## SUPPLEMENTARY MATERIALS

## S1. NMR spectra of extracted metabolites

Here below the <sup>1</sup>H-NMR spectra of fumarprotocetraric acid and atranorin are reported. Results are in accordance with those reported in literature (Figure S1 and 2).

**Fumarprotocetraric acid**: <sup>1</sup>H-NMR in DMSO-d6, δ (ppm): 10.57 (s, 1H, COH), 6.82 (s, 1H, CH), 6.62 (s, 1H, CHCH), 6.62 (s, 1H, CHCH), 5.28 (s, 2H, CH2), 2.46 (s, 3H, CH3), 2.42 (s, 3H, CH3).



**Atranorin:** <sup>1</sup>**H-NMR** in CDCl<sub>3</sub>, δ (ppm): 12.59 (s, 1H, OH), 12.53 (s, 1H, OH), 11.98 (s, 1H, OH), 10.40 (s, 1H, COH), 6.55 (s, 1H, CH), 6.44 (s, 1H, CH), 4.02 (s, 3H, OCH<sub>3</sub>), 2.72 (s, 3H, CH<sub>3</sub>), 2.58 (s, 3H, CH<sub>3</sub>), 2.13 (s, 3H, CH<sub>3</sub>).



A full characterization of extracted (-)-(*S*)-usnic acid was performed via mono- and bi-dimentional NMR analysis. Results are coherent with those reported in literature (Figure S3).



Figure S3: 1H-NMR (A), HSQC (B), 13C-DEPT (C) and 13C-NMR (D) of (-)-usnic acid after MAE procedure