

## Supplementary material

### Polyphenolic antioxidants in bilberry stems and leaves: non-targeted analysis by two-dimensional NMR spectroscopy and liquid chromatography – high-resolution mass spectrometry

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**Figure S1:** 2D  $^1\text{H}$ - $^{13}\text{C}$  HMBC spectrum of aqueous methanol extract of *V. myrtillus* leaves and stems

**Figure S2:** 2D  $^1\text{H}$ - $^{13}\text{C}$  HMBC spectrum of aqueous methanol extract of *V. uliginosum* leaves and stems

**Figure S3:** Tandem mass spectrum of the Caffeoyl-pentanediol-hexoside isomer (III) (retention time 10.2 min, precursor ion 427.1605) observed in negative ion detection mode;

**Figure S4:** Tandem mass spectrum of the *p*-Coumaroyl-pentanediol-hexoside-xyloside isomer (II) with two separate monosaccharides in structure (retention time 11.0 min, precursor ion 543.2087) observed in negative ion detection mode;

**Figure S5:** Tandem mass spectrum of the Caffeoyl hydroxydihydromonotropein (retention time 4.6 min, precursor ion 569.1512) observed in negative ion detection mode;

**Figure S6:** Tandem mass spectrum of the *p*-coumaroyl hydroxydihydromonotropein (retention time 6.6 min, precursor ion 553.1565) observed in negative ion detection mode;

**Figure S7:** Tandem mass spectrum of the Lyoniresinol-rhamnoside (retention time 9.4 min, precursor ion 565.2291) observed in negative ion detection mode.

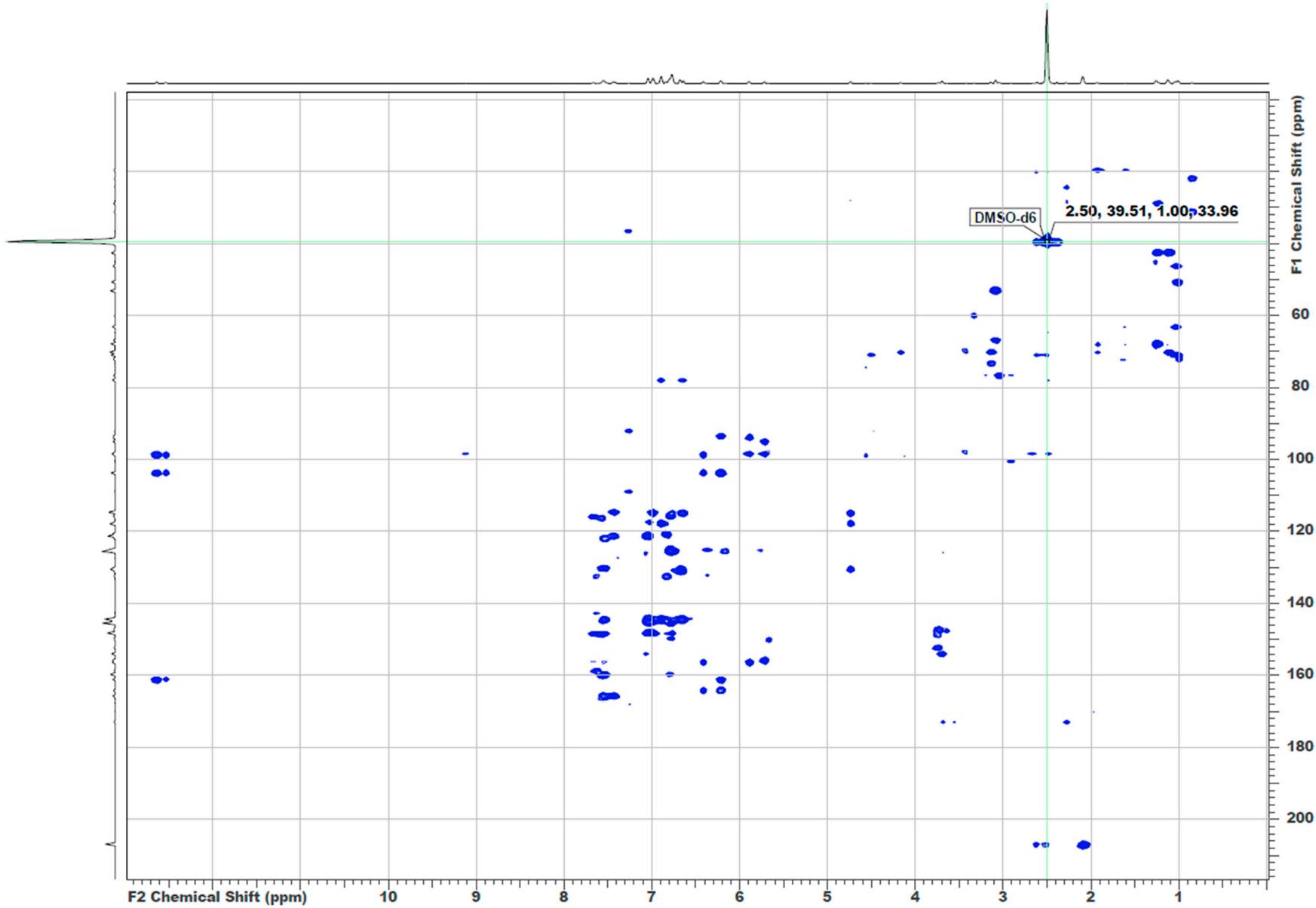


Figure S1: 2D  $^1\text{H}$ - $^{13}\text{C}$  HMBC spectrum of aqueous methanol extract of *V. myrtillus* leaves and stems

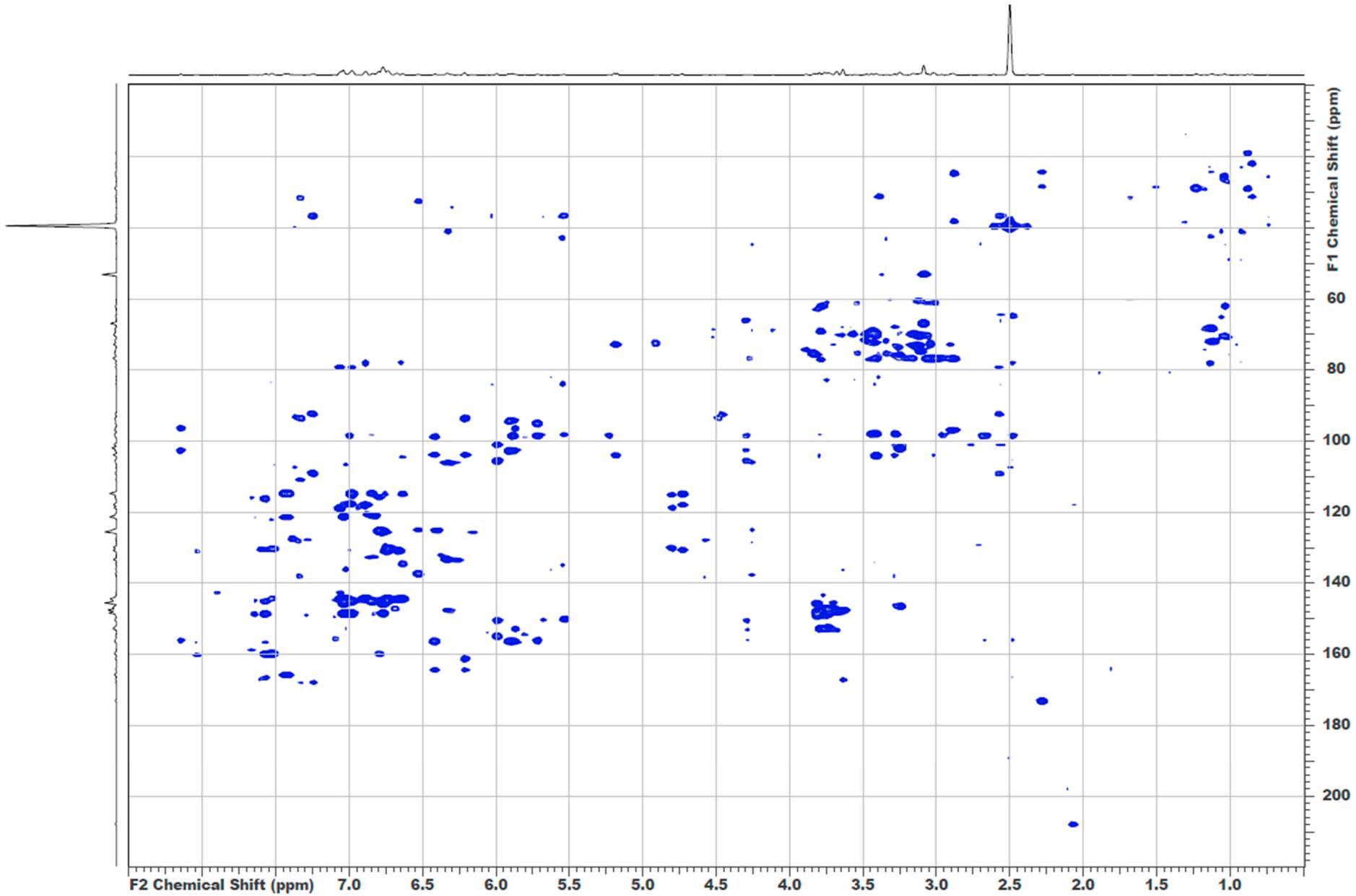


Figure S2: 2D  $^1\text{H}$ - $^{13}\text{C}$  HMBC spectrum of aqueous methanol extract of *V. uliginosum* leaves and stems

T: FTMS - p ESI d Full ms2 427.1609@hcd35.00 [65.0000-438.0000]

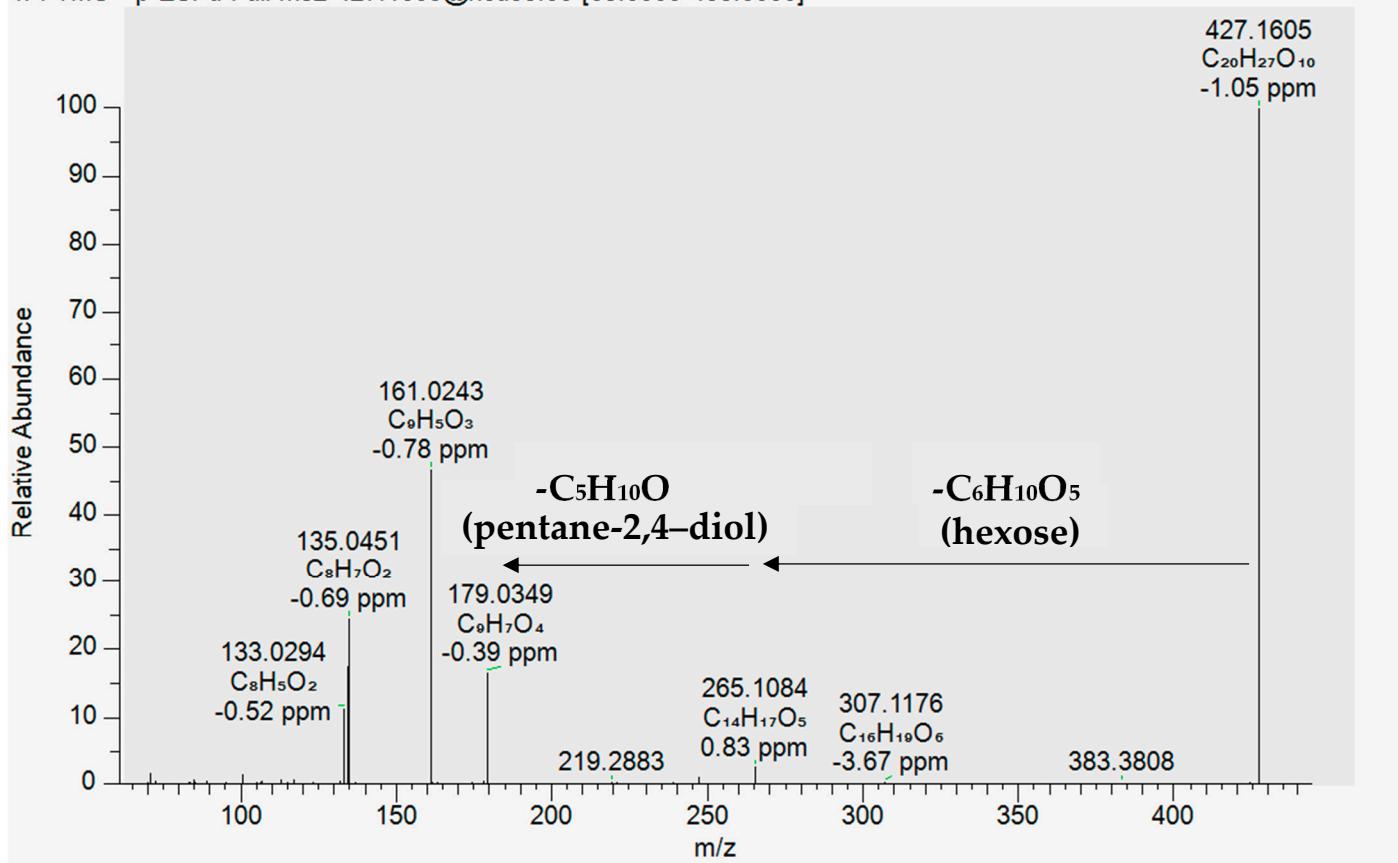
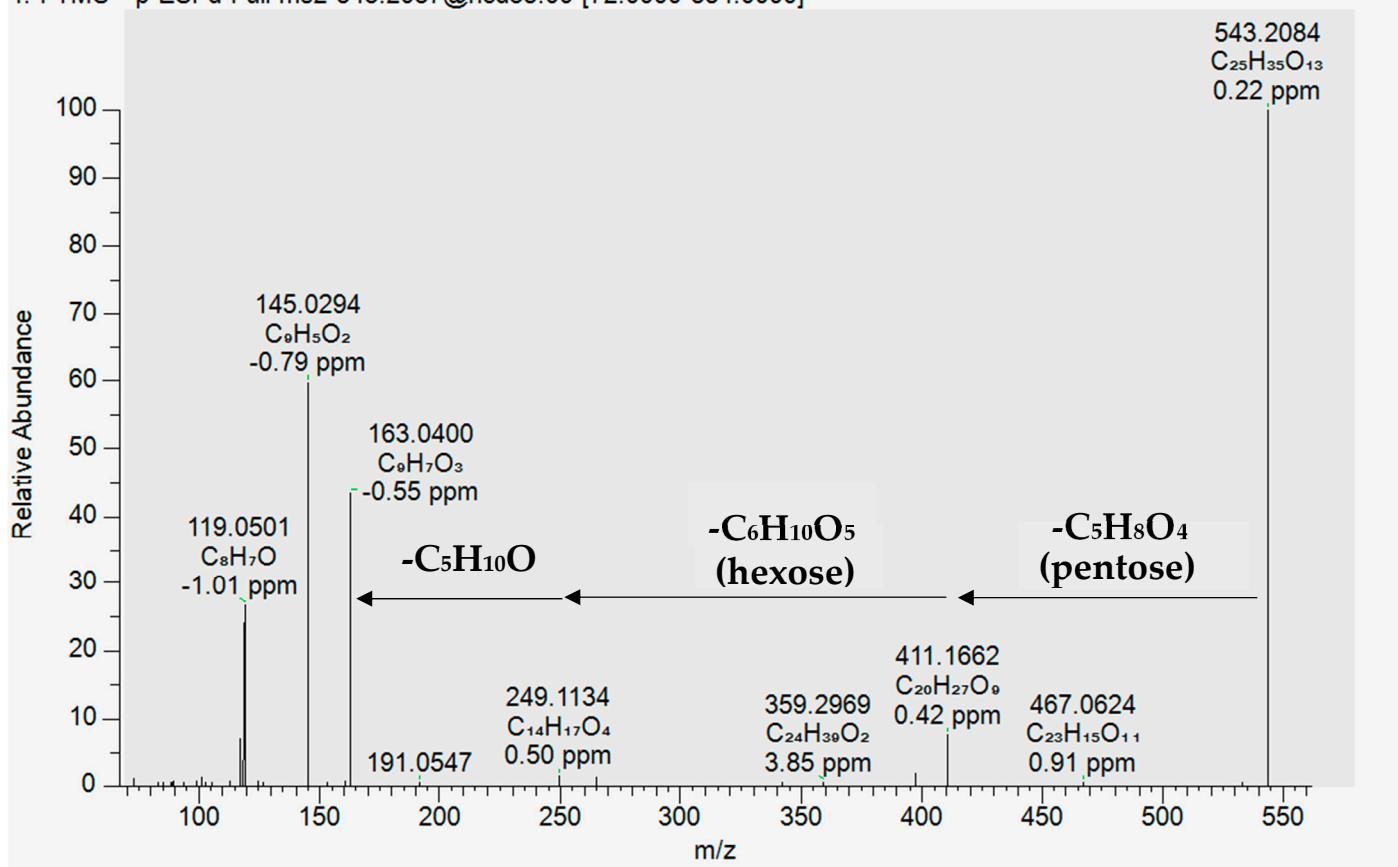


Figure S3: Tandem mass spectrum of the Caffeoyl-pentanediol-hexoside isomer (III) (retention time 10.2 min, precursor ion 427.1605) observed in negative ion detection mode

T: FTMS - p ESI d Full ms2 543.2087@hcd35.00 [72.0000-554.0000]



**Figure S4:** Tandem mass spectrum of the p-Coumaroyl-pentanediol-hexoside-xyloside isomer (II) with two separate monosaccharides in structure (retention time 11.0 min, precursor ion 543.2087) observed in negative ion detection mode

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T: FTMS - p ESI d Full ms2 569.1516@hcd35.00 [73.0000-580.0000]

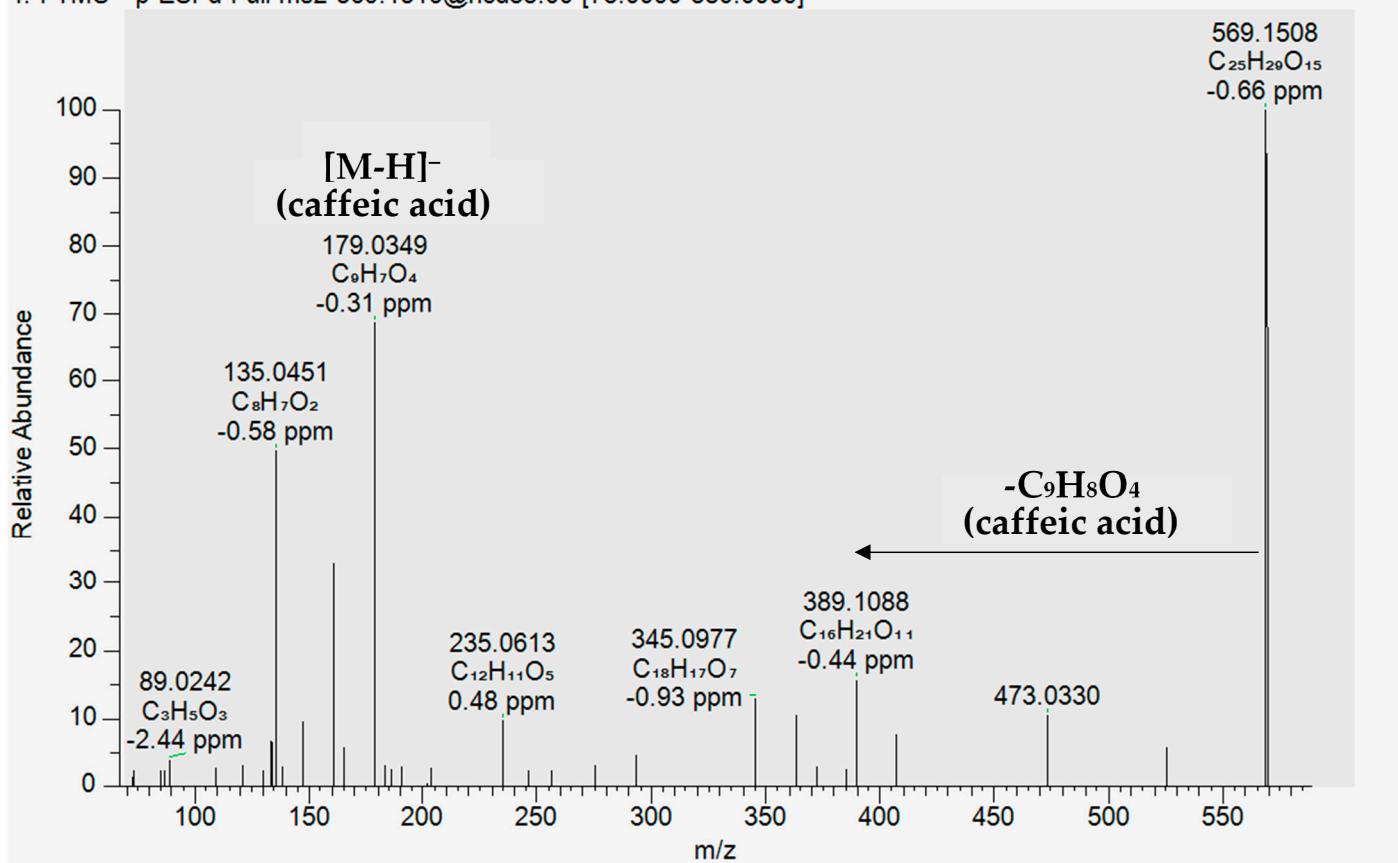
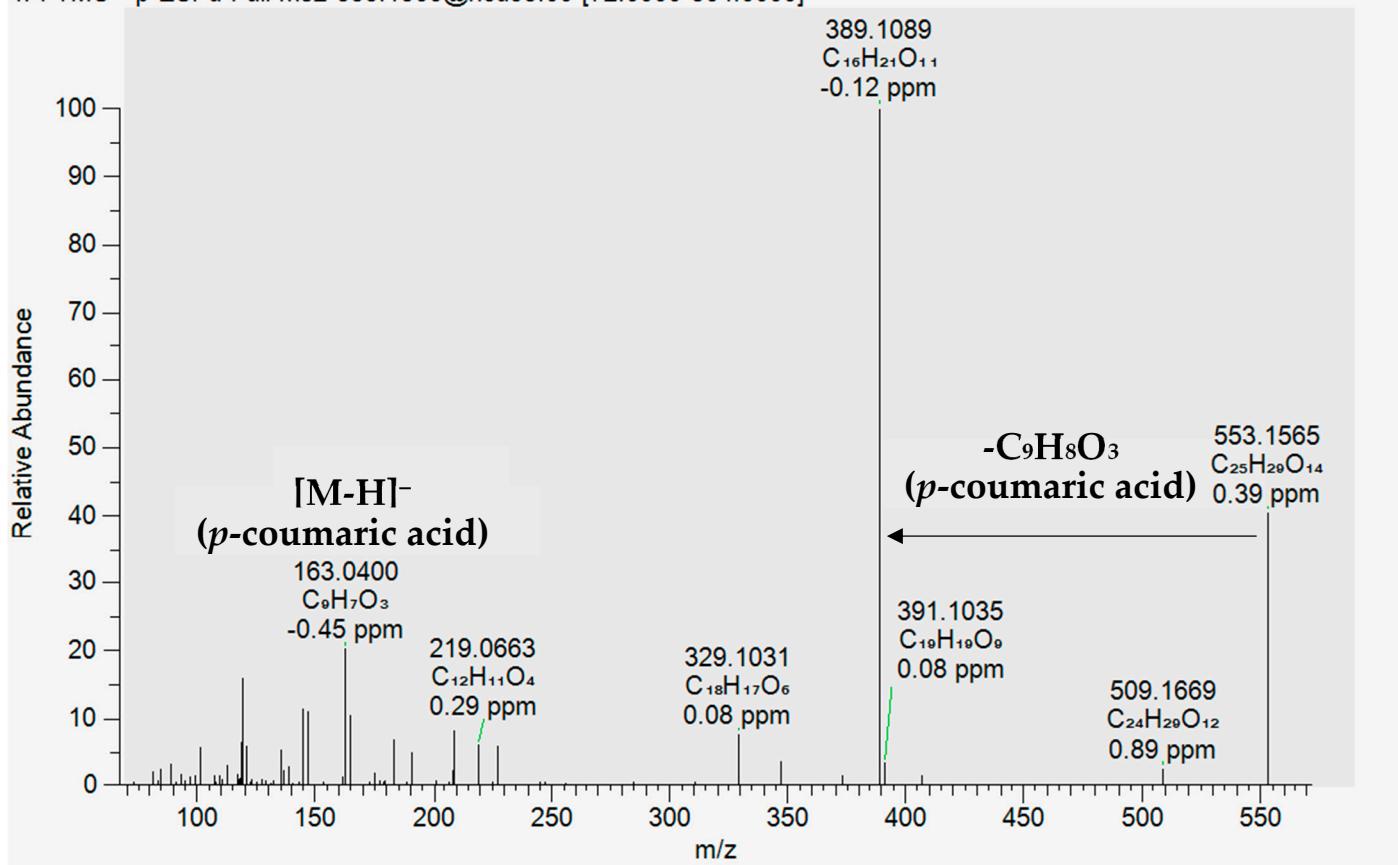


Figure S5: Tandem mass spectrum of the Caffeoyl hydroxydihydromonotropein (retention time 4.6 min, precursor ion 569.1512) observed in negative ion detection mode

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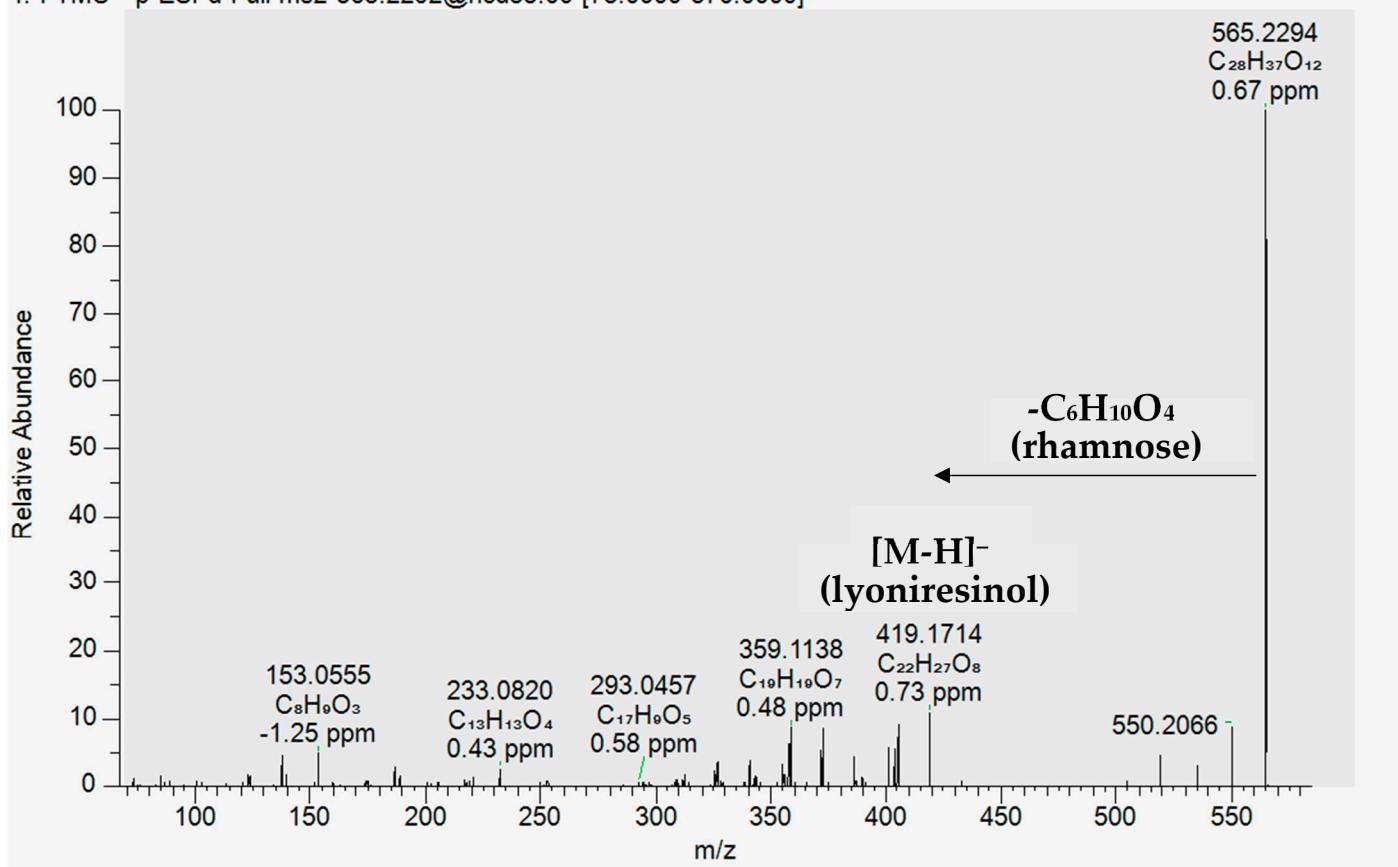
T: FTMS - p ESI d Full ms2 553.1566@hcd35.00 [72.0000-564.0000]



**Figure S6:** Tandem mass spectrum of the *p*-coumaroyl hydroxydihydromonotropein (retention time 6.6 min, precursor ion 553.1565) observed in negative ion detection mode

26  
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T: FTMS - p ESI d Full ms2 565.2292@hcd35.00 [73.0000-576.0000]



**Figure S7:** Tandem mass spectrum of the Lyoniresinol-rhamnoside (retention time 9.4 min, precursor ion 565.2291) observed in negative ion detection mode

33  
34  
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