

SUPPLEMENTARY DATA

Skin cuticule composition, waxes					
	Unit	GRE D-	GRE D+	CAR D-	CAR D+
C16 acid	mg/g	2.10	3.13	3.14	3.58
C18:2 acid	mg/g	0.88	0.05	3.47	2.89
C18:1 acid	mg/g	0.48	3.72	1.95	1.48
C18:0 acid	mg/g	0.80	1.05	0.91	1.15
C22 acid	mg/g	1.34	1.88	1.78	1.70
C24 acid	mg/g	2.28	2.69	1.69	1.71
C26 acid	mg/g	15.49	12.78	7.58	7.92
C28 acid	mg/g	23.17	20.94	16.52	18.39
C30 acid	mg/g	12.40	10.65	9.69	9.76
<i>Total fatty acids</i>	mg/g	58.95	56.91	46.71	48.58
C25 aldehyde	mg/g	11.43	12.11	6.62	6.99
C28 aldehyde	mg/g	14.76	15.09	8.69	8.56
C30 aldehyde	mg/g	9.57	9.88	6.77	6.19
C32 aldehyde	mg/g	10.84	11.29	6.93	6.74
<i>Total aldehydes</i>	mg/g	46.60	48.37	29.01	28.49
C26 alcohol	mg/g	15.62	18.34	11.24	12.17
C28 alcohol	mg/g	16.18	18.73	11.99	12.36
C30 alcohol	mg/g	5.04	6.04	4.71	4.81
<i>Total alcohols</i>	mg/g	36.84	43.10	27.95	29.37
oleanolic acid	mg/g	119.92	62.47	88.56	83.00
oleanolic aldehyde	mg/g	24.88	23.07	54.72	7.24
<i>Total terpenes</i>	mg/g	144.80	85.54	143.28	90.25
Skin cuticule composition, cutin monomers					
	Unit	GRE D-	GRE D+	CAR D-	CAR D+
<i>Fatty acids</i>					
p.coumaric acid	mg/g	1.81	0.79	2.84	1.49
C16 acid	mg/g	3.25	3.26	2.86	2.72
C18:2 acid	mg/g	2.43	1.57	3.66	2.31
C18:0 acid	mg/g	0.68	0.62	1.00	0.87
C26 acid	mg/g	0.26	0.12	0.31	0.27
<i>Hydroxy-fatty acids</i>					
10,16-dihydroxyhexanoic acid	mg/g	3.80	3.65	4.60	4.53
9,10 epoxy18-hydroxyoctadecenoic acid	mg/g	1.04	0.92	1.28	1.15
9,10 epoxy18-hydroxyoctadecanoic acid	mg/g	4.15	3.54	4.31	4.29
9,10,18-trihydroxyoctadecanoic acid	mg/g	0.40	0.52	0.36	0.61
octacosan-1,28-dioic acid	mg/g	0.97	0.51	0.73	0.90
<i>Sterols</i>					
sitosterol	mg/g	2.31	1.73	3.19	2.66

Table S1. Skin cuticule composition, waxes (a) and cutin monomers (b) of GRE and CAR berries at two different maturation stages.

Skin and pulp, analysis by ¹³ C solid-state NMR					
	Unit	GRE D-	GRE D+	CAR D-	CAR D+
pulp, tartaric acid	au	4	4	3	3
skin, tartaric acid	au	2	2	2	2
pulp, malic acid	au	0	0	0	0
skin, malic acid	au	0	0	0	0
pulp, polyphenolics / aromatics	au	1	1	2	2
skin, polyphenolics / aromatics	au	4	4	4	4
pulp, polysaccharides	au	5	5	5	5
skin, polysaccharides	au	5	5	5	5
pulp, amino-acids	au	3	3	3	3
skin, amino-acids	au	3	3	3	3
pulp, organic acids	au	2	2	2	2
skin, organic acids	au	3	3	3	3
Skin and pulp, neutral and acidic sugar composition					
	Unit	GRE D-	GRE D+	CAR D-	CAR D+
pulp, AIR	mg/g of pulp	8.8	10.5	10.7	9.4
skin, AIR	mg/g of skin	6.7	8.3	8.6	7.2
pulp, AIR	mg/g of berry	50.6	49.0	54.3	51.5
skin, AIR	mg/g of berry	9.9	8.3	9.0	10.1
pulp, AIR	mg/berry	83.5	91.1	98.8	92.2
skin, AIR	mg/berry	16.3	15.4	16.4	18.1
pulp, rhamnose	% AIR	1.3	1.4	2.3	2.2
skin, rhamnose	% AIR	1.4	1.3	2.0	2.2
pulp, fucose	% AIR	0.4	0.6	0.7	0.8
skin, fucose	% AIR	0.4	0.5	0.6	0.5
pulp, arabinose	% AIR	7.8	7.6	11.1	11.7
skin, arabinose	% AIR	6.6	6.6	9.2	10.3
pulp, xylose	% AIR	4.6	4.6	6.7	6.6
skin, xylose	% AIR	4.6	4.1	8.4	6.1
pulp, mannose	% AIR	3.8	3.7	2.7	2.4
skin, mannose	% AIR	4.2	3.9	2.3	2.1
pulp, galactose	% AIR	5.9	5.2	6.5	8.2
skin, galactose	% AIR	6.9	7.7	7.3	7.5
pulp, glucose	% AIR	34.5	35.2	30.7	28.4
skin, glucose	% AIR	36.8	36.5	27.6	27.8
pulp, galacturonic acid	% AIR	41.7	41.6	39.3	39.8
skin, galacturonic acid	% AIR	39.0	39.4	42.5	43.4

Table S2. Skin analysis by ¹³C solid-state NMR and by neutral and acidic sugar composition after polysaccharide depolymerization. au=arbitrary units. AIR = alcohol insoluble residue.

	Unit	GRE D-	GRE D+	CAR D-	CAR D+
<i>Skins:</i>					
hydrocinnamic acid	$\mu\text{g/g}$ fresh skin	382	382	160	108
benzoic acid	$\mu\text{g/g}$ fresh skin	1.63	2.78	3.38	5.01
anthocyanins	$\mu\text{g/g}$ fresh skin	1147	2352	6657	9068
non acylated anth.	$\mu\text{g/g}$ fresh skin	591	1524	3581	4132
para coumaroyl. anth.	$\mu\text{g/g}$ fresh skin	529	761	3581	4567
A-T and T-A dimers	$\mu\text{g/g}$ fresh skin	3.93	6.85	62.8	14.7
flavanols	$\mu\text{g/g}$ fresh skin	71	174	364	398
flavanols, monomers	$\mu\text{g/g}$ fresh skin	64.8	65.0	98.7	71.4
flavanols, dimers+trimers	$\mu\text{g/g}$ fresh skin	74.7	60.5	81.0	53.8
flavanols, total *	$\mu\text{g/g}$ fresh skin	11648	11465	10354	9788
flavanols, mDP		18.2	17.3	21.5	20.8
flavanols, tri-hydroxylated	% EGC (moles)	10.2	11.9	11.6	12.3
flavanols, galloylated	% EC-G (moles)	6.29	5.46	2.14	2.00
flavanols-SEC, mDP>3 *	$\mu\text{g/g}$ fresh skin	12203	12287	10703	12776
<i>Seeds:</i>					
flavanols, total	$\mu\text{g/g}$ seed	65681	57245	58616	51661
flavanols, mDP	-	6.11	5.99	6.30	6.00
flavanols, galloylated	% EC-G (moles)	24.8	23.1	23.0	21.9
flavanols-SEC, mDP>3 *	$\mu\text{g/g}$ seed	57852	65179	64807	48176

Table S3. Skins and seeds, polyphenols. * concentrations calculated in equivalent epicatechin.

	Unit	GRE D-	GRE D+	CAR D-	CAR D+
wine, yield	ml /kg of berry	607	603	624	618
wine, TAV	% vol.	10.89	14.16	11.10	12.34
wine, pH		3.30	3.48	3.32	3.41
wine, residual sugars	g/L	0.05	2.06	0.63	+9
wine, total acidity	g/L H ₂ SO ₄	4.95	4.30	5.69	5.13
wine, malic acid	g/L	0.83	1.27	2.15	2.09
wine, lactic acid	g/L	0.03	0.03	0.03	0.06
wine, L*		33.3	17.9	12.5	6.2
wine, a*		55.4	46.5	40.6	32.7
wine, b*		45.9	30.5	21.4	10.8
wine, total polyphenol index		29	44	43	57
wine, total pigments		7.4	21.6	25.7	42.6
wine, non bleachable pigments		0.57	0.80	1.10	1.30
wine, A420/520		0.75	0.54	0.47	0.41
wine, hydroxycinnamic acid	mg/L	144	207	33	36
wine, benzoic acid	mg/L	9.0	16.9	7.67	9.79
wine, total anthocyanins	mg/L	137	360	318	538
wine, non acylated antho.	mg/L	91	262	198	314
wine, para coumaroyl. antho.	mg/L	39	81	99	194
wine, A-T and T-A dimers	mg/L	0.30	0.65	0.32	0.71
wine, A-ethyl-T	mg/L	2.56	3.47	1.61	1.78
wine, pyranoanthocyanins	mg/L	3.89	14.17	8.05	13.68
wine, flavonols	mg/L	6.75	19.07	23.17	36.60
wine, T-ethyl-T	mg/L	0.22	0.43	0.31	0.41
wine, flavanol monomers	mg/L	35.9	44.2	29.6	33.7
wine, flavanol trimers	mg/L	31.6	34.1	29.4	28.6
wine, total flavanols (phloro)	mg/L	538	627	384	457
wine, mDP		5.6	5.6	5.0	5.1
wine, flavanols, trihydroxylated	% EGC (moles)	7.5	9.3	8.0	10.3
wine, flavanols, galloylated	% EC-G (moles)	6.7	7.1	3.9	3.6
wine, flavanols-SEC (mDP > 3)	mg eq. epicat/L	776	949	859	960
wine, polysacch., rhamnose	% PS	1.28	1.38	2.26	2.18
wine, polysacch., fucose	% PS	0.42	0.64	0.67	0.80
wine, polysacch., arabinose	% PS	7.85	7.58	11.11	11.7
wine, polysacch., xylose	% PS	4.56	4.61	6.72	6.56
wine, polysacch., mannose	% PS	3.79	3.74	2.69	2.37
wine, polysacch., galactose	% PS	5.88	5.22	6.34	8.17
wine, polysacch., glucose	% PS	34.5	35.2	30.7	28.4
wine, polysacch., galacturonic ac.	% PS	41.7	41.6	39.3	39.8

Table S4. Wine, polyphenols and polysaccharides.

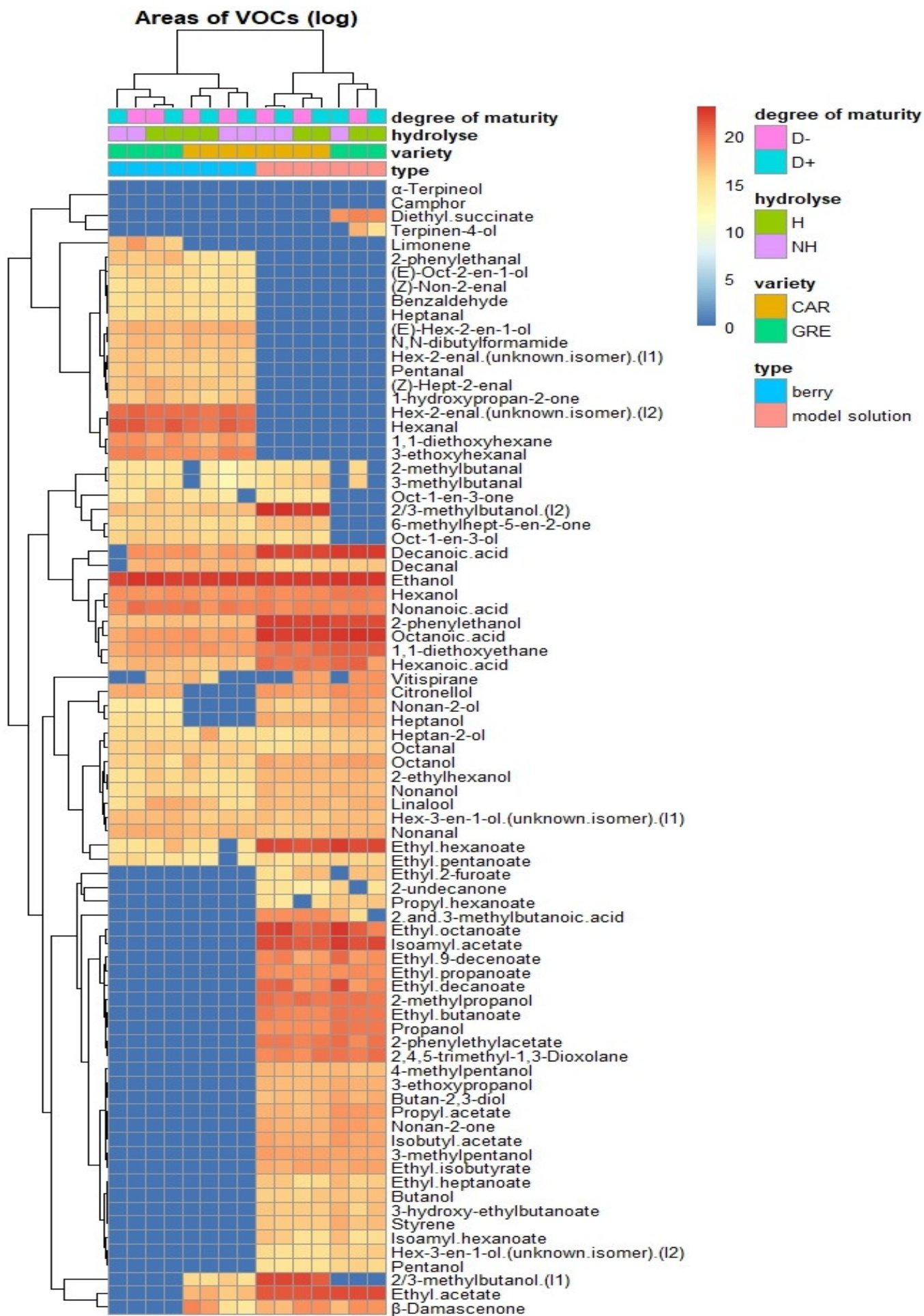


Figure S1. Heatmap of the logged intensities averaged across the three replicates.