**Suppl. Fig. 3** Chromatograms showing prunasin and sambunigrin peaks in (**a**) *Sambucus nigra* flower-bud extracts, (**b**) open flower (pre-anthesis stage) extracts, (**c**) senescing flower extracts and (**d**) mature leaf extracts

LC-MS using an LTQ Orbitrap XL system (Thermo Scientific, MA, USA). Chromatography was performed with a 150 mm × 3 mm (i.d.), 3 μm, Luna C18(2) column (Phenomenex) using a 400 μL min-1 mobile phase gradient mixed from H2O/MeOH/CH3CN + 1% HCOOH of 90:0:10 to 50:40:10 in 20 min. Concentrated aqueous ammonia was infused post column at 0.1 µL/min to augment ionisation. Quantification was performed on the ammoniated molecule at m/z 313.1394 (± 5ppm) extracted from a positive ion MS1 scan of m/z 125-600 at 30k resolution; low resolution ion trap MS2 data on m/z 313 were acquired simultaneously for confirmation. Standard curves were obtained from prunasin (Sigma-Aldrich Inc., UK) and sambunigrin (Toronto Research Chemicals Inc., Canada) which eluted at 10.1 min and 10.6 min respectively, under these conditions.

**(a)**



**(b)**



**(c)**



**(d)**

