

# Implication of the Polymeric Phenolic Fraction and Matrix Effect on the Antioxidant Activity, Bioaccessibility, and Bioavailability of Grape Stem Extracts

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**Table S1.** Chemical characterization of the isolated procyanidin fraction.

| Extracts | Catechin (%) | Epicatechin (%) | Epicatechin gallate (%) | Epigallocatechin (%) | mDP          |
|----------|--------------|-----------------|-------------------------|----------------------|--------------|
| HPE      | 14.59 ± 0.62 | 72.33 ± 0.49    | 12.40 ± 0.14            | 0.68 ± 0.11          | 12.22 ± 0.68 |
| LPE      | 16.58 ± 0.98 | 67.29 ± 2.53    | 15.59 ± 1.66            | 0.55 ± 0.05          | 12.18 ± 0.97 |

mDP = medium degree of polymerization.

**Table S2.** Calibration curves, LoD, LoQ and coefficient of determination of the reference standards.

| Phenolic compounds                 | Equation               | LoD<br>(mg/L) | LoQ<br>(mg/L) | R <sup>2</sup> |
|------------------------------------|------------------------|---------------|---------------|----------------|
| Gallic acid                        | $y = 109324x - 9.487$  | 0.393         | 1.190         | 0.9998         |
| Protocatechuic acid                | $y = 608845x - 2.291$  | 0.014         | 0.043         | 1.0000         |
| 4-Hydroxybenzoic acid              | $y = 65860x - 2.902$   | 0.198         | 0.600         | 0.9994         |
| Vanillic acid                      | $y = 12805x - 0.823$   | 0.546         | 1.655         | 0.9996         |
| Syringic acid                      | $y = 41846x - 0.4823$  | 0.171         | 0.519         | 0.9999         |
| Caftaric acid                      | $y = 107084x - 2.0433$ | 0.238         | 1.071         | 0.9996         |
| Caffeic acid                       | $y = 245503x - 5.766$  | 0.024         | 0.127         | 0.9999         |
| 3-Coumaric acid                    | $y = 69330x - 2.207$   | 0.045         | 0.160         | 0.9997         |
| Ethyl gallate                      | $y = 124694x - 3.274$  | 0.069         | 0.209         | 0.9998         |
| Ellagic acid                       | $y = 71898x - 3.854$   | 0.197         | 0.882         | 0.9996         |
| <i>trans</i> -Piceid               | $y = 240019x - 2.9723$ | 0.012         | 0.073         | 0.9999         |
| <i>trans</i> -Resveratrol          | $y = 255118x - 9.0471$ | 0.056         | 0.308         | 0.9995         |
| Catechin                           | $y = 14394x - 31.0908$ | 2.515         | 7.622         | 0.9998         |
| Epicatechin                        | $y = 10481x + 11.8033$ | 2.801         | 8.488         | 0.9995         |
| Epicatechin gallate                | $y = 37081x - 23.8862$ | 1.930         | 5.849         | 0.9995         |
| Dimer B <sub>1</sub>               | $y = 14342x - 15.8623$ | 2.208         | 6.690         | 0.9991         |
| Dimer B <sub>2</sub>               | $y = 10007x + 8.2927$  | 2.140         | 6.486         | 0.9994         |
| Quercetin-3- <i>O</i> -galactoside | $y = 65620x - 2.4850$  | 0.135         | 0.608         | 0.9995         |
| Quercetin-3- <i>O</i> -rutinoside  | $y = 48776x - 12.897$  | 0.108         | 0.381         | 0.9998         |
| Quercetin-3- <i>O</i> -glucuronide | $y = 58579x - 3.382$   | 0.158         | 0.558         | 0.9996         |
| Quercetin-3- <i>O</i> -glucoside   | $y = 86103x - 29.5653$ | 0.096         | 0.422         | 0.9997         |
| Quercetin                          | $y = 184585x + 4.1978$ | 0.035         | 0.190         | 0.9995         |

LoQ = limit of quantification. LoD = limit of detection.

**HPLC-PAD calibration parameters**

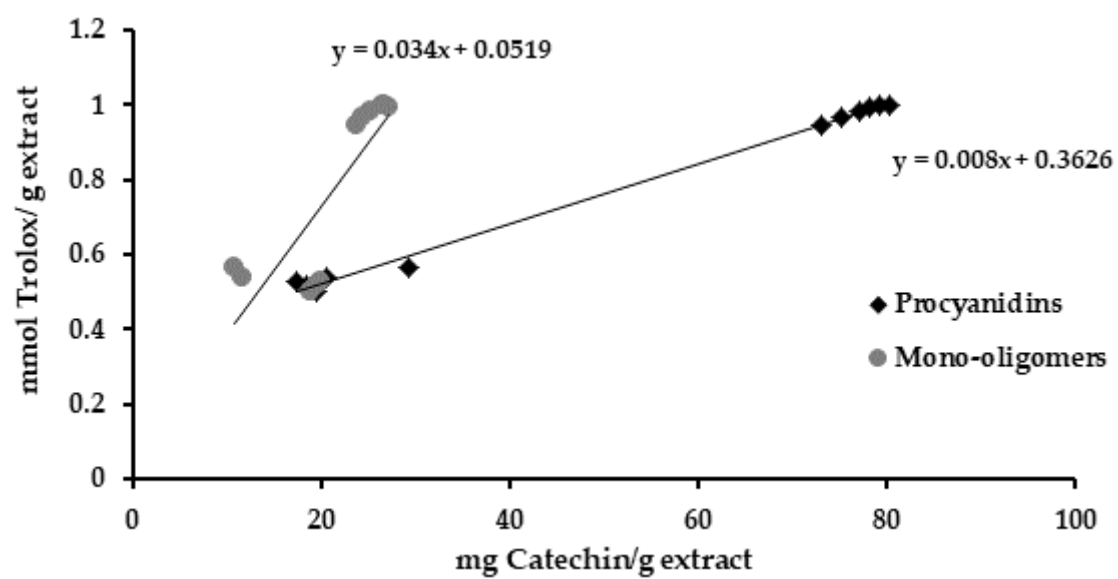
**Calibration curves:** Linearity was obtained from at least five different concentrations of standard solutions in triplicate.

**LODs and LOQs:** Limits of detection (LODs) and quantification (LOQs) were calculated based on the standard deviation of the regression line and its slope express as:

$$\text{LoD} = 3.3\sigma/S \text{ and } \text{LoQ} = 10\sigma/S$$

Where  $\sigma$  = standard deviation of the regression line

S = the slope of the regression line



**Figure S1.** Correlation between mono-oligomeric fraction (grey) and procyanidin fraction (black) content and antioxidant activity during gastrointestinal digestion of the HPE extract.