

Optimization of Phenolic Compounds Extraction from *Crataegi Fructus*

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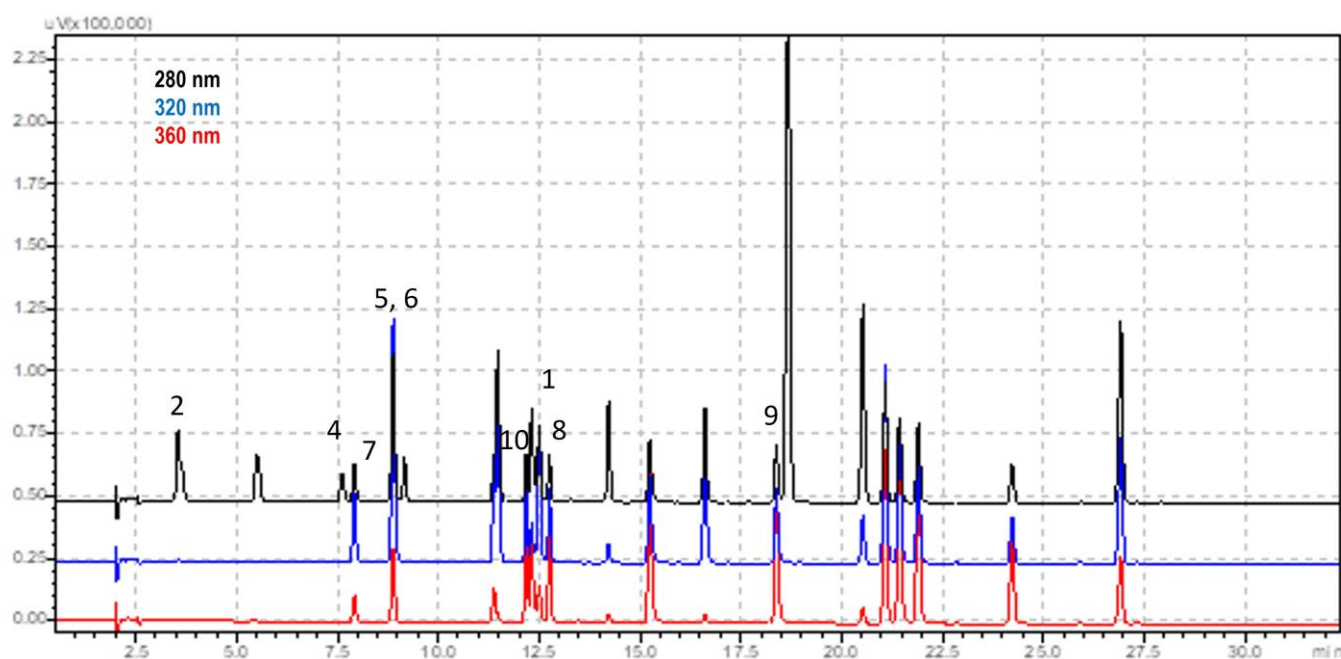


Figure S1. HPLC-PDA chromatogram of standard solution mixture recorded at 280, 320 and 360 nm (compounds identification: 1 - Hyperoside, 2 - Gallic acid, 3 - Syringic acid, 4 - (+)-Catechin, 5 - Procyanidin B2, 6 - (-)-Epicatechin, 7- Chlorogenic acid, 8 - Isoquercetin, 9 - Quercetin, 10 – Vitexin)* the HPLC method also involved the elution of other compounds that were not identified in the analyzed extracts.

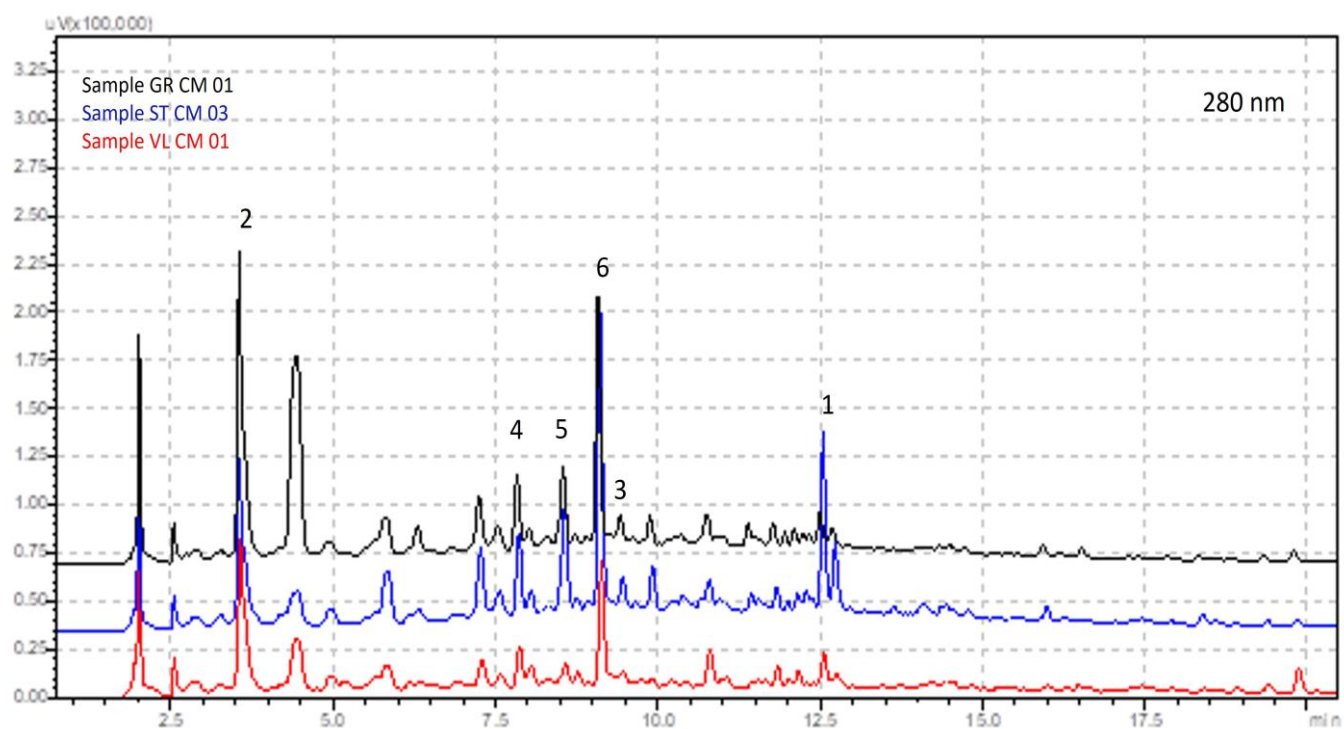


Figure S2. HPLC-PDA chromatograms of different genotypes of hawthorn extracts recorded at 280 nm (compounds identification: 1 - Hyperoside, 2 - Gallic acid, 3 - Syringic acid, 4 - (+)-Catechin, 5 - Procyanidin B2, 6 - (-)- Epicatechin).

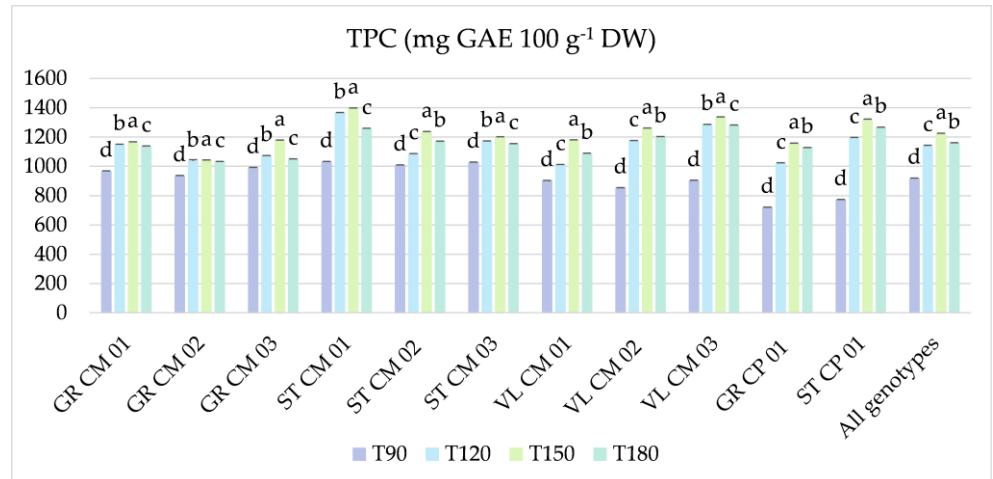


Figure S3. Extraction time effect on TPC depending on genotype. Different letters on the columns indicate statistically significant differences (Tukey test, $p < 0.05$). Error bars on graphs represent the standard deviation of the data.

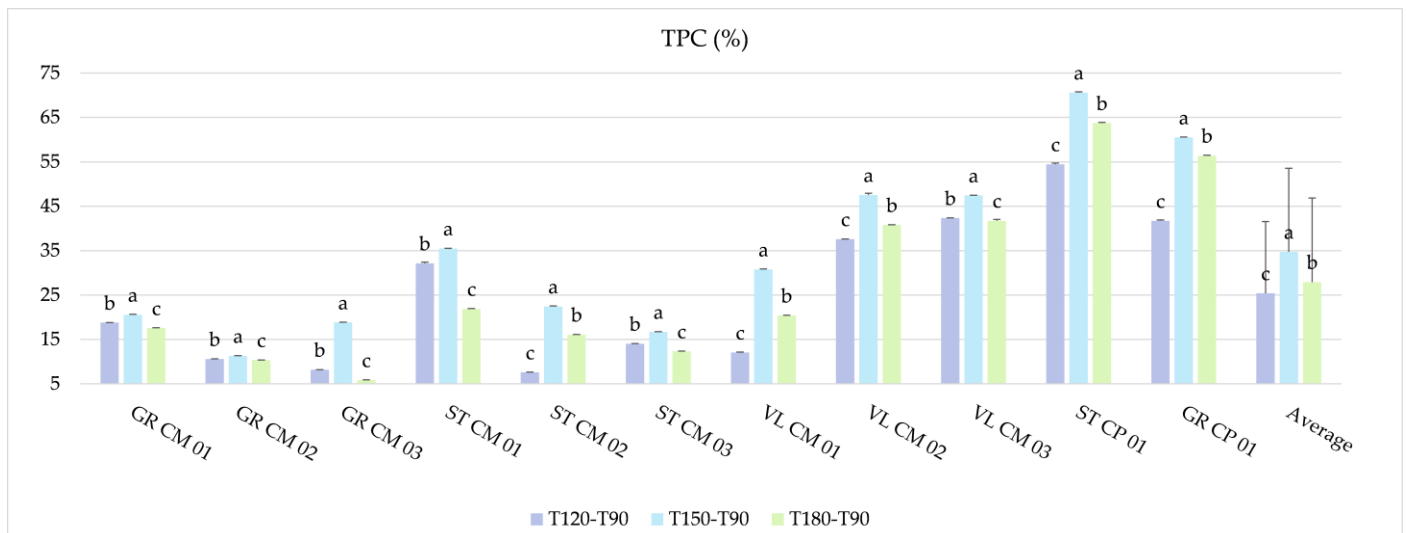


Figure S4. Percent of increase of TPC (%) extracted from *Crataegus* genotypes between two extraction times. Different letters on the columns indicate statistically significant differences (Tukey test, $p < 0.05$). Error bars on graphs represent the standard deviation of the data.

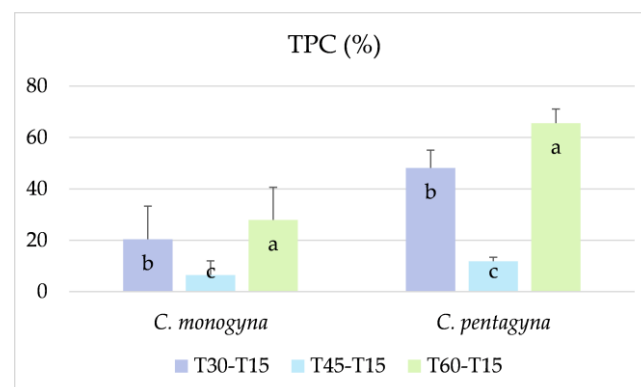


Figure S5. Percent of increase of TPC (%) extracted from *Crataegus* species between two extraction times. Different letters on the columns indicate statistically significant differences (Tukey test, $p < 0.05$). Error bars on graphs represent the standard deviation of the data.

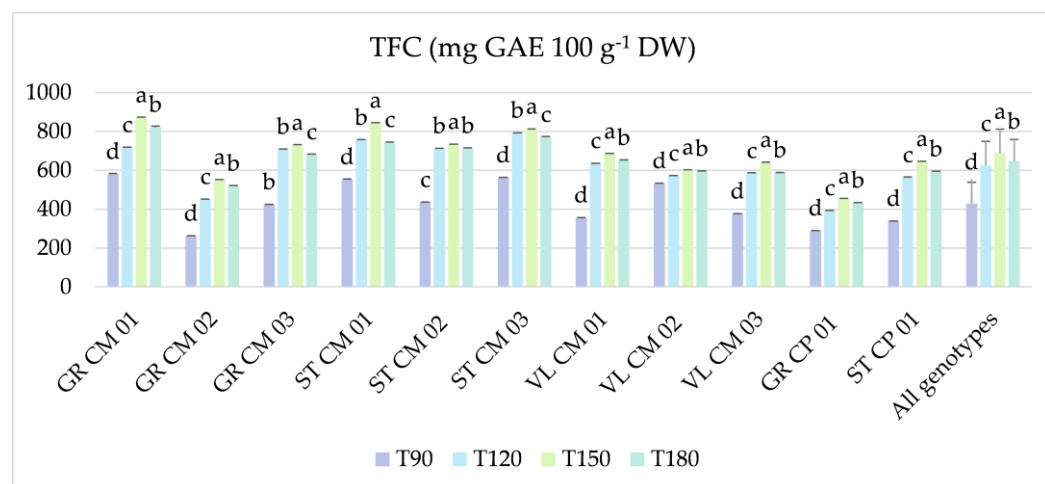


Figure S6. Extraction time effect on TFC depending on genotype. Different letters on the columns indicate statistically significant differences. Different letters on the columns indicate statistically significant differences (Tukey test, $p < 0.05$). Error bars on graphs represent the standard deviation of the data.

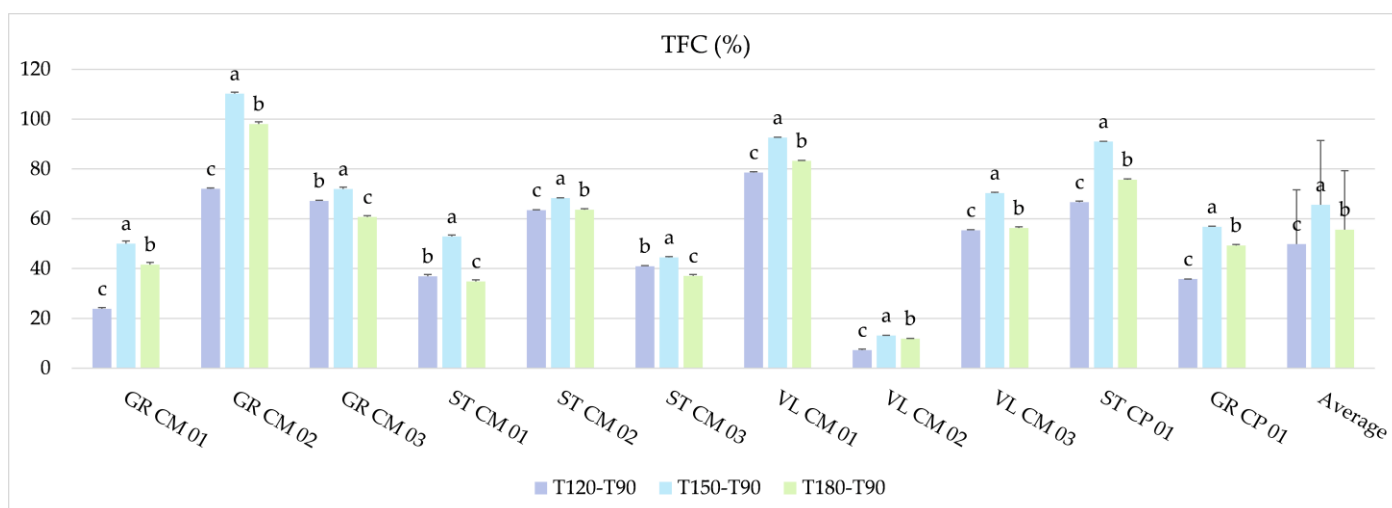


Figure S7. Percent of increase of TFC (%) extracted from *Crataegus* genotypes between two extraction times. Different letters on the columns indicate statistically significant differences (Tukey test, $p < 0.05$). Error bars on graphs represent the standard deviation of the data.

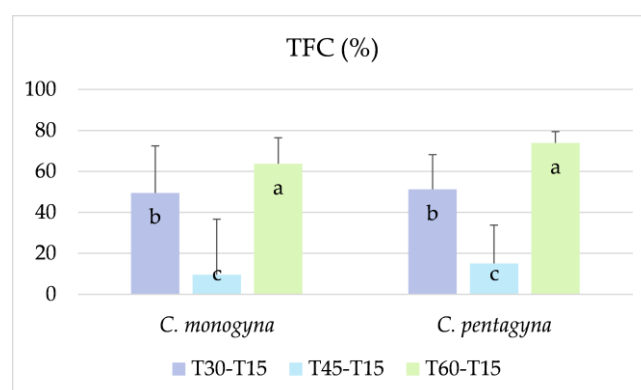


Figure S8. Percent of increase of TFC (%) extracted from *Crataegus* species between two extraction times. Different letters on the columns indicate statistically significant differences (Tukey test, $p < 0.05$). Error bars on graphs represent the standard deviation of the data.

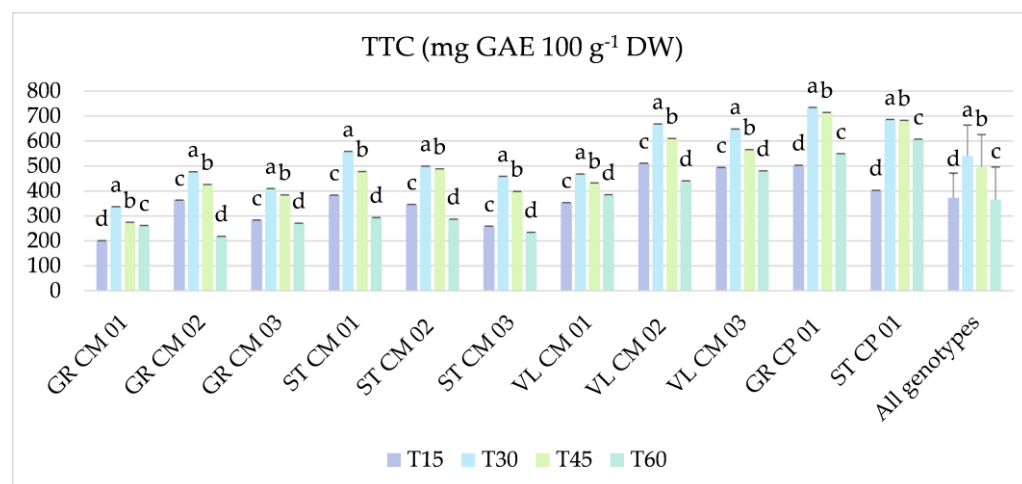


Figure S9. Extraction time effect on TTC depending on genotype. Different letters on the columns indicate statistically significant differences (Tukey test, $p < 0.05$). Error bars on graphs represent the standard deviation of the data.

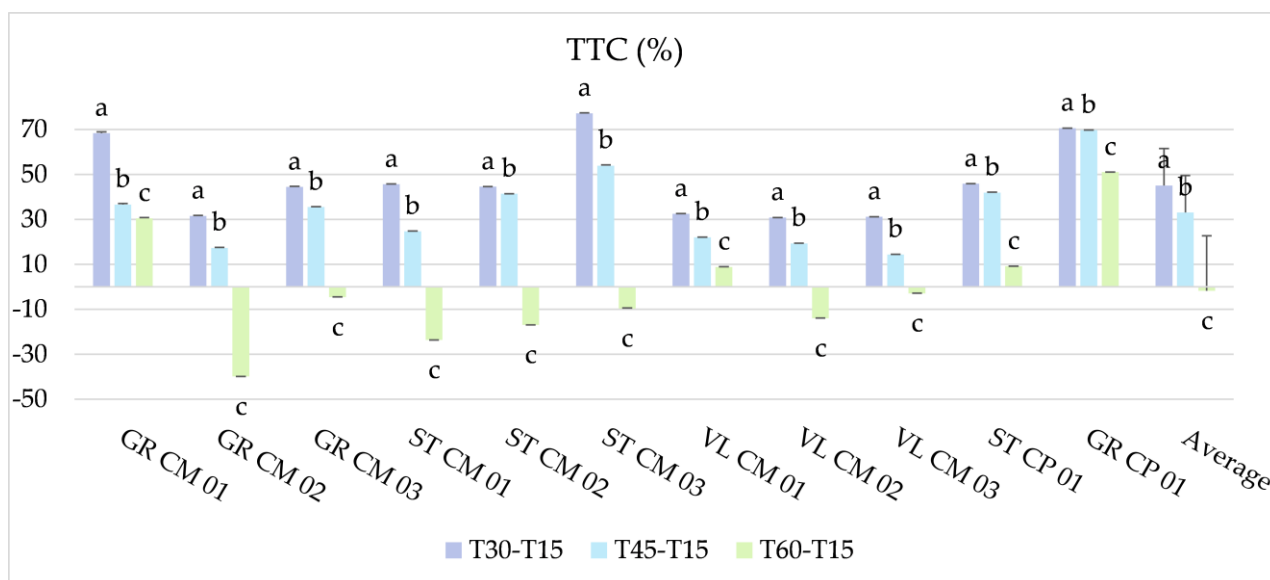


Figure S10. Percent of increase and decrease of TTC (%) extracted from *Crataegus* genotypes between two extraction times. Different letters on the columns indicate statistically significant differences (Tukey test, $p < 0.05$). Error bars on graphs represent the standard deviation of the data.

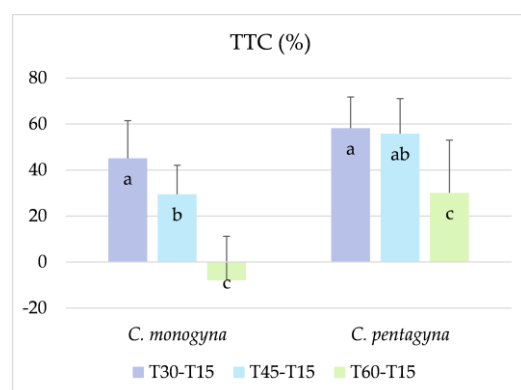


Figure S11. Percent of increase and decrease of TTC (%) extracted from *Crataegus* species between two extraction times. Different letters on the columns indicate statistically significant differences (Tukey test, $p < 0.05$). Error bars on graphs represent the standard deviation of the data.

Table S1. Limit of detection (LOD), limit of quantification (LOQ) and calibration curve parameters for phenolic compounds.

Compound	Retention time (min)	LOD (µg/mL)	LOQ (µg/mL)	Equation of calibration curve	R ²	Linearity range (µg/mL)
1	12.48	0.20	0.49	Y= 45963x - 28976	0.9990	0.5–50
2	3.55	0.16	0.53	Y= 25820x -1572	0.9992	0.5–50
3	9.40	0.32	0.48	Y= 38688x + 1029	0.9990	0.5–50
4	7.62	0.08	0.29	Y= 7627x + 648	0.9993	0.5–50
5	8.54	0.26	0.41	Y= 12008x - 8020	0.9993	0.5–50
6	9.16	0.11	0.23	Y= 8191x +2322	0.9995	0.5–50
7	7.99	0.16	0.37	Y= 15717x -3589	0.9999	0.5–50
8	12.75	0.07	0.32	Y= 18331x -1490	0.9995	0.5–50
9	18.41	0.24	0.39	Y= 43132x - 2292	0.9993	0.5–50
10	12.04	0.17	0.30	Y = 31603x -4407	0.9987	0.5–50

Table S2. Accuracy (% recovery) and precision (% RSD) of the HPLC method (n = 3).

Compound	Conc. (µg/mL)	% Recovery	% RSD	
			Intra-day	Inter-day
1	2.5	98.4	0.61	0.80
	10	100.5	0.10	1.15
	20	97.8	0.28	1.11
2	2.5	97.2	0.55	1.26
	10	98.9	0.83	1.08
	20	99.4	1.08	1.06
3	2.5	101.3	2.09	0.95
	10	101.8	1.95	1.23
	20	101.2	1.09	1.00
4	2.5	97.2	0.26	0.64
	10	95.8	0.56	2.19
	20	97.8	0.95	0.47
5	2.5	102.1	0.42	1.40
	10	102.4	0.33	1.69
	20	101.9	0.83	0.76
6	2.5	100.7	0.10	1.04
	10	99.9	0.41	1.30
	20	100.5	0.76	0.95
7	2.5	102.1	0.49	1.98
	10	102.4	0.58	1.09
	20	102.3	0.29	0.99
8	2.5	99.1	1.20	0.85
	10	98.4	1.99	0.63
	20	99.4	1.22	0.79
9	2.5	103.2	1.44	0.84
	10	102.9	1.09	0.86
	20	102.4	1.24	0.61
10	2.5	99.3	0.59	1.09
	10	97.3	0.61	1.17
	20	98.1	0.99	1.24

Table S3. Main bands in the ATR-FTIR spectra of hawthorn genotypes.

GR CM 01	GR CM 02	GR CM 03	ST CM 01	ST CM 02	ST CM 03	VL CM 01	VL CM 02	VL CM 03	GR CP 01	ST CP 01	Assignment
3270	3262	3267	3258	3258	3252	3217	3226	3216	3250	3268	Stretching O–H, N–H C–H, N–H asym [58]
										3011	=C–H groups that are related to olefins bands or unsaturated fatty acids L [58]
2923	2923	2921	2924	2927	2923	2922	2926	2922	2960	2920	ν_{asym} C–H L
2857	2857	2856	2856	2848	2856	2853	2855	2856	2853	2855	ν_{sym} C–H L
1736	1733	1736	1742	1736	1741	1738	1742	1741	1734	1737	ν C=O stretching due to lipids L
1611	1610	1606	1621	1621	1618	1609	1636	1617	1626	1625	Amide I (disordered structure -non-hydrogen bonded) [58]
											ν C=O, Amide I, stretching of protein P [59]
1517	1516	1532	1454	1518	1516	1511	1556	1516		1542	Amide II P
1425	1412	1406	1408	1410	1408	1425	1401		1411		δ_{asym} CH ₂ L
1368		1370	1369	1362	1366	1367	1323	1375	1370	1371	δ (CH ₂), ν (CC) (polysaccharides, pectin) [60]
1315	1316	1317	1312	1318	1316	1315		1314	1321	1312	Stretching C–N [61]
											Deformation N–H, δ CH ₂ [58] P
1236	1237	1232	1238	1238	1238	1233	1234	1234	1241	1236	Amide III P
1151							1147	1137		1149	C–O–C asym and sym stretch of various groups: cutin, cellulose, cell wall polysaccharide C [62]
			1060				1071				Stretching C–O deoxyribose C [58]
											Oligosaccharide C–OH stretching band, ν (CO), ν (CC), δ (OCH), ring (polysaccharides) C
1018	1020	1014	1019	1022	1021	1015	1021	1015	1021	1024	Vibrational frequency of –CH ₂ OH groups of carbohydrates (including glucose, fructose) C
											M – PO ₄ ³⁻
885	881	885	885	877	886	887	896	886		882	C–C, C–O deoxyribose C [58]
818	807	820		818	826	831	826	820		821	Ring C–H deformation [58]
							800	807		800	ρ (CH ₂) _n [58]
											CH out-of-plane bending vibrations

All wavenumber values are in cm^{–1}. **L** = lipids; **P** = proteins; **C** = carbohydrates; **M** = minerals