

Decoding the Proanthocyanins Profile of Italian Red Wines

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Table S1. Basic statistics and Anova analysis of the dimeric procyanidins

Group (Cultivar)	Number of samples per group	procyanidin B1				procyanidin B2			
		mg/L	±	Std. Deviation	Anova	mg/L	±	Std. Deviation	Anova
Sangiovese Romagna	7	26.09	±	5.83	a,b	23.77	±	8.73	a,b
Sangiovese Tuscany	12	22.54	±	8.22	a	22.59	±	5.91	a,b
Nebbiolo	11	39.69	±	11.14	a,b,c,d,e	34.18	±	15.51	b,c
Aglianico	10	47.97	±	9.39	d,e	49.68	±	25.35	c
Nerello Mascalese	3	30.31	±	12.87	a,b,c,d	11.54	±	5.07	a
Primitivo	11	28.39	±	9.45	a,b,c	26.41	±	8.95	a,b
Raboso Piave	10	40.18	±	14.52	b,c,d,e	13.47	±	4.35	a
Canonnau	9	29.10	±	12.97	a,b,c	16.44	±	7.94	a,b
Teroldego	11	23.54	±	10.60	a,b	24.54	±	12.75	a,b
Sagrantino	10	44.67	±	14.85	c,d,e	30.41	±	7.59	a,b,c
Montepulciano	9	29.89	±	10.20	a,b,c,d	22.59	±	9.88	a,b
Corvina	7	50.07	±	10.84	e	22.68	±	11.53	a,b
Total	111	34.34	±	14.13		25.87	±	14.86	

Anova: Means that do not share a letter are significantly different (significance value below 0.05)

Table S2. Basic statistics and Anova analysis of the free monomers' absolute values

Group (Cultivar)	Number of samples per group	catechin free			epicatechin free			galocatechin free			epigallocatechin free			catechin gallate free			Total monomers (mg/L)		
		mg/L	Std. Deviation	Anova	mg/L	Std. Deviation	Anova	mg/L	Std. Deviation	Anova	mg/L	Std. Deviation	Anova	mg/L	Std. Deviation	Anova	mg/L	Std. Deviation	Anova
Sangiovese Romagna	7	15.60	± 2.95	a	15.55	± 3.48	a,b	0.38	± 0.18	a,b	2.04	± 0.51	a,b,c	0.02	± 0.01	a	33.58	± 6.15	a,b
Sangiovese Tuscany	12	16.75	± 4.31	a	15.92	± 2.91	a,b	0.31	± 0.12	a,b	2.04	± 0.23	a,b,c	0.05	± 0.05	a	35.07	± 6.16	a,b
Nebbiolo	11	28.81	± 7.97	c,d	18.15	± 6.45	a,b	0.20	± 0.15	a,b	1.14	± 0.35	a	0.23	± 0.25	b	48.53	± 13.57	a,b
Aglianico	10	35.34	± 9.50	d	35.37	± 13.16	c	0.25	± 0.33	a,b	1.60	± 0.56	a,b,c	0.10	± 0.10	a,b	72.65	± 19.60	c
Nerello Mascalese	3	27.34	± 2.05	b,c,d	9.11	± 2.68	a	0.89	± 0.47	c	2.29	± 0.65	b,c	0.03	± 0.00	a	39.66	± 0.55	a,b
Primitivo	11	19.32	± 4.40	a,b,c	18.16	± 3.78	a,b	0.10	± 0.03	a	1.05	± 0.36	a	0.07	± 0.09	a	38.70	± 7.90	a,b
Raboso Piave	10	19.06	± 4.65	a,b,c	9.15	± 3.32	a	0.34	± 0.18	a,b	1.75	± 0.60	a,b,c	0.04	± 0.02	a	30.34	± 7.89	a,b
Canonnau	9	17.54	± 2.66	a,b	10.48	± 2.36	a	0.35	± 0.22	a,b	1.12	± 0.30	a	0.04	± 0.02	a	29.52	± 4.21	a
Teroldego	11	23.21	± 8.69	a,b,c	20.71	± 7.90	b	0.21	± 0.09	a,b	4.80	± 1.23	d	0.03	± 0.01	a	48.95	± 16.45	b
Sagrantino	10	24.03	± 8.01	a,b,c	22.15	± 6.27	b	0.15	± 0.05	a	1.73	± 0.56	a,b,c	0.04	± 0.02	a	48.10	± 13.68	a,b
Montepulciano	9	18.41	± 4.53	a,b,c	16.52	± 2.46	a,b	0.37	± 0.19	a,b	2.48	± 0.83	c	0.04	± 0.03	a	37.82	± 6.49	a,b
Corvina	7	27.36	± 6.93	b,c,d	15.76	± 5.48	a,b	0.46	± 0.17	b	1.45	± 0.45	a,b	0.03	± 0.00	a	45.05	± 12.43	a,b
Total	111	22.47	± 8.33		17.87	± 8.88		0.29	± 0.22		1.96	± 1.19		0.06	± 0.10		42.65	± 15.97	a,b

Anova: Means that do not share a letter are significantly different (significance value below 0.05)

Table S3. Basic statistics and Anova analysis of the free monomers' % values

Group (Cultivar)	Number of samples per group	catechin free %			epicatechin free %			gallo catechin free %			epigallocatechin free %			catechin gallate free %		
		free monomers %	Std. Deviation	Anova	free monomers %	Std. Deviation	Anova	free monomers %	Std. Deviation	Anova	free monomers %	Std. Deviation	Anova	free monomers %	Std. Deviation	Anova
Sangiovese Romagna	7	46.45 ± 3.24	a	46.17 ± 4.51	e	1.13 ± 0.53	a,b,c	6.18 ± 1.71	b,c	0.07 ± 0.05	a					
Sangiovese Tuscany	12	47.31 ± 6.24	a	45.72 ± 6.07	e	0.90 ± 0.34	b,c	5.92 ± 0.82	b,c	0.16 ± 0.17	a					
Nebbiolo	11	59.95 ± 6.08	b	36.56 ± 6.48	b,c,d	0.48 ± 0.50	a,b,c	2.45 ± 0.94	a	0.55 ± 0.54	b					
Aglianico	10	49.16 ± 6.69	a	47.88 ± 7.45	e	0.42 ± 0.65	a,b,c	2.39 ± 1.15	a	0.15 ± 0.17	a					
Nerello Mascalese	3	68.98 ± 6.01	c	22.93 ± 6.60	a	2.25 ± 1.21	e	5.76 ± 1.56	b,c	0.07 ± 0.00	a					
Primitivo	11	49.69 ± 3.08	a	47.05 ± 3.17	e	0.27 ± 0.10	a	2.76 ± 0.85	a	0.24 ± 0.44	a,b					
Raboso Piave	10	63.34 ± 4.01	b,c	29.65 ± 4.11	a,b	1.10 ± 0.50	b,c	5.76 ± 1.15	b,c	0.14 ± 0.07	a					
Canonnau	9	59.59 ± 4.71	b	35.30 ± 5.21	b,c	1.20 ± 0.80	c	3.79 ± 0.89	a,b	0.12 ± 0.04	a					
Teroldego	11	47.04 ± 4.79	a	41.93 ± 4.44	c,d,e	0.44 ± 0.19	a,b,c	10.53 ± 3.76	e	0.06 ± 0.03	a					
Sagrantino	10	49.71 ± 6.38	a	46.06 ± 6.98	e	0.36 ± 0.20	a,b	3.77 ± 1.20	a,b	0.10 ± 0.10	a					
Montepulciano	9	48.21 ± 5.30	a	44.15 ± 5.33	d,e	0.94 ± 0.40	a,b,c	6.59 ± 1.92	c	0.11 ± 0.10	a					
Corvina	7	61.30 ± 3.55	b	34.30 ± 4.40	b,c	1.07 ± 0.44	b,c	3.25 ± 0.92	a	0.08 ± 0.04	a					
Total	111	53.22 ± 8.34		40.93 ± 8.46		0.76 ± 0.62		4.92 ± 2.85		0.17 ± 0.27						

Anova: Means that do not share a letter are significantly different (significance value below 0.05)

Table S4. Basic statistics and Anova analysis of the terminal units' absolute values

Group (Cultivar)	Number of samples per group	catechin terminal			epicatechin terminal			galocatechin terminal			epigallocatechin terminal			catechin gallate terminal			total terminal units		
		mg/L	Std. Deviation	Anova	mg/L	Std. Deviation	Anova	mg/L	Std. Deviation	Anova	mg/L	Std. Deviation	Anova	mg/L	Std. Deviation	Anova	mg/L	Std. Deviation	Anova
		Sangiovese Romagna	7	40.02 ± 11.12	a,b,c	28.55 ± 14.12	a,b,c,d	11.86 ± 2.70	d,e	2.59 ± 0.96	b,c,d	0.19 ± 0.06	a,b	83.21 ± 27.07	a,b,c				
Sangiovese Tuscany	12	48.33 ± 12.69	a,b,c	29.08 ± 7.84	a,b,c,d	12.25 ± 3.47	d,e	2.49 ± 0.73	b,c,d	0.19 ± 0.08	a,b	92.35 ± 21.06	a,b,c						
Nebbiolo	11	72.66 ± 25.65	c	34.91 ± 18.49	b,c,d	12.17 ± 3.45	d,e	1.81 ± 0.76	a,b,c	0.25 ± 0.20	a	121.80 ± 45.79	b,c						
Aglianico	10	72.79 ± 26.31	c	49.45 ± 16.01	d	5.75 ± 2.40	a,b,c	2.57 ± 1.36	b,c,d	0.19 ± 0.11	a,b	130.76 ± 42.41	c,d						
Nerello Mascalese	3	57.11 ± 17.04	a,b,c	17.06 ± 10.80	a,b	20.16 ± 2.30	f	2.82 ± 0.49	c,d	0.15 ± 0.01	a,b	97.30 ± 26.11	a,b,c						
Primitivo	11	66.84 ± 12.64	b,c	46.17 ± 12.00	c,d	5.05 ± 1.31	a,b	1.97 ± 1.33	a,b,c	0.17 ± 0.09	a,b	120.21 ± 25.11	b,c						
Raboso Piave	10	66.84 ± 31.15	b,c	21.00 ± 16.39	a,b	12.31 ± 5.54	c,d,e	2.53 ± 1.70	b,c,d	0.19 ± 0.07	a,b	101.71 ± 53.16	a,b,c						
Canonnau	9	50.21 ± 23.30	a,b,c	15.29 ± 7.07	a,b	10.43 ± 4.08	b,c,d	1.41 ± 0.53	a,b,c	0.16 ± 0.04	a,b	77.49 ± 33.51	a,b,c						
Teroldego	11	34.47 ± 10.83	a,b	25.19 ± 5.87	a,b,c	6.43 ± 1.66	a,b,c,d	0.96 ± 0.63	a,b	0.17 ± 0.04	a,b	67.23 ± 16.70	a,b						
Sagrantino	10	123.40 ± 34.02	e	42.65 ± 21.65	c,d	16.91 ± 5.45	e,f	3.77 ± 1.29	d	0.32 ± 0.17	b	187.06 ± 58.59	d						
Montepulciano	9	52.25 ± 13.19	a,b,c	27.93 ± 8.63	a,b,c,d	11.52 ± 3.82	c,d,e	2.45 ± 0.71	b,c,d	0.17 ± 0.04	a,b	94.33 ± 22.93	a,b,c						
Corvina	7	25.50 ± 12.24	a	9.54 ± 7.67	a	3.42 ± 1.48	a	0.58 ± 0.39	a	0.15 ± 0.02	a	39.19 ± 20.76	a						
Total	111	60.42 ± 31.70		30.35 ± 17.29		10.14 ± 5.34		2.14 ± 1.27		0.20 ± 0.11		103.26 ± 49.50							

Anova: Means that do not share a letter are significantly different (significance value below 0.05)

Table S5. Basic statistics and Anova analysis of the terminal units' % values

Group (Cultivar)	Number of samples per group	catechin terminal %			epicatechin terminal %			galocatechin terminal %			epigallocatechin terminal %			catechin gallate terminal %		
		terminal monomers %	Std. Deviation	Anova	terminal unit %	Std. Deviation	Anova	terminal unit %	Std. Deviation	Anova	terminal unit %	Std. Deviation	Anova	terminal unit %	Std. Deviation	Anova
Sangiovese Romagna	7	48.87	± 5.48	a,b	33.08	± 5.71	d,e	14.69	± 2.64	b,c	3.12	± 1.02	b,c	0.24	± 0.05	b
Sangiovese Tuscany	12	52.08	± 4.73	a	31.65	± 5.23	d,e	13.33	± 2.23	c	2.72	± 0.66	c	0.21	± 0.09	b
Nebbiolo	11	60.41	± 4.16	c,d,e	26.91	± 6.78	b,c,d	10.90	± 3.36	b,c	1.58	± 0.76	a,b	0.20	± 0.11	b
Aglianico	10	55.07	± 5.59	a,b,c	38.20	± 4.73	e	4.32	± 0.95	a	2.26	± 1.55	a,b,c	0.15	± 0.07	b
Nerello Mascalese	3	58.36	± 2.06	b,c,d	16.49	± 6.13	a	22.01	± 7.27	e	2.98	± 0.60	c	0.16	± 0.04	b
Primitivo	11	55.88	± 2.93	a,b,c,d	38.13	± 2.95	e	4.31	± 1.14	a	1.54	± 0.67	a,b	0.14	± 0.08	b
Raboso Piave	10	66.32	± 5.78	e	18.06	± 7.29	a,b	13.14	± 3.18	b,c	2.24	± 0.68	a,b,c	0.24	± 0.14	b
Canonnau	9	63.39	± 5.50	d,e	19.60	± 4.28	a,b	14.87	± 5.89	c	1.89	± 0.61	a,b,c	0.26	± 0.18	b
Teroldego	11	50.26	± 7.01	a	38.43	± 7.45	e	9.68	± 1.80	b	1.36	± 0.74	a	0.27	± 0.09	b
Sagrantino	10	66.90	± 4.51	e	21.68	± 5.78	a,b,c	9.21	± 2.00	b	2.05	± 0.59	a,b,c	0.17	± 0.06	b
Montepulciano	9	55.30	± 3.69	a,b,c	29.54	± 4.78	c,d,e	12.34	± 2.90	b,c	2.63	± 0.61	a,b,c	0.19	± 0.05	b
Corvina	7	67.03	± 6.72	e	21.26	± 7.94	a,b,c	9.72	± 3.31	b	1.49	± 0.73	a,b	0.50	± 0.29	a
Total	111	58.23	± 7.93		28.75	± 9.45		10.71	± 4.90		2.09	± 0.95		0.22	± 0.14	

Anova: Means that do not share a letter are significantly different (significance value below 0.05)

Table S6. Basic statistics and Anova analysis of the upper units' absolute values

Group (Cultivar)	Number of samples per group	epicatechin-PhI			epigallocatechin-PhI			epicatechin gallate-PhI			total upper units		
		mg/L	Std. Deviation	Anova	mg/L	Std. Deviation	Anova	mg/L	Std. Deviation	Anova	mg/L	Std. Deviation	Anova
Sangiovese Romagna	7	946.64	± 164.34	a,b	453.17	± 77.92	c,d	117.61	± 39.63	b,c	1517.41	± 273.37	b,c
Sangiovese Tuscany	12	972.01	± 196.03	a,b	454.42	± 102.39	c,d	135.71	± 51.13	b,c	1562.13	± 340.08	b,c
Nebbiolo	11	1387.48	± 277.46	d	503.09	± 131.62	c,d	178.95	± 58.39	c	2069.51	± 453.97	c,d
Aglianico	10	1210.01	± 246.26	c,d	204.31	± 72.54	a,b	133.93	± 49.24	b,c	1548.24	± 346.47	b,c
Nerello Mascalese	3	899.88	± 110.66	a,b	534.90	± 54.72	d	78.01	± 7.99	a,b	1512.79	± 171.37	b,c
Primitivo	11	972.32	± 172.73	a,b	188.47	± 54.40	a,b	90.73	± 26.62	a,b	1251.52	± 229.41	b
Raboso Piave	10	879.04	± 357.78	a,b	356.93	± 178.87	b,c	107.87	± 76.76	b,c	1343.84	± 607.13	b
Canonnau	9	892.96	± 379.34	a,b	290.51	± 126.24	b	88.09	± 62.10	a,b	1271.55	± 560.06	b
Teroldego	11	659.63	± 155.67	b	281.65	± 87.20	b	76.33	± 24.92	a,b	1017.62	± 251.72	b
Sagrantino	10	1805.28	± 343.94	e	491.48	± 128.68	c,d	268.44	± 88.37	d	2565.20	± 547.39	d
Montepulciano	9	739.34	± 236.14	b	250.92	± 107.45	b	89.62	± 56.00	a,b	1079.87	± 386.52	b
Corvina	7	299.18	± 176.04	a	68.62	± 44.94	a	15.99	± 15.83	a	383.79	± 235.34	a
Total	111	993.75	± 437.68		332.87	± 169.46		120.03	± 79.26		1446.65	± 646.78	

Anova: Means that do not share a letter are significantly different (significance value below 0.05)

Table S7. Basic statistics and Anova analysis of the upper units' % values

Group (Cultivar)	Number of samples per group	epicatechin-PhI %				epigallocatechin-PhI %				epicatechin gallate-PhI %			
		Upper unit %	±	Std. Deviation	Anova	Upper unit %	±	Std. Deviation	Anova	Upper unit %	±	Std. Deviation	Anova
Sangiovese Romagna	7	62.48	±	1.93	a,b	29.94	±	2.12	f,g	7.59	±	1.13	c,d
Sangiovese Tuscany	12	62.43	±	2.37	a,b	29.12	±	2.05	g	8.45	±	1.47	b,c,d
Nebbiolo	11	67.38	±	2.32	c,d	24.11	±	1.79	d,e	8.51	±	1.33	c,d
Aglianico	10	78.51	±	2.98	e	12.97	±	2.80	a	8.52	±	1.87	c,d
Nerello Mascalese	3	59.44	±	1.00	a	35.40	±	0.79	h	5.16	±	0.21	a,b
Primitivo	11	77.89	±	3.11	e	14.99	±	2.96	a,b	7.12	±	1.23	b,c
Raboso Piave	10	66.84	±	4.09	c,d	25.80	±	3.42	d,e,f,g	7.36	±	2.03	b,c
Canonnau	9	70.62	±	2.17	d	22.98	±	2.21	d	6.40	±	1.74	b,c
Teroldego	11	65.21	±	3.42	b,c	27.27	±	3.82	e,f,g	7.52	±	1.38	b,c,d
Sagrantino	10	70.78	±	2.69	d	18.99	±	1.84	c	10.23	±	1.71	d
Montepulciano	9	69.24	±	3.82	c,d	23.05	±	3.40	d	7.70	±	2.85	b,c,d
Corvina	7	78.82	±	2.62	e	17.53	±	2.36	b,c	3.65	±	1.31	a
Total	111	69.58	±	6.50		22.84	±	6.28		7.58	±	2.20	

Anova: Means that do not share a letter are significantly different (significance value below 0.05)

Formulas for the calculations

From the Table S3

- **Free catechin + epicatechin %** = “catechin free %” + “epicatechin free %”
- **Free C-ring *trans/cis*** = (“catechin free %” + “gallocatechin free %”)/ (“epicatechin free %” + “epigallocatechin free %”)
- **Free B-ring 3xOH/2xOH** = (“gallocatechin free %” + “epigallocatechin free %”)/ (“catechin free %” + “epicatechin free %”)
- **Free galloylated %** = “catechin gallate free %”

From the Table S5

- **Terminal C-ring *trans/cis*** = (“catechin terminal %” + “gallocatechin terminal %”)/ (“epicatechin terminal %” + “epigallocatechin terminal %”)
- **Terminal B-ring 3xOH/2xOH** = (“gallocatechin terminal %” + “epigallocatechin terminal %”)/ (“catechin terminal %” + “epicatechin terminal %”)
- **Terminal galloylated %** = “catechin gallate terminal %”

From the Table S7

- **Upper galloylated %** = “epicatechin gallate-PhI %”

For the formulas were used information about the biosynthesis and the chemistry of the flavan-3-ols [1-4], and previous similar studies [5-12].

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