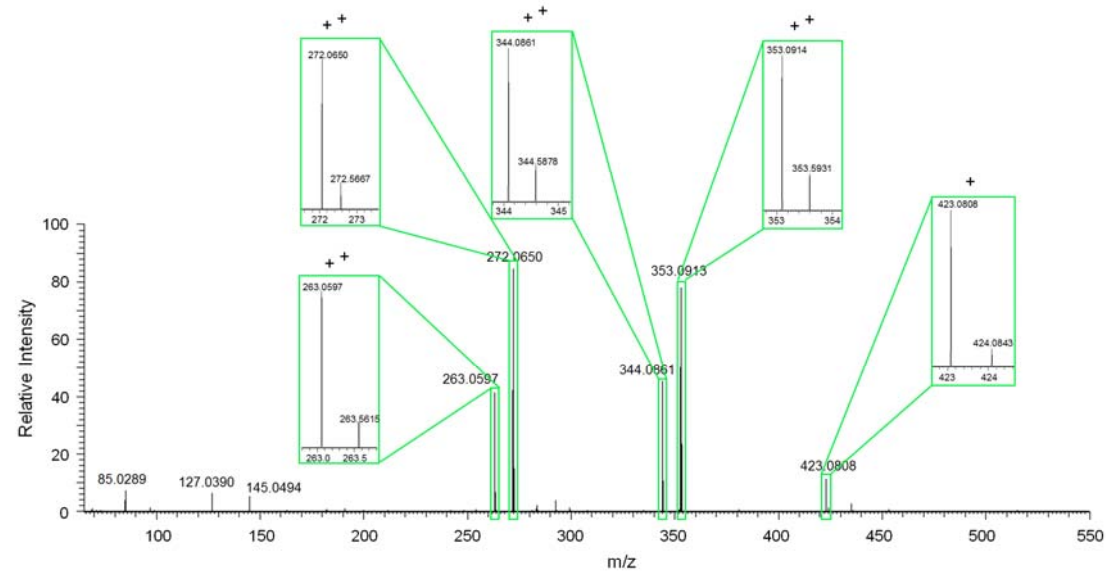


Supplementary Figure S4. Tentative marker identification. MS/MS spectra acquired for marker ion with m/z 515.1444 obtained by analysing a representative extract of a syrup sample in positive ionization mode and applying HCD fragmentation with normalized collision energy of 23%. It was possible to inspect the isotopic distribution of five out of nine product ions, which indicated that four of them were doubly charged product ions (++) and one of them was a singly charged product ion (+), as reported above each inset of the fragmentation spectrum (A).

The lower panel (B) shows the corresponding HCD fragmentation spectrum in which we reported a potential molecular formula together with mass uncertainty with respect to the theoretical value (Δ ppm) for the observed product ions. The left part of the spectrum displays three ions (i.e. m/z 127.0390, 145.0494, 163.0600) characterized by a series of water losses (i.e. mass difference of 18.011 m/z). On the right part of the spectrum, we proposed a potassium adduct for the singly charged ion with m/z 423.0808 given that potassium was present in the precursor ion. In the central part of the spectrum, we observed four doubly charged ions. We proposed a doubly charged adduct for ion with m/z 272.0650 (i.e. adduct $[M+H+K]^{++}$) and its doubly charged water loss (i.e. mass difference of 9.005 m/z) for ion with m/z 263.0597 (i.e. adduct $[M-H_2O+H+K]^{++}$).

Finally, we tentatively inferred similar adducts for ions with m/z 344.0861 and 353.0913. One of the possible calculated adducts for ion with m/z 344.0861 is $[C_{31}H_{36}O_{15}+H+K]^{++}$ that could be interpreted as $[C_{25}H_{28}O_{11}+C_6H_8O_4+H+K]^{++}$, thus representing a potassium adduct of M associated to another of the observed singly charged product ions (i.e. m/z 145.0494). In a similar way, one of the possible calculated adducts for ion with m/z 353.0861 is $[C_{31}H_{38}O_{16}+H+K]^{++}$ that could be interpreted as $[C_{25}H_{28}O_{11}+C_6H_{10}O_5+H+K]^{++}$, thus representing a potassium adduct of M associated to another of the observed singly charged product ions (i.e. m/z 163.0600).

A.



B.

