

Supplemental Data for:

Li S, Wilkinson KL and Bindon KA. 2018.

Compositional variability in commercial tannin and mannoprotein products.

Am J Enol Vitic 69:176-181. doi: 10.5344/ajev.2017.17057.

Supplemental Table 1 Enotannin and mannoprotein (MP) products used in the study, showing their codes and grouped according to common manufacturers.

Producer group	Enotannin code	Mannoprotein code
1	skin1	MP2
	skin2	
	skin3	
	seed1	
	seed2	
2	skin+seed3	MP1
		MP4
		MP7
3	skin4	MP3
	seed3	MP5
	skin+seed1 skin+seed2	MP6
4	skin5	
	seed4	
5	skin6	
	seed5	
6		MP8

Supplemental Table 2 Reference compounds and their source used for comparison in the Fourier transform mid-infrared spectroscopic analysis of enotannin products.

Reference standard	Supplier reference
Arabinogalactan	Sigma Aldrich, St. Louis, MO
Ascorbic acid	Merck, Bayswater, VIC, Australia
Calcium tartrate	Sigma Aldrich, St. Louis, MO
(+)-Catechin hydrate	Sigma Aldrich, St. Louis, MO
Cellulose	Sigma Aldrich, St. Louis, MO
Citric acid	Sigma Aldrich, St. Louis, MO
D-fructose	Sigma Aldrich, St. Louis, MO
D-glucose	Merck, Bayswater, VIC, Australia
Ellagic acid	Sigma Aldrich, St. Louis, MO
(-)-Epicatechin	Sigma Aldrich, St. Louis, MO
Gallic acid	Sigma Aldrich, St. Louis, MO
Grape marc seeds (white)	Hixson et al. 2015. J Agric Food Chem 63:9954-9962
Malvidin-3-glucoside	Vidal et al. 2004. J Agric Food Chem 52:713-719
Pectin from Apple P-8471 SIGMA	Sigma Aldrich, St. Louis, MO
Polygalacturonic acid Sigma P3889-5G	Sigma Aldrich, St. Louis, MO
Potassium hydrogen tartrate	Sigma Aldrich, St. Louis, MO
Potassium metabisulfite	Sigma Aldrich, St. Louis, MO
Preveraison seed tannin (Tannat)	Hixson et al. 2015. J Agric Food Chem 63:9954-9962
Preveraison skin tannin (Tannat)	Hixson et al. 2015. J Agric Food Chem 63:9954-9962
Purified grape skin cell walls (marc)	Bindon and Smith. 2013. Food Chem 136:917-928
Purified yeast lees (red wine)	AWRI database, unpublished
Quercetin	Sigma Aldrich, St. Louis, MO
Red wine tannin	McRae et al. 2013. J Agric Food Chem 61:11618-11627
Rhamnogalacturonan (soy)	Megazyme, Irishtown, Bray, Co. Wicklow, Ireland
Seed tannin (ripe)	Cheah et al. 2014. PLoS ONE 9:e98921
Seed tannin (ripe)	Bindon et al. 2010. J Agric Food Chem 58:10736-10746
Skin tannin (ripe)	Bindon et al. 2016. J Agric Food Chem 64:8406-8419
Tannic acid	Sigma Aldrich, St. Louis, MO
Tartaric acid	Sigma Aldrich, St. Louis, MO
Wine protein	Bindon et al. 2016. J Agric Food Chem 64:8406-8419

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Supplemental Table 3 Monomeric phenolic compounds (mg) contained in 1 g of the enotannin products.^a

	Catechin (mg/g)	Epicatechin (mg/g)	Gallic acid (mg/g)	Anthocyanin (mg/g)	Total (mg/g)
Skin1	3.4 ± 0.4	22.4 ± 0.3	2.2 ± 0.0	n.d. ^b	28.0
Skin2	15.0 ± 0.1	13.8 ± 0.2	2.8 ± 0.1	n.d.	31.6
Skin3	22.2 ± 0.2	18.5 ± 0.1	5.5 ± 0.1	n.d.	46.2
Skin4	46.9 ± 0.5	49.0 ± 0.6	7.1 ± 0.1	n.d.	103.0
Skin5	c.n.q. ^c	c.n.q.	11.6 ± 0.4	111.6 ± 0.3	123.2
Skin6	15.2 ± 0.2	22.8 ± 1.4	5.4 ± 0.0	n.d.	43.4
Seed1	21.4 ± 0.1	17.8 ± 0.1	5.1 ± 0.1	n.d.	44.3
Seed2	3.3 ± 0.0	c.n.q.	7.3 ± 0.0	n.d.	10.6
Seed3	46.8 ± 0.3	30.9 ± 0.3	2.0 ± 0.2	n.d.	79.7
Seed4	22.7 ± 0.4	c.n.q.	20.6 ± 0.7	n.d.	43.3
Seed5	39.7 ± 1.0	20.4 ± 0.2	2.5 ± 0.1	n.d.	62.6
Skin+seed1	37.4 ± 0.8	18.0 ± 0.6	12.2 ± 0.1	n.d.	67.6
Skin+seed2	29.6 ± 0.2	25.3 ± 0.1	1.1 ± 0.1	n.d.	56.0
Skin+seed3	19.3 ± 0.4	15.8 ± 0.3	19.3 ± 1.2	n.d.	54.4

^aValues are expressed as mg/g of product and are means of three replicates ± standard error.

^bn.d.: not detected.

^cc.n.q.: could not be quantified. For skin5, catechin and epicatechin could not be quantified due to co-eluting with anthocyanins, which have high absorbance at 280 nm. In all other cases, compounds could not be quantified because they were present at concentrations lower than the quantification threshold.

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Supplemental Table 4 Subunit composition (%), mean degree of polymerization (mDP), and average molecular weight derived from phloroglucinolysis analysis, and average molecular weight derived from gel permeation chromatography (GPC) of commercial enotannin products.^a

	% epigallo- catechin (ext.)	% catechin (ext.)	% epicatechin (ext.)	% epicatechin- gallate (ext.)	% catechin (ter.)	% epicatechin (ter.)	% epicatechin- gallate (ter.)	mDP	% mass conversion	Molecular mass (subunit) (g/mol)	Molecular mass (GPC) (g/mol)
Skin1	4.0±0.2	9.8±0.3	52.5±1.0	8.1±0.1	13.5±0.3	8.1±0.4	4.1±0.2	3.91±0.12	13.2±0.5	1209±36	1263±4
Skin2	3.5±0.1	10.0±0.2	53.3±0.5	7.6±0.1	11.4±0.5	7.6±0.2	3.5±0.1	3.91±0.09	50.8±1.4	1202±26	1923±17
Skin3	4.3±0.1	9.6±0.1	53.2±0.2	6.5±0.1	12.4±0.1	10.5±0.3	3.3±0.0	3.81±0.06	51.6±1.4	1165±19	1591±10
Skin4	9.5±0.0	7.3±0.0	53.7±0.7	3.7±0.1	13.1±0.9	12.2±0.2	0.5±0.1	3.87±0.10	90.0±4.1	1155±30	998±9
Skin5	24.6±0.5	5.7±0.5	51.1±0.5	3.5±0.1	8.9±0.3	5.5±0.2	0.8±0.2	6.60±0.21	49.1±1.6	1984±62	1413±22
Skin6	3.4±0.1	3.4±0.1	60.3±0.4	8.2±0.2	10.3±0.6	6.7±0.2	2.7±0.3	4.91±0.00	40.6±2.5	1559±60	1599±32
Seed1	4.7±0.4	4.7±0.3	51.6±1.9	6.2±0.3	13.3±1.2	11.1±1.0	3.3±0.1	3.63±0.30	57.8±5.9	1110±92	1539±18
Seed2	1.5±0.0	10.8±0.2	54.6±0.3	8.4±0.1	13.1±0.8	8.3±0.2	3.3±0.2	4.01±0.01	24.6±1.0	1251±21	1360±8
Seed3	1.2±0.1	8.5±0.1	55.0±0.6	10.1±0.1	11.3±0.4	10.0±0.4	4.1±0.2	3.96±0.10	55.4±1.6	1237±32	1741±5
Seed4	6.7±0.2	13.1±0.2	46.0±0.1	7.1±0.1	13.3±0.1	12.6±0.4	1.3±0.1	3.67±0.07	32.5±1.1	1116±20	1960±8
Seed5	2.6±0.2	8.7±0.1	62.5±0.5	9.5±0.1	7.6±0.5	6.1±0.1	3.1±0.1	5.97±0.21	50.8±1.8	1851±65	2029±12
Skin+seed1	2.0±0.1	8.4±0.0	57.3±0.2	7.0±0.2	11.5±0.1	11.1±0.2	2.7±0.0	3.95±0.04	56.4±1.0	1205±13	1728±1
Skin+seed2	2.2±0.2	7.6±0.2	55.2±0.2	10.7±0.2	9.6±0.0	9.8±0.1	4.9±0.2	4.14±0.00	50.0±1.2	1293±12	1973±8
Skin+seed3	2.1±0.3	9.6±0.4	60.8±0.4	9.8±0.3	6.3±0.6	9.7±0.3	1.6±0.2	5.68±0.32	49.2±2.7	1750±98	1963±28

^aValues are means of three replicates ± standard error; ext. = extension subunit; ter. = terminal subunit.

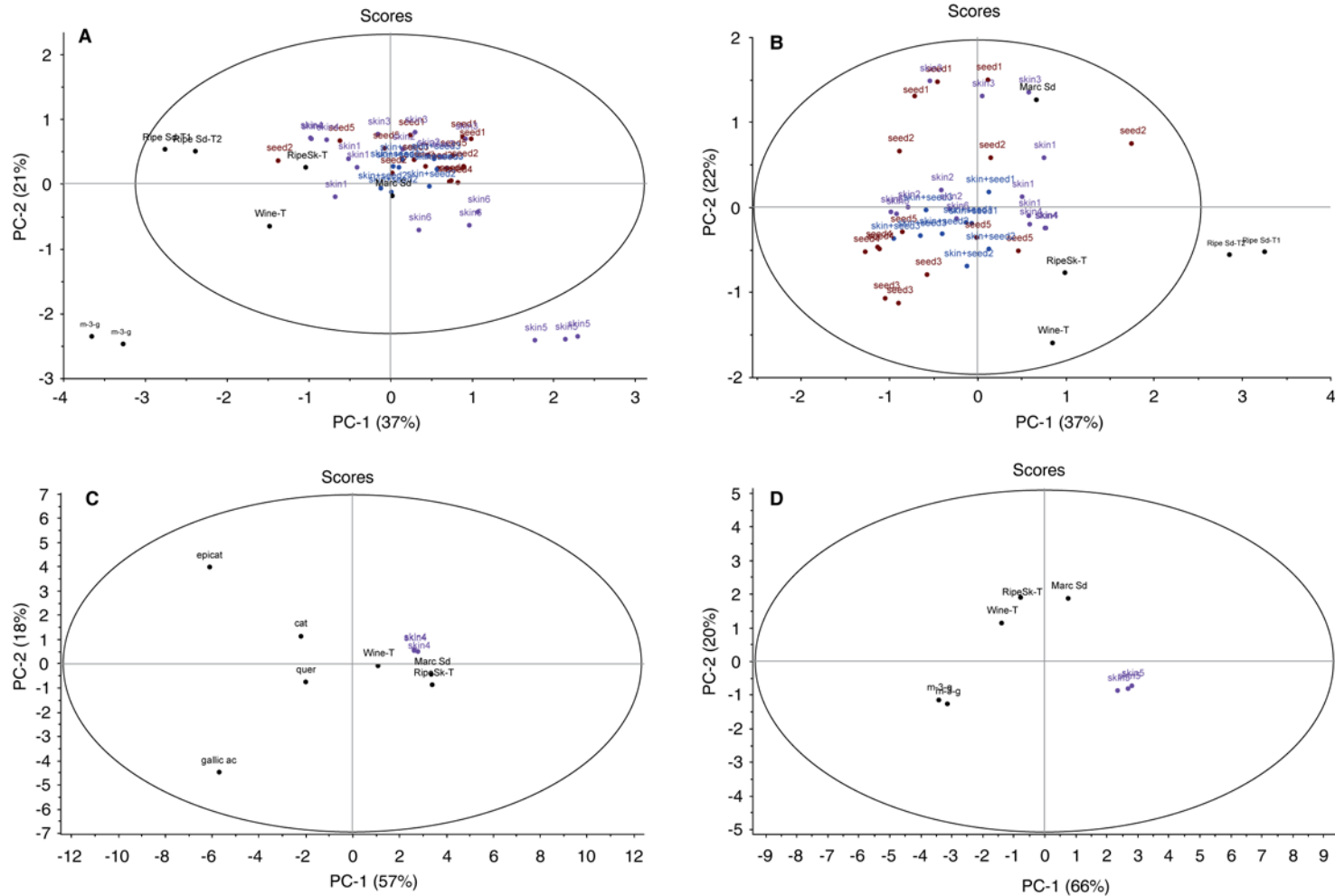
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Enotannins: seed1 to seed5; skin1 to skin6; skin+seed1 to skin+seed3. Abbreviations for reference spectra: cat = (+)-catechin; epicat = (-)-epicatechin; quer = quercetin; gallic ac = gallic acid; m-3-g = malvidin-3-glucoside; Wine-T = red wine tannin; Ripe Sk-T = ripe skin tannin; Ripe Sd-T = ripe seed (two reference samples); Marc Sd = ground and dried seeds from marc. tannin.



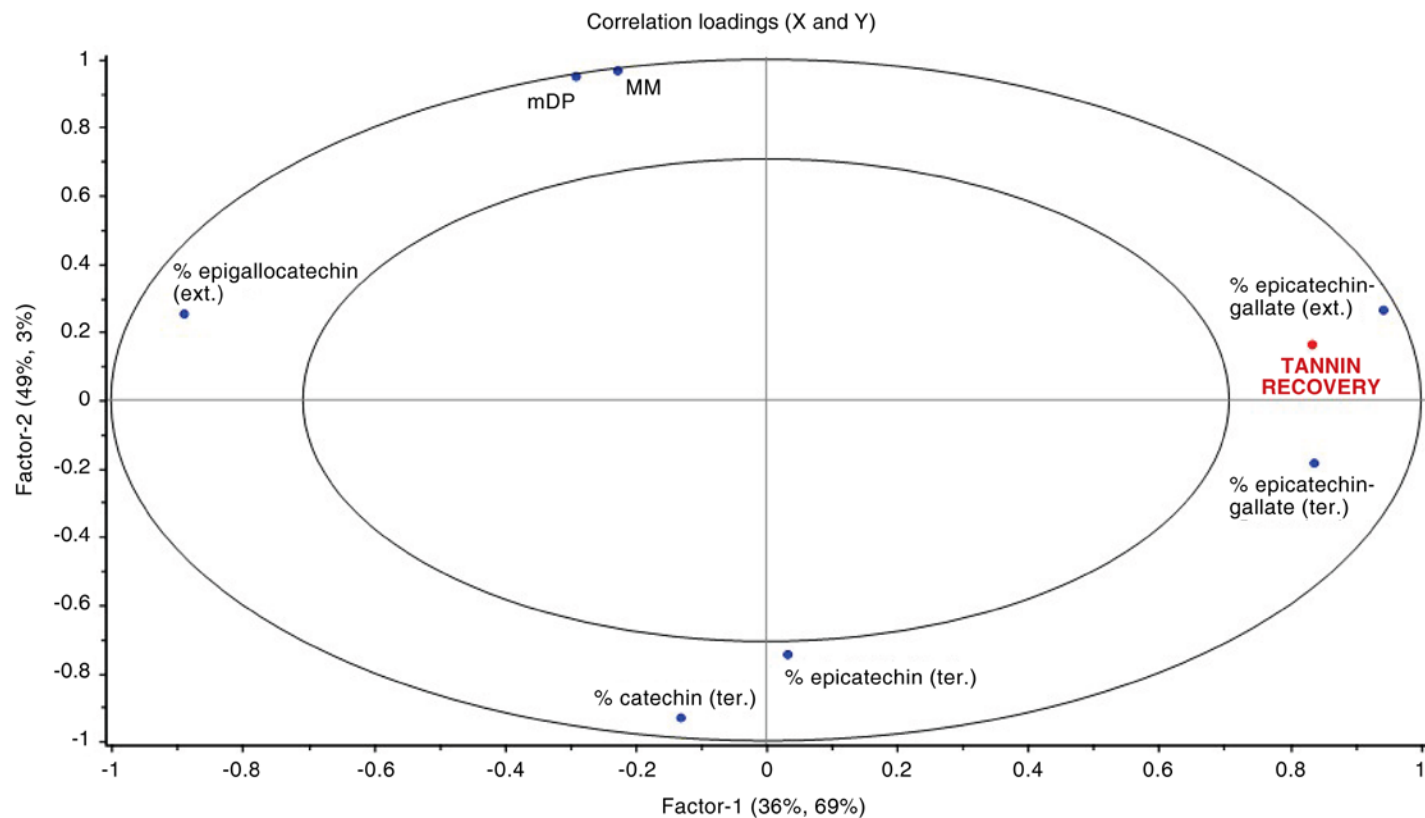
Supplemental Figure 1 Principal component analysis comparing Fourier transform mid-infrared spectra of dried enotannin products with significant reference compounds. Ellipse indicates spectral similarity defined by Hotelling's T-squared distribution (dissimilar or non-significant reference spectra were omitted from the final analysis). (A) all enotannins and significant reference spectra; (B) excluding skin5 and malvidin-3-glucoside; (C) skin4 and significant reference spectra; (D) skin5 and malvidin-3-glucoside spectra.

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Supplemental Figure 2 Partial least squares regression model (R^2 of calibration 0.86; R^2 of validation 0.69) to predict tannin recovery (% w/w) by methyl-cellulose precipitable tannin in enotannin products from significant tannin compositional variables.