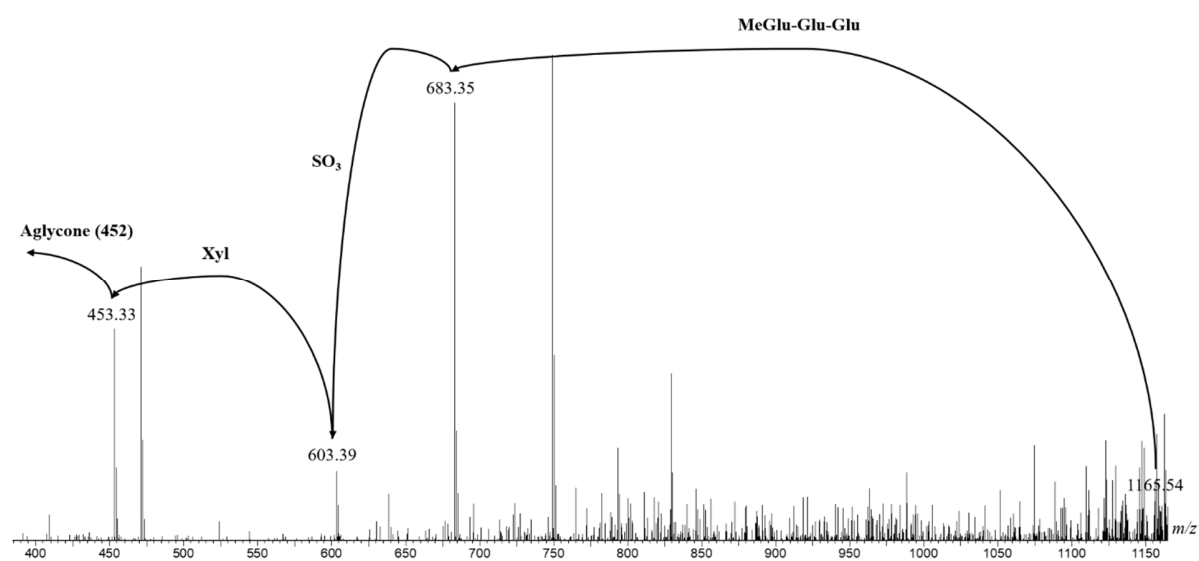


Figure S12. LC-MS/MS(+) analysis of *H. (H.) algeriensis* saponin extract: CID spectrum recorded for the m/z 1165 precursor ions $[M+H]^+$ at 11.3 min retention time (Saponin G).

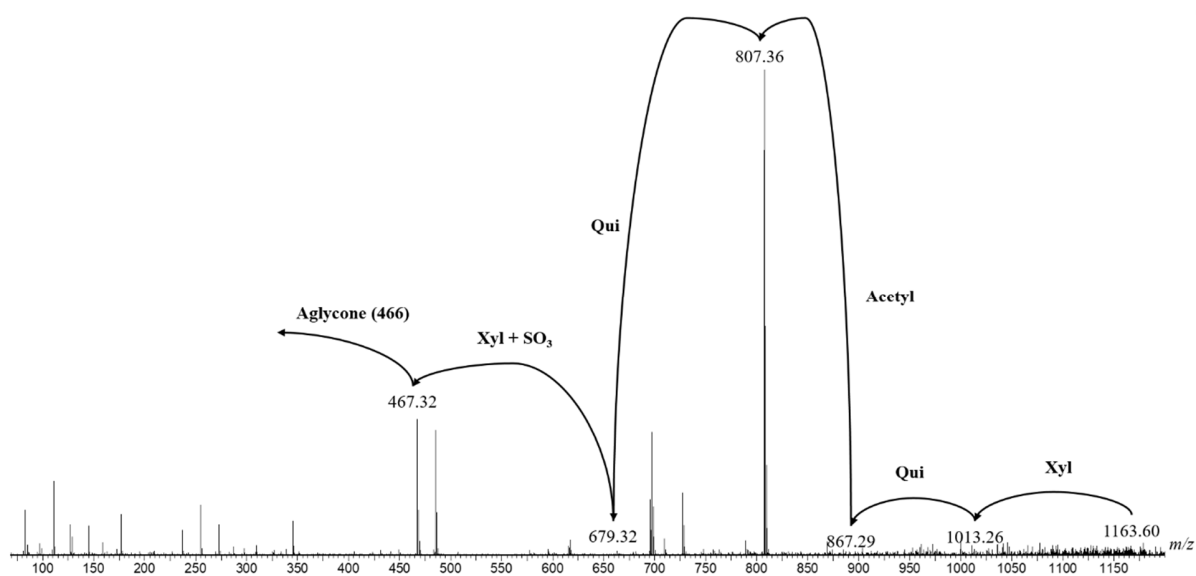


Figure S13. LC-MS/MS(+) analysis of *H. (H.) algeriensis* saponin extract: CID spectrum recorded for the m/z 1163 precursor ions $[M+H]^+$ at 7.6 min retention time (Saponin H).

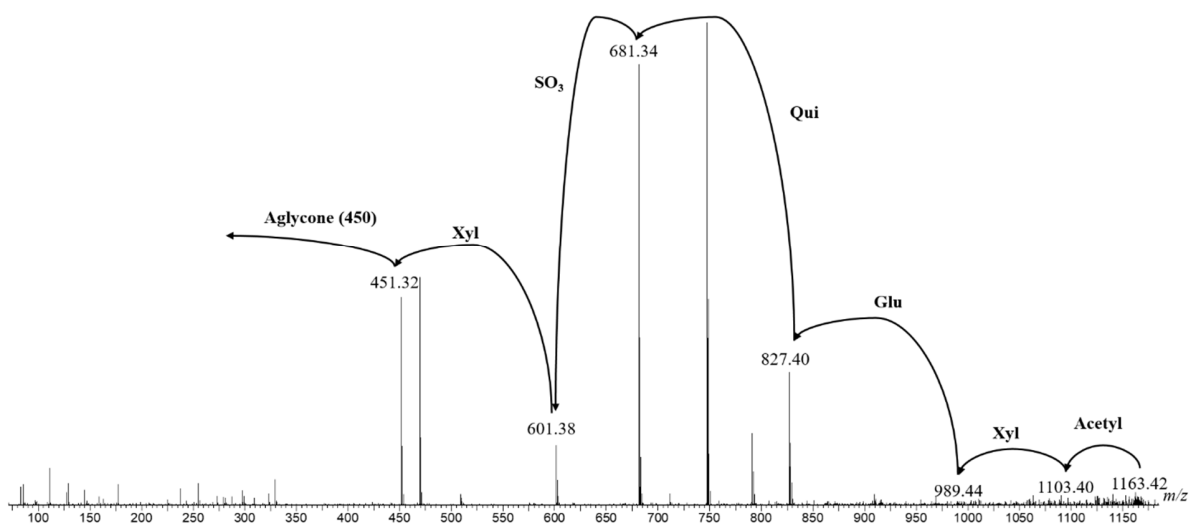


Figure S14. LC-MS/MS(+) analysis of *H. (H.) algeriensis* saponin extract: CID spectrum recorded for the m/z 1163 precursor ions $[M+H]^+$ at 7.9 min retention time (Saponin I).

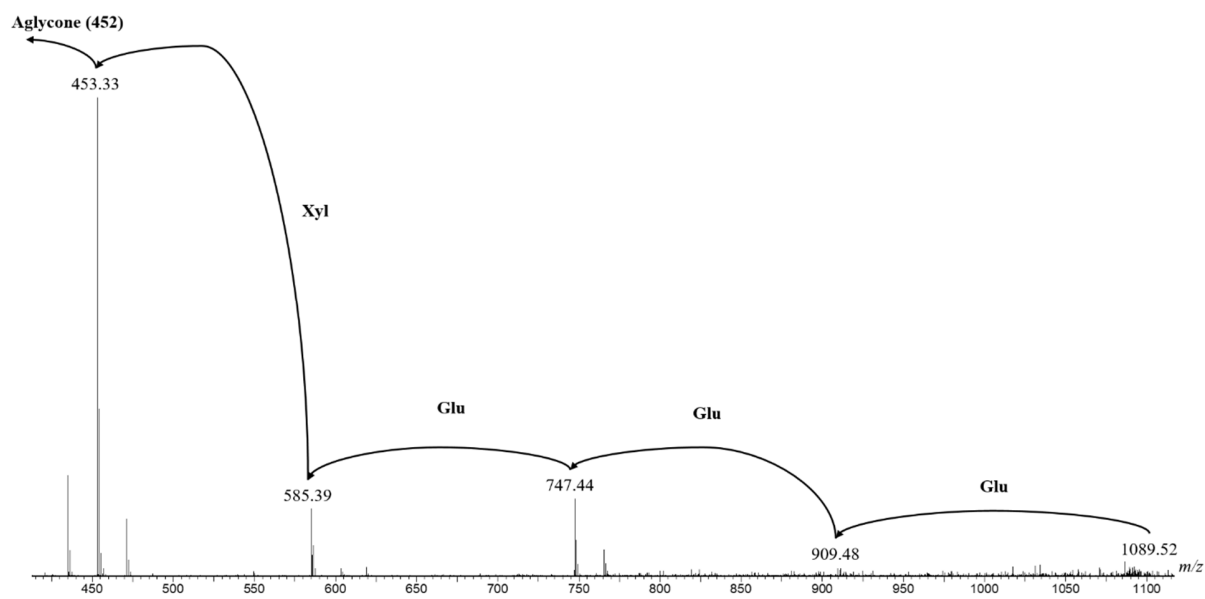


Figure S15. LC-MSMS(+) analysis of *H. (H.) algeriensis* saponin extract: CID spectrum recorded for the m/z 1089 precursor ions $[M+H]^+$ at 9.3 min retention time (Saponin J).

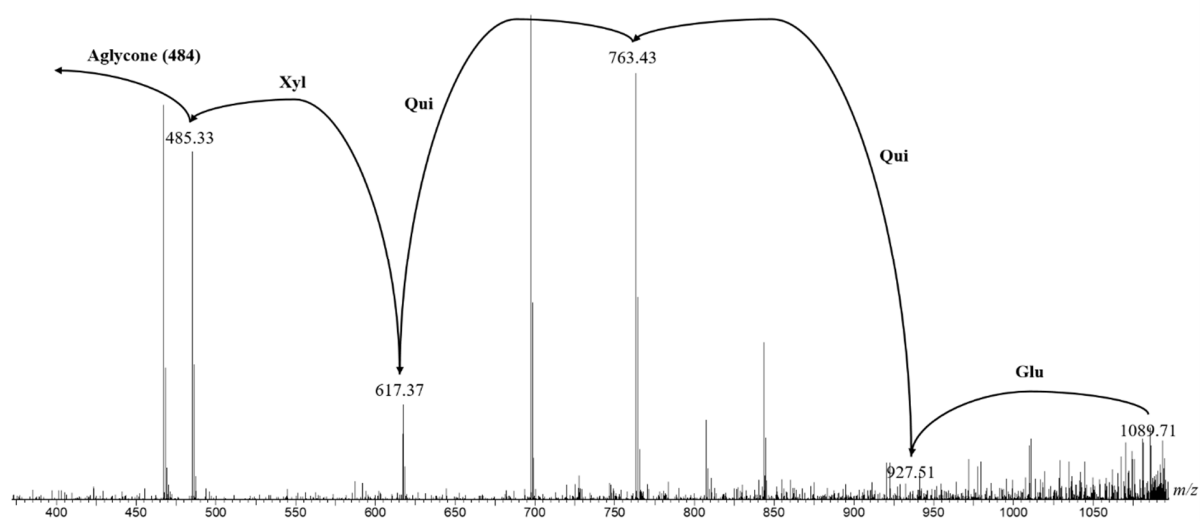


Figure S16. LC-MSMS(+) analysis of *H. (H.) algeriensis* saponin extract: CID spectrum recorded for the m/z 1089 precursor ions $[M+H]^+$ at 7.6 min retention time (Saponin K).

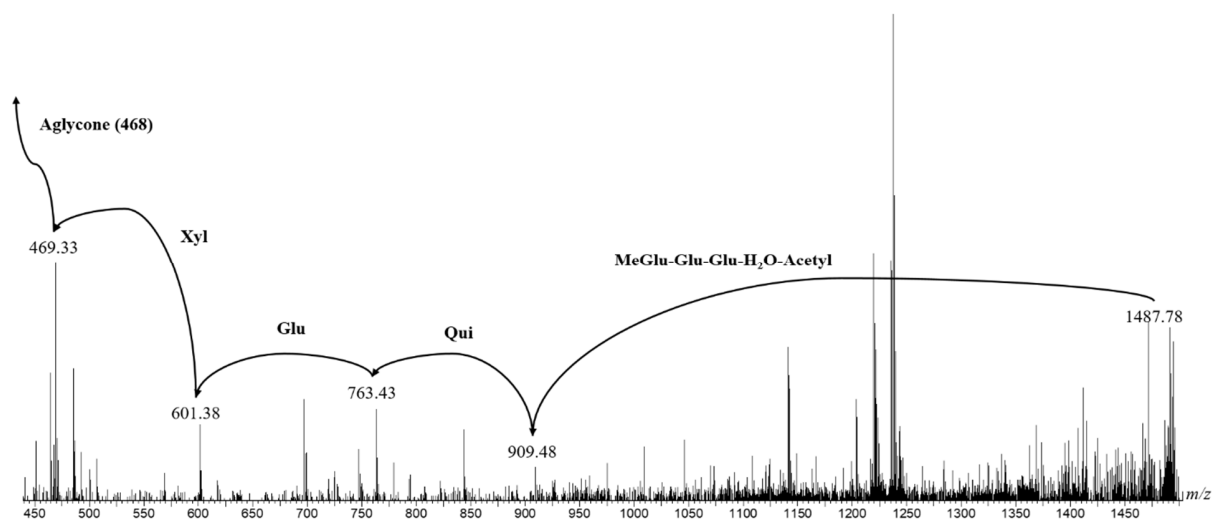


Figure S17. LC-MS/MS(+) analysis of *H. (R.) arguinensis* saponin extract: CID spectrum recorded for the m/z 1487 precursor ions $[M+H]^+$ at 7.6 min retention time (Saponin 1).

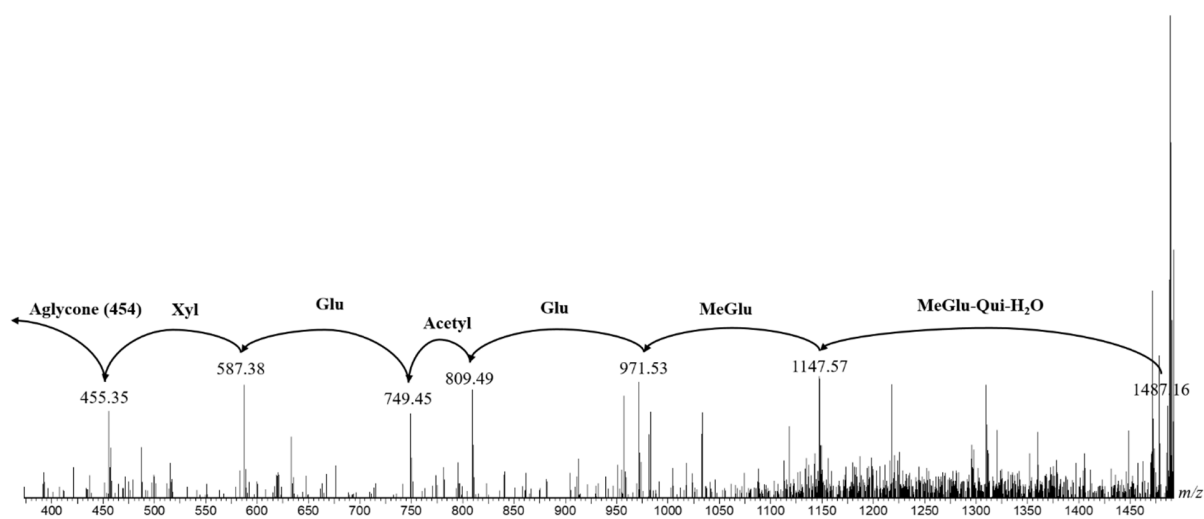


Figure S18. LC-MS/MS(+) analysis of *H. (R.) arguinensis* saponin extract: CID spectrum recorded for the m/z 1487 precursor ions $[M+H]^+$ at 8.2 min retention time (Saponin 2).

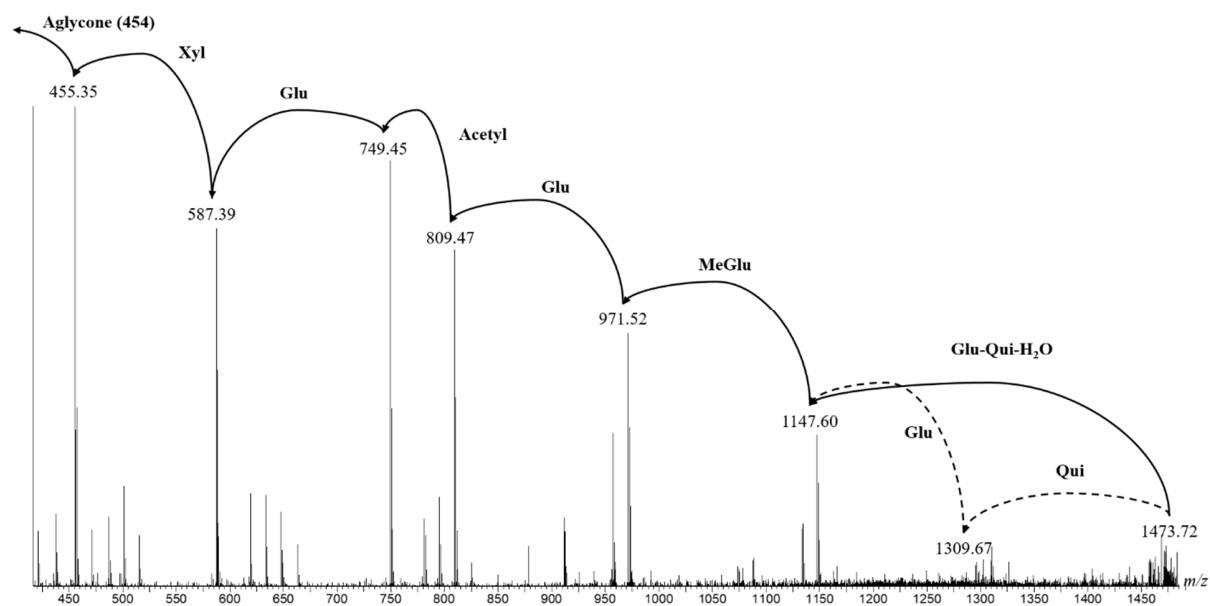


Figure S19. LC-MS/MS(+) analysis of *H. (R.) arguinensis* saponin extract: CID spectrum recorded for the m/z 1473 precursor ions $[M+H]^+$ at 8.2 min retention time (Saponin 3).

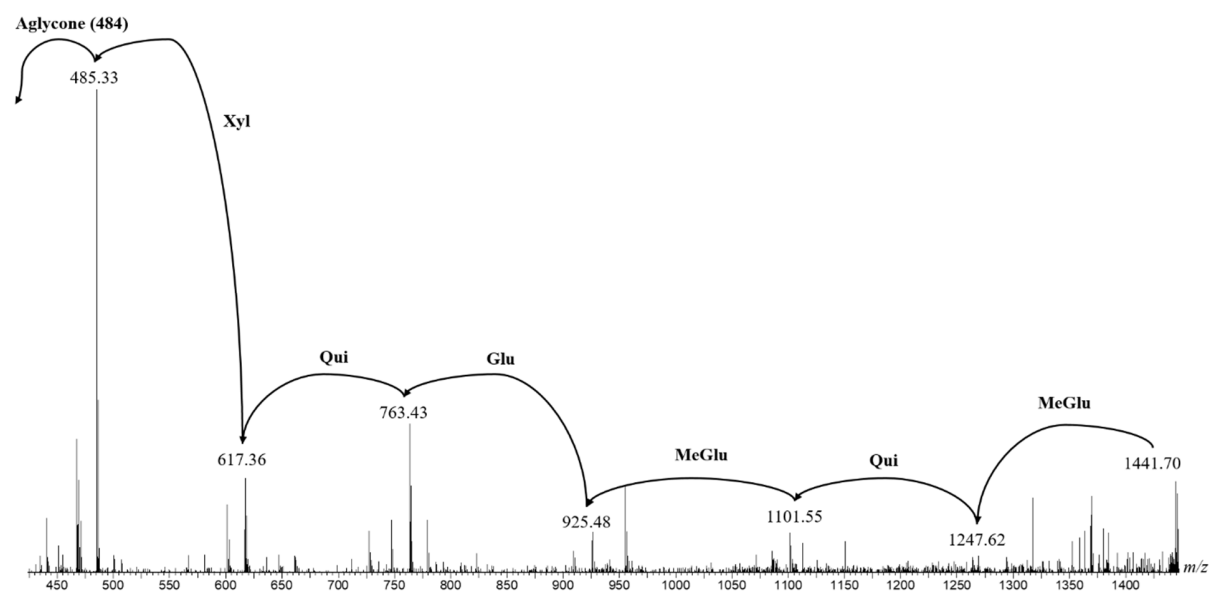


Figure S20. LC-MS/MS(+) analysis of *H. (R.) arguinensis* saponin extract: CID spectrum recorded for the m/z 1141 precursor ions $[M+H]^+$ at 7.3 min retention time (Saponin 4).

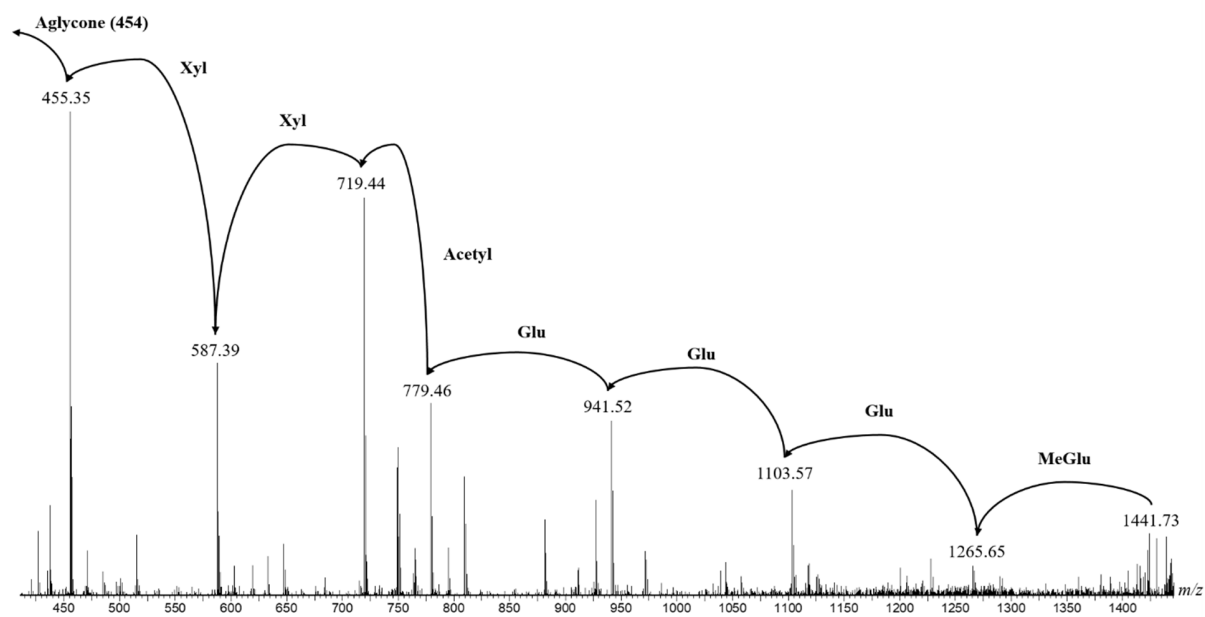


Figure S21. LC-MS/MS(+) analysis of *H. (R.) arguinensis* saponin extract: CID spectrum recorded for the m/z 1141 precursor ions $[M+H]^+$ at 8.4 min retention time (Saponin 5).

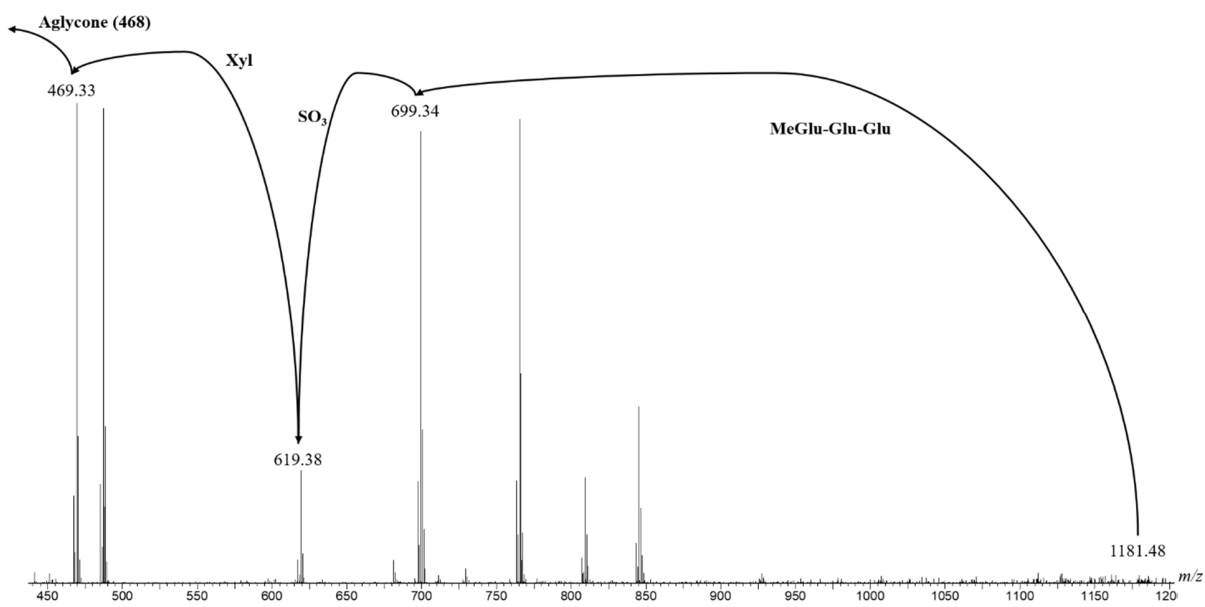


Figure S22. LC-MS/MS(+) analysis of *H. (R.) arguinensis* saponin extract: CID spectrum recorded for the m/z 1181 precursor ions $[M+H]^+$ at 7.4 min retention time (Saponin 6).

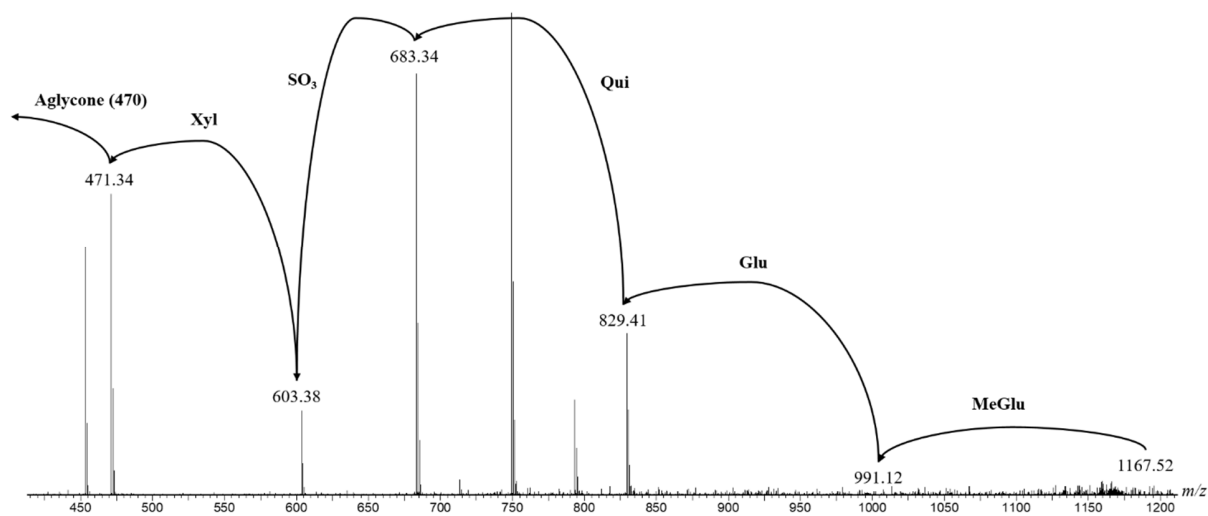


Figure S23. LC-MS/MS(+) analysis of *H. (R.) arguinensis* saponin extract: CID spectrum recorded for the m/z 1167 precursor ions $[M+H]^+$ at 11.3 min retention time (Saponin 7).

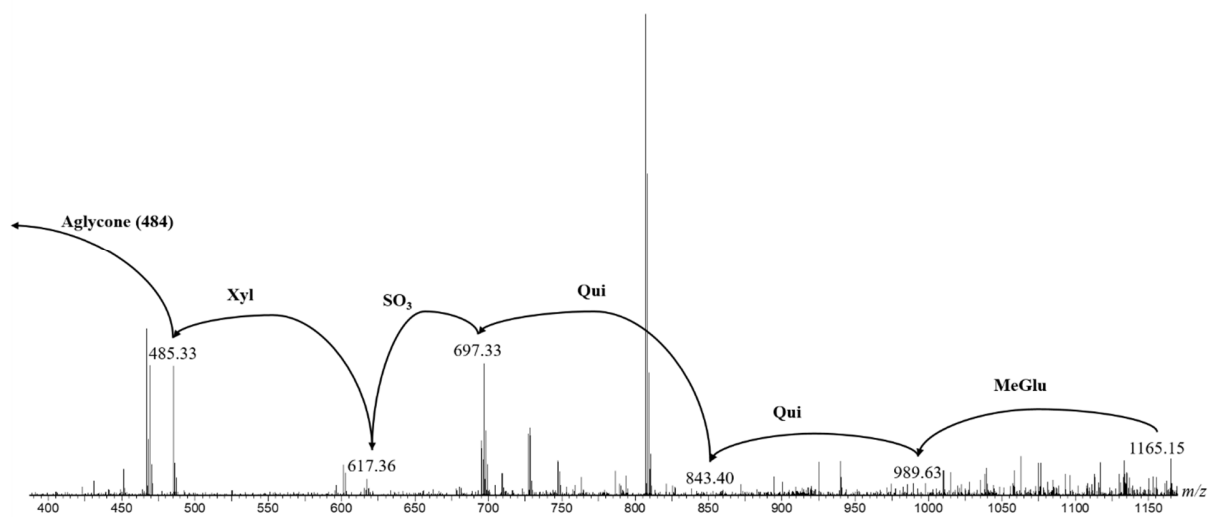


Figure S24. LC-MS/MS(+) analysis of *H. (R.) arguinensis* saponin extract: CID spectrum recorded for the m/z 1165 precursor ions $[M+H]^+$ at 7.6 min retention time (Saponin 8).

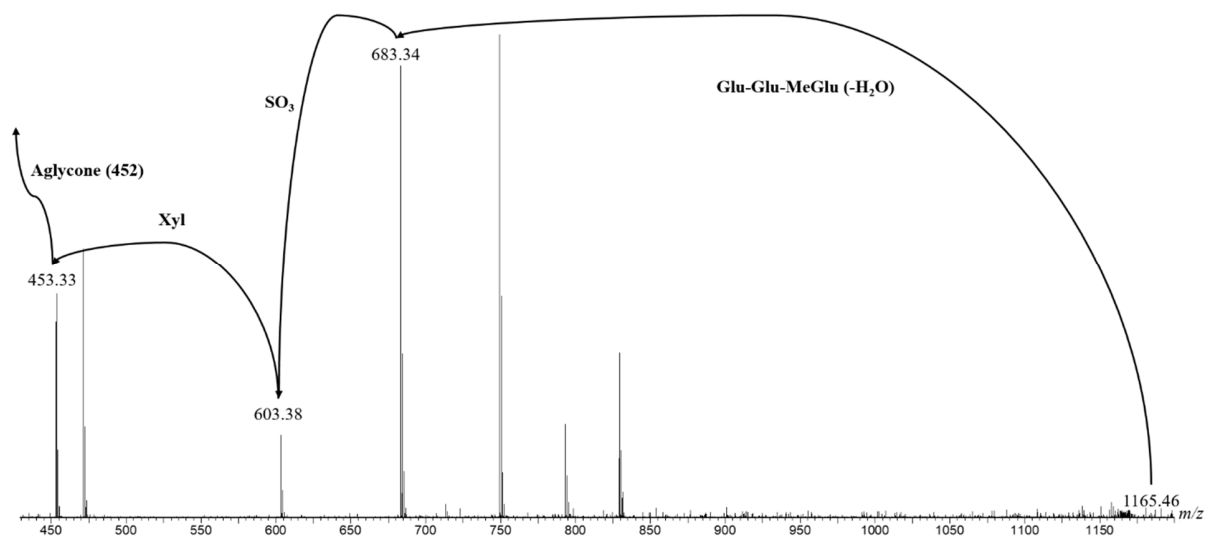


Figure S25. LC-MS/MS(+) analysis of *H. (R.) arguinensis* saponin extract: CID spectrum recorded for the m/z 1165 precursor ions $[M+H]^+$ at 11.3 min retention time (Saponin 9).

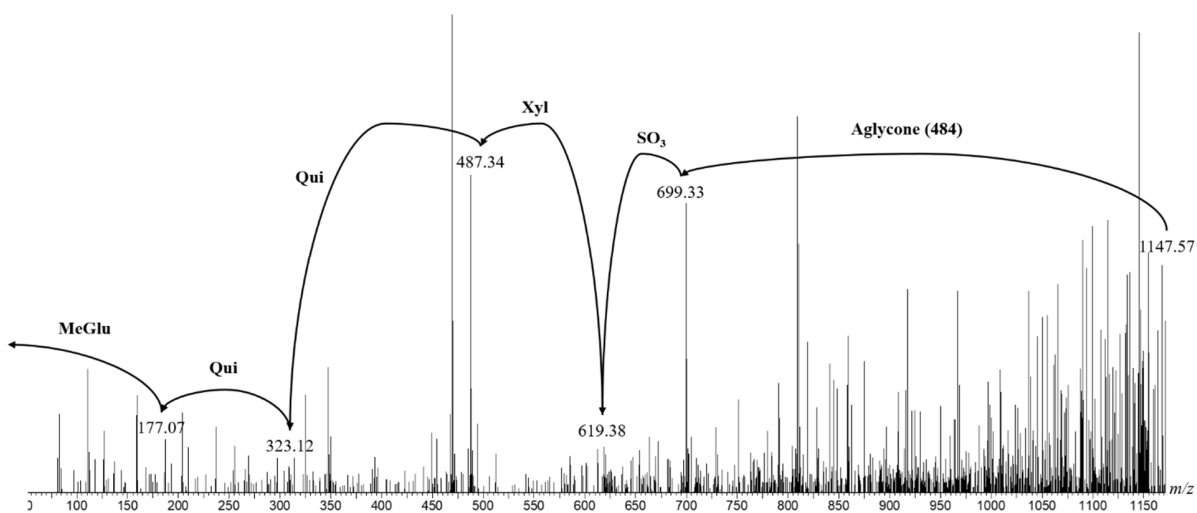


Figure S26. LC-MS/MS(+) analysis of *H. (R.) arguinensis* saponin extract: CID spectrum recorded for the m/z 1147 precursor ions $[M+H]^+$ at 7.4 min retention time (Saponin 10).

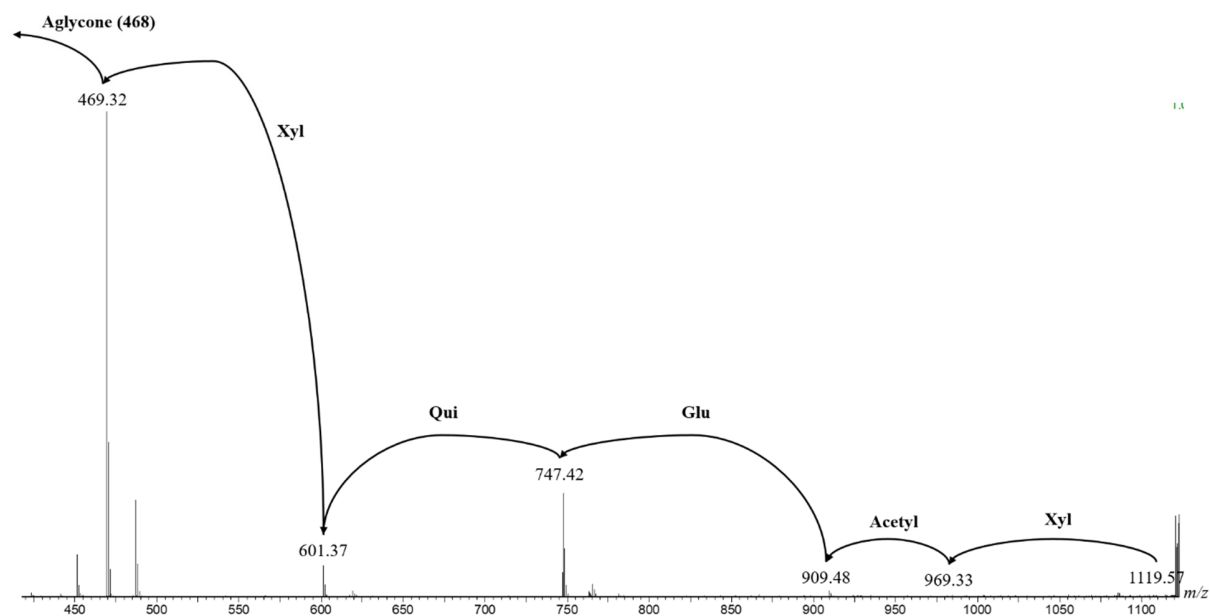


Figure S27. LC-MS/MS(+) analysis of *H. (R.) arguinensis* saponin extract: CID spectrum recorded for the m/z 1119 precursor ions $[M+H]^+$ at 10.1 min retention time (Saponin 11).

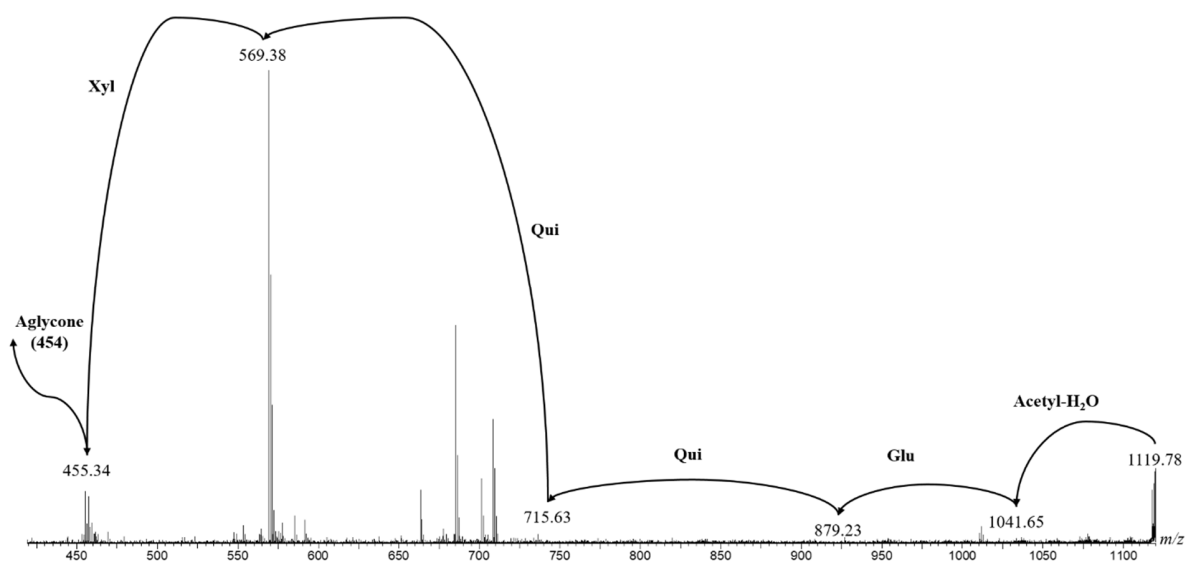


Figure S28. LC-MS/MS(+) analysis of *H. (R.) arguinensis* saponin extract: CID spectrum recorded for the m/z 1119 precursor ions $[M+H]^+$ at 13.6 min retention time (Saponin 12).

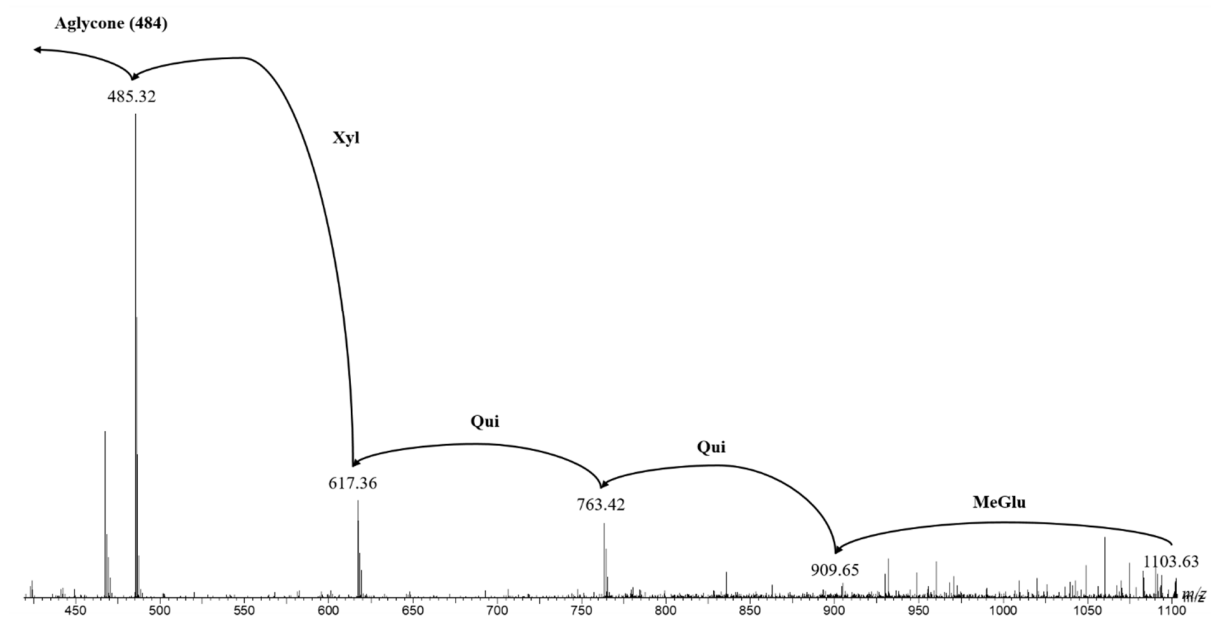


Figure S29. LC-MS/MS(+) analysis of *H. (R.) arguinensis* saponin extract: CID spectrum recorded for the m/z 1103 precursor ions $[M+H]^+$ at 7.6 min retention time (Saponin 13).

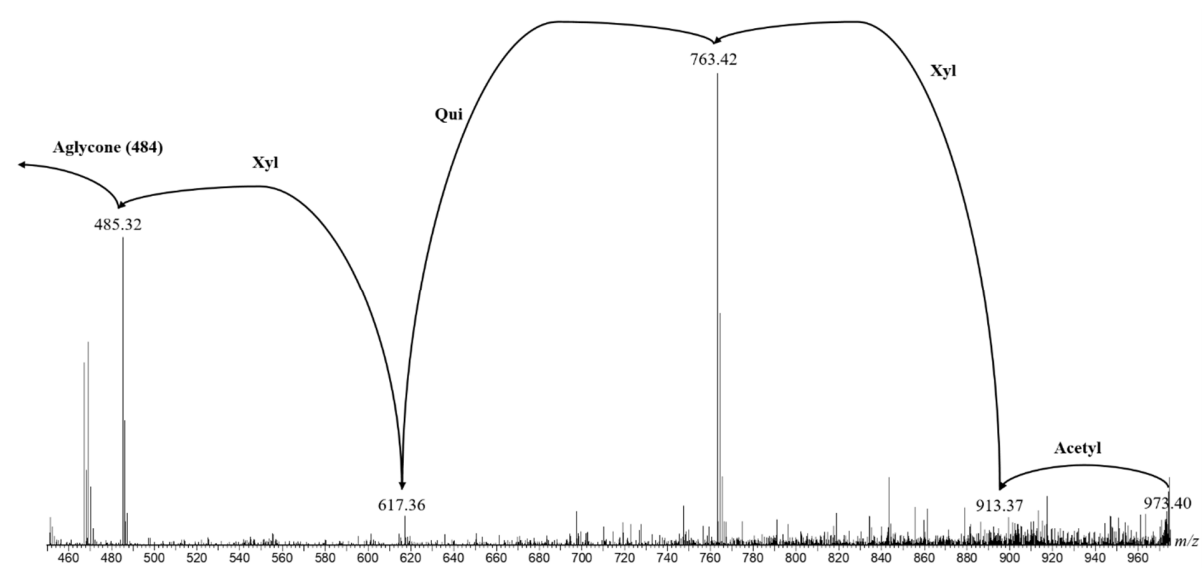


Figure S30. LC-MS/MS(+) analysis of *H. (R.) arguinensis* saponin extract: CID spectrum recorded for the m/z 973 precursor ions $[M+H]^+$ at 10.1 min retention time (Saponin 14).

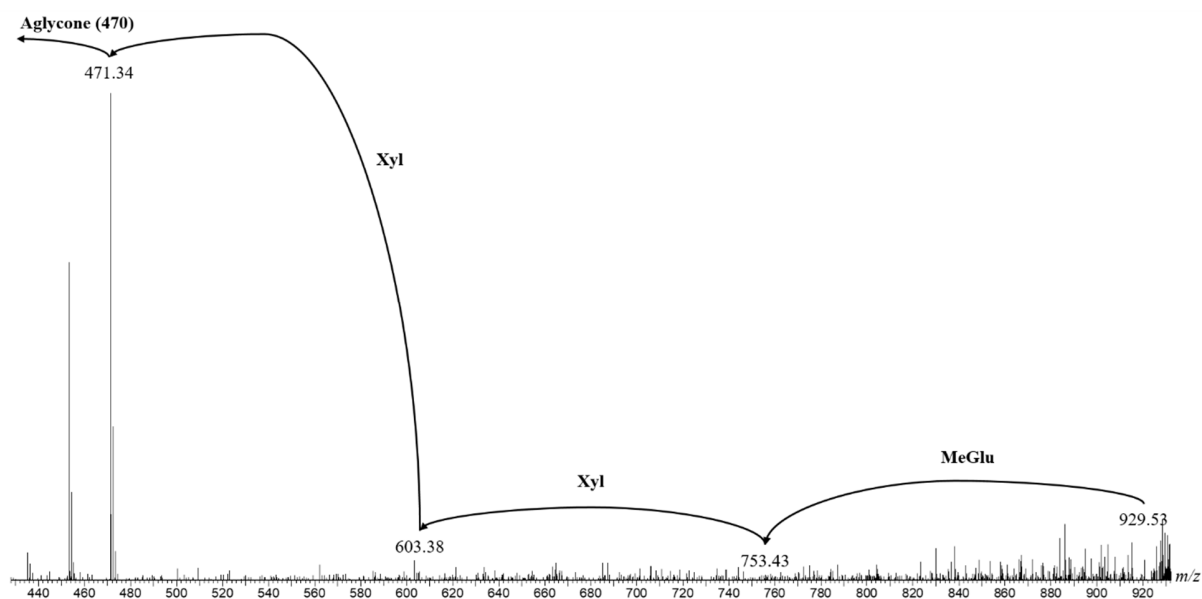


Figure S31. LC-MS/MS(+) analysis of *H. (R.) arguinensis* saponin extract: CID spectrum recorded for the m/z 929 precursor ions $[M+H]^+$ at 11.6 min retention time (Saponin 15).

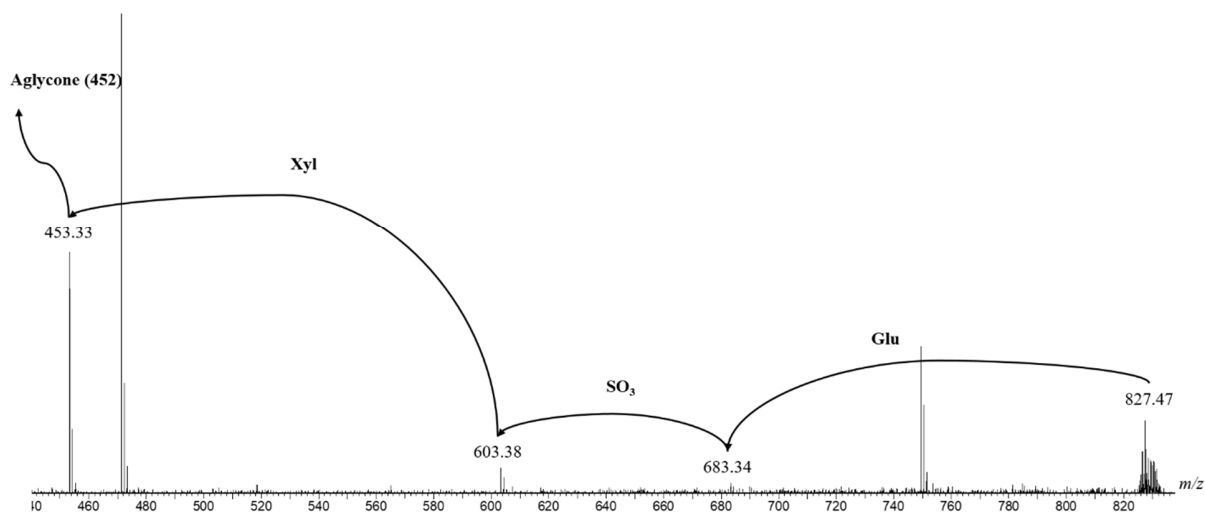


Figure S32. LC-MS/MS(+) analysis of *H. (R.) arguinensis* saponin extract: CID spectrum recorded for the m/z 827 precursor ions $[M+H]^+$ at 12.0 min retention time (Saponin 16).