A versatile targeted metabolomics method for rapid quantification of multiple classes of phenolics in fruit and beverages

Authors: Urska Vrhovsek*, Domenico Masuero, Mattia Gasperotti, Pietro Franceschi, Lorenzo Caputi, Roberto Viola and Fulvio Mattivi

SUPPORTING INFORMATION DESCRIPTION

Table S1. List of the compounds included in the study, including CAS number, Metlin ID, KEGG ID, chemical formula, molecular weight, concentration in the mixture, number of mixture and supplier.

Table S2. Analytical parameters.

Table S3. Metabolites quantification.

Figure S1. Intra-day precision of the Retention Time both for standard compounds and for metabolites detected in matrices.

Figure S2. High-resolution spectra of *trans*- and *cis*-piceid (panel A) and of phloridzin (panel B) in grape and apple extracts.

Table S1. List of the compounds included in the study, including CAS number, Metlin ID, KEGG ID, chemical formula, molecular weight, concentration in the mixture, number of mixture and supplier.

Compound	CAS nº	METLIN ID	KEGG ID	Chemical formula	MW (Da)	Mixture number	Concentration in the mixture (mg/L)	Supplier
Benzoic acid derivatives								
Catechol	120-80-9	282	C00090	C6H6O2	110.11	3	100	Sigma
Benzoic acid	65-85-0	1297	C00180	C7H6O2	122.12	1	100	Fluka
3-Hydroxybenzaldehyde	100-83-4	na	C03067	C7H6O2	122.12	1	100	Fluka
Salicylic acid	69-72-7	616	C00805	C7H6O3	138.12	2	100	Aldrich
4-Hydroxybenzoic acid	99-96-7	3263	C00156	C7H6O3	138.12	1	100	Aldrich
2,4-Dihydroxybenzoic acid	89-86-1	na	na	C7H6O4	154.12	2	100	Fluka
2,5-Dihydroxybenzoic acid	490-79-9	618	C00628	C7H6O4	154.12	2	100	Aldrich
2,6-Dihydroxybenzoic acid	303-07-1	na	na	C7H6O4	154.12	2	100	Fluka
3,4-Dihydroxybenzoic acid	99-50-3	3227	C00230	C7H6O4	154.12	2	100	Carl Roth
3,5-Dihydroxybenzoic acid	99-10-5	na	na	C7H6O4	154.12	2	100	Fluka
Gallic acid	149-91-7	3295	C01424	C7H6O5	170.12	1	100	Aldrich
Vanillin	121-33-5	62927	C00755	C8H8O3	152.14	1	100	Carlo Erba
Vanillic acid	121-34-6	5471	na	C8H8O4	168.14	1	100	Carl Roth
Methyl gallate	99-24-1	44726	na	C8H8O5	184.14	2	100	Fluka
Cinnamic acid	621-82-9	310	C10438	C9H8O2	148.15	1	100	Aldrich
Acetovanillone	498-02-2	na	C11380	C9H10O3	166.17	1	100	Aldrich
Syringaldehyde	134-96-3	na	na	C9H10O4	182.17	2	100	Aldrich
Syringic acid	530-57-4	2256	C10833	C9H10O5	198.17	2	100	Fluka
Salicin	138-52-3	6948	C01451	C13H18O7	286.27	2	100	Sigma
Ellagic acid	476-66-4	3430	C10788	C14H6O8	302.19	3	100	Fluka
Coumarins								
4-Hydroxycoumarin	1076-38-6	na	na	C9H6O3	162.14	4	100	Carl Roth
Umbelliferone	93-35-6	44642	na	C9H6O3	162.14	4	100	Fluka
4-Methylumbelliferone	90-33-5	na	na	C10H8O3	176.17	4	100	Carl Roth
Daphnetin	486-35-1	na	na	C9H6O4	178.14	4	100	Biomedicals

Compound	CAS nº	METLIN ID	KEGG ID	Chemical formula	MW (Da)	Mixture number	Concentration in the mixture (mg/L)	Supplier
Esculetin	305-01-1	43936	C09263	C9H6O4	178.14	4	100	Carl Roth
Esculin	531-75-9	na	na	C15H16O9	340.29	4	100	Carl Roth
Scopoletin	92-61-5	na	na	C10H8O4	192.16	4	100	Fluka
Fraxin	524-30-1	na	na	C16H18O10	370.31	4	100	Carl Roth
Phenylpropanoids								
p-Coumaric acid	501-98-4	307	C00811	C9H8O3	164.16	5	100	Sigma
m-Coumaric acid	588-30-7	305	C12621	C9H8O3	164.16	5	100	Carl Roth
o-Coumaric acid	583-17-5	306	C01772	C9H8O3	164.16	5	100	Carl Roth
Caffeic acid	331-39-5	3316	C01481	C9H8O4	180.16	5	100	Sigma
Ferulic acid	1135-24-6	4156	C01494	C10H10O4	194.18	5	100	Carl Roth
Sinapic acid	530-59-6	45738	C00482	C11H12O5	224.21	5	100	Sigma
Caftaric acid	67879-58-7	na	na	C13H12O9	312.23	5	100	Isolated
Neochlorogenic acid	906-33-2	na	na	C16H18O9	354.31	5	100	TransMIT
Cryptochlorogenic acid	905-99-7	na	na	C16H18O9	354.31	5	100	TransMIT
Chlorogenic acid	327-97-9	3498	C00852	C16H18O9	354.31	5	100	TransMIT
1,3-Dicaffeoylquinic acid	1182-34-9	na	na	C25H24O12	516.45	6	100	TransMIT
1,5-Dicaffeoylquinic acid	30964-13-7	na	na	C25H24O12	516.45	6	100	TransMIT
Rosmarinic acid	537-15-5	na	na	C18H16O8	360.31	6	100	Aldrich
Coniferyl aldehyde	458-36-6	63108	C02666	C10H10O3	178.18	6	100	Aldrich
Coniferyl alcohol	458-35-5	44742	C00590	C10H12O3	180.20	6	100	Aldrich
Sinapyl alcohol	537-33-7	44805	C02325	C11H14O4	210.23	6	100	Aldrich
Fertaric acid	na	na	na	C14H14O9	326.25	6	100	Isolated
trans-Coutaric acid	27174-07-8	na	na	C13H12O8	296.23	6	100	Isolated
Raspberry ketone	5471-51-2	na	na	C10H12O2	164.20	6	100	Lancaster
Stilbenes								
4-Hydroxystilbene	6554-98-9	na	na	C14H12O	196.25	7	100	Aldrich
trans-Resveratrol	501-36-0	6979	C03582	C14H12O3	228.24	7	140	Isolated
cis-Resveratrol	61434-67-1	44878	na	C14H12O3	228.24	7	100	Isolated
Piceatannol	10083-24-6	7029	C05901	C14H12O4	244.24	7	100	TransMIT
Pterostilbene	537-42-8	45423	na	C16H16O3	256.30	7	50	TransMIT

Compound	CAS nº	METLIN ID	KEGG ID	Chemical formula	MW (Da)	Mixture number	Concentration in the mixture (mg/L)	Supplier
trans-Piceid	27208-80-6	53240	C10275	C20H22O8	390.38	7	123	Isolated
cis-Piceid	na	na	na	C20H22O8	390.38	7	100	Isolated
Astringin	29884-49-9	53235	C10245	C20H22O9	406.38	7	100	Polyphenols
Isorhapontin	32727-29-0	53238	C10266	C21H24O9	420.41	7	100	Polyphenols
cis-ε-Viniferin	62218-08-0	na	na	C28H22O6	454.47	8	10	Isolated
trans-ε-Viniferin	na	na	na	C28H22O6	454.47	8	10	Isolated
cis-ω-Viniferin	na	na	na	C28H22O6	454.47	8	10	Isolated
trans-ω-Viniferin	na	na	na	C28H22O6	454.47	8	10	Isolated
Caffeic acid + Catechin condensation product	na	na	na	C24H20O9	452.40	8	10	Isolated
Pallidol	105037-88-5	na	na	C28H22O6	454.47	8	10	Isolated
Ampelopsin D + Quadrangularin A	149418-37-1	na	na	C28H22O6	454.47	8	10	Isolated
α-Viniferin	62218-13-7	na	na	C42H30O9	678.66	8	10	Isolated
E-*cis*-miyabenol	na	na	na	C42H32O9	680.68	8	10	Isolated
Z-miyabenol C	na	na	na	C42H32O9	680.68	8	10	Isolated
Isohopeaphenol	na	na	na	C56H42O12	906.92	9	10	Isolated
Ampelopsin H	na	na	na	C56H42O12	906.92	9	10	Isolated
Vaticanol C-like isomer	na	na	na	C56H42O12	906.92	9	10	Isolated
Dihydrochalcones								
Phloretin	60-82-2	3405	C00774	C15H14O5	274.26	9	100	TransMIT
Phloridzin	60-81-1	3535	C01604	C21H24O10	436.41	9	100	TransMIT
Trilobatin	4192-90-9	na	na	C21H24O10	532.45	9	100	Extrasynthese
Isoflavones								
Daidzein	486-66-8	43572	C10208	C15H10O4	254.23	9	100	Extrasynthese
Genistein	446-72-0	3398	C06563	C15H10O5	270.24	9	100	Extrasynthese
Flavones								
6-Methoxyflavone	26964-24-9	na	na	C16H12O3	252.27	10	100	Carl Roth
Chrysin	480-40-0	44046	C10028	C15H10O4	254.24	10	100	Carl Roth
Apigenin	520-36-5	3397	C01477	C15H10O5	270.24	10	100	Carl Roth

Compound	CAS nº	METLIN ID	KEGG ID	Chemical formula	MW (Da)	Mixture number	Concentration in the mixture (mg/L)	Supplier
Apigenin-7-*O*-glucoside	578-74-5	64218	C04608	C21H20O10	432.38	11	100	Sigma
Apiin	26544-34-3	44510	C04858	C26H28O14	564.49	10	100	Carbosynth
Sinensetin	2306-27-6	49674	na	C20H20O7	372.36	10	100	Extrasynthese
Morin	480-16-0	3431	na	C15H10O7	302.24	10	100	Carl Roth
Eupatorin-5-methylether	21764-09-0	na	na	C19H18O7	358.34	10	100	Extrasynthese
Luteolin	491-70-3	3409	C01514	C15H10O6	286.24	10	100	Sigma
Luteolin-7-*O*-Glucoside	68321-11-9	na	C03951	C21H20O11	448.37	10	100	Sigma
Luteolin-8-*C*-Glucoside	28608-75-5	4891	C10114	C21H20O11	448.37	11	100	Sigma
Baicalein	491-67-8	43859	C10023	C15H10O5	270.24	10	100	Sigma
Hesperetin	520-33-2	44508	C01709	C16H14O6	302.28	11	100	Carl Roth
Hesperidin	520-26-3	3678	C09755	C28H34O15	610.56	11	100	Sigma
Galangin	548-83-4	45739	C10044	C15H10O5	270.24	16	100	Carl Roth
Flavanones								
Naringenin	480-41-1	3401	C00509	C15H12O5	272.25	11	100	Carl Roth
Naringenin-7-*O*-glucoside	529-55-5	44786	C09099	C21H22O10	434.39	11	100	Carl Roth
Sakuranetin	2957-21-3	na	C09833	C16H14O5	286.28	11	100	Carl Roth
Eriodictyol	552-58-9	3415	C05631	C15H12O6	288.25	11	100	Carl Roth
Flavan-3-ols								
Catechin	88191-48-4	3419	C06562	C15H14O6	290.27	12	100	Extrasynthese
Epicatechin	490-46-0	3420	C09727	C15H14O6	290.27	12	100	Extrasynthese
Gallocatechin	970-73-0	47219	C12127	C15H14O7	306.27	12	100	Sigma
Epigallocatechin	970-74-1	47220	C12136	C15H14O7	306.27	12	100	Sigma
Catechin gallate	130405-40-2	47305	na	C22H18O10	442.37	12	100	Sigma
Epicatechin gallate	1257-08-5	47306	na	C22H18O10	442.37	12	10	Sigma
Gallocatechin gallate	4233-96-9	47336	na	C22H18O11	458.37	12	100	Sigma
Epigallocatechin gallate	989-51-5	3550	C09731	C22H18O11	458.37	12	100	Sigma
Procyanidin A2	41743-41-3	na	C10237	C30H24O12	576.50	13	100	Extrasynthese
Procyanidin B1	20315-25-7	na	na	C30H26O12	578.52	13	100	TransMIT
Procyanidin B2	29106-49-8	na	na	C30H26O12	578.52	13	100	TransMIT
procyanidin B3	23567-23-9	na	na	C30H26O12	578.52	13	10	Leuven

Compound	CAS nº	METLIN ID	KEGG ID	Chemical formula	MW (Da)	Mixture number	Concentration in the mixture (mg/L)	Supplier
Procyanidin B4	29206-51-2	na	na	C30H26O12	578.52	13	100	Bioproducts Leuven Bioproducts
Flavonols								
Quercetin	117-39-5	409	C00389	C15H10O7	302.24	13	50	Fluka
Quercetin-3-sulfate	6089-05-6	50720	C00616	C15H10O10S	382.30	14	100	ICC Indofine
Quercetin-3-O-rhamnoside	522-12-3	43747	C01750	C21H20O11	448.38	14	100	Fluka
Quercetin-3-O-glucoside	21637-25-2	64227	C05623	C21H20O12	464.38	14	100	Extrasynthese
Quercetin-4'-O-glucoside	20229-56-5	na	na	C21H20O12	464.38	14	100	Extrasynthese
Quercetin-3-O-galactoside	482-36-0	50457	C10073	C21H20O12	464.38	14	100	Extrasynthese
Quercetin-3-O-glucose-6'-acetate	54542-51-7	na	na	C23H22O13	506.41	15	100	ICC Indofine
Quercetin-3-O-glucuronide	22688-79-5	na	na	C21H18O13	478.37	16	100	Extrasynthese
Rutin	153-18-4	3677	C05625	C27H30O16	610.52	16	100	Extrasynthese
Peltatoside	23284-18-6	na	na	C26H28O16	596.50	15	50	Extrasynthese
Quercetin-3,4'-diglucoside	29125-80-2	na	na	C27H30O17	626.51	16	100	Extrasynthese
Taxifolin	480-18-2	3434	C01617	C15H12O7	304.25	13	100	Sigma
Kaempferol	520-18-3	3410	C05903	C15H10O6	286.23	13	100	Carl Roth
Kaempferol-3-O-glucoside	480-10-4	64226	C12249	C21H20O11	448.37	14	100	Extrasynthese
Kaempferol-3-O-glucuronide	22688-78-4	na	na	C21H18O12	462.37	16	100	Extrasynthese
Kaempferol-3-O-rutinoside	17650-84-9	50150	na	C27H30O15	594.53	15	100	Extrasynthese
Robinin	301-19-9	na	C10178	C33H40O19	740.66	16	100	Carl Roth
Dihydrokaempferol	480-20-6	3416	C00974	C15H12O6	288.25	16	100	TransMIT
Myricetin	529-44-2	3448	C10107	C15H10O8	318.23	14	100	Extrasynthese
Myricitrin	17912-87-7	50852	C10108	C21H20O12	464.37	14	100	Carl Roth
Laricitrin	53472-37-0	50898	C12633	C16H12O8	332.26	14	100	Extrasynthese
Syringetin	4423-37-4	50914	C11620	C17H14O8	346.29	14	100	Extrasynthese
Syringetin-3-O-glucoside	40039-49-4	50904	na	C23H24O13	508.43	15	100	Extrasynthese
Syringetin-3-O-galactoside	55025-56-4	50900	na	C23H24O13	508.43	15	100	Extrasynthese

Compound	CAS nº	METLIN ID	KEGG ID	Chemical formula	MW (Da)	Mixture number	Concentration in the mixture (mg/L)	Supplier
Rhamnetin	90-19-7	43977	C10176	C16H12O7	316.26	13	100	Extrasynthese
Isorhamnetin	480-19-3	3445	C10084	C16H12O7	316.26	13	100	Extrasynthese
Isorhamnetin-3-O-glucoside	5041-82-7	49007	na	C22H22O12	478.41	15	100	Extrasynthese
Isorhamnetin-3-rutinoside	604-80-8	na	na	C28H32O16	624.55	16	100	Extrasynthese

na= not available

Table S2. Analytical parameters.

Compound	Linear range (ng/mL)	Slope (a)	Δ(a)	Offset (b)	Δ(b)	R^2	Weighting	LOQ (pg)
Benzoic acid derivatives								
Catechol	200-20000	429	16	64	34	0,992	1/x	400
Benzoic acid	80-60000	151	4	-5	10	0,994	1/x	160
3-Hydroxybenzaldehyde	40-10000	5466	163	147	123	0,991	1/x	80
Salicylic acid	100-20000	3018	59	-54	83	0,997	1/x	200
4-Hydroxybenzoic acid	20-10000	3503	65	43	36	0,996	1/x	40
2,4-Dihydroxybenzoic acid	40-8000	7450	244	376	153	0,990	1/x	80
2,6-Dihydroxybenzoic acid	40-10000	20284	468	1665	315	0,995	1/x	80
2,5-Dihydroxybenzoic acid	2-20000	4591	87	0	20	0,995	1/x	4
3,4-Dihydroxybenzoic acid	60-20000	546	11	-9	10	0,996	1/x	120
3,5-Dihydroxybenzoic acid	8-20000	5738	81	-15	30	0,997	1/x	16
Gallic acid	80-60000	616	8	-57	16	0,998	1/x	160
Vanillin	4-10000	42882	802	279	197	0,995	1/x	8
Vanillic acid	10-10000	15849	359	57	141	0,993	1/x	20
Methyl gallate	4-10000	25231	511	-83	117	0,995	1/x	8
Cinnamic acid	6-10000	20036	369	104	115	0,996	1/x	12
Acetovanillone	4-10000	20616	360	29	81	0,995	1/x	8
Syringaldehyde	8-20000	23901	453	54	173	0,995	1/x	16
Syringic acid	8-20000	2161	47	-19	18	0,994	1/x	16
Salicin	80-10000	324	11	13	12	0,992	1/x	160
Ellagic acid	400-20000	525	15	68	44	0,994	1/x	800
Coumarins								
4-Hydroxycoumarin	20-8000	6885	195	85	85	0,991	1/x	40
Umbelliferone	4-6000	31068	653	123	97	0,995	1/x	8
4-Methylumbelliferone	4-6000	22089	564	113	84	0,993	1/x	8
Daphnetin	4-6000	23300	519	45	79	0,994	1/x	8
Esculetin	2-6000	32544	716	1	86	0,993	1/x	4

Esculin	1-20000	20843	371	-39	68	0,995	1/x	2
Scopoletin	2-6000	51804	1227	282	160	0,993	1/x	4
Fraxin	4-6000	16437	348	1	56	0,995	1/x	8
Phenylpropanoids								
p-Coumaric acid	6-10000	11188	371	113	114	0,990	1/x	12
m-Coumaric acid	6-10000	13179	328	92	86	0,992	1/x	12
o-Coumaric acid	8-8000	8029	109	42	27	0,998	1/x	16
Caffeic acid	6-10000	5124	107	32	26	0,994	1/x	12
Ferulic acid	1-8000	27411	542	16	69	0,995	1/x	2
Sinapic acid	40-8000	1346	35	-16	18	0,993	1/x	80
Caftaric acid	60-2000	355	23	-36	20	0,970	none	120
Neochlorogenic acid	1-40000	8945	101	-39	25	0,998	1/x	2
Cryptochlorogenic acid	40-1000	1121	79	-3	4	0,971	1/x	120
Chlorogenic acid	60-1000	652	34	-43	9	0,984	1/x	120
1,3-Dicaffeoylquinic acid	40-10000	2992	174	-10	26	0,977	1/x	80
1,5-Dicaffeoylquinic acid	20-10000	5210	91	-17	15	0,997	1/x	40
Rosmarinic acid	40-2000	3462	127	-143	26	0,993	1/x	80
Coniferyl aldehyde	4-10000	23402	501	84	112	0,992	1/x	8
Coniferyl alcohol	1-10000	12457	204	10	30	0,995	1/x	2
Sinapyl alcohol	4-10000	11059	173	33	42	0,996	1/x	8
Fertaric acid	20-4000	7235	371	-21	30	0,982	1/x	40
trans-Coutaric acid	8-10000	10154	247	-36	39	0,994	1/x	16
Raspberry ketone	20-10000	7434	135	94	70	0,996	1/x	40
Stilbenes								
4-Hydroxystilbene	100-4000	128	5	20	3	0,996	1/x	200
trans-Resveratrol	112-28000	717	20	-12	34	0,993	1/x	224
cis-Resveratrol	4-8000	12580	307	5	55	0,991	1/x	8
Piceatannol	6-20000	12828	225	-65	76	0,995	1/x	12
Pterostilbene	20-2000	1752	61	103	48	0,994	none	40
trans-Piceide	7-12300	14198	245	-54	82	0,996	1/x	15
cis-Piceide	4-40000	21004	259	-69	98	0,998	1/x	8

Astringin	4-20000	18607	114	-46	21	1,000	1/x	8
Isorhapontin	4-20000	7286	111	-13	31	0,996	1/x	8
cis-ε-Viniferin	20-8000	651	15	-38	47	0,995	none	40
trans-ε-Viniferin	60-8000	1163	22	-61	69	0,997	none	120
cis-ω-Viniferin	80-6000	1007	38	9	101	0,992	none	160
trans-ω-Viniferin	200-10000	70	3	4	5	0,992	1/x	400
Caffeic acid + Catechin condensation product	10-4000	5305	222	-12	16	0,990	1/x	20
Pallidol	6-10000	2804	36	-17	10	0,998	1/x	12
Ampelopsin D + Quadrangularin A	40-10000	1575	35	-5	6	0,996	1/x	80
α-Viniferin	80-8000	610	17	10	14	0,995	1/x	160
E-*cis*-miyabenol	20-10000	931	16	5	9	0,997	1/x	40
Z-miyabenol C	80-10000	425	10	-25	11	0,995	1/x	160
Isohopeaphenol	20-6000	2024	23	-18	8	0,999	1/x	40
Ampelopsin H + Vaticanol C-like isomer	40-2000	838	16	-15	5	0,998	1/x	80
Dihydrochalcones								
Phloretin	1-2000	46632	740	-79	40	0,997	1/x	2
Phloridzin	2-60000	15908	231	-83	84	0,996	1/x	4
Trilobatin	10-20000	5401	105	-19	22	0,997	1/x	20
Isoflavones								
Daidzein	100-8000	24	1	9	3	0,992	none	200
Genistein	400-10000	9	0	6	1	0,991	1/x	800
Flavones								
6-Methoxyflavone	200-8000	209079	8488	74330	10775	0,992	1/x	400
Chrysin	200-8000	5725	369	2615	460	0,984	1/x	400
Apigenin	200-8000	18814	1196	8228	1618	0,980	1/x	400
Apigenin-7-*O*-glucoside	2-10000	34433	640	19	117	0,994	1/x	4
Apiin	8-20000	26035	600	320	229	0,993	1/x	16
Sinensetin	80-10000	104481	5245	11458	4993	0,985	1/x	160

Morin dihydrate	10-20000	4935	76	-19	42	0,997	1/x	20
Eupatorin-5-methylether	100-10000	116438	6004	18194	7701	0,984	1/x	200
Luteolin	100-8000	32817	1441	2642	1407	0,990	1/x	200
Luteolin-7-*O*-Glucoside	6-20000	29384	441	113	149	0,996	1/x	12
Luteolin-8-*C*-Glucoside (Orientin)	4-20000	3773	59	-7	16	0,996	1/x	8
Baicalein	10-8000	64124	1985	2513	664	0,992	1/x	20
Hesperetin	40-10000	110	3	2	2	0,992	1/x	80
Hesperidin	2-20000	3119	38	-5	9	0,997	1/x	4
Galangin	400-20000	135	6	4	50	0,989	none	800
Flavanones								
Naringenin	2-2000	34736	1016	56	69	0,991	1/x	4
Naringenin-7-*O*-glucoside	20-8000	652	19	6	9	0,992	1/x	40
Sakuranetin	200-20000	39	1	4	10	0,993	none	400
Eriodictyol	100-20000	79	2	3	4	0,992	1/x	200
Flavan-3-ols								
Catechin	10-40000	1786	26	-15	12	0,997	1/x	20
Epicatechin	200-20000	1474	60	236	108	0,990	1/x	400
Gallocatechin	10-20000	3610	70	-45	28	0,995	1/x	20
Epigallocatechin	8-20000	5254	87	-131	42	0,997	1/x	16
Catechin gallate	10-8000	2434	120	-59	40	0,976	1/x	20
Epicatechin gallate	1-800	24413	1180	-93	47	0,977	1/x	2
Gallocatechin gallate	8-1000	1395	74	-19	8	0,983	1/x	16
Epigallocatechin gallate	10-1000	2335	177	-38	20	0,961	1/x	20
Procyanidin A2	20-60000	1180	34	-43	29	0,989	1/x	40
Procyanidin B1	60-10000	632	33	-3	6	0,970	1/x	120
Procyanidin B2 + Procyanidin B4	40-60000	1360	35	-60	31	0,993	1/x	80
Procyanidin B3	10-6000	354	13	-7	4	0,990	1/x	20
Flavonols								
Quercetin	4-10000	6200	118	-40	29	0,995	1/x	8

Quercetin-3-sulfate	10-10000	9626	325	-29	53	0,990	1/x	20
Quercetin-3-O-rhamnoside	4-20000	3384	31	-13	10	0,999	1/x	8
Quercetin-3-O-glucoside	6-20000	6491	95	-44	35	0,997	1/x	12
Quercetin-4-O-glucoside	4-20000	10474	130	2	40	0,997	1/x	8
Quercetin-3-O-galactoside	10-20000	4168	100	-36	52	0,993	1/x	20
Quercetin-3-O-glucoside acetate	8-10000	4449	108	-1	47	0,993	1/x	16
Quercetin-3-O-glucuronide	20-40000	6857	112	-54	86	0,997	1/x	40
Rutin (Quercetin-Glc-Rha)	8-20000	6761	87	-8	39	0,998	1/x	16
Peltatoside	10-20000	5224	118	-57	61	0,995	1/x	20
Quercetin-3,4'-diglucoside	10-20000	4692	82	-11	43	0,996	1/x	20
Taxifolin	6-20000	5845	63	29	23	0,998	1/x	12
Kaempferol	4-8000	14114	370	6	81	0,992	1/x	8
Kaempferol-3-O-glucoside	6-20000	8556	120	-38	40	0,997	1/x	12
Kaempferol-3-O-glucuronide	4-20000	11856	143	-26	48	0,998	1/x	8
Kaempferol-3-O-rutinoside	2-20000	7951	144	-19	34	0,995	1/x	4
Robinin	6-20000	6733	140	-1	48	0,993	1/x	12
Dihydrokaempferol	10-20000	4725	94	-2	50	0,995	1/x	20
Myricetin	8-20000	7838	115	-25	24	0,997	1/x	16
Myricitrin	10-40000	2530	25	-28	17	0,999	1/x	20
Laricitrin	6-10000	6041	143	-17	45	0,993	1/x	12
Syringetin	2-8000	10054	250	22	37	0,991	1/x	4
Syringetin-3-O-glucoside + Syringetin-3-O-galactoside	4-8000	8106	179	36	33	0,993	1/x	8
Rhamnetin	6-10000	7212	173	-20	48	0,993	1/x	12
Isorhamnetin	8-6000	19195	445	-14	98	0,994	1/x	16
Isorhamnetin-3-Glc	4-10000	8958	206	-27	42	0,992	1/x	8
Isorhamnetin-3-rutinoside	4-20000	7473	143	-11	52	0,995	1/x	8

Table S3. Metabolites quantification.

Compound	Apple	Grape	Strawberry	Raspberry	Cherry	Green tea	Wine
	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/ml
3-Hydroxybenzaldehyde			1,30*				
4-Hydroxybenzoic acid		1,10*	1,30*	0,25*	0,55*	7,90*	1,39
Cinnamic Acid						0,31*	
Vanillin					0,15*	**1,20***	
Acetovanillone							**0,07***
Vanillic acid		**0,28***			**0,37***	0,10*	**0,06**
Gallic acid		**5,75***		0,55*	**0,49***	**71,05**	**28,60**
2,4-Dihydroxybenzoic acid						**21,85***	
3,5-Dihydroxybenzoic acid		0,17*			1,02*	5,63*	1,70*
3,4-Dihydroxybenzoic acid					0,50*	**4,06***	**1,36***
2,5-Dihydroxybenzoic acid							**0.41***
Methyl gallate		0,02*	0,03*	0,02*		**1,21***	0,01*
syrangaldehyde						**0,13***	0,10
Syringic acid		0,02*					0,74
Catechol							0,62*
Ellagic acid	1,00*	1,85*	13,50	0,34			8,67*
Umbelliferone				0,02*			
Scopoletin						**0,18***	
Esculin					0,02*	**0,88***	
p-Coumaric acid				**0,27**		**2,01***	**1,50**
Caffeic acid				0,28*		0,37*	**1,08**
Ferulic acid				**0,13***	0,05*	**0,30***	**0,14**
Sinapic acid				0,11*			
Caftaric acid		**> 20**		3,43*			**> 50**

Neochlorogenic acid	**0,17**		**0,19***	**0,18**	**> 200**	**15,95**	0,10*
Cryptochlorogenic acid	**2,29**				**> 7,5**	**> 30***	
Chlorogenic acid	**> 50**		0,60		> 10	**> 30**	
Rosmarinic Acid						0,72*	
Sinapyl alcohol				**0,68***		1,16*	
Fertaric acid		3,20*					**4,52***
trans-Coutaric acid		1,96				0,63*	**> 10**
trans-Resveratrol							1,01
cis-Resveratrol							**0,42**
Piceatannol		0,08					0,26
trans-Piceide	0,04*	0,27	0,10*	0,04*	0,06*	0,14*	**1,36**
cis-Piceide	0,02*	0,02*	0,03*	0,02*	0,03*	0,53*	1,19
Astringin		0,69*					**0,28***
Isorhapontin		0,08*					**0,48***
trans-ε-Viniferin		0,32*					0,06
Caffeic acid + Catechin condensation product					0,23*		**0,79***
Pallidol		0,04*					**3,38**
Isohopeaphenol		0,19*					0,81*
Phloretin						**0,10***	0,01*
Phloridzin	**8,51**	0,08*	**0,60***	0,16*	0,43*	**3,14***	**0,28***
Trilobatin			0,07*				
Luteolin-7-*O*-Glucoside		0,18*				2,21*	
Luteolin-8-*C*-Glucoside						**10,19***	
Apigenin-7-*O*-glucoside						**4,12***	
Naringenin				0,04*	0,02*	**0,57***	**0,07**
Naringenin-7-O-glucoside	> 300*	8,29*	67,65*	9,45*	> 40*	> 100*	> 8
Catechin	**3,05**	**26,40**	**34,65**	**0,54**	**8,30**	**85,85**	**6,19**

Epicatechin	**42,45**	**66,15**	**2,85**	**43,55**	**49,00**	**9,62**	**10,24**
Epigallocatechin		**0,41**				**> 200**	**0,55**
Gallocatechin		**0,52***			0,25*	**>200**	**2,53**
Catechin gallate		**1,38***				**> 50***	
Epicatechin gallate		**1,29**				**> 50**	
Gallocatechin gallate						**> 200**	
Epigallocatechin gallate	0,05*	3,69*	0,12	0,19*	0,01	**> 400**	
Procyanidin A2					0,53*		
Procyanidin B1	**15,06***	**21,74**	**33,50**		**20,50**	**18,45**	**> 20**
Procyanidin B2 + B4	**72,56**	**59,94**		**31,84**	**25,55**	**> 300**	**15,71**
Procyanidin B3		19,67	> 30	3,59*		> 30	> 6
Kaempferol		0,52*	**0,04***			**6,84***	**0,10**
Quercetin		**0,55***			**0,49***	**7,56***	**2,39**
Taxifolin		**0,20***			0,02*	**0,48***	**1,06***
Isorhamnetin		0,01*					**0,06**
Myricetin		**1,96***				**3,40***	**1,71**
Laricitrin		0,02*					**0,12**
Syringetin		0,02*					0,02
Quercetin-3-*O*-rhamnoside	**7,73**	0,07*				**12,11***	0,54
Kaempferol-3-*O*-glucoside		**8,01***	**4,45**			**77,57**	
Myrcitin							0,11
Quercetin-3-*O*-glucoside	**2,25**	**79,78***	0,49*	0,78	**14,08***	**121,72***	**0,07**
Quercetin-4-*O*-glucoside		**0,31***			**1,01***		
Quercetin-3-*O*-galactoside	**17,18**	**17,68**		**0,67***		**64,02**	**0,35***
Isorhamnetin-3-*O*-glucoside		2,26*				0,73*	
Quercetin-3-O-glucoside acetate						1,95*	

Syringetin-3-*O*-glucoside + Syringetin-3-*O*-galactoside		**1,06***				**0,39***	**0,87***
Kaempferol-3-*O*-rutinoside			**0,71***		**8,12***	**112,82**	
Peltatoside					0,12*		
Rutin	0,35	1,32*	**0,05***	**0,04**	**82,30***	**> 100**	
Isorhamnetin-3-rutinoside					0,23*	**2,63***	
Quercetin-3,4'-diglucoside		**4,07***		0,83*			**0,19***
Robinin						0,06	
Quercetin-3-*O*-glucuronide		**42,85**	**9,11**	**3,42**	0,09*	**0,59***	**3,91***
Kaempferol-3-*O*-glucuronide		0,58*	**7,43**	0,25*		0,35	**0,04***

Legend :

1) Metabolites which concentrations were out of linear range are signed with > and their values are an extrapolation of the calibration curves.

2) * The compounds which were found with this method and are not reported in Polyphenol explorer

3) The compounds signed in **bold** are confirmed with the expected ratio between the area of the qualifier 1 and the quantifier. All other compounds remain tentatively identified.

Figure S1. Intra-day precision of the retention time both for standard compounds (panel A) and for metabolites detected in matrices (panel B). In both experiments the samples were injected 5 times.

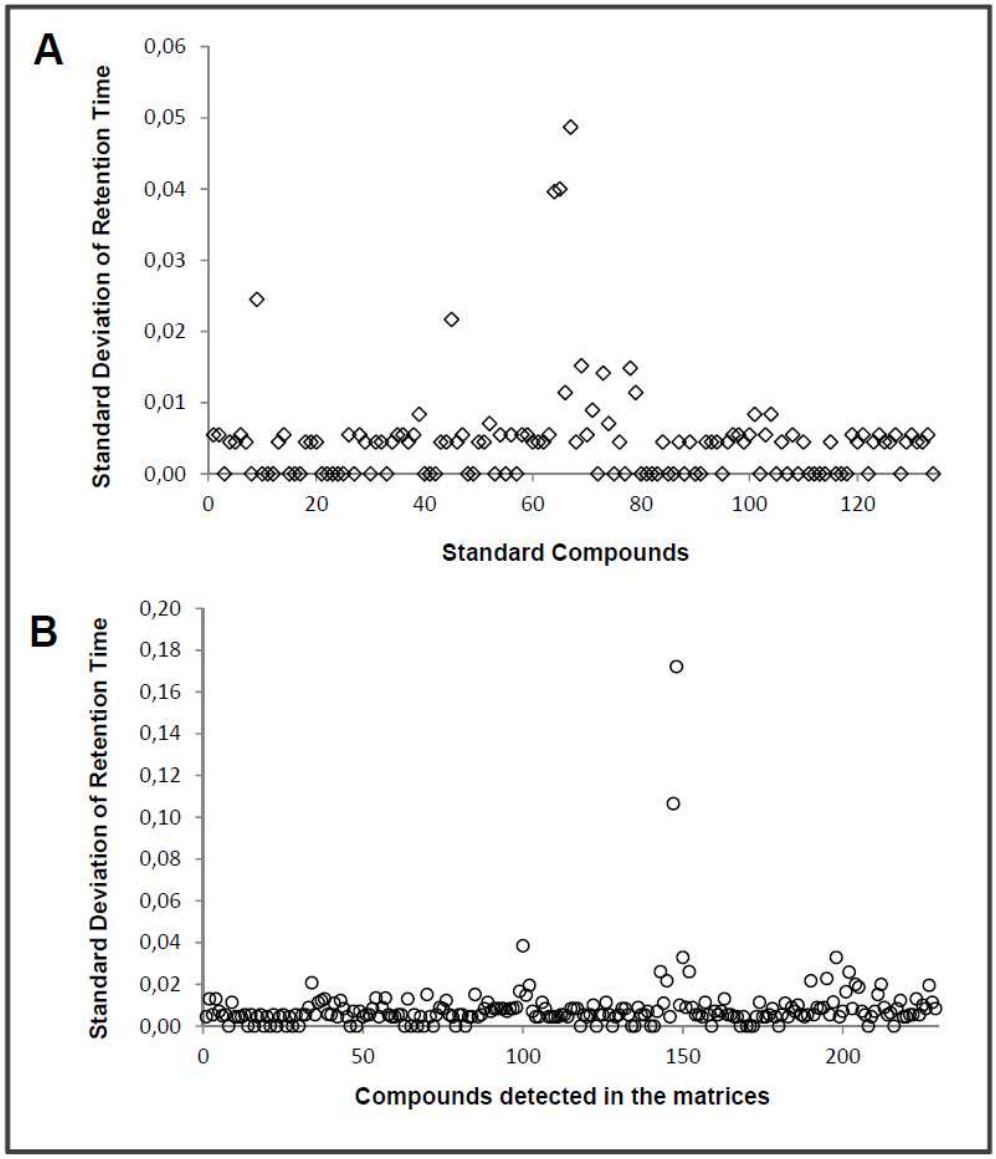

Figure S2. High-resolution spectra of *trans*-piceid (panel A) and *cis*-piceid (panel B) and of phloridzin (panel C) in grape and apple extracts.

Figure S1. Panel A

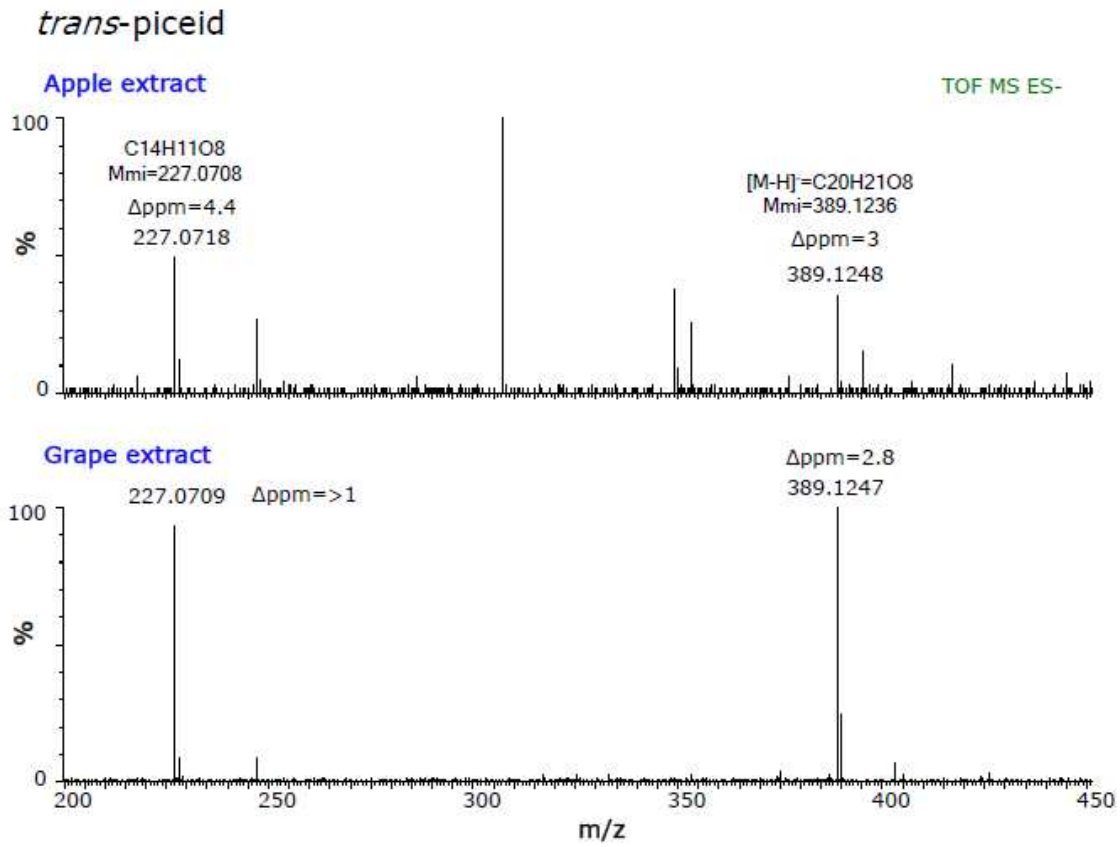

Figure S1. Panel B

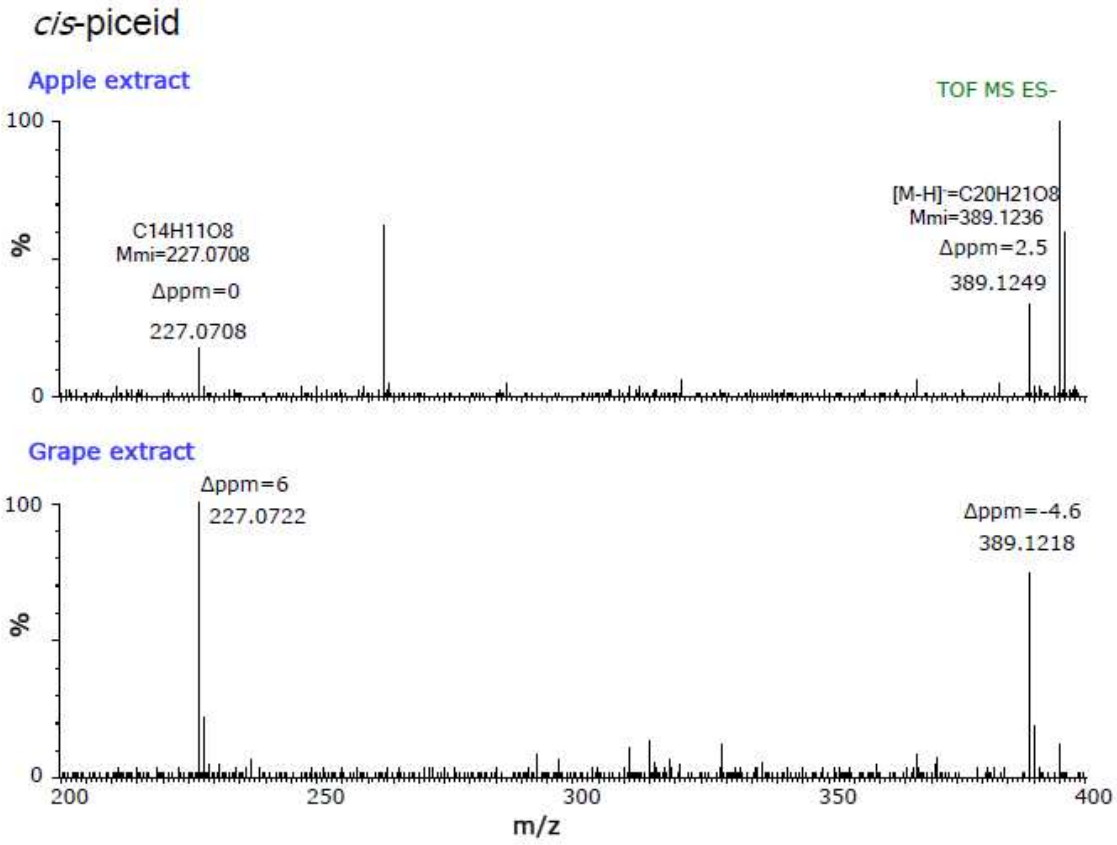

Figure 1S. Panel C