

SUPPLEMENTARY DATA

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Supplemental Material

TABLE S1. Analyte identification.

ID numbers	Compound	2019						2020					
		CF0	CF0	CF1	CF1	CF2	CF2	CF0	CF0	CF1	CF1	CF2	CF2
		Mean	sd	Mean	sd	Mean	sd	Mean	sd	Mean	sd	Mean	sd
m1	L-proline	77170.468	484751.266	16965.928	323349.391	49422.789	334262.049	7110.872	439951.273	23199.326	292870.487	52560.906	412289.450
m2	L-leucine	1589.743	30799.445	4476.453	32881.854	3403.779	25775.556	5727.521	42415.180	4283.908	31691.734	6281.562	62770.488
m3	L-isoleucine	5076.022	59408.677	3813.662	60139.578	9577.547	64787.579	10297.374	80528.371	3247.853	57730.058	15459.272	109108.975
m4	L-phenylalanine	2417.423	25904.053	1941.102	29652.701	177.801	47682.480	3102.054	27222.278	4799.188	32528.513	6844.017	76670.425
m5	L-tyrosine	1861.759	22624.612	1669.023	18761.038	2899.888	18144.303	4418.766	30640.760	3649.509	25540.154	5000.225	41836.569
m6	L-tryptophan	6590.009	60133.906	7974.666	59279.889	12.153	58230.680	10565.679	74746.105	5943.557	60241.623	7206.670	85155.745
m7	cyanidin-3-O-glucoside	1616.181	12740.794	4800.809	32463.099	60.060	77178.258	491.738	7012.132	6836.262	47668.357	2523.184	82284.603
m8	peonidin-3-O-glucoside	719.614	70846.572	8359.982	100274.088	10387.985	141089.157	1503.665	48590.627	12897.074	127176.879	13150.622	160518.777
m9	delphinidin-3-O-glucoside	3127.959	49804.227	11475.375	156657.308	17812.608	206792.365	1358.554	27339.770	23709.325	164780.312	5688.943	206635.396
m10	petunidin-3-O-glucoside	3205.111	74799.300	23331.296	189129.548	21686.445	176150.916	1527.462	48686.566	24404.260	171529.310	7298.321	184585.217
m11	cyanidin-3-O-(6-O-acetyl)-glucoside	91.930	1677.310	652.736	7505.642	501.079	14327.421	59.858	1203.421	597.248	9320.256	719.389	16441.817
m12	malvidin-3-O-glucoside	43840.333	324584.720	19293.500	427748.814	16775.507	282678.553	9985.424	318935.425	41512.775	370092.970	22824.865	280520.060
m13	petunidin-3-O-(6-O-acetyl)-glucoside	1464.828	21700.632	7154.479	75063.228	7345.389	55645.296	448.776	13338.350	9416.262	63089.311	2744.140	57470.609
m14	malvidin-3-O-(6-O-acetyl)-glucoside	24980.236	228876.571	16521.783	221410.514	5708.610	113823.820	12743.280	238540.632	15873.036	167130.603	9822.061	103217.806
m15	petunidin-3-O-(6-p-coumaroyl)-glucoside	2622.397	18810.375	3404.395	31881.581	958.564	16213.676	2793.721	22586.931	1227.056	17618.725	2031.756	13420.673
m16	malvidin-3-O-(6-p-coumaroyl)-glucoside	22214.659	171327.995	11402.255	122464.949	2974.390	46964.236	22454.185	208644.005	11412.870	76473.810	4311.879	36073.684
m17	malvidin-3,5-O-diglucoside	32.688	923.769	123.704	1091.956	243.695	1348.128	135.985	1568.330	139.651	977.926	67.466	660.355
m18	gallic acid	29.892	513.190	58.164	435.197	11.416	340.889	14.722	100.180	21.168	182.328	55.304	633.456
m19	citric acid	980.715	9948.375	1445.279	10841.319	1307.251	11761.746	1437.452	10761.691	528.982	9487.439	711.840	13246.691
m20	resveratrol	10.200	68.514	8.921	75.088	7.548	82.603	1.280	29.217	14.033	91.179	17.855	232.488
m21	piceatannol	5.088	22.488	9.140	62.004	1.045	26.960	1.131	3.512	0.718	18.460	0.795	33.024
m22	catechin	319.149	2646.657	44.136	4228.429	842.111	5786.689	136.653	1238.060	143.043	4562.476	1290.811	12070.170
m23	epicatechin	468.742	3186.480	126.609	3483.906	95.693	3900.516	118.258	966.936	434.643	3608.138	651.675	9049.814

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m24	coutaric acid	918.080	6201.355	277.929	6259.129	644.460	7977.517	338.624	5401.953	1169.331	9137.717	611.544	12022.749
m25	caftaric acid	970.529	9802.907	462.669	12165.262	1955.404	16364.925	1059.465	10105.213	2330.446	16486.957	1041.667	21735.640
m26	fertaric acid	196.569	1324.936	65.509	1046.442	169.515	1177.444	154.254	1287.129	160.099	1579.111	67.043	1480.074
m27	piceid	262.089	1965.586	33.791	401.764	43.293	1193.467	83.064	555.748	66.764	384.539	119.203	1041.511
m28	catechin gallate	52.237	264.835	122.210	848.543	107.544	1337.044	16.131	205.952	63.536	1023.730	92.643	1567.878
m29	kaempferol-3-O-glucoside	20.782	655.450	106.064	1095.972	84.031	605.166	47.203	484.676	81.603	1388.750	148.309	1463.945
m30	pallidol	36.032	152.421	4.632	35.732	18.662	95.965	4.163	38.460	1.674	29.453	2.571	72.111
m31	e-viniferin	na	na	4.912	14.697	25.277	82.696	2.157	22.059	10.321	42.217	1.667	93.441
m32	quercetin-3-O-glucoside	288.453	2318.705	221.967	4621.284	411.820	4517.405	299.280	2017.993	343.001	5753.733	506.633	7624.238
m33	quercetin-3-O-glucuronide	568.908	3865.539	670.898	4320.114	313.081	6201.804	108.917	2221.329	318.174	6097.129	773.531	9289.002
m34	myricetin-hexoside1	134.465	1074.196	223.190	1609.689	127.310	2648.630	68.597	762.911	218.815	2225.158	214.656	2627.818
m35	myricetin glucoside	683.321	5247.285	778.392	5982.257	39.463	2536.702	503.023	4360.656	450.431	4780.851	338.773	4032.133
m36	495 quercetin derivative	112.220	1256.822	280.189	4190.229	517.013	4280.198	43.228	809.763	11.130	3438.825	270.489	4148.882
m37	procyanidinB1	300.828	2488.741	145.084	1849.781	59.079	1826.253	42.606	2019.378	153.154	2701.540	267.810	3671.464
m38	procyanidinB2	92.127	4732.629	80.366	1738.027	226.419	2572.160	360.996	2827.046	239.312	2699.168	424.596	3197.548
m39	procyanidinB3	175.977	1414.580	103.129	740.613	67.663	940.131	69.375	891.300	101.060	844.980	149.325	1768.428
m40	procyanidinB4	183.399	2181.195	43.357	1552.356	174.712	1326.706	106.618	993.091	135.947	1537.116	221.075	2307.704
m41	kaempferol-3-O-rutinoside	9.768	109.378	35.520	293.325	22.832	208.499	4.168	80.807	31.143	334.064	19.554	422.404
m42	procyanidin gallate 1	93.474	883.009	79.669	373.014	14.950	823.547	98.131	969.685	87.651	691.110	194.188	2114.555
m43	procyanidin trimer 2	176.912	1487.506	141.868	1097.554	168.915	1378.399	80.893	1034.772	153.055	1517.803	60.256	2142.829
m44	procyanidin gallate 2	81.311	736.403	38.583	300.174	6.407	287.102	93.050	647.659	27.765	290.355	46.493	313.305
m45	procyanidin trimer1	115.481	852.153	25.223	749.702	115.599	856.095	56.988	649.812	114.938	1081.040	149.858	1669.301

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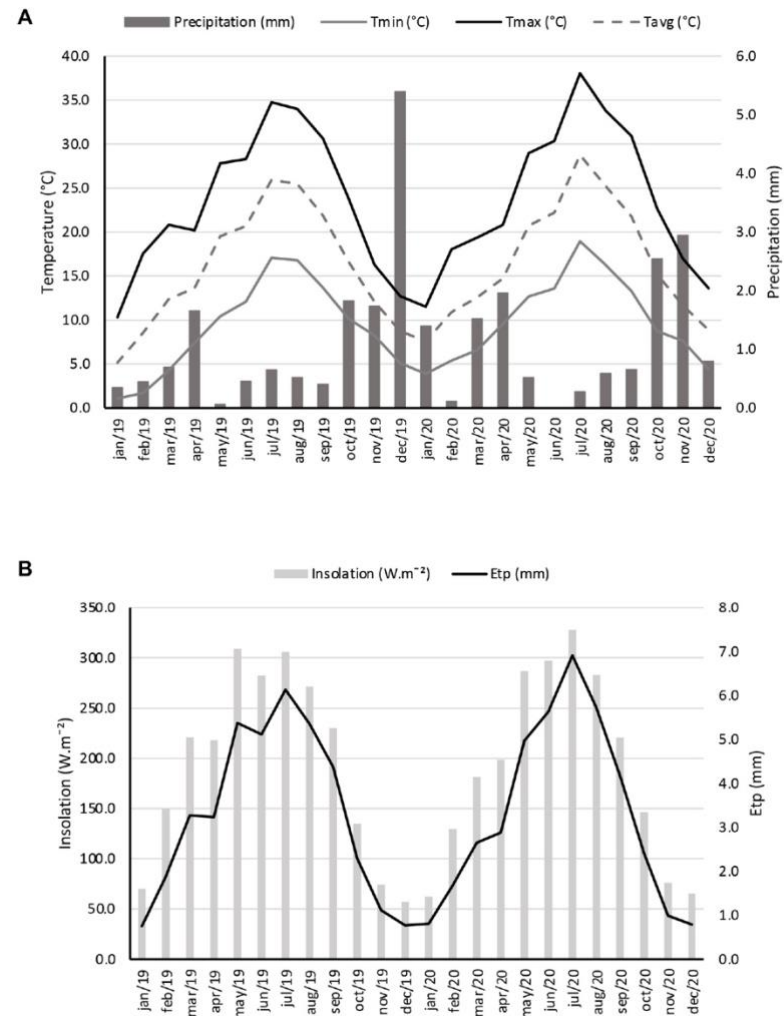


FIGURE S1. Monthly mean climatic conditions occurred during the 2019 and 2020 vintage in the vineyard Quinta do Ataíde from the Douro Superior sub-region. **(A)** Precipitation (mm); Maximum temperature -Tmax-(°C); Minimum temperature – Tmin (°C) and Average temperature – Tavg (°C). **(B)** Evapotranspiration - Etp (mm); Insolation – Insol. (W/m²).

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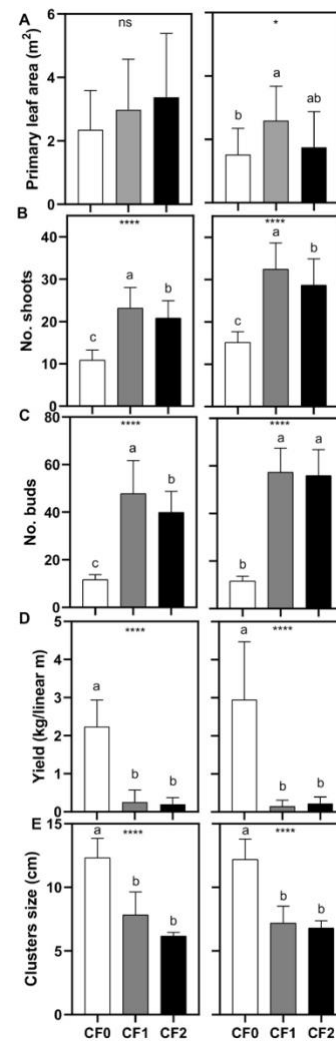


FIGURE S2. Effect of second pruning on **A)** number of shoots per plant; **B)** primary foliar area per plant; **C)** number of buds and **D)** clusters size and **E)** yield per linear length in 2019 and 2020 vintages of grape cv. 'Touriga Nacional' in different pruning conditions. Pruning conditions: CF0 = plants with no second pruning; CF1 = plants submitted to CF 15 days after fruit set; CF2 = plants submitted to CF 30 days after fruit set. Results represent mean \pm SD of four replicates.

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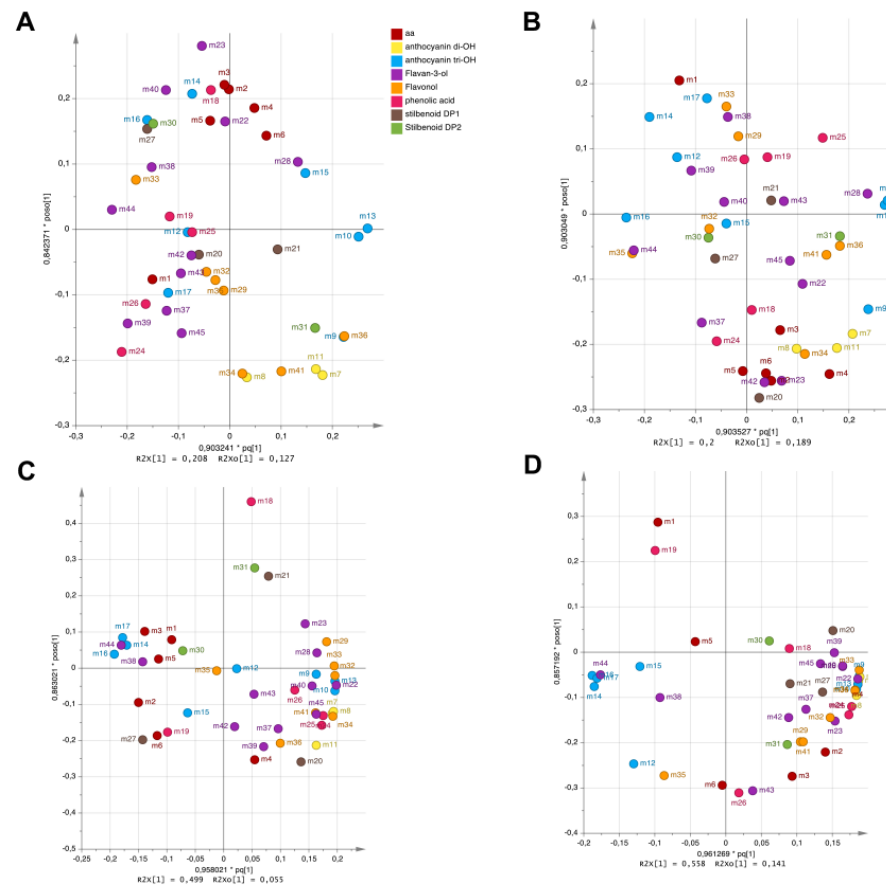


FIGURE S3. Supervised classification using OPLS-DA with crop forcing (CF1 and CF2) as dependent variables on metabolomic data from grape berries cv. “Touriga Nacional” at harvest in the vintages of 2019 (A and B) and 2020 (C and D). Variables in loading plots were colored according to metabolic class. Numbers indicate the ID of metabolites as given in Material and Method part.