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PROFILING THE PROCYANIDINS FROM *CINNAMMOMUM ZEYLANICUM* BY LIQUID CHROMATOGRAPHY/TANDEM MASS SPECTROMETRY

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Proanthocyanidins (PAs) are a group of structurally diverse biologically active polyphenolic compounds which are oligomers of flavan-3-ol units, and are ubiquitous in nature. PAs that consist exclusively of (epi)catechins are procyanidins (PCs), while PAs that contain at least one subunit of (epi)afzelechin or (epi)gallocatechin are called propelargonidin and prodelphinidin respectively. PAs are classified into two groups, A-type and B-type PAs, according to the nature of the inter-flavanol linkages. B-type PAs, in which the inter-flavanol linkages are C-C bonds between C4 of one flavanol unit and C8 or C6 of another flavanol unit, are encountered more frequently in nature. The double linked A-type PAs have a bond between either C2-O7 or C2-O5 in addition to the C4-C8. In this study PAs of *Cinnammomum zeylanicum* were investigated qualitatively by liquid chromatography/tandem mass spectrometry. An aqueous methanolic (70%) extract of cinnamon powder was used for LC-MS^n, to ensure an efficient extraction of phenolics, especially PAs. The C_{18} amide reverse phase HPLC column was used as it was found to be more efficient in the separation of PAs and allowed the separation of different oligomers with the same molecular mass. For the LC-MS measurements negative ion mode was used to obtain better tandem mass spectra and high resolution mass spectra. For all the compounds the high resolution mass data were in good agreement with the theoretical molecular formulae, all displaying a mass error of below 5 ppm thus confirming their elemental composition. A total of 37 A-type and B-type PCs and their monomers, catechin and epicatechin at *m/z* 289 $[M-H]^-$ were detected. Five A-type PC dimers (epi)cat-4,8'/2,7'-(epi)cat *m/z* 575 $[M-H]^-$; three B-type PC dimers (epi)cat-4,8'-(epi)cat *m/z* 577 $[M-H]^-$; one A-type PC trimer (epi)cat-4,8'/2,7'-(epi)cat-4',8''/2',7''-(epi)cat), *m/z* 861 $[M-H]^-$; four A-type PC trimers (epi)cat-4,8'/2,7'-(epi)cat-4',8''-(epi)cat), *m/z* 863 $[M-H]^-$; three B-type PC trimers (epi)cat-4,8'-(epi)cat-4',8''-(epi)cat, *m/z* 865 $[M-H]^-$; two A-type PC tetramers (epi)cat-4,8'/2,7'-(epi)cat-4',8''-(epi)cat-4'',8'''-(epi)cat, *m/z* 1151 $[M-H]^-$; six A-type PC tetramers (epi)cat-4,8'-(epi)cat-4',8''/2',7''-(epi)cat-4'',8'''-(epi)cat, *m/z* 1151 $[M-H]^-$, ten B-type PC tetramers (epi)cat-4,8'-(epi)cat-4',8''-(epi)cat-4'',8'''-(epi)cat, *m/z* 1153 $[M-H]^-$; a PC pentamer with one A-type linkage *m/z* 1439 $[M-H]^-$; two B-type PC pentamers, *m/z* 1441$[M-H]^-$ were identified on the basis of their unique multi step fragmentation pattern in the negative ion mode of tandem mass spectra.

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