

## **Addition of grape skin and stems extracts in wines during the storage to reduce the Sulphur dioxide: impact on red wine quality**

Rocío Casquete; María José Benito\*; Francisco Pérez-Nevado; Ana Martínez; Alberto Martín; María de Guía Córdoba

### **SUPPLEMENTAL MATERIAL**

This article contains the methodology for analysis by HPLC-ES-QTOF of SFE extract compounds and 1 supplementary table.

### **METHODOLOGY FOR HPLC-ES-QTOF ANALYSIS**

**INSTRUMENT:** LC-ESI-QTOF (Agilent HPLC-QTOF Model G6530, Agilent Technologies, Palo Alto, CA, USA).

**MASS\_SPECTROMETRY:** Ion mode negative; Collision energy 10-40 eV (N<sub>2</sub>); Scanning m/z 100-1700.

**CHROMATOGRAPHY:** Column C18 (4.6 x 1.50 mm, x 4.8 µm), Agilent Technologies; Temperature 30°C; Solvents: water with 0.1% formic acid (A) and methanol with 0.1% formic acid (B). Gradient: hold 5 min at 95A/5B, linear from 95A/5B to 10A/90B 10 min, hold 5 min at 10A/90B, linear from 10A/90B to 95A/5B 5 min, reequilibration 95A/5B (5 min). Flow rate: 0.35 mL/min.

Table S1. Tentatively identification, retention times, characteristic ions, and abundance (Arbitrary area units) of the majority compounds from stem and grape-skin extract analyzed by HPLC-ESI-QTOF.

Proposed compound	RT <sup>1</sup>	[M-H] <sup>-</sup>	MS/MS ions	Stem	Grape-skin
<b>Phenolic compounds</b>					
Derivate feliric acid	3,01	311	<b>103</b> ;193; 149	6386957	
Sinapyl aldehyde	3,04	<b>149</b>			146843
Dihydroxycoumarin	3,15	<b>133</b>			71786
1,3-Dicaffeoylquinic acid	3,17	353	<b>179</b> ; 191	20130	
Galic acid hexoside	10,94	331	<b>125</b> ; 169,01	1153575	
Protocatechuic acid hexoside	11,314	315	<b>108,01</b> ; 109; 152,01	602744	
Derivate syringic acid	12,192	197,01	122,99; <b>138,01</b> ; 166,97; 182	102363	
Proanthocyanidin <i>dimer</i>	12,53	577,07	<b>289,07</b> ; 245,08; 407,07; 425; 451	184667	42245
Malvidin-3-O-glucoside	12,64	491,17	<b>329,06</b> ; 313; 314; 330	37770	23172
Proanthocyanidin <i>dimer</i>	12,82	577,07	<b>289,07</b> ; 407,07;	31895	15796
Proanthocyanidin <i>dimer</i>	13,037	425	<b>289,07</b> ; 245,08; 109,03; 577	534888	107290
Malvidin-acetil-hexoside	13,19	533,12	<b>329</b> ; 314; 299;	96943	4286
Proanthocyanidin <i>trimer</i>	13,22	867,19	<b>865,19</b> ; 866,19;		56504
Syringic acid	13,23	<b>197,04</b>	153,02	20786	
Proanthocyanidin <i>trimer</i>	13,29	695	<b>289</b> ; 407; 451; 577	50201	16901
Vanillin	13,33	<b>151</b>		54498	
(+)-Catechin	13,39	<b>289,07</b>	245,08; 125,02	294047	24935
Proanthocyanidin <i>dimer</i>	13,42	577	<b>407</b>	117662	77629
Rutin	13,518	<b>609,14</b>	300,03	90261	
Quercetin-3-O-galactoside	13,783	<b>463,08</b>	300,01	910189	
Quercetin-3-O-glucuronide	13,883	<b>477,08</b>	301,04;151	2149033	24449
Syringetin-3-O-glucoside	14,081	<b>507,06</b>	344,01;447,04	321049	

Quercitina	15,573	<b>301,03</b>	151	843172
<b>Terpenoids</b>				
Ursolic acid	16,427	457,35	<b>455,35</b> ; 456,35	25082072
<b>Fatty acids and derivates</b>				
FA 18:1 +3O	16,14	<b>329,22</b>	139; 171; 211,13	146304
13-HOTrE®(13S-hydroxy-6Z,9Z,11E-octadecatrienoic acid)	18,05	<b>221,15</b>	177,09; 220,15; 192	42966
Linoleic acid	18,68	280,23	<b>279,23</b>	91957554
13-HOTrE/13-KODE	19,48	<b>293</b>	275,3	47374
Stearic acid	19,67	284,26	<b>283,26</b>	8706431
9-HODE (9S-hydroxy-10E,12Z-octadecadienoic acid)	20,225	<b>295,22</b>	171,09; 277,21	184443
Heptadecanoic acid	20,8	<b>267,19</b>		66406 509636
Palmitic acid	23,09	<b>255,23</b>	254	17992020
Oleic acid	24,07	<b>281,25</b>	282,25	11740911
<b>Unknown</b>				
Unknown 1	14,57	<b>549</b>	345; 344; 301	37168
Unknown 2	20,76	<b>469</b>	423	329642
Unknown 3	20,7	270,21	<b>269,2</b>	505044

<sup>1</sup>RT: Retention time (min)

<sup>3</sup>Majority ion