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SUPPLEMENTARY DATA

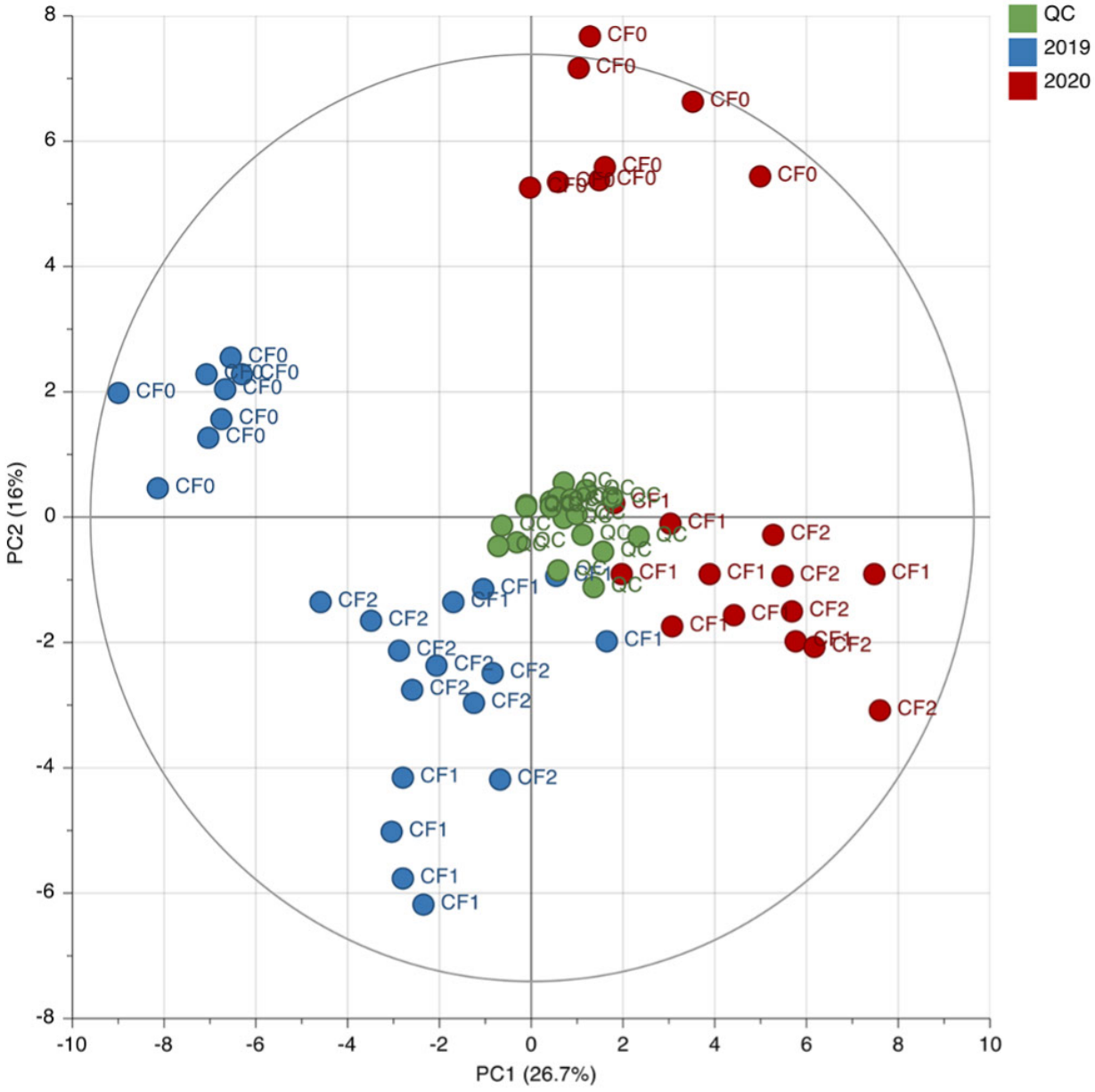


Figure S1. Principal component analysis (PCA) of grapevine cane metabolic compounds in two vintages. Score plots of UPLC–MS-based metabolomic data from hydro-ethanolic extracts of canes under different crop forcing treatments (CF0, CF1, CF2). QC: Quality control samples.

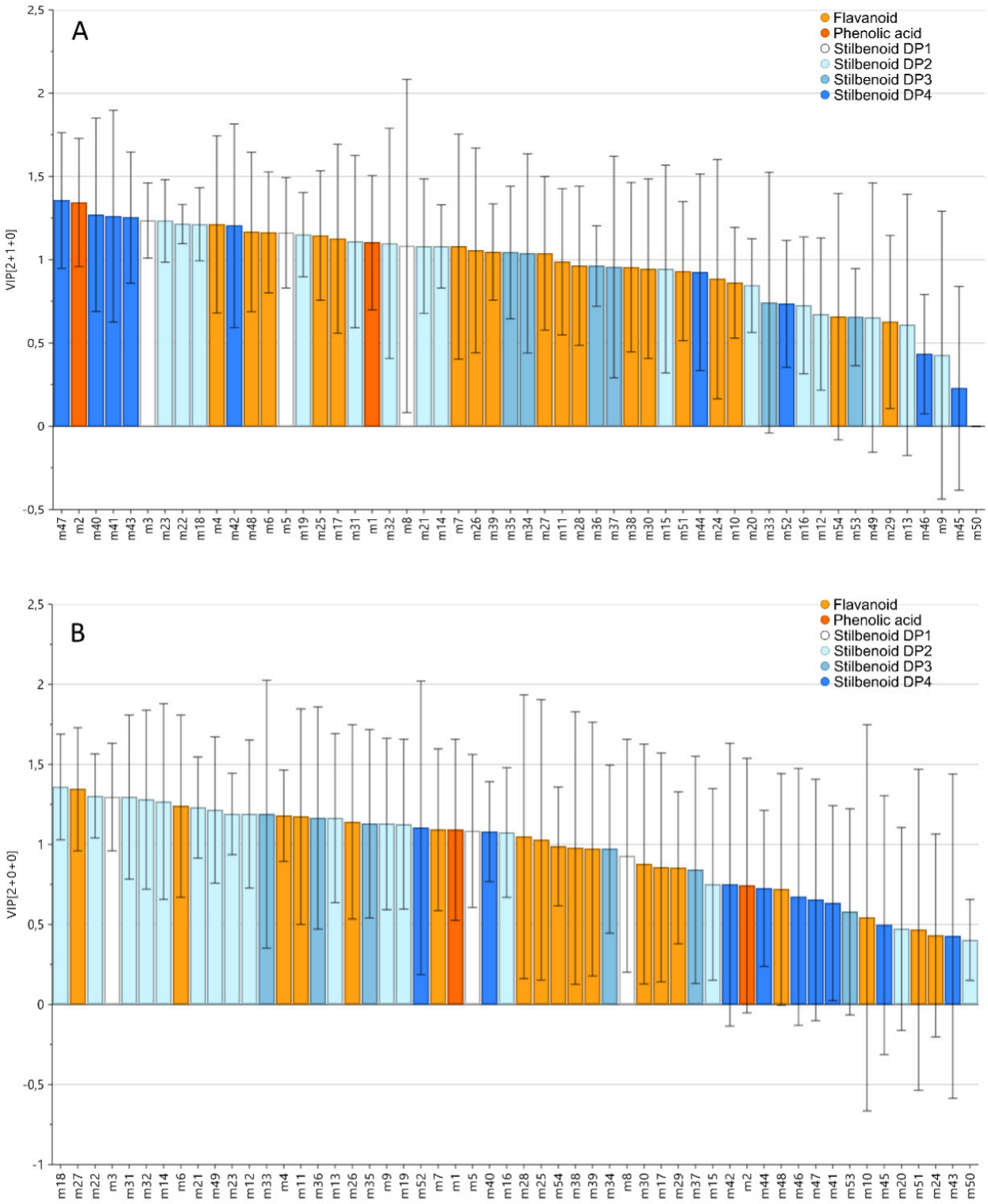


Figure S2. VIP-scores of the OPLS-DA models performed with crop forcing as dependent variables on metabolomic data from grapevine canes of cv. 'Touriga Nacional' in the vintages of 2019 (A) and 2020 (B). Each variable was colored according to the polyphenol class and numbers indicated the ID of the compound as given in Table S1.

SUPPLEMENTARY DATA
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Table S1. List of metabolites identified after UPLC-MS-based metabolic profiling of grape cane extracts following crop forcing.

Peak	Metabolites class	Compound assignment	Rt	m/z [M-H]-	Productions (ES-)	m/z [M+H]+	Productions (ES+)	λ_{max} (nm)	References	Identification confidence
m1	Phenolic acid	Gallic acid	1,94	169	-	171	-	218, 271	Standard	1
m2	Phenolic acid	Caffeic acid	3,67	179	-	nd	-	-	Standard	1
m3	Stilbenoid DP1	*E*-resveratrol	10,31	227	-	229	-	305, 317	Standard	1
m4	Flavonoid	Catechin	4,83	289	578, 245, 205, 179	291	139, 123	203, 279	Standard	1
m5	Stilbenoid DP1	*E*-piceatannol	8,55	243	175	-	-	323	Standard	1
m6	Flavonoid	Epicatechin	5,98	289	578, 245, 203	291	139, 123, 147	202, 279	Standard	1
m7	Flavonoid	Gallocatechin 1	3,07	305	109	307	-	206	Ehrhardt *et al.*, 2014	2
m8	Stilbenoid DP1	*E*-piceid	7,78	389	227	391	-	307, 319	Standard	1
m9	Stilbenoid DP2	Vitisinol C1	13,49	427	-	429	-	-	Mattivi *et al.*, 2011	4
m10	Flavonoid	Epicatechin-3-*O*-gallate	7,82	441	169	443	291, 123	203, 276.7	Standard	1
m11	Flavonoid	Astilbin	8,35	449	-	-	-	-	Souquet *et al.*, 2000	5
m12	Stilbenoid DP2	Pallidol	9,56	453	-	-	-	-	Standard	1
m13	Stilbenoid DP2	*Z*-ε-viniferin	12,73	453	-	455	-	223sh, 283,7	Mullinaci *et al.*,2010	3
m14	Stilbenoid DP2	*E*-ε-viniferin	13,09	453	499, 255	455	349	225,7sh, 323,7	Standard	1
m15	Stilbenoid DP2	ω-viniferin	14,18	453	266	455	-	225sh, 323	Pussa *et al.*, 2006	3
m16	Stilbenoid DP2	δ-viniferin	14,71	453	-	455	-	225sh, 309	Pezet *et al.*, 2003; Mullinacci *et al.*, 2010	3
m17	Flavonoid	Isoquercetin	8,23	463	301	465	-	-	Standard	1
m18	Stilbenoid DP2	Ampelopsin A	8,28	469	451	471	-	281,7	Standard	1

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m19	Stilbenoid DP2	Scirpusin A1	9,41	469	-	471	-	-	Kong *et al.*, 2010; Moss *et al.*, 2013	4
m20	Stilbenoid DP2	Scirpusin A2	10,44	469	-	471	-	-	Kong *et al.*, 2010; Moss *et al.*, 2013	4
m21	Stilbenoid DP2	Restrytisol 1	6,76	471	-	-	-	-	Mullinaci *et al.*,2010	4
m22	Stilbenoid DP2	Restrytisol 2	7,73	471	377, 227	-	-	-	Mullinaci *et al.*,2010	2
m23	Stilbenoid DP2	Restrytisol 3	8,29	471	-	-	-	-	Mullinaci *et al.*,2010	5
m24	Flavonoid	Quercetin-3-*O*-glucuronide	7,84	477	301	479	-	256, 355	Ehrhardt *et al.*, 2014; Souquet *et al.*, 2000	2
m25	Flavonoid	Procyanidin B1	4,28	577	289	579	291	201, 279	Standard	1
m26	Flavonoid	Procyanidin B3	4,61	577	289	579	291	201, 279	Standard	1
m27	Flavonoid	Procyanidin B4	5,25	577	289	579	139	203, 279	Standard	1
m28	Flavonoid	Procyanidin B2	5,40	577	425, 289, 137	579	139	203, 279	Standard	2
m29	Flavonoid	Procyanidin dimer 5	6,03	577	289	579	-	-	Rzeppa *et al.*, 2011	2
m30	Flavonoid	Procyanidin dimer 6	6,66	577	289	579	409	202, 276	Rzeppa *et al.*, 2011	2
m31	Stilbenoid DP2	Resveratrol dimer glycoside 1	9,81	615	453	617	-	-	Moss *et al.*, 2013	2
m32	Stilbenoid DP2	Resveratrol dimer glycoside 2	11,21	615	453	617	-	-	Moss *et al.*, 2013	2
m33	Stilbenoid DP3	Resveratrol trimer 1	11,22	679	-	681	-	-	Moss *et al.*, 2013; Pussa *et al.*, 2006	4
m34	Stilbenoid DP3	Resveratrol trimer 2	11,68	679	491	681	-	-	Moss *et al.*, 2013; Pussa *et al.*, 2006	2
m35	Stilbenoid DP3	*E*-miyabenol C	13,41	679	453	681	-	205, 328	Standard	1
m36	Stilbenoid DP3	Resveratrol trimer 3	13,82	679	453	681	-	-	Moss *et al.*, 2013; Pussa *et al.*, 2006	3

m37	Stilbenoid DP3	Resveratrol trimer 4	14,66	679	453	681	-	-	Moss *et al.*, 2013; Pussa *et al.*, 2006	3
m38	Flavonoid	Procyanidin C1	4,90	865	425, 289	867	-	279	Standard	1
m39	Flavonoid	Procyanidin trimer 2	6,27	865	289	867	-	279	Monagas *et al.*, 2006; Rzeppa *et al.*, 2011	2
m40	Stilbenoid DP4	Resveratrol dehydrogenated tetramer	13,77	904	679	906	-	-	Ito *et al.*, 1999	3
m41	Stilbenoid DP4	Hopeaphenol	11,50	905	679	907	-	280,7	Standard	1
m42	Stilbenoid DP4	Isohopeaphenol	11,89	905	717	907	-	281,7	Lambert *et al.*, 2013; Moss *et al.*, 2013	2
m43	Stilbenoid DP4	Resveratrol tetramer 1	12,39	905	-	907	-	-	Pussa *et al.*, 2006; Flamini *et al.*, 2013; Moss *et al.*, 2013	3
m44	Stilbenoid DP4	Resveratrol tetramer 2	14,05	905	-	907	-	-	Pussa *et al.*, 2006; Flamini *et al.*, 2013; Moss *et al.*, 2013	4
m45	Stilbenoid DP4	Resveratrol tetramer 3	14,79	905	-	907	-	-	Pussa *et al.*, 2006; Flamini *et al.*, 2013; Moss *et al.*, 2013	3
m46	Stilbenoid DP4	*E*-vitisin B	15,53	905	811	907	-	325,7	Standard	1
m47	Stilbenoid DP4	Viniferol E	11,22	923	-	925	-	-	Escobar-Avello, 2021	4
m48	Flavonoid	Gallocatechin 2	4,38	305	-	-	-	205	Ehrhardt *et al.*, 2014	3
m49	Stilbenoid DP2	Vitisinol C2	14,08	427	-	429	-	-	Mattivi *et al.*, 2011	4
m50	Stilbenoid DP2	Scirpusin A3	11,96	469	-	471	-	-	Kong *et al.*, 2010; Moss *et al.*, 2013	4
m51	Flavonoid	Procyanidin A1	7,67	575	289	577	-	278	Standard	1

m52	Stilbenoid DP4	Resveratrol tetramer 4	15,36	905	717	907	-	-	Pussa *et al.*, 2006; Flamini *et al.*, 2013; Moss *et al.*, 2013	3
m53	Stilbenoid DP3	Resveratrol trimer 5	15,51	679	-	681	-	-	Moss *et al.*, 2013; Pussa *et al.*, 2006	4
m54	Flavonoid	Procyanidin dimer 7	7,95	577	451	579	-	-	Rzeppa *et al.*, 2011	2

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