**Supporting information S2.**

Ion adducts and in-source fragments from UPLC-QToF analysis supporting the tentative identification of M = 496.2299 as atractyligenin glucuronide.

|  |  |  |  |
| --- | --- | --- | --- |
| *m/z* | RT | ESI +/- | Ion adduct or fragment |
| 520.225 | 11.3 | + | [M+Na]+ 13C isotope |
| 519.221 | 11.3 | + | [M+Na]+ |
| 497.156 | 11.3 | + | [M+H]+ |
| 495.226 | 11.3 | - | [M-H]- |
| 479.199 | 11.3 | + | [M+H-H2O]+ |
| 322.202 | 11.3 | + | [M+H-AnhGlu]+ 13C isotope |
| 321.194 | 11.3 | + | [M+H-AnhGlu]+ |
| 303.195 | 11.3 | + | [M+H-AnhGlu-H2O]+ |
| 285.187 | 11.3 | + | [M+H-AnhGlu-2H2O]+ |
| 257.191 | 11.3 | + | [M+H-AnhGlu-2H2O-CO]+ |

High resolution MS data (LTQ Orbitrap) supporting the identification of atractyligenin glucuronides.



1. Extracted ion chromatogram *m/z* 495.2234 of a non-hydrolyzed urine from a high coffee consumer showing three peaks at RT 12.3, 12.99 and 13.53 min. These peaks correspond respectively to those observed at RT 10.1, 10.8 and 11.3 min with the UPLC-QTof analysis. Similarities between isotopic patterns (inset) suggest that these three peaks are different glucuronide conjugates of atractyligenin.
2. Collision-induced dissociation spectrum of *m/z* 495.2234 produces two major fragments, *m/z* 193.0369 and *m/z* 319.1947, corresponding to [M-H]- of glucuronic acid and [M-H]- of atractyligenin.
3. MS3 spectra obtained from the successive collision-induced dissociation of the ion *m/z* 495.2234 and the daughter ion *m/z* 319.1945 produces identical fragmentation patterns for the three isomers.
4. Extracted ion chromatogram *m/z* 319.1945 from the urine of a high coffee consumer after *β*-glucuronidase-sulfatase hydrolysis, showing only one peak.
5. Collision-induced dissociation spectrum of *m/z* 319.1945 in hydrolyzed urine produces similar fragments to those produced by MS3 spectra of non-hydrolyzed urine (C). The main fragments are derived from combined losses of H2O, CO, CO2 and HCOOH, and are consistent with the fragmentation patterns predicted by Mass FrontierTM software for the proposed identification of atractyligenin glucuronide.