

Characterization of Free Sugars in Hawthorn (*Crataegus* spp.) Species

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Free sugar contents were detected by HPLC in the fruits of 20 genotypes belonging to 5 different species (*Crataegus* spp.) collected from Malatya (eastern Turkey). The fresh fruits of *C. orientalis*, *C. aronia*, *C. meyeri*, *C. tanacetifolia* and *C. pontica* contain in average 1.36- 1.84 g/100 g sucrose, 4.18-5.33 g/100 g fructose, 0.42-1.12 g/100g maltose and 2.58-3.62 g/100 g glucose, respectively. The contents of sucrose, fructose, maltose and glucose did not differ by the species statistically. The main sugar was fructose in all hawthorn species, followed by glucose, sucrose and maltose. The mean percentages of fructose, glucose, sucrose and maltose within the total amount of these 4 sugars were 47.9, 29.4, 15.2 and 7.4 %, respectively. In addition, the species averagely had soluble solids content (SSC) 13.6-17.6 %.

Key Words: *Crataegus* spp., Hawthorn, Fruit, Malatya, Free sugars.

INTRODUCTION

Hawthorn belonging to the family *Rosaceae* and the genus *Crataegus* is native to Turkey. In different regions of Turkey, hawthorns are known with many synonymes such as aliç, yemsen, guhusk and haziran. Turkey is rich in genetic resources of hawthorn^{1,2}. It has been reported that it has about 200 species in the world^{3,4}. Hawthorns are deciduous plants and they usually prefer alkaline soils. Owing to individual variations, it is not easy to separate their species. The ripe fruit of hawthorn is small, its fruit can have yellowish, orange, reddish, black and dark blue colours depending on the species. The dry matter percentage of hawthorn fruit is 44.8-50.7% in *C. monogyna*⁵. Hawthorn fruits which contain vitamin C, flavonoids, glycosides, anthocynaidins, saponins, tannins, antioxidants and phenolics in addition to sugars⁶ have medicinal values⁶⁻¹⁰.

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HPLC has been extensively used to separate sugars^{11,12}. References regarding sugar contents of hawthorn species are very limited. In hawthorn fruit, the major sugar is fructose^{13,14}. The contents of fructose and glucose account for about 3 % of fresh fruit weight and the percentage of the remaining sugar components which are sucrose, sugar alcohol, sorbitol is only 0.5%¹⁴. Bignami *et al.*⁶ reported that fruits of *C. azarolus* contain 13.06-15.87% total sugars (as percentage of fresh weight). The objective of this study was to detect based on species the free sugars of hawthorns growing in Darende district (Malatya, eastern Turkey). Hawthorns are wild grown in Malatya located in eastern Turkey. In the district. hawthorn genetic resources have not been previously identified.

EXPERIMENTAL

The material of this study constituted hawthorn genotypes belonging to five different *Crataegus* species from native hawthorn population of Darende (district Malatya) located in eastern Turkey. Fresh fruits of genotypes were collected from hawthorn bushes growing in Darende in middle and late September. After fresh fruits of hawthorn were transported in polypropylene bags, they were held at room temperature and cleaned by manual. The species of hawthorn genotypes were morphologically separated⁴. Fruits belonged to five hawthorn species *C. orientalis*, *C. tanacetifolia*, *C. pontica*, *C. aronia* and *C. meyeri*. In addition, four genotypes for each species were marked. The soluble solids contents (SSC %) of fruits were also determined by refractometer.

Determination of free sugars: The analysis of free sugars was done by modifying the methods reported by Torije *et al.*¹⁵ and Karkacier *et al.*¹². 2 g of fresh fruit sample was ground into powder in liquid nitrogen and 40 mL of methanol was added. After the mixture was incubated on a magnetic stirrer at 65°C for 0.5 h, it was centrifuged at 4°C, 1300 rpm for 40 min. The supernatant was transferred in clean tube and made up to 50 mL with methanol. Subsequent to removing methanol by rotary evaporator, the residue was dissolved in 25 mL double distilled water. The extract was passed through Sep-Pak C₁₈ cartridge and 2.5 mL filtrate was mixed with 7.5 mL acetonitrile. It was filtrated by 0.45 µm membrane filter and injected into HPLC. The column was calibrated by known standards of fructose, sucrose, glucose and maltose. Free sugars were expressed as g/100 g in fresh fruit weight.

Statistical analysis: For statistical analysis of data, a completely randomized design with three replications was used. 10 Fruits was randomly chosen per replicate for soluble solid contents analyses. The means were separated by Duncan's multiple range test. Significant differences were found at $p < 0.01$. Statistical package program Minitab was used for the

analysis of variance. In addition, the correlation and regression analyses were conducted to conclude relationships among sugar contents of species.

RESULTS AND DISCUSSION

Table-1 shows free sugar contents and SSC % of fruits which belonged to five hawthorn species. The species which were *C. orientalis*, *C. aronia*, *C. meyeri*, *C. tanacetifolia* and *C. pontica* averagely contained 1.36-1.84 g/100 g sucrose, 4.18-5.33 g/100 g fructose, 0.42-1.12 g/100 g maltose and 2.58-3.62 g/100 g glucose, respectively. The contents of sucrose, fructose, maltose and glucose did not differ by the species statistically.

In fresh fruits of genotypes, sucrose content was detected between 1.40-2.78 g/100 g in *C. orientalis*, 1.00- 1.90 g/100 g in *C. aronia*, 1.30-1.80 g/100 g in *C. meyeri*, 1.18-2.40 g/100 g in *C. tanacetifolia* and 0.81-2.10 g/100 g in *C. pontica*. The content of fructose was between 2.90-6.22 g/100 g in *C. orientalis*, 3.44-6.30 g/100 g in *C. aronia*, 4.10-4.50 g/100 g in *C. meyeri*, 2.30-7.90 g/100 g in *C. tanacetifolia* and 4.01-7.27 g/100 g in *C. pontica*. The content of maltose was between 0.10-0.97 g/100 g in *C. orientalis*, 0.10-1.70 g/100 g in *C. aronia*, 0.15-2.07 g/100 g in *C. meyeri*, 0.17-1.30 g/100 g in *C. tanacetifolia* and 0.25-0.80 g/100 g in *C. pontica*. Glucose contents in *C. orientalis*, *C. aronia*, *C. meyeri*, *C. tanacetifolia* and *C. pontica* were determined as 2.13-2.50 g/100 g, 2.04-3.96 g/100 g, 2.47-5.22 g/100 g, 1.63-3.80 g/100 g and 1.82-3.90 g/100 g, respectively. Within free sugars, the main sugar was fructose in all hawthorn species. It was followed by glucose, sucrose and maltose, respectively. However, as mean values of all species, the mean percentages of fructose, glucose, sucrose and maltose within the total amount of these four sugars were 47.9, 29.4, 15.2 and 7.4 %, respectively.

As regards sugar contents of hawthorn species, there exists a limited reference. Bignami *et al.*⁶ recorded that fruits of *Crateagus azarolus* contain 13.06-15.87 % total sugars (as percentage of fresh weight), total sugars consist of 3.9-7.6 % fructose, 3.04-6.73 % glucose, 0.03-6.64 % sucrose and 1.31-2.30 % sorbitol and the percentages of fructose, glucose and sucrose within total sugars are 30.6-45.7, 22.01-42.4 and 0.2-45.3 %, respectively, depending on five different accessions represented by two regions of Italy. Chapman and Horvat¹⁴ reported that the major sugar is fructose in a ripen hawthorn fruit, contents of fructose and glucose account for about 3 % of fresh fruit weight and the percentage of the remaining sugar components which are sucrose, sugar alcohol, sorbitol is only 0.5 %. Trappey *et al.*¹³ determined that fruit juice extract of hawthorn (*C. opaca*) contains 1.02-1.99 % fructose and 0.65-1.36 % glucose. In this study, fructose content was close to values to those reported by Bignami *et al.*⁶, higher than those by Chapman and Horvat¹⁴ and Trappey *et al.*¹³. Glucose content

TABLE-1
 FREE SUGAR CONTENTS (AS g/100 g IN DRY FRUIT WEIGHT AND % OF
 TOTAL AMOUNT OF FOUR SUGARS) AND SOLUBLE SOLIDS IN TWENTY
 HAWTHORN GENOTYPES BELONGING TO FIVE SPECIES FROM
 DARENDE (MALATYA, TURKEY)

Hawthorn species	Genotypes	Sucrose		Fructose		Maltose		Glucose		Total* (g/100 g)	SSC (%)
		(g/100 g)	%	(g/100 g)	%	(g/100 g)	%	(g/100 g)	%		
<i>Crataegus orientalis</i> Palas ex. M. Bieb. var. <i>orientalis</i>	O-01	1.40	15.4	4.70	51.9	0.44	13.0	2.50	27.6	9.04	11.8
	O-33	1.60	13.0	6.22	50.5	0.97	7.8	3.51	28.5	12.30	13.6
	O-38	1.59	23.4	2.90	42.7	0.16	2.3	2.13	31.4	6.78	16.9
	O-43	2.78	33.9	2.90	26.7	0.10	1.2	2.41	29.4	8.19	14.0
<i>Crataegus aronia</i> (L.) Bosc. ex. DC. var. <i>aronia</i>	A-06	1.40	13.6	6.10	59.4	0.10	0.9	2.66	25.9	10.26	14.2
	A-34	1.00	8.6	5.62	48.4	1.70	14.6	3.29	28.3	11.61	18.5
	A-36	1.06	15.5	3.44	50.2	0.30	4.3	2.04	29.8	6.84	17.0
	A-40	1.90	14.5	6.30	48.2	0.90	6.8	3.96	30.3	13.06	19.7
<i>Crataegus meyeri</i> Pojark	M-04	1.68	20.0	4.10	48.8	0.15	1.7	2.47	29.4	8.40	23.7
	M-11	1.70	13.2	4.50	35.0	1.41	10.9	5.22	40.6	12.83	15.8
	M-13	1.30	14.5	4.14	46.3	0.86	9.6	2.63	29.4	8.93	13.2
	M-14	1.80	14.7	4.14	33.9	2.07	16.9	4.18	34.2	12.19	16.8
<i>Crataegus tanacetifolia</i> (Lam.) Pers	T-26	2.40	26.4	3.50	38.5	1.30	14.3	1.89	20.7	9.09	12.6
	T-28	1.27	9.3	7.30	53.9	1.17	8.6	3.80	28.0	13.54	14.2
	T-29	1.18	20.3	2.30	39.5	0.70	12.0	1.63	28.0	5.81	13.2
	T-37	1.40	10.6	7.90	60.1	0.81	6.1	3.03	23.0	13.14	14.3
<i>Crataegus pontica</i> C. Koch	P-17	1.34	11.9	5.20	46.2	0.80	7.1	3.90	34.7	11.24	12.1
	P-21	1.20	9.8	7.27	59.6	0.41	3.3	3.30	27.0	12.18	18.3
	P-39	0.81	8.6	4.86	52.1	0.25	2.6	3.40	36.4	9.32	18.0
	P-41	2.10	25.4	4.01	48.5	0.33	3.9	1.82	22.0	8.26	15.9
<i>Mean of C. orientalis</i>		1.84	20.2	4.18	46.0	0.42	4.6	2.64	29.0	9.08	14.1
<i>Mean of C. aronia</i>		1.34	12.8	5.37	51.3	0.75	7.1	2.99	28.6	10.45	17.4
<i>Mean of C. meyeri</i>		1.62	15.3	4.22	39.8	1.12	10.5	3.62	34.2	10.58	17.4
<i>Mean of C. tanacetifolia</i>		1.56	15.0	5.25	50.5	0.99	9.5	2.58	24.8	10.38	13.6
<i>Mean of C. pontica</i>		1.36	13.2	5.33	52.0	0.45	4.3	3.10	30.2	10.24	16.1
Mean		1.55	15.2	4.87	47.9	0.75	7.4	2.99	29.4	10.15	15.7
Significance		NS		NS		NS		NS		NS	
LSD (0.01)		—		—		—		—		—	

NS: non-significant; *The total amount of sucrose, fructose, maltose and glucose.

was usually lower than those reported by Bignami *et al.*⁶, higher than those by Chapman and Horvat¹⁴ and Trappey *et al.*¹³. The content of sucrose was usually lower than those of Bignami *et al.*⁶. In addition, some genotypes individually had higher fructose, glucose and sucrose contents than those reported in the references.

In addition, the average species had soluble solids content (SSC) 13.6-17.6 %. In addition, although SSC % did not differ by the species statistically, *C. aronia* and *C. meyeri* averagely had higher SSC % than other species. Ozcan *et al.*¹⁶ recorded 32.31 % SSC for fresh wild hawthorn fruits collected from Konya (Derbent) in Turkey. Türkoglu *et al.*¹ averagely determined 15.23-15.28 % SSC in fruits of *C. orientalis* grown in Van. The SSC from this study had close values with those by Türkoglu *et al.*¹, while it was lower than reported by Özcan *et al.*¹⁶.

On the other hand, relationships among sugar contents of hawthorn genotypes were also studied (Table-2). While the relationships of sucrose-fructose ($r = -0.324$) and sucrose-glucose ($r = -0.142$) had low negative correlation coefficients, relationships of glucose-fructose (Fig. 1) and glucose-maltose (Fig. 2) resulted in higher positive correlation coefficients with $r = 0.507$ and $r = 0.556$, respectively.

TABLE-2
RELATIONSHIPS AMONG SUGAR CONTENTS IN
THE FRUITS OF HAWTHORN GENOTYPES

Correlation coefficients (r)	Maltose	Glucose	Fructose
Sucrose	0.002	-0.142	-0.324
Maltose	–	0.556	0.169
Glucose	–	–	0.507

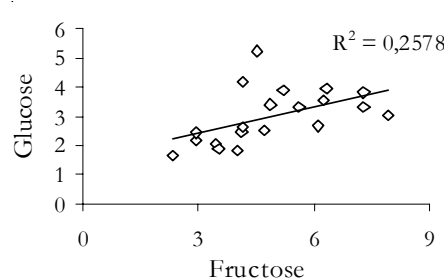


Fig. 1. Relationship of fructose and glucose in fruits of hawthorn genotypes

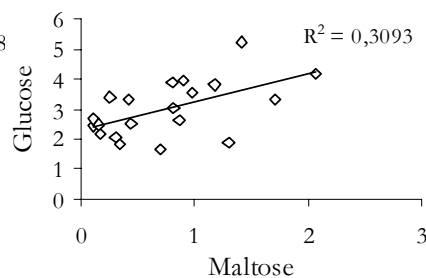


Fig. 2. Relationship of maltose and glucose in fruits of hawthorn genotypes

Findings in respect of free sugar contents of hawthorn species are limited in the references. Therefore, new compositional findings of this work will contribute to nutritional breeding efforts of hawthorn species and studies in this matter.

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(Received: 9 January 2007;

Accepted: 19 June 2007)

AJC-5754