

Supplemental material

Table S1. Tentative identification of phenolic compounds in extra early clementine varieties, *Citrus clementina* Hort ex Tan.

Peak	Rt	λ_{max}	Molecular ion [M-H] ⁻ (m/z)	MS2 (m/z)	Tentative identification
1	5.2	272	385	281(78), 223(5),193(12),133(10)	Sinapoyl-glucoside1
2	6.4	324	385	367(9),209(27),191(100),173(3),147(15),129(19)	Feruloyl-glucaric acid2
3	6.8	266	341	179(100),135(52)	Caffeoyl-hexoside3
4	9.1	274,sh328	355	295(2),235(4),217(13),193(28),175(100)	Feruloyl-6'-O-glucoside2
5	9.5	332	593	575(2),503(9),473(20),383(18),353(23)	Vicenin II (apigenin-6,8-di-C-glucoside)4
6	10.7	282,sh336	433	271(100)	Naringenin-O-hexoside5
7	10.9	284,sh338	443	399(3),381(4),341(2),299(14),281(15)	Dihydrophaseic acid glucoside
8	11.6	268	281	237(95),189(29),171(100),145(12),139(19),123(54)	Dihydrophaseic acid
9	13.0	338	623	605(3),533(5),503(31),413(11),383(22),312(8)	Diosmetin-6,8-di-C-glucoside6
10	14.9	286,sh336	427	385(7),367(27),223(9),205(50),179(10),153(100),138(19)	Hydroxycinnamoyl derivative7
11	16.9	326	561	367(100),337(10),193(84),191(33),173(29),134(18)	Dihydroferulic-feruloylquinic acid dimer2
12	17.4	326	561	367(100),337(8),193(92),191(29),173(26),134(14)	Dihydroferulic-feruloylquinic acid dimer2
13	18.2	356	609	301(100)	Rutin (quercetin-3-O-rutinoside)8
14	19.8	280,sh334	579	271(100)	Narirutin/naringin5
15	22.5	284,sh340	609	301(100)	Hesperidin/Neohesperidin9
16	23.1	348	693	633(2),595(9),507(3),395(4)	Nomilin-glucoside9
17	30.8	345	593	285(100)	Kaempferol-O-deoxyhexosyl-hexoside10

Retention time (Rt), wavelengths of maximum absorption in the visible region (λ_{max}), mass spectral data.

Table S2. Full quantification (mg/g of extract) of phenolic compounds in extra early clementine varieties, *Citrus clementina* Hort ex Tan. (mean \pm SD, n=9).

Season	1			2			3		
Tentative identification	Basol	Clemenrubí	Clemensoon	Basol	Clemenrubí	Clemensoon	Basol	Clemenrubí	Clemensoon
Sinapoyl-glucoside ¹	3.4 \pm 0.2	2.04 \pm 0.01	3.92 \pm 0.01	1.09 \pm 0.01	1.40 \pm 0.04	0.88 \pm 0.01	1.20 \pm 0.02	0.93 \pm 0.01	0.90 \pm 0.01
Feruloyl-glucaric acid ²	0.99 \pm 0.01	1.01 \pm 0.03	2.95 \pm 0.05	0.49 \pm 0.01	0.46 \pm 0.03	0.58 \pm 0.01	0.65 \pm 0.03	0.62 \pm 0.01	0.45 \pm 0.02
Caffeoyl-hexoside ³	1.56 \pm 0.03	1.58 \pm 0.07	3.26 \pm 0.07	1.03 \pm 0.02	0.90 \pm 0.01	0.72 \pm 0.01	1.09 \pm 0.02	0.93 \pm 0.03	0.85 \pm 0.01
Feruloyl-6'-O-glucoside ²	1.07 \pm 0.01	0.68 \pm 0.03	1.32 \pm 0.05	0.15 \pm 0.01	0.20 \pm 0.01	0.19 \pm 0.01	0.25 \pm 0.01	0.23 \pm 0.01	0.16 \pm 0.01
Vicenin II (apigenin-6,8-di-C-glucoside) ⁴	2.80 \pm 0.01	0.88 \pm 0.01	1.84 \pm 0.01	0.42 \pm 0.01	0.46 \pm 0.01	0.37 \pm 0.01	0.84 \pm 0.01	0.69 \pm 0.02	0.63 \pm 0.01
Naringenin-O-hexoside ⁵	0.80 \pm 0.01	0.47 \pm 0.02	1.38 \pm 0.01	0.16 \pm 0.01	0.17 \pm 0.01	0.13 \pm 0.01	0.18 \pm 0.01	0.12 \pm 0.01	0.09 \pm 0.01
Dihydrophaseic acid glucoside	nq	nq	nq	nq	nq	nq	nq	nq	nq
Dihydrophaseic acid	nq	nq	nq	nq	nq	nq	nq	nq	nq
Diosmetin-6,8-di-C-glucoside ⁶	0.54 \pm 0.01	0.251 \pm 0.005	0.50 \pm 0.01	0.17 \pm 0.01	0.22 \pm 0.01	0.16 \pm 0.01	0.20 \pm 0.01	0.18 \pm 0.01	0.12 \pm 0.01
Hydroxycinnamoyl derivative ⁷	0.14 \pm 0.01	0.099 \pm 0.001	0.217 \pm 0.001	0.09 \pm 0.01	0.09 \pm 0.01	0.04 \pm 0.01	0.11 \pm 0.01	0.09 \pm 0.01	0.05 \pm 0.01
Dihydroferulic-feruloylquinic acid dimer ²	1.32 \pm 0.03	0.91 \pm 0.01	1.671 \pm 0.001	0.25 \pm 0.01	0.20 \pm 0.02	0.13 \pm 0.01	0.14 \pm 0.01	0.16 \pm 0.01	0.09 \pm 0.01
Dihydroferulic-feruloylquinic acid dimer ²	2.23 \pm 0.02	1.223 \pm 0.003	2.597 \pm 0.004	0.26 \pm 0.02	0.27 \pm 0.01	0.13 \pm 0.01	0.24 \pm 0.01	0.22 \pm 0.01	0.16 \pm 0.01
Rutin (quercetin-3-O-rutinoside) ⁸	1.35 \pm 0.01	0.48 \pm 0.01	1.51 \pm 0.01	0.23 \pm 0.01	0.24 \pm 0.01	0.32 \pm 0.01	0.22 \pm 0.01	0.36 \pm 0.01	0.20 \pm 0.01
Narirutin/naringin ⁵	4.15 \pm 0.01	2.563 \pm 0.011	5.82 \pm 0.01	0.80 \pm 0.01	0.91 \pm 0.01	0.75 \pm 0.01	0.81 \pm 0.01	0.76 \pm 0.01	0.63 \pm 0.01
Hesperidin/Neohesperidin ⁹	4.52 \pm 0.02	2.98 \pm 0.02	5.25 \pm 0.02	0.51 \pm 0.01	0.65 \pm 0.01	0.34 \pm 0.01	0.59 \pm 0.01	0.54 \pm 0.01	0.39 \pm 0.01
Nomilin-glucoside ⁹	0.197 \pm 0.001	0.056 \pm 0.001	0.115 \pm 0.001	0.04 \pm 0.01	0.03 \pm 0.01	0.04 \pm 0.01	0.04 \pm 0.01	0.04 \pm 0.01	0.03 \pm 0.01
Kaempferol-O-deoxyhexosyl-hexoside ¹⁰	0.25 \pm 0.01	0.12 \pm 0.01	0.419 \pm 0.001	0.25 \pm 0.01	0.18 \pm 0.01	0.14 \pm 0.01	0.21 \pm 0.01	0.18 \pm 0.01	0.20 \pm 0.01
Total flavonoids	13.81 \pm 0.02b	7.33 \pm 0.04c	15.46 \pm 0.01a	3.36 \pm 0.02b	3.53 \pm 0.01a	2.66 \pm 0.01c	3.67 \pm 0.01a	3.17 \pm 0.04b	2.66 \pm 0.01c
Total phenolic acids	10.51 \pm 0.50b	7.45 \pm 0.21c	15.73 \pm 0.07a	2.58 \pm 0.02b	2.84 \pm 0.02a	2.24 \pm 0.01c	3.10 \pm 0.01a	2.86 \pm 0.05b	2.28 \pm 0.02c
Total phenolic compounds	25.27 \pm 0.53b	15.35 \pm 0.21c	32.78 \pm 0.08a	5.94 \pm 0.01b	6.37 \pm 0.01a	4.91 \pm 0.01c	6.78 \pm 0.01a	6.03 \pm 0.09b	4.94 \pm 0.03c

nq - not quantified. Calibration curves used: 1- sinapic acid ($y=270.42x+62.29$; $R^2=0.999$); 2- ferulic acid ($y=525.36x+233.82$; $R^2=0.999$); 3- caffeic acid ($y=359.01x+488.40$; $R^2=0.998$); 4- apigenin-6-C-glucoside ($y=179.52x+116.83$; $R^2=0.999$); 5- naringenin ($y=539.98x+161.46$; $R^2=0.995$); 6- luteolin-6-C-glucoside ($y=423.95x+91.13$; $R^2=0.999$); 7- cinnamic acid ($y=1979x+787.15$; $R^2=0.994$); 8- quercetin-3-O-rutinoside ($y=280.87x+373.73$; $R^2=0.998$); 9-hesperetin ($y=792.22x-76.88$; $R^2=0.999$); 10- kaempferol-3-O-rutinoside ($y=182.94x+96.64$; $R^2=0.999$). In each row per season different letters mean significant differences ($p<0.05$).