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Carotenoid and polyphenol content of heritage tomatoes: 2022

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Report for:

Mark Christensen, Heritage Food Crops Research Trust, Whanganui

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Executive summary

Carotenoid and polyphenol content of heritage tomatoes: 2022

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As in previous years, carotenoids and metabolites were measured in tomato (*Solanum lycopersicum*) samples provided by Mark Christensen, Heritage Food Crops Research Trust (HFCRT). Twelve samples of tomato were provided. The highest concentration of tetra-*cis*-lycopene was 5.9 mg/100 g FW in the golden tomato sample Moonbeam.

Similar to the 2021 results, the concentrations of the carotenoids phytoene, phytofluene and zeta-carotene, which are biosynthetic precursors to tetra-*cis*-lycopene, tended to be higher when tetra-*cis*-lycopene was present, and lower for tomatoes that contained beta-carotene and all-trans-lycopene.

Chlorogenic acids (both mono-caffeoyl and di-caffeoyl) were the major polyphenols in these tomatoes. Relatively low concentrations of flavonoids were detected, and the concentrations of these compounds were variable between cultivars.

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1 Introduction

The Heritage Food Crops Research Trust (HRCFT) want to understand the health benefits of tomato (*Solanum lycopersicum*) for consumers and are interested in identifying tomato cultivars and selections that have greater concentrations of carotenoids and polyphenols than conventionally grown commercial tomatoes. The New Zealand Institute for Plant and Food Research Limited (PFR) has measured carotenoids and polyphenols for several years by means of a series of projects (Cordiner 2020; McGhie & Cordiner 2021). Here we report the results for tomato samples collected during the 2022 summer.

2 Materials and methods

Twelve samples of tomato were provided by Mark Christensen, Heritage Food Crops; details are provided in Table 1. All samples were stored at −20°C from when they were received at PFR, Palmerston North, until analysis.

Lab reference: TM47

Table 1. Details of the tomato samples supplied for analysis.

Sample name	Description
African Oracle2 M	HFCRT selection of ‘African Oracle’ that has beta-carotene concentration reduced to zero and increased concentration of tetra-cis-lycopene
Amish Yellowish Orange Oxheart 2	Amish heirloom variety. Early producing, oxheart-shaped golden fruit with higher concentrations of tetra-cis-lycopene
Best Optical M	HRCRT selection of ‘Optical’ with high concentrations of beta-carotene
Geary Tomato	Grown from HFCRT seed by Mrs Geary; fruit returned morphed. Oblate and ribbed golden fruit with very high concentrations of chlorogenic acid
Golden Bell	NZ natural cross from ‘Oxheart’ and small orange tomato. Bright orange bell shaped tomato
Golden Emperor	Large beefsteak-type of golden tomato
Moonbeam	HFCRT selection from ‘Moonglow’
Oley	HFCRT selection from ‘Wally’s Spanish’
Optical best at S	HFCRT selection from ‘Optical’
Oracle 2 SBO M	HFCRT selection from ‘Oracle’ in 2022. Fruit contains tetra-cis-lycopene rather than beta-carotene and good polyphenol concentrations
Red Oracle orange S	HFCRT selection from orange ‘Oracle’ that changed to red in 2021 and back to orange in 2022
Roma Belle	HFCRT selection from ‘Golden Belle’ with a ‘Roma’-style shape

HRCFT = The Heritage Food Crops Research Trust.

2.1 Metabolite analysis

The analytical method used for the measurement of carotenoids in this study was similar to that used in the previous study (McGhie & Cordiner 2020). Authentic standards for tetra-*cis*-lycopene, phytoene, phytofluene and zeta-carotene were not available and the concentrations for these carotenoids were calculated using surrogate standards, with corrections based on relative extinction coefficients at the wavelengths used to detect each carotenoid (Table 2). Tetra-*cis*-lycopene concentrations were calculated using an all-*trans*-lycopene standard, whereas phytoene, phytofluene and zeta-carotene concentrations were calculated using a beta-carotene standard. The accuracy of the absolute concentration values should be treated with caution and comparison with quantitative data from other studies should only be made with care.

The method used for the analysis of polyphenols was similar, but an additional feature was added to the liquid chromatography–mass spectrometry (LCMS) method that had a marked impact on the concentrations calculated for (E)-caffeoyl 3-glucoside and (E)-caffeoyl 4-glucoside, which is described in the discussion.

Details of the carotenoids and polyphenols measured are shown in Tables 2 and 3, respectively.

Table 2. Carotenoids measured in tomatoes in 2022.

Compound	CAS#	Formula	Exact mass	Detection wavelength (nm)
lutein	127-40-2	$C_{40}H_{56}O_2$	568.4280	445
all-trans-lycopene	502-65-8	$C_{40}H_{56}$	536.4382	505
tetra-cis-lycopene	2361-24-2	$C_{40}H_{56}$	536.4382	436
phytoene	13920-14-4	$C_{40}H_{64}$	544.5008	286
phytofluene	540-15-6	$C_{40}H_{62}$	542.4852	348
zeta-carotene	13587-06-9	$C_{40}H_{60}$	540.4695	400
beta-carotene	7235-40-7	$C_{40}H_{56}$	536.4382	450

Table 3. Polyphenols measured in tomatoes in 2022.

Compound	Abbreviation	CAS#	Formula	Exact mass	Equivalence
(E)-caffeoyl 3-glucoside	EC3-glu	143729-78-6	$C_{15}H_{18}O_9$	342.0951	chlorogenic acid
(E)-caffeoyl 4-glucoside	EC4-glu	147511-61-3	$C_{15}H_{18}O_9$	342.0951	chlorogenic acid
3,4-dicaffeoylquinic acid	3,4-dCGA	14534-61-3	$C_{25}H_{24}O_{12}$	516.1268	chlorogenic acid
3,5-dicaffeoylquinic acid	3,5-dCGA	2450-53-5	$C_{25}H_{24}O_{12}$	516.1268	chlorogenic acid
4,5-dicaffeoylquinic acid	4,5-dCGA	57378-72-0	$C_{25}H_{24}O_{12}$	516.1268	chlorogenic acid
catechin	Cat	154-24-4	$C_{15}H_{14}O_6$	290.0790	epicatechin
chlorogenic acid	CGA	327-97-9	$C_{16}H_{18}O_9$	354.0951	chlorogenic acid
cryptochlorogenic acid	cCGA	905-99-7	$C_{16}H_{18}O_9$	354.0951	chlorogenic acid
epicatechin	epiCat	490-49-0	$C_{15}H_{14}O_6$	290.0790	epicatechin
kaempferol 3-rutinoside	K-rut	17650-84-9	$C_{27}H_{30}O_{15}$	594.1585	quercetin 3-rutinoside
naringenin	Nar	480-41-1	$C_{15}H_{12}O_5$	272.0685	quercetin
neochlorogenic acid	nCGA	202650-88-2	$C_{16}H_{18}O_9$	354.0951	chlorogenic acid
procyanidin B1	ProCy B1	20315-25-7	$C_{30}H_{26}O_{12}$	578.1424	procyanidin B2
procyanidin B2	ProCy B2	29106-49-8	$C_{30}H_{26}O_{12}$	578.1424	procyanidin B2
procyanidin B5	ProCy B5	12798-57-1	$C_{30}H_{26}O_{12}$	578.1425	procyanidin B2
procyanidin B7	ProCy B7	12798-59-3	$C_{30}H_{26}O_{12}$	578.1425	procyanidin B2
procyanidin C1	ProCy C1	37064-30-5	$C_{45}H_{38}O_{18}$	866.2058	procyanidin B2
quercetin	Q	117-39-5	$C_{15}H_{10}O_7$	302.0427	quercetin
quercetin 3-arabinopyranoside	Q-arapy	22255-13-6	$C_{20}H_{18}O_{11}$	434.0849	quercetin 3-rutinoside
quercetin 3-galactoside	Q-gal	482-36-0	$C_{21}H_{20}O_{12}$	464.0955	quercetin 3-rutinoside
quercetin 3-glucoside	Q-glu	482-35-9	$C_{21}H_{20}O_{12}$	464.0955	quercetin 3-rutinoside
quercetin 3-rhamnoside	Q-rha	522-12-3	$C_{21}H_{20}O_{11}$	448.1006	quercetin 3-rutinoside
quercetin 3-rutinoside	Q-rut	153-18-4	$C_{27}H_{30}O_{16}$	610.1534	quercetin 3-rutinoside
quercetin 3-xyloside	Q-xyl	549-32-6	$C_{20}H_{18}O_{11}$	434.0849	quercetin 3-rutinoside
quercetin 3-xylosylrutinoside	Q-xylrut	129235-39-8	$C_{32}H_{38}O_{20}$	742.1956	quercetin 3-rutinoside
trans-4-p-coumaroyl quinic acid	t4CQA	1108200-72-1	$C_{16}H_{18}O_8$	338.1002	trans-4-p-coumaroyl quinic acid
trans-5-p-coumaroyl quinic acid	t5CQA	5746-55-4	$C_{16}H_{18}O_8$	338.1002	trans-4-p-coumaroyl quinic acid

3 Results

3.1 Metabolite concentrations

Carotenoid concentrations for the 12 tomato samples are shown in Table 4. As noted above, because authentic standards were not available for tetra-*cis*-lycopene, phytoene, phytofluene and zeta-carotene, the accuracy of the absolute concentration values should be treated with caution and comparison with quantitative data from other studies should only be made with care.

The concentrations of tetra-*cis*-lycopene were generally similar to those in previous years; however, the relative concentration between samples seems to vary year-to-year. The differences between tetra-*cis*-lycopene, all-*trans*-lycopene and beta carotene concentrations tend to align with the colour of the tomato. For example, red tomatoes contain all-*trans*-lycopene, orange tomatoes often contain beta-carotene, and golden tomatoes contain tetra-*cis*-lycopene.

The concentrations of phytoene, phytofluene and zeta-carotene are somewhat correlated with each other and tend to be elevated when tetra-*cis*-lycopene is present, and lower for tomatoes that contain beta-carotene and all-trans-lycopene. Phytoene, phytofluene and zeta-carotene have a lower intensity of colour than other carotenoids measured in this study owing to a lesser number of double bonds in their molecular structure. Therefore, these carotenoids will have a lower impact on the colour of the fruit but appear to be present at higher concentrations. Possibly the higher concentrations of phytoene, phytofluene and zeta-carotene will have an impact on factors such as health. These compounds are generally not available in a pure form and consequently appear to have been little studied with respect to health benefits (Mapelli-Brahm & Meléndez-Martínez 2021).

Polyphenol concentrations for the 12 tomato samples are shown in Table 5. The phenolic compounds detected generally agree with those reported by Gómez-Romero et al. (2010).

The major polyphenolic metabolites in these tomatoes are caffeic acid conjugates with quinic acid, also known as chlorogenic acids. A number of monocaffeoyl and dicaffeoyl quinic acid conjugates were detected. Standards are not available for all these metabolites and were therefore these were quantified as chlorogenic acid equivalents.

As mentioned earlier, the change to the analytical method did not affect the measurement of most of the polyphenols. However, the quantitation of (E)-caffeoyl 3-glucoside and (E)-caffeoyl 4-glucoside was substantially affected and the quantitative results are different from those reported in 2021. Neither (E)-caffeoyl 3-glucoside nor (E)-caffeoyl 4-glucoside are available as authentic standards and therefore these compounds were quantified as chlorogenic acid equivalents. The ratio of the response of the mass spectrometer between chlorogenic acid and (E)-caffeoyl 3-glucoside and (E)-caffeoyl 3-glucoside had a marked impact on the concentration calculated for (E)-caffeoyl 3-glucoside and (E)-caffeoyl 4-glucoside, and this response ratio was very different with the analytical method used this year compared with previous years. Consequently, the concentrations of (E)-caffeoyl 3-glucoside and (E)-caffeoyl 4-glucoside can be compared only between cultivars analysed with the same method. Comparison of concentrations between years for (E)-caffeoyl 3-glucoside and (E)-caffeoyl 4-glucoside is not valid.

The concentrations reported for naringenin probably include both naringenin and naringenin chalcone, as described above. Naringenin/naringenin chalcone is a key intermediate in the flavonoid biosynthetic pathway and interestingly the concentrations found in the samples varied substantially. However, the concentrations of naringenin/naringenin chalcone did not appear to be related to the concentrations of quercetin 3-rutinoside, the main flavonoid in these tomatoes.

Table 4. Carotenoid concentrations (mg/100 g fresh weight) for the 12 tomato samples analysed in this study. n.d. = not detected.

Sample	tetra-cis-lycopene	phytoene	phytofluene	beta-carotene	all-trans-lycopene	lutein	zeta-carotene
African Oracle2, M	2.95	5.47	4.82	n.d.	0.24	n.d.	6.27
Amish Yellowish Orange Oxheart 2	5.30	12.65	11.89	n.d.	0.09	n.d.	11.47
Best Optical M	n.d.	1.26	n.d.	6.27	0.23	n.d.	0.28
Geary Tomato	4.87	9.96	13.14	n.d.	n.d.	n.d.	13.22
Golden Bell	3.98	3.86	4.40	n.d.	n.d.	0.10	5.10
Golden Emperor	2.44	4.91	6.06	n.d.	n.d.	n.d.	8.62
Moonbeam	5.89	6.01	6.74	n.d.	0.15	n.d.	8.25
Oley	3.54	9.63	11.83	n.d.	0.12	n.d.	17.38
Optical best at S	n.d.	1.87	n.d.	4.34	n.d.	0.02	n.d.
Oracle 2 SBO M	4.38	4.86	5.33	n.d.	0.32	0.08	4.98
Red Oracle orange S	2.28	6.35	6.45	n.d.	n.d.	0.10	2.90
Roma Belle	2.16	0.67	10.89	n.d.	n.d.	0.00	16.39

Table 5. Polyphenol concentrations (mg/100 g fresh weight) for the 12 tomato samples analysed in this study. n.d. = not detected. Table 3 lists the analytes that were analysed, and a number of these were not detected. These were: catechin, epicatechin, procyanidin B1, procyanidin B2, procyanidin B5, procyanidin B7, procyanidin C1, quercetin 3-arabinopyranoside, quercetin 3-galactoside, quercetin 3-glucoside, quercetin 3-rhamnoside, quercetin 3-xyloside, kaempferol 3-rutinoside and trans-4-p-coumarylquinic acid.

Sample	CGA	nCGA	3,4-dCGA	3,5-dCGA	4,5-dCGA	EC3-glu	EC4-glu	t5CQA	Nar	Q-rut	Q-xylrut
African Oracle2, M	4.23	0.40	3.19	2.20	11.97	11.78	14.18	1.11	0.01	0.84	0.35
Amish Yellowish Orange Oxheart 2	8.47	0.44	5.71	3.42	26.17	15.84	25.50	1.02	0.01	0.89	0.29
Best Optical M	10.22	0.82	1.32	5.91	8.63	13.79	11.97	7.12	0.00	1.38	0.68
Geary Tomato	4.59	0.41	4.83	5.20	53.29	19.05	33.46	1.25	0.52	3.32	0.84
Golden Bell	1.30	0.26	3.08	1.00	4.87	10.79	5.50	0.59	0.71	0.38	0.39
Golden Emperor	2.18	0.10	1.33	0.95	9.85	10.57	14.43	0.64	1.20	0.34	0.11
Moonbeam	0.79	0.33	2.46	0.95	5.99	15.26	20.51	0.15	0.26	0.94	0.19
Oley	0.89	0.32	1.94	0.79	4.13	15.56	20.04	0.09	0.20	0.73	0.16
Optical best at S	11.65	0.35	0.85	6.03	7.36	9.09	12.89	8.17	0.00	2.45	0.54
Oracle 2 SBO M	4.86	1.65	12.16	7.06	25.43	24.36	23.61	8.24	0.30	1.88	0.35
Red Oracle orange S	8.31	0.50	0.99	5.15	8.74	14.86	20.34	1.29	0.24	1.88	0.57
Roma Belle	1.35	0.42	1.21	0.82	4.83	11.06	7.31	2.04	0.00	0.54	0.23

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