

Characterization of the (Poly)Phenolic Fraction of Fig Peel: Comparison among Twelve Cultivars Harvested in Tuscany

Luca Calani ¹, Letizia Bresciani ^{1,*}, Margherita Rodolfi ¹, Daniele Del Rio ¹, Raffaella Petruccelli ², Cecilia Faraloni ² and Tommaso Ganino ^{1,2,*}

¹ Department of Food and Drug, University of Parma, Parco Area delle Scienze 27/A, 43124 Parma, Italy

² Institute of BioEconomy (IBE-CNR), via Madonna del Piano 10, 50019 Sesto Fiorentino (FI), Italy

* Correspondence: letizia.bresciani@unipr.it (L.B.); tommaso.ganino@unipr.it (T.G.); Tel.: +39-0521-903906 (L.B.); +39-0521-905597 (T.G.)

Supplementary Material

Table S1. Chromatographic and mass spectrometric characteristics of (poly)phenols identified in fig peels and whole dried fig.

| Compound | RT (min) | [M-H] ⁻ (m/z) | MS ² ions (m/z) | MS ³ ions (m/z) | Standard compound used for quantification |
|------------------------------------|-------------|-----------------------------|-------------------------------|-------------------------------|--|
| Phenolic acids | | | | | |
| Vanillic acid derivative I | 7.46 | 167 | 152,167 | | |
| Vanillic acid derivative II | 8.96 | 167 | 123,152 | | |
| Dihydroxybenzoic acid-O-pentoside | 3.21 | 285 | 153,152,165,151,163,225,109 | (153)109,135 | |
| Hydroxybenzoic acid-O-hexoside | 4.07 | 299 | 137 | (137)93 | |
| Dihydroxybenzoic acid-O-hexoside | 1.75 | 315 | 153,152,165,109 | (153)109,153,108 | |
| Caffeic acid-O-hexoside | 3.86 | 341 | 179,297,113,143,173 | | |
| Homovanillic acid-O-hexoside | 2.97 | 343 | 181,137,163 | | |
| 3-Caffeoylquinic acid | 2.70 | 353 | 191,179 | (191)127,173,85,93 | 3-Caffeoylquinic acid |
| 5-Caffeoylquinic acid | 6.24 | 353 | 191,179 | (191)127,173,85,93 | 5-Caffeoylquinic acid |
| Caffeoylquinic acid isomer | 7.27 | 353 | 191,179 | (191)127,173,85,93 | 5-Caffeoylquinic acid |
| Ferulic acid-O-hexoside** | 6.14 | 401 | 355,193 | (355)193 | |
| Sinapic acid-O-hexoside** | 6.93 | 431 | 385,223,269 | (385)223 | |
| Flavan-3-ols | | | | | |
| (+)-Catechin | 4.25 | 289 | 245,205,179,231 | | (+)-Catechin |
| (-)-Epicatechin | 7.19 | 289 | 245,205,179,231 | | (+)-Catechin |
| Procyanidin dimer B-type | 3.57 | 577 | 425,451,407,289,287,467 | | Procyanidin B2 |
| Flavanones | | | | | |
| Pinocembrin | 12.39 | 255 | 213,211,151,187 | | |
| Naringenin | 12.17 | 271 | 151,177 | | |
| Naringenin-like | 12.33 | 271 | 151,177 | | |
| Naringenin-O-hexoside | 10.74 | 433 | 271,295 | (271)151,177,107 | |
| Flavones | | | | | |
| Apigenin | 12.51 | 269 | 269,225,149,201,151,226,227 | (269)269,225,149,181 | |
| Vitexin | 8.88 | 431 | 311,341 | | Vitexin |
| Apigenin-C-hexoside | 9.07 | 431 | 311,341,413 | | Vitexin |
| Luteolin-C-hexoside | 8.58 | 447 | 327,357,429,285 | (327)299,284,327,283 | Vitexin |
| Apigenin-C-hexoside-C-pentoside I | 8.46 | 563 | 443,473,545,503,353,383 | | Vitexin |
| Apigenin-C-hexoside-C-pentoside II | 8.51 | 563 | 443,473,545,503,353,383 | | Vitexin |
| Apigenin-O-rutinoside | 7.96 | 577 | 269,283,225,311 | | Rutin |
| Apigenin-O-rhamnoside-C-hexoside | 9.02 | 577 | 413,293,457,341 | | Vitexin |

| | | | | | |
|---------------------------------------|-------|-------|---|----------------------------------|-------------------------|
| Luteolin-C-hexoside-O-rhamnoside | 8.54 | 593 | 473 ,429,285,357,339,309,284,327 | | Vitexin |
| Methyluteolin-O-rhamnoside-C-hexoside | 9.21 | 607 | 443 ,323,353,487 | | Vitexin |
| Flavonols | | | | | |
| Quercetin-O-hexoside | 9.28 | 463 | 301 ,300,302 | (301)179,151,273,257,283 | Rutin |
| Taxifolin-O-hexoside | 5.69 | 465 | 303 ,285 | (303)285,177,125,259 | |
| Kaempferol-O-acetylhexoside | 10.22 | 489 | 285 ,327 | (285)257,267,241,229,163,199,213 | Rutin |
| Quercetin-O-acetylhexoside I | 9.40 | 505 | 301 ,300,463 | (301)179,151,257,229 | Rutin |
| Quercetin-O-acetylhexoside II | 9.58 | 505 | 301 ,300,463 | (301)179,151,257,229 | Rutin |
| Kaempferol-O-rutinoside | 9.66 | 593 | 285 ,286,257 | (285)257,267,229,241,213 | Rutin |
| Quercetin-3-O-rutinoside | 9.1 | 609 | 301 ,299,343 | (301)179,151,257,273 | Rutin |
| Anthocyanins | | | | | |
| Cyanidin-3-O-glucoside | 6.95 | 449* | 287 ,286 | (287)287,213,231,241,259,189 | Cyanidin-3-O-glucoside |
| Cyanidin-O-malonylglucoside | 8.86 | 535* | 287 ,535,491,449 | (287)287,213,259,241,231,269,189 | Cyanidin-3-O-glucoside |
| Cyanidin-3-O-rutinoside | 7.41 | 595* | 595 ,287,449 | (595)287,449 | Cyanidin-3-O-rutinoside |
| Cyanidin-O-dihexoside | 5.57 | 611* | 611 | (611)449,287 | Cyanidin-3-O-glucoside |
| (epi)catechin-cyanidin-rutinoside | 6.33 | 883* | 883 | (883)575,423,737,329,557 | Cyanidin-3-O-rutinoside |
| Cyanidin-O-rutinoside dimer I | 6.63 | 1189* | 1189 | (1189)881,1043,735,573 | Cyanidin-3-O-rutinoside |
| Cyanidin-O-rutinoside dimer II | 7.57 | 1189* | 1189 | (1189)881,1043,735,573 | Cyanidin-3-O-rutinoside |
| Cyanidin-O-rutinoside dimer III | 8.34 | 1189* | 1189 | (1189)881,1043,735,573 | Cyanidin-3-O-rutinoside |

*Anthocyanins analysed in ESI+ [M]⁺. ** Formate adduct. Product ions are listed in their order of relative ionic abundance and the highest fragment ion is reported in bold type.

Figure S1. Chromatographic profiles of caffeoylquinic acids and their MS/MS spectra.

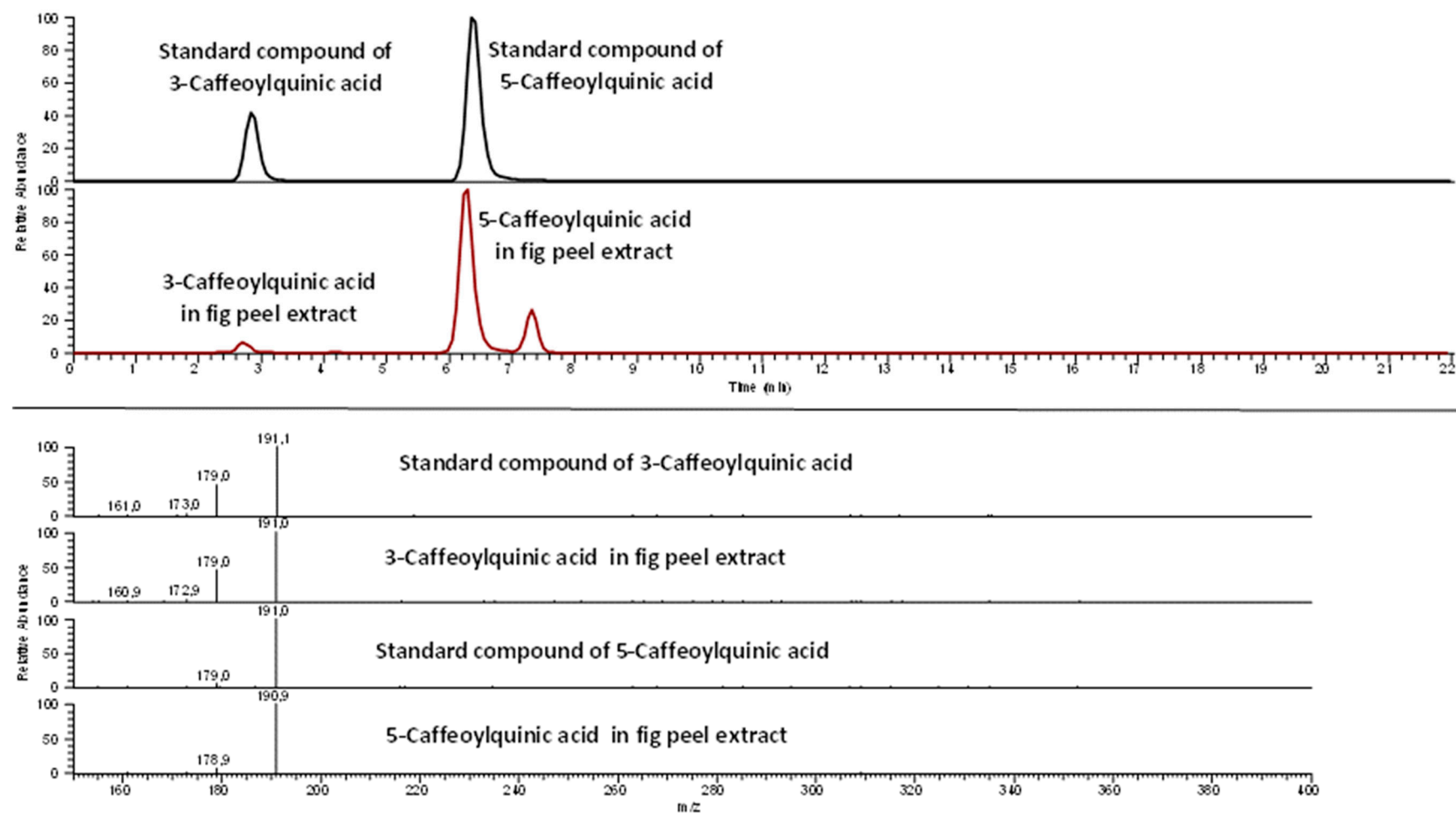


Figure S2. Chromatographic profile of quercetin-3-O-rutinoside and its MS/MS spectra.

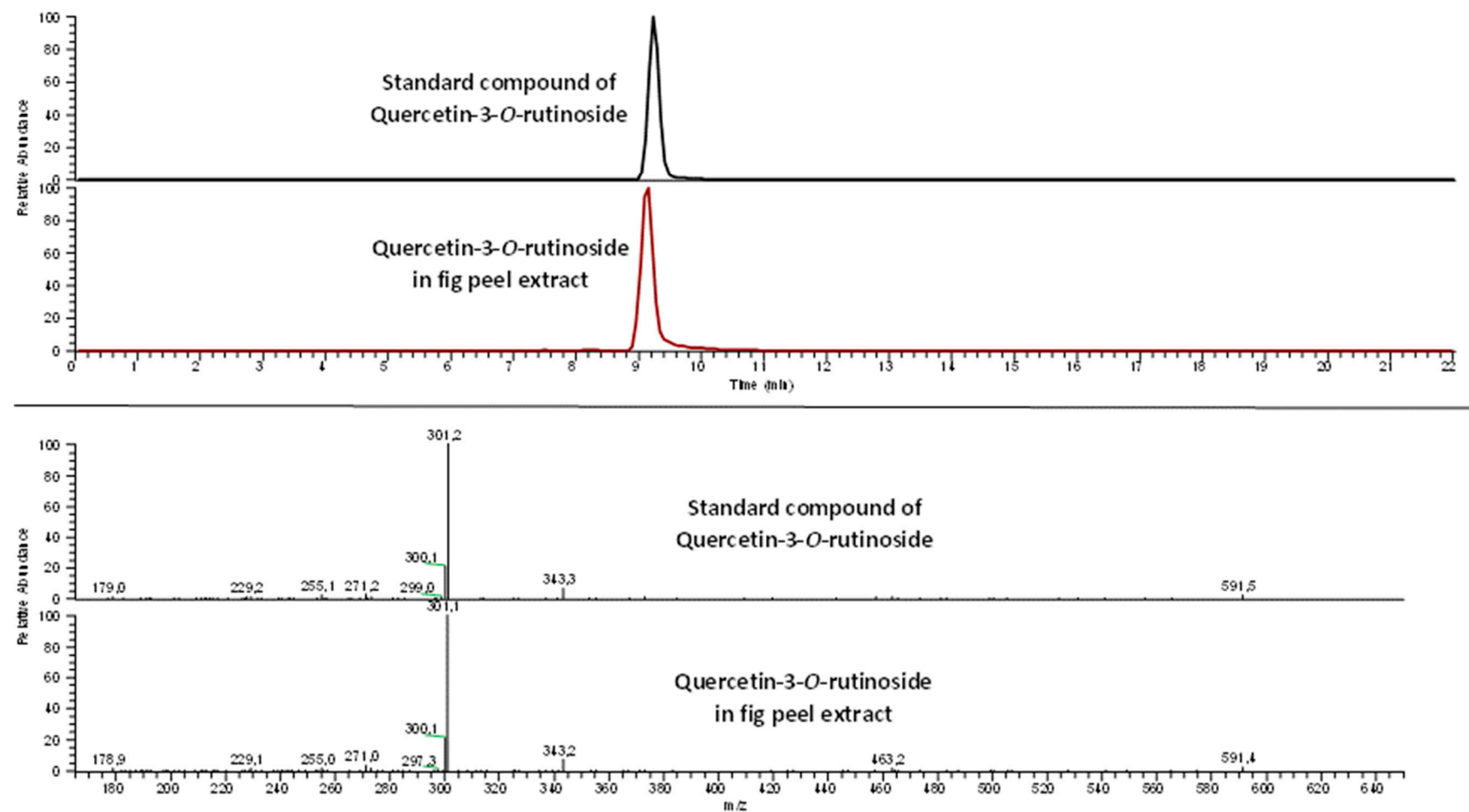


Figure S3. Chromatographic profiles of cyanidin-3-*O*-glucoside and cyanidin-3-*O*-rutinoside with their MS/MS spectra.

