*antioxidants*

MDPI

# Supplementary Materials:

# Contribution of Individual Polyphenols to Antioxidant Activity of *Cotoneaster bullatus* and *Cotoneaster zabelii* Leaves - Structural Relationships, Synergy Effects and Application for Quality Control

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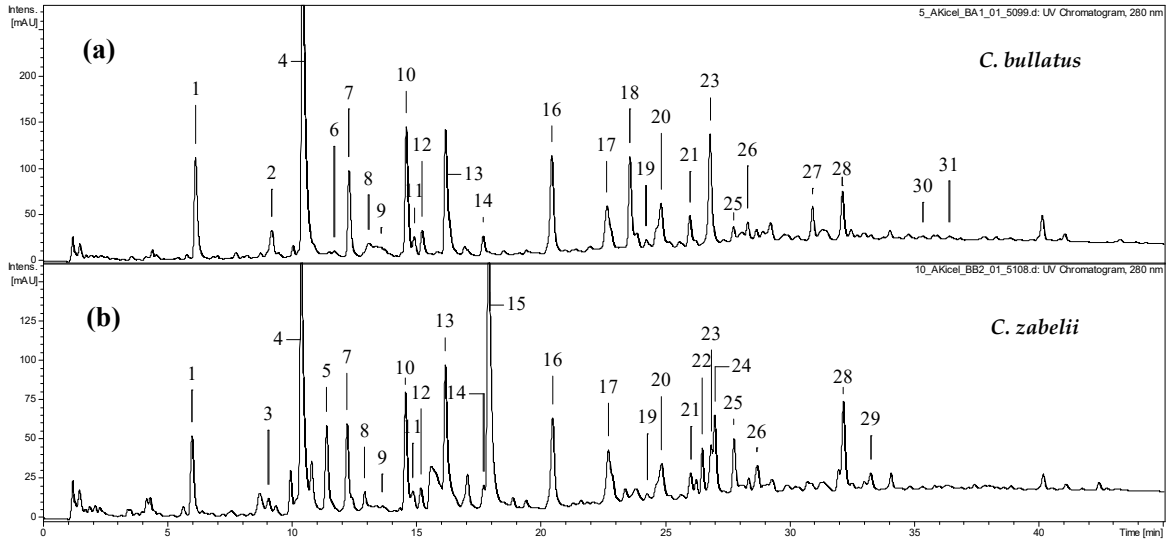


**Figure S1.** Representative UHPLC-UV chromatograms of the methanol-water (7;3, *v*/*v*) extracts from the leaves of *C. bullatus* **(a)** and *C. zabelii* **(b)** at 280 nm. The peak numbers refer to those applied in Table S1.

**Table S1.** UHPLC-PDA-ESI-MS$^3$ data of polyphenols identified in the methanol-water (7:3, *v*/*v*) extracts from the leaves of *C. bullatus* and *C. zabelii*.

| Peak | Analyte | $R_t$ [a] (min) | UV $\lambda_{max}$ [b] (nm) | $[M-H]^-$ [c] (m/z) | $MS^2$ | $MS^3$ | ME Extracts [d] |
|---|---|---|---|---|---|---|---|
| **1** | neochlorogenic acid (3-*O*-caffeoylquinic acid, **NCHA**) * | 6.1 | 325 | 353 | 191, 179, 135 | | CB, CZ |
| **2** | procyanidin dimer B-type | 9.0 | 280 | 577 | 451, **425**, 407, 289 | 407, 273 | CB |
| **3** | caffeic acid derivative | 9.7 | 325 | 451 | 405, 179 | | CZ |
| **4** | chlorogenic acid (5-*O*-caffeoylquinic acid, **CHA**)* | 10.4 | 325 | 353 | 191, 179 | | CB, CZ |
| **5** | dicaffeoylquinic acid isomer | 11.1 | 325 | 515 | 395, 379, 285 | | CZ |
| **6** | procyanidin dimer B-type | 11.7 | 280 | 577 | 451, **425**, 407, 289 | 407, 273 | CB |
| **7** | cryptochlorogenic acid 4-*O*-caffeoylquinic acid, **CCHA**)* | 12.3 | 325 | 353 | 191, 179, 173 | | CB, CZ |
| **8** | dicaffeoylquinic acid isomer | 12.8 | 325 | 515 | 395, 379, 285 | | CB, CZ |
| **9** | procyanidin dimer B-type | 13.5 | 280 | 577 | 451, **425**, 407, 289 | 407, 273 | CB, CZ |
| **10** | procyanidin B2 (**PB2**)* | 14.6 | 280 | 577 | 451, **425**, 407, 289 | 407, 273 | CB, CZ |
| **11** | procyanidin trimer B-type | 15.0 | 280 | 865 | 739, **713**, 695, 577 | 695, 425, 407 | CB, CZ |
| **12** | 5-*p*-coumaroylquinic acid | 15.3 | 310 | 337 | 191, 163 | | CB, CZ |
| **13** | (-)-epicatechin (**ECA**)* | 16.1 | 280 | 289 | 245, 205, 179, 137 | | CB, CZ |
| **14** | procyanidin tetramer B-type | 17.7 | 280 | 1153 | 1027, 863, 739, 501, 491, 289 | | CB, CZ |
| **15** | caffeic acid derivative (**CAD**) | 18.2 | 290, 328 | 613 | 457, 339, 295, 179 | | CZ |
| **16** | procyanidin C1 (**PC1**)* | 20.4 | 280 | 865 | **713**, 695, 577 | 695, 425, 407 | CB, CZ |
| **17** | procyanidin tetramer B-type | 22.9 | 280 | 1153 | 1027, 863, 739, 501, 491, 289 | | CB, CZ |
| **18** | quercetin pentoside-hexoside (**QPH**) | 23.6 | 268, 355 | 595 | 463, 445, 301 | | CB |
| **19** | procyanidin tetramer B-type | 24.3 | 280 | 1153 | 1027, 863, 739, 501, 491, 289 | | CB, CZ |
| **20** | procyanidin dimer hexoside | 24.9 | 280 | 739 | 587, 577, 451, 289 | | CB, CZ |
| **21** | quercetin rhamnoside-hexoside | 26.4 | 255, 355 | 609 | **447**, 343, 301 | 301 | CB, CZ |
| **22** | quercetin dirhamnoside | 26.6 | 255, 350 | 593 | **447**, 301 | 301 | CZ |
| **23** | hyperoside (quercetin 3-*O*-ß-galactoside, **HP**)* | 26.9 | 255, 353 | 463 | 301 | | CB, CZ |
| **24** | rutin (quercetin 3-*O*-ß-(6´´-*O*-α-rhamnosyl)-glucoside , **RT**)* | 27.3 | 265, 350 | 609 | 463, 343, 301 | | CZ |
| **25** | isoquercitrin (quercetin-*O*-ß-glucoside, **IQ**)* | 27.9 | 275, 350 | 463 | 301 | | CB, CZ |
| **26** | procyanidin dimer B-type | 28.5 | 280 | 577 | 425, 407, 289 | | CB, CZ |
| **27** | quercetin rhamnoside-hexoside | 31.0 | 265, 355 | 609 | 447, 301 | | CB |
| **28** | quercitrin (quercetin 3-*O*-ß-rhamnoside, **QR**)* | 32.2 | 275, 350 | 447 | 301 | | CB, CZ |
| **29** | quercetin hexoside derivative | 33.3 | 265, 355 | 505 | 463, 337, 301 | | CZ |
| **30** | quercetin dirhamnoside | 35.3 | 365, 355 | 593 | 447, 301 | | CB |
| **31** | dicaffeoylquinic acid isomer | 36.3 | 325 | 515 | 379, **353**, 299, 203 | 191, 179, 173 | CB |

* identified with authentic standards; [a] $R_t$, retention time; [b] UV λmax, absorbance maxima in PDA spectra; [c] $[M-H]^-$, pseudomolecular ion in MS spectra recorded in a negative mode; [d] **ME** extracts, methanol-water (7:3, *v*/*v*) leaf extracts; **CB**, *C. bullatus*; **CZ**, *C. zabelii*.

**Table S2.** Chromatographic properties of the optimized HPLC-PDA method.

| Analyte | $t_R$ (*min*) | *RSD* $t_R$ (%) | $R_s$ | *T* | *w* | *F* |
|---|---|---|---|---|---|---|
| **NCHA** | 3.58 | 2.28 | - | 1.021 | 2.616 | 1.281 |
| **CHA** | 6.19 | 0.88 | 16.337 | 1.038 | 1.558 | 0.750 |
| **CCHA** | 6.82 | 0.58 | 5.242 | 1.052 | 1.460 | 0.694 |
| **PB2** | 7.33 | 0.99 | 5.125 | 1.036 | 1.409 | 0.680 |
| **ECA** | 7.91 | 0.48 | 5.785 | 1.143 | 1.215 | 0.532 |
| **PC1** | 8.71 | 1.04 | 7.601 | 1.061 | 1.361 | 0.641 |
| **CAD** | 9.12 | 1.54 | 3.102 | 1.121 | 1.260 | 0.562 |
| **QPH** | 9.54 | 1.12 | 6.914 | 1.308 | 1.260 | 0.482 |
| **RT** | 10.23 | 0.53 | 8.787 | 1.087 | 1.111 | 0.511 |
| **HP** | 10.49 | 0.66 | 1.703 | 1.112 | 1.158 | 0.520 |
| **IQ** | 10.85 | 0.70 | 2.022 | 1.109 | 1.142 | 0.515 |
| **QR** | 11.83 | 0.82 | 12.006 | 1.119 | 1.215 | 0.543 |

$t_R$, retention time; *RSD* $t_R$ values for retention times ($t_R$); resolution ($R_s$) and symmetry ($T$) factors between analyte peaks were calculated using the following equations: $R_s = 2.0 \times (t_{R2} - t_{R1})/(w_2 + w_1)$ and $T = w/2F$, where ($t_{R2} - t_{R1}$) is the difference between retention times of two peaks; ($w_2 + w_1$) is the sum of peak widths at baseline between tangent lines drawn at 50% of peak heights; $w$ is the peak width at 5% of peak height; and $F$ is the time from width start point at 5% of peak height to $t_R$.