

LC–MS-Based Metabolomics Discriminates Premium from Standard Chilean cv. Cabernet Sauvignon Wines from Different Valleys

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Figure S2. schematic representation of tryptophan catabolites, stilbenoids and cinnamic acids according to the valley. **Li:**Limarí, **Val:** valparaíso (Aconcagua valley), **Cur:** Curicó, **Mau:** Maule, **Ca:** Cachapoal, **Col:**Colchagua, **It:**Itata and **Mai:** Maipo.

Figure S3. Correlation plot clustered between sulfonated metabolites and anthocyanidins-pigments compounds in premium and standard Cabernet Sauvignon wines ($\alpha=0.05$).

Figure S4. The Heatmap used for the Figures F3-F7 for P1, P2, S1 and S2 quality groups. *(Separated file)*

Supplementary Table S7: Enological parameters measured in grape must according to Premium (P) and Standard (S) quality groups.

Parameter	P	S	<i>p</i> -value
Brix°	24.1±2.5	22.7±1.4	0.02
Ammonium (g/L)	82±50.3	85.8±29.7	0.74
PAN (g/L)	55.4±29.5	61.8±20.8	0.39
YAN(g/L)	148.8±65.9	147.7±47.0	0.97

Supplementary Table S8: Enological parameters in grape must according to subquality groups.

Parameter	P1	P2	S1	S2	<i>p</i> -value
Brix°	25.07±1.16 ^a	23.66±2.8 ^a	22.52±1.53 ^b	22.92±1.38 ^a	≤0.05
Ammonium (g/L)	104.31±79.36	73.32±32.62	92.09±30.90	76.46±26.50	≥0.05
PAN (g/L)	65.18±31.72	51.66±28.63	64.44±15.60	57.71±27.25	≥0.05
YAN(g/L)	195.76±76.95 ^a	130.02±52.62 ^b	156.79±44.10 ^a	134.15±50.15 ^a	≤0.05

Letters indicated pairwise comparison with post-hoc Tukey test after anova one-way. Different superscript letters indicated statistically difference (*p*-value≤0.005) between P1, P2, S1 and S2 groups.

Supplementary Table S9: Enological parameters of experimental Cabernet Sauvignon wines according to Premium (P) and Standard (S) quality groups.

Parameter	P	S	<i>p</i> -value
pH	3.45±0.04	3.46±0.03	0.24
TSO2 (ppm)	45.2±5.06	47.4±5.66	0.16
F SO2 (ppm)	38.3±4.82	41.7±5.34	0.02
A (% v/v)	13.3 ±0.89	13.3±0.88	0.30

Supplementary Table S10: Enological parameters of experimental Cabernet Sauvignon wines according to subquality groups.

Parameter	P1	P2	S1	S2	<i>p</i> -value
pH	3.45±0.04	3.44±0.04	3.45±0.03	3.46±0.03	≥0.05
TSO2 (ppm)	43.42±4.3	45.93±5.26	47.83±6.39	46.72±4.59	≥0.05
F SO2 (ppm)	37.21±3.88	38.68±5.17	41.47±6.28	41.92±3.79	≥0.05
A (% v/v)	13.55±0.22 ^{a,b}	13.79±0.52 ^a	12.70±0.94 ^b	13.07±0.84 ^{a,b}	≤0.05

Letters indicated pairwise comparison with post-hoc Tukey test after one-way ANOVA. Different superscript letters indicated statistically difference (*p*-value≤0.005) between P1, P2, S1 and S2 groups.

Supplementary Table S11: Integration means from raw files for amino acids, peptides, and non-flavonoids according to subquality groups.

compound	P1	P2	S1	S2
valine	13.09±2.60 ^b	14.59±3.27 ^{a,b}	19.04±6.73 ^a	16.96±3.40 ^a
arginine	14.19±6.98 ^{a,b}	8.21±3.51 ^b	17.74±10.35 ^a	9.28±7.95 ^b
leucine	3.08±1.11 ^a	2.18±0.62 ^b	2.37±1.53 ^b	1.80±0.80 ^b
isoleucine	0.35±0.15 ^{a,b}	0.26±0.09 ^b	0.38±0.28 ^a	0.24±0.12 ^b
proline	168.82±14.22 ^a	144.38±25.11 ^b	141.90±21.94 ^b	121.74±30.16 ^c
tyrosine	9.58±2.17 ^a	7.32±1.12 ^b	9.18±3.93 ^a	7.06±1.50 ^b
tryptophan	1.32±0.59 ^a	0.79±0.31 ^b	1.16±1.02 ^a	0.59±0.28 ^b
phenylalanine	9.60±3.42 ^a	6.61±1.74 ^b	8.51±5.65 ^a	5.87±2.67 ^b
tryptophol 2-sulfate	2.79± 0.77 ^b	3.73±1.18 ^{a,b}	4.35±1.76 ^a	4.90±1.79 ^a
indole 3 lactic-acid	28.44±8.67 ^b	34.36±22.97 ^b	62.13±51.22 ^a	40.13±18.04 ^b
indole lactic acid glucoside	1667.22±95.47	1601.63±165.29	1645.20±290.03	1590.56±320.95
indole lactic glucoside sulfonate	13.39±4.08 ^b	18.16±4.69 ^b	21.99±9.89 ^a	22.40±6.84 ^a
beta-glucogallin	19.05±3.80 ^a	14.34±3.57 ^b	13.62±8.52 ^b	12.37±4.10 ^b
galloyl hexoside	7.69±6.58 ^a	6.68±6.12 ^a	1.20±2.04 ^b	1.78±2.27 ^b
Cysteine sulfonate	1.19±0.23	1.81±2.63	1.61±0.78	1.30±0.63
3,4-hydroxybenzoic acid	1.33±0.36 ^a	1.10±0.42 ^a	0.79±0.55 ^b	0.82±0.40 ^b
4-hydroxybenzoic acid	5.54±1.58 ^a	4.36±0.99 ^b	3.55±1.02 ^b	3.85±1.00 ^b
trans-fertaric acid	12.22±2.06 ^a	9.94±1.80 ^b	8.76±1.52 ^c	10.05±1.49 ^b
O-coumaric acid	2.20±0.63 ^b	3.20±1.23 ^a	3.87±1.54 ^a	3.44±1.61 ^a
caftaric acid	8.70±1.84 ^a	8.08±1.75 ^{a,b,c}	7.36±1.83 ^c	9.37±2.25 ^a
trans-coutaric acid	49.40±11.79 ^{a,b}	44.13±7.76 ^{b,c}	40.41±8.83 ^c	50.29±10.74 ^a
caffeic.acid	29.93±7.39 ^c	35.45±9.29 ^b	42.10±11.29 ^a	39.88±13.52 ^{a,b}
cis-coutaric acid	3.37±0.49	3.42±0.73	3.19±0.54	3.46±0.46
Leu-leu-leu	1.51±0.81	0.92±0.41	1.44±1.55	0.79±0.51
Ethyl-caffeate	67.44±13.20 ^b	89.97±27.39 ^a	98.06±30.54 ^a	101.98±42.05 ^a
vanillic acid	5.69±0.93 ^a	4.68±0.89 ^b	3.76±1.23 ^c	4.03±0.83 ^c
trans-resveratrol	5.89±2.13 ^c	7.97±3.96 ^b	9.32±3.66 ^b	13.94±6.42 ^{a,b}
trans-piceid	22.46±10.35 ^c	25.29±13.28 ^{b,c}	27.59±20.12 ^b	39.34±25.70 ^a
trans-piceatannol	3.61±1.28 ^b	4.34±2.52 ^b	4.18±1.54 ^b	5.50±2.51 ^a
pallidol	1.97±0.98 ^b	2.22±2.36 ^b	2.71±2.74 ^b	5.05±4.34 ^a
ferulic acid-O-glucoside	2.00±0.56 ^a	1.63±0.57 ^b	1.54±0.55 ^b	1.63±0.40 ^b
gallic acid	54.62±11.75 ^a	46.00±6.89 ^b	44.33±8.07 ^b	42.18±6.08 ^b
egallic acid	95.52±28.06 ^a	73.28±21.23 ^b	62.50±19.26 ^b	75.19±40.43 ^b
α-aminoadipic acid	1.82±0.20 ^a	1.73±0.268 ^{a,b}	1.61±0.27 ^{b,c}	1.53±0.32 ^c
glutathione	2.21±0.38 ^a	1.23±0.44 ^b	1.09±0.39 ^b	1.21±0.89 ^b
glutathione S-Sulfonate	22.46±4.35 ^a	23.99±18.37 ^a	15.03±10.73 ^{a,b}	14.82±7.07 ^b
tyr-ala	1.60±0.78 ^a	1.05±0.41 ^b	1.59±1.33 ^a	0.94±0.44 ^b
pro-thr	2.37±0.75	1.98±0.45	2.48±1.56	2.07±0.62

t 4-hydroxy proline	0.26±0.08	0.26±0.09	0.29±0.08	0.24±0.08
gly-his	0.17±0.10 ^b	0.13±0.08 ^b	0.30±0.33 ^a	0.10±0.06 ^b

Letters indicated pairwise comparison with HSD Tukey test after one-way ANOVA. Different superscript letters indicated statistically difference (p -value \leq 0.005) between P1, P2, S1 and S2 groups.

Supplementary Table S12: Integrated areas means and standard deviation from raw files for tryptophan catabolites, stilbenoids and cinnamic acids for analyzed wines according to the valley.

compound	Cachapoal	Colchagua	Curicó	Itata	Limarí	Maipo	Maule	Aconcagua
tryptophan	0.57±0.25 ^b	0.87±0.36 ^a	1.25±1.49 ^a	1.13±0.23 ^a	0.70±0.34 ^b	1.39±0.52 ^a	0.77±0.26 ^b	0.64±0.11 ^b
indole 3-lactic acid	39.58±21.67	31.48±14.47	41.96±13.18	20.87±0.89	53.72±15.71	36.90±26.48	55.78±54.36	44.52±0.49
indole lactic glucoside	1562.97±187.71 ^b	1672.11±190.71 ^b	1677.81±198.81 ^b	1850.43±44.77 ^a	2002.54±291.35 ^a	1693.27±101.41 ^b	1469.67±254.00 ^b	1793.31±58.40 ^{a,b}
indole lactic glucoside sulfonate	18.11±5.36 ^b	19.81±4.81 ^{a,b}	20.87±4.71 ^{a,b}	16.91±1.95 ^b	29.13±3.63 ^a	14.71±5.49 ^b	20.37±10.56 ^{a,b}	23.23±2.38 ^{a,b}
tryptophol sulfonate	4.72±2.34 ^a	3.83±1.31 ^a	4.10±0.87 ^a	4.05±0.60 ^a	4.65±0.84 ^a	2.86±0.81 ^b	4.32±1.85 ^a	4.56±1.13 ^a
trans-resveratrol	8.50±3.27 ^{a,b}	6.54±3.75 ^b	10.27±3.07 ^a	10.78±0.46 ^a	11.82±4.47 ^a	6.29±1.71 ^b	12.21±6.46 ^a	7.78±0.17 ^{a,b}
trans-piceid	25.89±9.52	26.83±18.28	36.13±21.37	21.48±1.71	26.62±2.95	22.54±9.94	31.46±24.93	16.27±1.97
trans-piceatannol	4.30±1.86 ^a	3.74±2.22 ^b	4.17±0.85 ^a	3.53±0.27 ^b	5.10±1.23 ^a	3.50±1.27 ^b	5.53±2.82 ^a	3.95±0.13 ^{a,b}
pallidol	1.81±1.13	3.25±3.75	3.51±2.65	0.88±0.11	3.09±1.23	1.96±0.89	3.56±3.92	0.82±0.09
3,4-hydroxybenzoic acid	1.04±0.49	1.14±0.50	0.93±0.47	1.18±0.10	0.53±0.22	1.12±0.44	0.84±0.50	1.06±0.09
4-hydroxybenzoic acid	4.07±1.03 ^b	3.99±0.83 ^b	3.44±0.95 ^b	5.48±0.08 ^a	3.94±0.94 ^b	5.27±1.68 ^a	4.06±1.22 ^b	4.25±0.35 ^a

Letters indicated pairwise comparison with HSD Tukey test after one-way ANOVA. Different superscript letters indicated statistically difference (p -values≤0.005) between different origin valley.

Supplementary Table S13: Integrated areas means and standard deviation from raw files for the flavonoids and the anthocyanins of Figure 5-6.

compound	P1	P2	S1	S2
naringenin	13.44±2.98	15.32±5.63	13.32±5.15	15.32±4.02
luteolin	2.92±0.70 ^a	2.39±0.55 ^b	2.01±0.65 ^b	2.48±0.80 ^b
luteolin 7-glucoside	35.81±15.81 ^a	16.48±17.81 ^b	4.93±7.90 ^c	13.10±12.63 ^{b,c}
quercetin	553.09±102.89 ^a	504.30±177.90 ^a	358.62±238.32 ^b	502.01±235.36 ^a
quercetin 3-glucoside	607.56±266.15 ^a	249.08±257.74 ^b	75.35±122.32 ^c	202.75±181.31 ^{b,c}
quercetin 3-glucuronide	608.52±127.66 ^a	418.62±160.01 ^b	310.98±120.95 ^c	405.53±189.08 ^b
quercetin 4-glucoside	157.32±61.02 ^a	84.72±68.05 ^b	50.82±48.36 ^c	110.31±81.79 ^b
quercetin -xyloside	4.40±2.72 ^a	2.51±3.04 ^b	1.35±1.92 ^b	2.53±2.02 ^b
isorhamnetin	115.71±23.47 ^a	127.10±71.67 ^a	86.78±65.68 ^b	115.53±71.75 ^a
isorhamnetin 3-glucoside	168.90±61.70 ^a	93.63±63.22 ^b	37.66±34.70 ^c	77.64±44.68 ^b
isorhamnetin 3-(6"-acetyl)-glucoside	27.83±5.70 ^a	20.04±6.03 ^b	15.32±4.92 ^c	16.60±5.69 ^c
cyanidin 3-glucoside	43.21±28.48 ^a	37.62±19.83 ^a	24.90±12.12 ^b	33.95±23.03 ^{a,b}
cyanidin 3-(6"-acetyl)-glucoside	35.14±21.18 ^a	29.52±15.33 ^a	18.94±10.43 ^b	27.28±17.63 ^a
cyanidin 3-(6"-p-coumaroyl)-glucoside	11.10±6.78 ^a	9.76±3.61 ^a	7.31±3.36 ^b	10.58±8.47 ^{a,b}
peonidin 3-glucoside	410.28±132.24 ^a	365.63±95.94 ^a	309.70±103.09 ^b	337.55±125.94 ^{a,b}
peonidin3-(6"-acetyl)-glucoside	287.05±71.35 ^a	254.66±55.61 ^a	211.38±66.11 ^b	236.76±76.99 ^b
peonidin3-(6"-p-coumaroyl)-glucoside	131.60±41.16	121.34±35.23	108.34±40.82	122.52±66.45
dihydrokaempferol	7.058±1.68	7.14±1.62	6.61±1.99	6.88±1.10
dihydroquercetin rhamnoside	64.33±23.04 ^a	48.42±16.73 ^b	42.22±16.98 ^b	51.51±32.74 ^{a,b}
kaempferol	164.30±72.93 ^a	109.92±81.98 ^a	37.44±51.94 ^b	108.25±127.33 ^a
kaempferol 3-glucoside	92.46±66.04 ^a	35.63±39.75 ^b	14.86±13.58 ^c	29.91±21.20 ^{b,c}
kaempferol 3-glucuronide	13.87±3.23 ^a	9.37±4.36 ^b	6.58±3.46 ^c	9.09±4.59 ^b
myricetin	200.23±36.04	233.01±49.50	245.40±86.21	240.71±94.00
myricetin 3-glucoside	843.23±193.25 ^a	516.90±213.39 ^b	283.53±188.23 ^c	463.82±251.21 ^b
myricetin 3-rhamnoside	3.94±1.59	4.00±2.35	3.916±2.94	3.27±2.12
laricitrin	10.84±2.14	15.66±10.81	18.60±15.21	17.47±16.69
laricitrin 3-(6"-acetyl)-glucoside	1.69±0.67 ^a	1.43±0.80 ^a	1.02±0.68 ^b	1.22±0.72 ^a
syringetin	16.57±4.49 ^a	13.34±2.73 ^b	13.75±4.736 ^b	13.36±3.49 ^{a,b}
syringetin 3-glucoside	234.64±35.48 ^a	192.79±43.60 ^b	173.72±38.66 ^b	170.99±39.48 ^b
syringetin 3-(6"-acetyl)-glucoside	1.15±0.34 ^b	1.22±0.51 ^b	2.44±1.63 ^a	1.04±0.68 ^c
delphinidin 3-glucoside	654.00±224.65	680.83±232.79	570.56±252.80	690.12±335.34
delphinidin 3-(6"-p-coumaroyl)-glucoside	45.12±17.33	42.28±12.92	38.43±17.12	54.44±43.05
delphinidin 3-(6"-acetyl)-glucoside	277.74±90.69 ^a	264.31±99.840 ^a	206.36±101.63 ^b	269.35±130.54 ^{a,b}
delphinidin 3,5-diglucoside	39.15±15.93 ^{a,b}	50.70±25.85 ^a	20.82±17.80 ^c	36.51±20.45 ^b
petunidin 3-glucoside	960.07±230.30 ^{a,b,c}	959.88±258.62 ^b	775.00±286.67 ^c	973.86±444.31 ^a
petunidin 3-(6"-p-coumaroyl)-glucoside	92.33±27.89	81.89±23.56	69.95±27.67	94.36±67.79
petunidin 3-(6"-acetyl)-glucoside	448.14±116.62 ^a	408.13±125.98 ^a	320.03±133.33 ^b	417.52±196.08 ^a
malvidin 3-glucoside	7724.31±868.99	7598.47±852.24	7710.51±1436.24	7617.66±1553.8
malvidin 3-(6"-acetyl)-glucoside	4911.33±669.09	4448.10±575.81	4395.39±868.68	4429.66±979.11

malvidin 3-(6''-p-coumaroyl)-glucoside	1111.71±206.67	988.98±198.20	1013.63±270.54	1062.49±408.33
catechin/epicatechin ethyl malvidin 3-glucoside	28.32±17.66 ^a	14.54±8.34 ^b	10.27±5.90 ^c	10.24±7.18 ^c
catechin/epicatechin ethyl malvidin 3-glucoside	11.10±6.91 ^a	5.38±5.90 ^b	3.19±1.51 ^c	3.16±2.35 ^c
catechin/epicatechin malvidin 3-glucoside	116.86±24.27 ^a	111.28±15.16 ^a	100.40±25.70 ^b	119.69±37.38 ^c
catechin/epicatechin-ethyl-malvidin 3-(6''-p-coumaroyl)-glucoside	13.77±8.35 ^a	6.40±2.85 ^b	5.18±1.75 ^b	5.64±3.59 ^b
malvidin 3-glucoside-4vinylphenol	20.84±6.73	21.66±10.75	22.51±10.87	30.56±29.02
pyranomalvidin 3-(6''-acetyl)-glucoside	126.10±63.84 ^a	52.63±36.77 ^b	48.19±24.16 ^b	23.79±18.51 ^b
pyranomalvidin 3-(6''-p-coumaroyl)-glucoside	42.99±25.39 ^a	16.38±13.049 ^b	15.03±9.28 ^b	9.06±9.40 ^b
carboxypyranomalvidin 3-(6''-acetyl)-glucoside	168.96±29.47 ^a	108.20±32.42 ^b	101.04±32.84 ^b	88.00±30.30 ^b
carboxypyranomalvidin 3-(6''-p-coumaroyl)-glucoside	56.22±13.22 ^a	35.23±32.42 ^b	34.67±10.61 ^b	34.59±17.05 ^b
methyl-pyrano-malvidin 3-glucoside	73.21±17.78 ^a	48.49±18.99 ^b	33.26±13.22 ^c	28.73±10.29 ^c
Pinotin	88.52±17.24	82.51±23.71	71.63±26.35	101.04±84.05
Pinotin A	86.07±13.91 ^{a,b}	82.40±23.50 ^{a,b}	71.81±26.35 ^b	100.56±83.62 ^a
Oxovitisin A	10.51±3.57 ^a	5.77±2.66 ^b	5.11±1.50 ^c	3.73±1.71 ^c

Letters indicated pairwise comparison with HSD Tukey test after one-way ANOVA. Different superscript letters indicated statistically difference (p -value \leq 0.005) between P1, P2, S1 and S2.

Supplementary Table S14: Integrated areas means and standard deviation from raw files for the flavonols of Figure 7A.

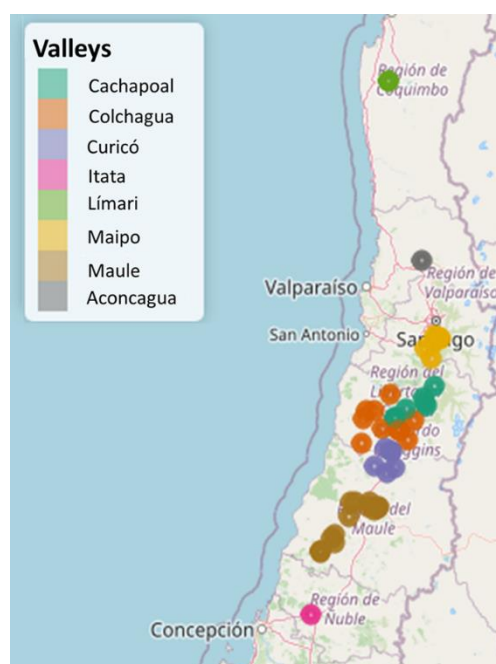
compound	P1	P2	S1	S2
Epicatechin	146.44±49.27 ^a	121.63±35.23 ^b	110.68±29.87 ^{b,c}	95.683±18.83 ^c
Catechin	232.58±68.80 ^a	178.00±39.95 ^b	161.50±32.65 ^{b,c}	152.37±20.94 ^c
PB3	38.45±15.01 ^a	29.34±7.79 ^b	28.16±9.37 ^b	23.134±2.62 ^b
PB4	26.58±9.63 ^a	20.49±4.91 ^b	18.37±4.82 ^b	18.917±4.18 ^b
PB2	190.04±39.32 ^a	159.53±30.02 ^b	158.41±24.05 ^b	156.488±14.77 ^b
caffeic acid-catechin condensation product	0.32±0.29 ^a	0.26±0.18 ^a	0.21±0.18 ^b	0.439±0.43 ^a
Proanthocyanidin trimer	3.58±1.25 ^a	2.65±0.96 ^b	2.61±1.04 ^b	3.167±1.18 ^b
Proanthocyanidin trimer	1.93±0.56 ^a	1.36±0.56 ^b	1.38±0.59 ^b	1.658±0.55 ^b
Proanthocyanidin trimer	5.90±2.19 ^a	4.41±1.14 ^b	4.09±1.30 ^b	5.151±1.14 ^b
Proanthocyanidin trimer	3.57±1.58 ^a	2.70±0.80 ^b	2.50±0.61 ^b	3.313±0.89 ^b
Proanthocyanidin trimer	2.94±1.61 ^a	1.79±0.77 ^b	1.76±0.66 ^c	2.029±0.48 ^b
Proanthocyanidin dimer	58.94±14.07 ^a	47.16±8.51 ^b	47.67±7.60 ^b	53.211±7.66 ^b
Proanthocyanidin dimer	44.38±11.32 ^a	36.54±7.94 ^b	39.91±8.02 ^b	41.153±7.82 ^b
Proanthocyanidin dimer	6.34±2.29 ^a	5.10±1.12 ^b	4.64±0.73 ^c	4.700±0.72 ^c
Proanthocyanidin dimer	10.42±2.95 ^a	7.49±1.58 ^b	8.28±1.75 ^b	8.810±2.32 ^b
flavan-3-ol hexoside	3.47±1.76 ^a	2.81±1.48 ^a	1.62±1.24 ^b	1.472±0.64 ^b
flavan-3-ol hexoside	12.72±4.74 ^a	11.35±5.02 ^a	8.47±3.41 ^b	7.070±2.70 ^b
epicatechin sulfonate	10.43±2.67 ^b	12.63±3.19 ^{a,b}	11.55±2.88 ^b	15.184±4.48 ^a
procyanidin B2-4β-sulfonate	0.47±0.23 ^b	0.61±0.30 ^a	0.49±0.23 ^{a,b}	0.809±0.42 ^a
prodelphinidin-4β-sulfonate	1.88±0.53 ^b	2.34±1.02 ^b	2.75±1.17 ^b	3.626±1.99 ^a
prodelphinidin-4β-sulfonate	2.18±0.41 ^b	3.55±1.16 ^b	3.26±1.45 ^b	4.575±1.54 ^a

Letters indicated pairwise comparison with HSD Tukey test after one-way ANOVA. Different superscript letters indicated statistically difference (p -value≤0.005) between P1, P2, S1 and S2.

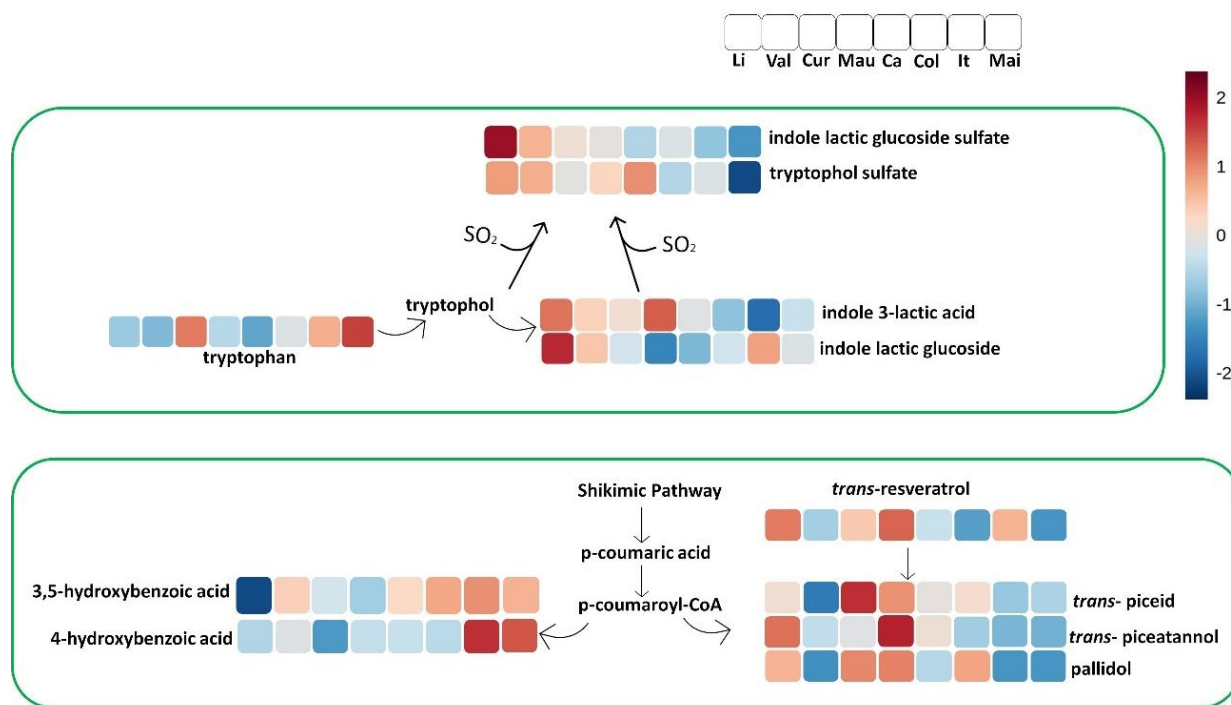
Supplementary Table S15: Integrated areas means and standard deviation from raw files for metabolites of Figure 7B.

compound	P1	P2	S1	S2
D-pantothenic acid	2.58±0.48 ^a	2.03±0.38 ^b	1.81±0.54 ^b	1.40±0.40 ^c
uridine monophosphate	18.20±5.93 ^a	16.05±4.01 ^a	6.76±3.86 ^c	13.36±4.96 ^b
hypoxanthine	18.74±2.60 ^{a,b}	15.21±3.34 ^b	17.84±5.67 ^a	17.58±2.48 ^{a,b}
xanthine	74.41±5.95 ^b	80.11±5.74 ^{a,b}	72.03±13.93 ^b	82.91±7.42 ^a
uridine or pseudouridine	7.84±2.31 ^{a,b}	5.91±1.21 ^b	9.70±5.40 ^a	5.52±1.15 ^b
tartaric acid	289.33±11.57	287.04±17.51	283.83±7.86	281.97±14.60
riboflavina	12.25±1.27 ^a	9.80±1.29 ^b	11.48±2.66 ^a	9.30±1.85 ^b
choline	121.77±19.63 ^b	133.33±17.75 ^{a,b}	146.63±45.81 ^a	129.62±14.10 ^{a,b}
pantotheine sulfonate	6.93±2.46	7.58±5.69	7.73±2.80	6.42±2.21
malic acid	4.99±0.63 ^b	5.78±1.26 ^{a,b}	5.79±1.15 ^b	5.95±0.94 ^a
Uracil	2.07±0.28 ^b	2.23±0.39 ^b	2.46±0.51 ^{a,b}	2.89±0.78 ^a

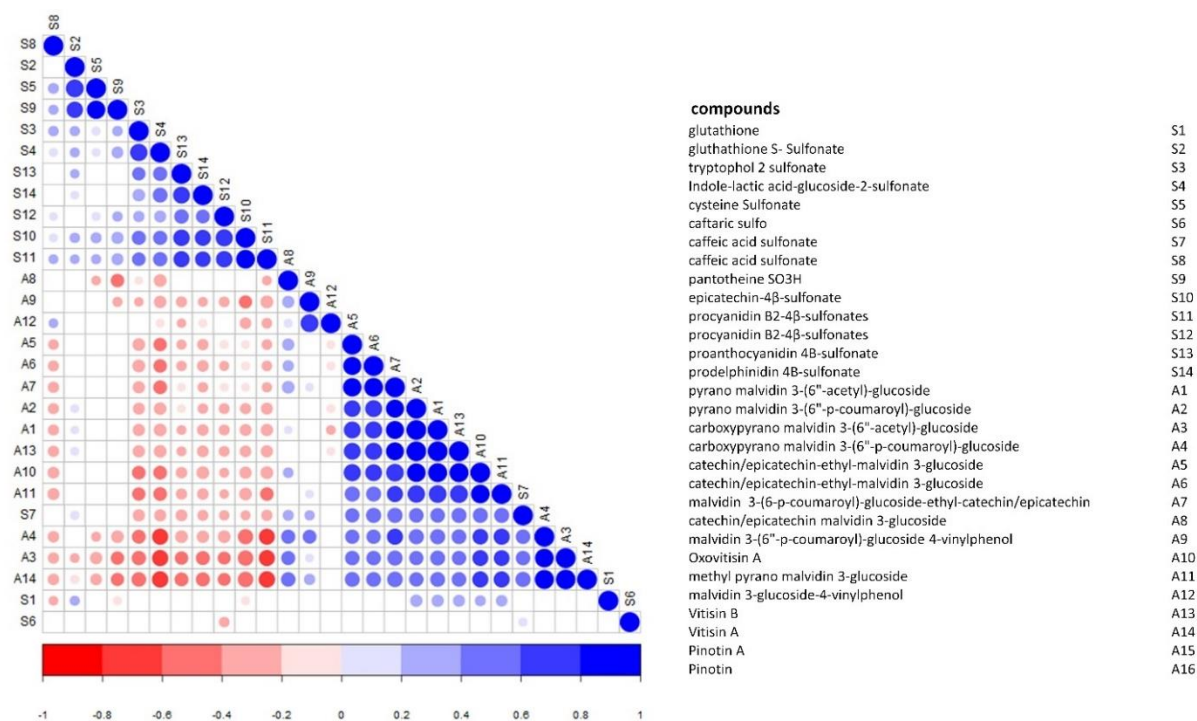
Letters indicated pairwise comparison with HSD Tukey test after one-way ANOVA. Different superscript letters indicated statistically difference (p -value≤0.005) between P1, P2, S1 and S2.



Supplementary Figure S1: valley geographic distribution of wine samples.



Supplementary Figure S2: schematic representation of tryptophan catabolites, stilbenoids and cinnamic acids according to the valley. **Li:**Limarí, **Val:** valparaíso (Aconcagua valley), **Cur:** Curicó, **Mau:** Maule, **Ca:** Cachapoal, **Col:**Colchagua, **It:**Itata and **Mai:** Maipo.



Supplementary Figure S3: Correlation plot clustered between sulfonated metabolites and anthocyanidins-pigments compounds in premium and standard Cabernet Sauvignon wines ($\alpha=0.05$).

Safety Statement

This study does not include any new or unexpected significant hazards or risks associated material. A Table with all the chemicals and their Classification/Hazardous Identification can be found below.

Material Name	Material CAS-No	Classification according to Regulation (EC) No 1272/2008
Methanol	67-56-1	Flammable liquids (Category 2), H225 Acute toxicity, Oral (Category 3), H301 Acute toxicity, Inhalation (Category 3), H331 Acute toxicity, Dermal (Category 3), H311 Specific target organ toxicity - single exposure (Category 1), Eyes, Central nervous system, H370
Acetonitrile	75-05-8	Flammable liquids (Category 2), H225 Acute toxicity, Oral (Category 4), H302 Acute toxicity, Inhalation (Category 4), H332 Acute toxicity, Dermal (Category 4), H312 Eye irritation (Category 2), H319
Formic acid	64-18-6	Flammable liquids (Category 3), H226 Acute toxicity, Oral (Category 4), H302 Acute toxicity, Inhalation (Category 3), H331 Skin corrosion (Sub-category 1A), H314 Serious eye damage (Category 1), H318
2-Propanol	67-63-0	Flammable liquids (Category 2), H225 Eye irritation (Category 2), H319 Specific target organ toxicity - single exposure (Category 3), Central nervous system, H336
Leucine Enkephalin	81678-16-2	Not a hazardous substance or mixture according to Regulation (EC) No. 1272/2008.
Sodium Hydroxide	1310-73-2	Corrosive to Metals (Category 1), H290 Skin corrosion (Sub-category 1A), H314 Serious eye damage (Category 1), H318