

## Electronic Supplementary Information

**Table S1:** UHPLC-MS characteristics of polyphenols identified in red grape pomace.

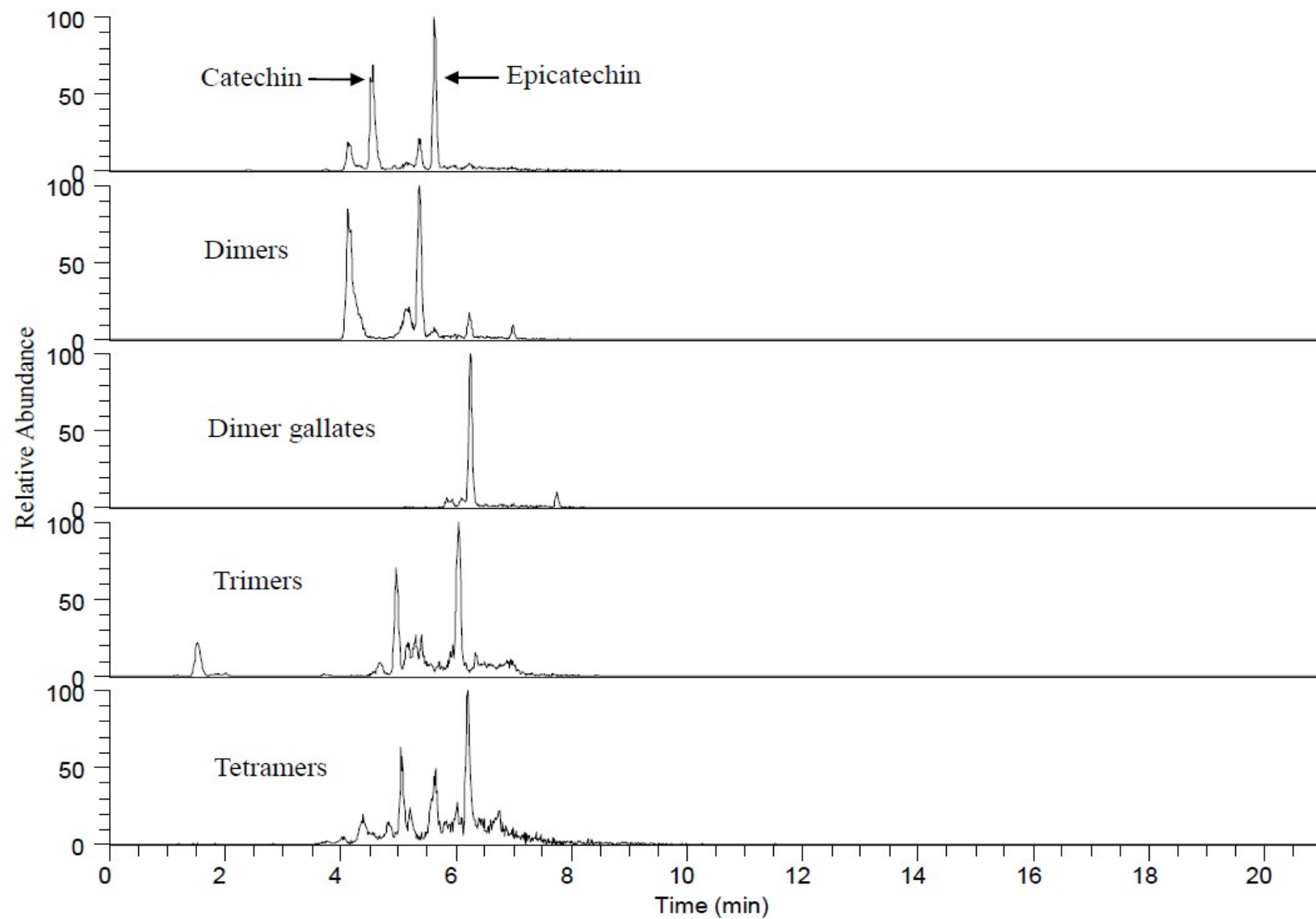
Compound	rt (min)	[M-H] <sup>-</sup> (m/z)	MS <sup>2</sup> ions (m/z)	MS <sup>3</sup> ions (m/z)
Galloylquinic acid	1.36	343	169, 173, 325, 228, 125, 191	(169) 125
Procyanidin trimer B-type	1.53	865	695, 575, 577, 713, 739, 847, 287	(695) 543, 405, 363, 451, 289, 243
Gallic acid- <i>O</i> -hexoside	1.66	331	169	125
Hydroxytyrosol	2.07	153	123	
Caftaric acid	2.69	311	149, 179	(149) 131, 103, 87, 59
Procyanidin dimer B-type	4.13	577	425, 451, 407, 289, 559, 287	(425) 407, 273, 381
Procyanidin tetramer B-type	4.44	1153.5	1027, 983, 865, 1135, 863, 575, 739, 577,	
Catechin	4.56	289	245, 205, 179, 231, 203	(245) 203, 187, 227, 161, 175, 188
(Epi)catechin- <i>O</i> -hexoside	4.70	451	289, 331	(289) 245, 205, 179, 137, 231, 125
Procyanidin trimer B-type	4.70	865	695, 739, 577, 713, 575, 587, 425, 407	(695) 543, 677, 243, 525, 407, 451
Procyanidin tetramer B-type	4.84	1153.5	863, 1027, 865, 983, 575, 577, 1135	
Procyanidin trimer B-type	4.97	865	695, 577, 739, 713, 575, 449, 287	(695) 543, 677, 243, 525, 407, 451
Procyanidin dimer B-type	5.16	577	425, 451, 407, 559, 289, 287	(425) 407, 273
Procyanidin trimer B-type	5.25	865	695, 575, 739, 577, 713, 847, 287	(695) 543, 677, 243, 525, 407, 451
Procyanidin dimer B-type	5.36	577	425, 451, 407, 559, 289, 287	(425) 407, 273
Procyanidin trimer gallate B-type	5.57	1017	729, 847, 891, 999, 865, 727, 677, 575	(729) 577, 559, 407, 425, 449, 313, 287, 303
Epicatechin	5.63	289	245, 205, 179, 231, 271	(245) 203, 187, 227, 161, 175, 188, 230
Procyanidin dimer gallate B-type	5.83	729	577, 559, 407, 425, 603, 451, 449, 439	(577) 451, 407, 425, 559, 289, 287
Procyanidin hexamer -B-type	5.87	864.5*	779, 575, 789, 695, 577, 739, 1151, 1153, 719, 1439	
Procyanidin trimer B-type	6.04	865	695, 739, 713, 577, 575, 587, 407, 847	(695) 543, 243, 289, 405, 451, 677, 363
Procyanidin dimer gallate B-type	6.25	729	559, 577, 603, 407, 441, 711, 451, 289	(559) 407; (577) 559, 451, 407, 289
Procyanidin trimer B-type	6.34	865	695, 575, 739, 577, 713, 847, 287	(695) 543, 677, 243, 525, 407, 451
Procyanidin hexamer -B-type	6.54	864.5*	1151, 779, 719, 577, 788, 1153, 712, 575	
Ellagic acid	6.90	301	301, 257, 229, 185, 258	(301) 301, 229, 257, 284, 213
Procyanidin dimer B-type	6.99	577	425, 451, 407, 287, 289, 559	(425) 407, 273, 381
Quercetin-3- <i>O</i> -glucoronide	7.08	477	301	179, 151, 257, 273, 193

Secoisolariciresinol- <i>O</i> -hexoside	7.11	523	361, 347, 329, 343	(361) 346, 165, 179, 313, 331, 343, 298
Dihydroquercetin- <i>O</i> -rhamnoside	7.20	449	303, 285, 151	(303) 285, 177, 125
Secoisolariciresinol- <i>O</i> -hexoside	7.24	523	361, 329, 347, 343	(361) 346, 165, 313, 179, 343, 331, 121
Procyanidin tetramer B-type	6.20	1153.5	1135, 1027, 983, 863, 865, 739, 577, 575	
Procyanidin octamer B-type	6.79	1152.7*	1727, 1439, 1441, 1067, 1007, 865, 863, 575	
Syringetin- <i>O</i> -hexoside	7.66	507	344, 345, 387, 346	(344) 316, 330, 301, 273, 329, 315, 287
Resveratrol- <i>O</i> -glucoside	7.84	389	227	185, 183, 159, 157, 143

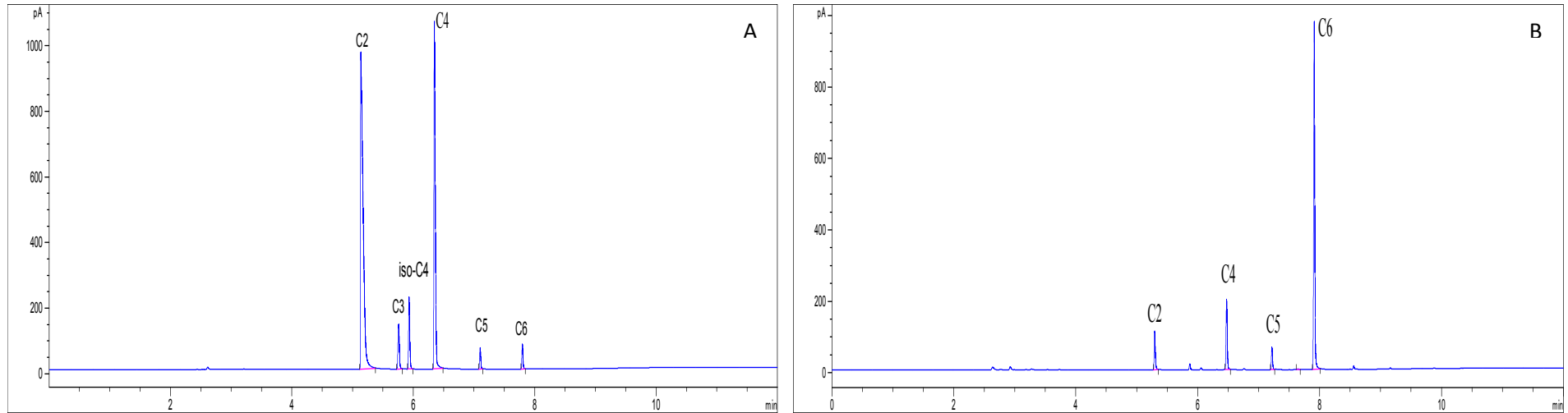
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Fragment ions are listed in order of relative abundances. \*Doubly-charged molecular ions. The ions in parentheses were fragmented in MS<sup>3</sup> experiment.

**Figure S1:** Chromatographic traces of monomers, dimers, dimer gallates, trimers and tetramers of B-type procyanidins



**Figure S2:** Gas chromatographic-FID detection of volatile fatty acids, namely: acetic (C2), propionic (C3), butyric (C4), isobutyric (iso-C4), valeric (C5) and hexanoic (C6) acids. (A)- Liquid fraction of the GP that was first dephenolised and then anaerobically digested, diluted 2.5 times. (B)- Liquid fraction of the GP that was anaerobically digested, diluted 13.3 times.



**Figure S3:** Polyhydroxyalkanoates quantification. (A)- PHAs content and polymer composition determined by GC-FID detection of short chain length polyhydroxyalkanoates: the internal standard was the benzoic acid (11.6 min) and only hydroxybutyrate (HB; 5.2 min) was detected. (B)- PHAs content determined by TGA of the dried pellets for the conditions 40% of  $GP_{Deph}^{Acid}$  (black) and  $SimGP_{Deph}^{Acid}$  (red) contents in the accumulation media (% v/v).

