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#### Artículo Original | Original Article

## Study on peel components and juice quality of three mandarin hybrids (*Citrus reticulata*) on sour orange rootstock cultivated in Ramsar, Iran

[Estudio sobre los componentes de la cáscara y la calidad del jugo de tres híbridos de mandarina (*Citrus reticulata*) en patrones de naranja agria cultivados en Ramsar, Irán]

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Abstract: The peel components and juice quality of three mandarin hybrids were investigated in this study. Peel components were extracted using the cold-press method and analyzed using GC-FID and GC-MS. Total soluble solids, total acid, pH value, ascorbic acid as well as density were determined in juice obtained from mandarin hybrids. Twenty-six, thirty-five and nineteen peel components were identified in Fortune, Robinson and Osceola respectively including: aldehydes, alcohols, esters, monoterpenes, sesquiterpenes and other components. The major components were limonene,  $\gamma$ -terpinene, (E)- $\beta$ -ocimene,  $\beta$ -myrcene, sabinene, linalool and  $\alpha$ -Pinene. Among the three scions examined, Fortune showed the highest content of aldehydes and Robinson showed the highest content of TSS. This study shows that scion has a profound influence on aldehyd and TSS that are important to quality improvement.

Keywords: aromatic plants; terpene; carvone; limonene; beta-caryophyllene; 1,8-cineole

**Resumen:** Los componentes de la cáscara y la calidad del jugo de tres híbridos de mandarina fueron investigados en este estudio. Los componentes de la cáscara fueron extraídos por el método de prensado en frío y se analizaron mediante GC-FID y GC-MS. el total de sólidos solubles, acidez total, pH, ácido ascórbico, así como la densidad se determinaron en el jugo obtenido a partir de híbridos de mandarina. Veintiséis, treinta y cinco y diecinueve componentes de la cáscara de Fortuna, Robinson y Osceola respectivamente fueron identificados, incluyendo: aldehídos, alcoholes, ésteres, monoterpenos, sesquiterpenos y otros componentes. Los componentes principales eran limoneno,  $\gamma$ -terpineno, (E) - $\beta$ -ocimeno,  $\beta$ -mirceno, sabineno, linalool y  $\alpha$ -pineno. Entre los tres vástagos examinados, Fortune mostró el mayor contenido de aldehídos y Robinson mostró el mayor contenido de SST. Este estudio muestra que el vástago tiene una profunda influencia en aldehído y SST que son importantes para mejorar la calidad.

Palabras clave: plantas aromáticas; terpeno; carvona; limoneno; beta-cariofileno; 1,8-cineol

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#### INTRODUCTION

Citrus is one of the most economically important crops in Iran. By 2012, the total annual Citrus production in Iran has been 82500 tons (FAO, 2016). Mandarin hybrids are so variable as the result of hybridization between many fine-quality mandarins and Citrus species. Many of these varieties or cultivars are now being used successfully for juice production and fresh fruit. Fortune resulted from the hybridization of Clementine and Dancy tangerines in 1964. It became important in South Texas because of its late maturity. Robinson and Osceola resulted from a cross between Clementine and Orlando tangelo in 1942 (Fotouhi & Fattahi, 2007). They are three of the most important mandarin cultivars used in the world. Although they are important cultivars, the flavor components of Fortune, Robinson and Osceola have been investigated very little before.

Citrus oils occur naturally in special oil glands in flowers, leaves, peel and juice. These valuable essential oils are composed of many compounds including: terpenes, sesquiterpenes, aldehydes, alcohols, esters and sterols. They may also be described as mixtures of hydrocarbons, oxygenated compounds and nonvolatile residues. Essential oils of Citrus are commercially used for flavoring foods, beverages, perfumes, cosmetics and medicines (Babazadeh-Dariazi, 2009). In addition, identified recent studies have insecticidal, antimicrobial, antioxidative and antitumor properties for Citrus peel oils (Shahidi & Zhong, 2005).

Although oxygenated compounds occurring in relatively small amounts, they have been found to be responsible for the specific odor and flavor of Citrus fruits. The quality of an essential oil can be calculated from the quantity of oxygenated compounds present in the oil. The quantity of oxygenated compounds in an oil depends on several factors including rootstock (Verzera *et al.*, 2003), scion or cultivar (Lota *et al.*, 2000; Lota *et al.*, 2001; Fanciullino *et al.*, 2006), degree of maturity (Kesterson & Hendrickson, 1962), climat (Scora & Torrisi, 1966).

Branched aldehydes and alcohols are important flavor compounds, extensively used in food products (Babazadeh-Darjazi, 2009). Several studies have shown that the tangerine-like smell is mainly a result of the presence of carbonyl compounds such as octanal, citronellal, decanal, neral, geranial, dodecanal (Buettner *et al.*, 2003). The quality of a honey can be calculated from the quantity of oxygenated components present in the honey (Alissandrakis *et al.*, 2003; Alistair *et al.*, 1993). In addition, type of flowers may influence the quality of volatile flavor components present in the honey. The effect of oxygenated compounds in the attraction of the pollinators has been proven. Therefore, the presence of oxygenated compounds can encourage the agricultural yield (Kite *et al.*, 1991; Andrews *et al.*, 2007).

Citrus juice is the most popular beverage in the world because of the fantastic flavor and abundant nutrition. The juice quality of Citrus is an important economic factor in an industry that buys its fruit based on the sugar content and processes over 95% (Rouse, 2000). The best juices are consumed by the food and beverage industries. The quality of a juice may be calculated not only with the amount of oxygenated components present in the juice but also with a concentration of compositions such as TSS, acids and vitamin C (Babazadeh-Darjazi *et al.*, 2009).

Juice, TSS and TA content are the main internal parameters used to determine Citrus quality in the world (Antonucci *et al.*, 2011). TSS content also forms the basis of payment for fruit by some juice processors in a number of countries, especially where the trade in juice is based on frozen concentrate (Hardy & Sanderson, 2010). The amount of TSS present in the juice is variable and depends upon a number of factors including: rootstock, scion or variety, degree of maturity, seasonal effects, climate, nutrition, tree age and etc (Hardy & Sanderson, 2010).

Several studies have shown that the scion or cultivar used may influence the quantity of chemical compositions (TSS, TA and vitamin C) present in the juice (Nematollahi, 2005). Compared with orange juice, very little research has been carried out on mandarin juice. Therefore, it is very important to be able to assess the differences between mandarin hybrids in terms of quantity of compositions (TSS, acids and vitamin C).

In this study, we compare the peel volatile compounds isolated from three mandarin scions with the aim of determining whether the quantity of oxygenated compounds influenced by the scions. Also the present study report the effects of scion on the juice quality parameters with the aim of verifying if they influenced by the scion.

#### MATERIALS AND METHODS

#### Mandarin scions

In 1989, mandarin scions that was grafted on Sour orange rootstock, were planted at  $8\times4$  m with three replication at Ramsar research station [Latitude  $36^{\circ}54'$  N, longitude  $50^{\circ}40'$  E; Caspian Sea climate,

average rainfall and temperature were 970 mm and 16.25° C per year, respectively; soil was classified as loam-clay, pH ranged from 6.9 to 7]. Fortune, Robinson and Osceola were used as scions in this experiment (Table 1).

 

 Table 1

 Common and botanical names for Citrus taxa used as scions and rootstock (Fotouhi & Fattahi, 2007)

Common name	botanical name	Parents	category
Fortune (scion)	Citrus reticulata cv. Fortune	Clementine mandarin× Dancy tangerine	Mandarin hybrid
Robinson (scion)	Citrus reticulata cv. Robinson	Clementine mandarin×Orlando tangelo	Mandarin hybrid
Osceola (scion)	Citrus reticulata cv. Osceola	Clementine mandarin×Orlando tangelo	Mandarin hybrid
Sour orange (Rootstock)	Citrus aurantium	Mandarin ×Pomelo	Sour orange

#### Preparation of peel sample

In the last week of January 2014, at least 10 mature fruit were collected from many parts of the same trees located in Ramsar research station. About 150 g of fresh peel was cold-pressed and then the oil was separated from the crude extract by centrifugation (at 4000 RPM for 15 min at 4° C). The supernatant was dehydrated with anhydrous sodium sulfate at 5° C for 24h and then filtered. The oil was stored at -25° C until analyzed.

#### Preparation of juice sample

In the last week of January 2014, at least 10 mature fruit were collected from many parts of the same trees located in Ramsar research station. Juice was obtained using the Indelicate Super Automatic, Type A2 104 extractor. After extraction, juice was screened to remove peel, membrane, pulp and seed pieces according to the standard operating procedure. Each juice replicate was made with 10 mandarins. Three replicates were used for the quantitative analysis (n = 3).

#### Chemical methods

The total titratable acidity was assessed by titration with sodium hydroxide (0.1 N) and expressed as % citric acid. Total soluble solids, expressed as Brix, were determined using a Carl Zeiss, Jena (Germany) refractometer. The pH value was measured using a digital pH meter (WTW Inolab pH-L1, Germany). Ascorbic acid was determined by titration with Potassium iodide. The density of the juice was measured using a pycnometer and ash was determined by igniting a weighed sample in a muffle furnace at 550° C to a constant weight (Majedi, 1994).

#### GC and GC-MS

An Agilent 6890N gas chromatograph (USA) equipped with a DB-5 (30 m  $\times 0.25$  mm i.d; film thickness = 0.25 µm) fused silica capillary column (J&W Scientific) and a flame ionization detector (FID) was used. The column temperature was programmed from 60° C (3 min) to 250° C (20 min) at a rate of 3° C/min. The injector and detector temperatures were 260° C and helium was used as the carrier gas at a flow rate of 1.00 ml/min and a linear velocity of 22 cm/s. The linear retention indices (LRIs) were calculated for all volatile components using a homologous series of n-alkanes (C9-C22) under the same GC conditions. The weight percent of each peak was calculated according to the response factor to the FID. Gas chromatography-mass spectrometry was used to identify the volatile components. The analysis was carried out with a Varian Saturn 2000R, 3800 GC linked with a Varian Saturn 2000R MS.

#### Table 2

Statistical analysis of variation in peel flavor Components of mandarin scions (see Materials and methods). Mean is average composition in % over the different scions used with three replicates. St. err = standard error. F value is accompanied by its significance, indicated by: NS = not significant, \* = significant at P = 0.05, \*\* = significant at P = 0.01.

Compounds	For	Fortune		Robinson		Osceola	
	Mean	St.err	Mean	St.err	Mean	St.err	F value
Oxygenated compounds							
a) Aldehyds							
1) Octanal	0.08	0.01	0.17	0.01	0.19	0.04	F**
2) Nonanal			0.06	0.006	0.05	0.01	
3) Citronellal	0.04	0.006	0.03	0	0.02	0.006	
4) Decanal	0.03	0.006	0.08	0.006	0.12	0.02	F**
5) Geranial	0.02	0.006	0.01	0	0.01	0.006	
6) Perilla aldehyde	0.02	0.01	0.02	0.01	0.02	0.01	
7) Undecanal			0.01	0.006			
8) Dodecanal			0.01	0.002			
9) α-sinensal	0.39	0.04	0.1	0.02	0.05	0.01	F**
Total	0.58	0.07	0.49	0.06	0.46	0.10	
b) Alcohols							
1) linalool	0.83	0.05	1.03	0.04	0.54	0.07	F**
2)(Z) p-mentha-2,8-dien-1-ol					0.02	0.006	
3) Terpinen-4-ol	0.04	0.01					
4) α-terpineol			0.13	0.02	0.03	0.01	
5) β-citronellol	0.04	0	0.02	0.01			
6) Thymol			0.04	0.01			
7) Elemol	0.04	0.01	0.03	0.01			
Total	0.95	0.07	1.25	0.09	0.59	0.08	
c) Esters							
1) Citronellyl acetate	0.05	0.01					
Monoterpenes							
1) α-thujene			0.12	0.006			
2) α-pinene	0.47	0.05	0.8	0.01	0.39	0.05	F**
3) Sabinene	1.04	0.02	0.16	0.02	0.41	0.04	F**
4) β- pinene	0.03	0.01	0.28	0.03			
5) β-myrcene	1.56	0.18	1.57	0.05	1.42	0.26	NS
6) α-terpinene			0.03	0			
7) Limonene	90.8	1.15	87.79	1.13	91.4	1.08	NS
8) (Z)-β-ocimene	0.02	0					
9) (E)-β-ocimene	2.38	0.13	1.2	0.18	1.73	0.12	F**
10) γ-terpinene	0.61	0.09	4.45	0.28			
11) α-terpinolene			0.18	0.04			
12) Cis-limonene oxide					0.02	0.006	
Total	96.94	1.63	96.58	1.74	95.37	1.55	
Sesquiterpenes							
1) δ-elemene			0.1	0.01			

Compounds	Fortune		Robinson		Osceola		
	Mean	St.err	Mean	St.err	Mean	St.err	F value
2) α-copaene	0.07	0.006	0.01	0	0.02	0.006	
<b>3)β -cubebene</b>	0.05	0.006			0.02	0.006	
4) β-elemene	0.05	0.006	0.04	0.01			
5) γ-elemene			0.05	0.01			
6) α-humulene			0.01	0			
7) Germacrene D	0.04	0.006	0.08	0.01			
8) Bicyclogermacrene	0.01	0.002	0.01	0			
9) E,E-α-farnesene	0.06	0.006	0.01	0			
10) δ-cadinene	0.06	0.02	0.008	0.003	0.02	0.01	
11) Germacrene B			0.02	0.006			
Total	0.33	0.05	0.33	0.04	0.06	0.02	
Other compounds							
1)Thymol methyl ether			0.03	0			
Total oxygenated compounds	1.58	0.15	1.74	0.15	1.05	0.18	
Total	98.85	1.84	98.69	1.945	96.48	1.76	

						Tabl	le 3				
		Peel v	olatile co	mponen	ts of 1	nanc	larin hybrids. (*Theı	e is in oi	l)		
	Component	Fortune	Robinson	Osceola	KI		Component	Fortune	Robinson	Osceola	KI
1	α- thujene		*		928	22	Thymol methyl ether		*		1236
2	α - Pinene	*	*	*	935	23	Geranial	*	*	*	1275
3	Sabinene	*	*	*	975	24	Perilla aldehyde	*	*	*	1282
4	β -pinene	*	*		979	25	Thymol		*		1291
5	β -myrcene	*	*	*	991	26	Undecanal		*		1307
6	octanal	*	*	*	1003	27	δ- elemene		*		1344
7	$\alpha$ -terpinene		*		1021	28	Citronellyl acetate	*			1349
8	Limonene	*	*	*	1036	29	α -copaene	*	*	*	1385
9	(Z)-β- ocimene	*			1040	30	β-cubebene	*		*	1396
10	(E)- β - ocimene	*	*	*	1049	31	β -elemene	*	*		1399
11	$\gamma$ - terpinene	*	*		1061	32	Dodecanal		*		1409
12	$\alpha$ -terpinolene		*		1091	33	γ - elemene		*		1440
13	Linalool	*	*	*	1100	34	α - humulene		*		1466
14	Nonanal		*	*	1109	35	Germacrene D	*	*		1493
15	(Z) p-mentha-2,8- dien-1-ol			*	1124	36	Bicyclogermacrene	*	*		1504
16	Cis-limonene oxide			*	1137	37	E,E, α - farnesene	*	*		1514
17	Citronellal	*	*	*	1154	38	δ-cadinene	*	*	*	1532
18	Terpinene-4-ol	*			1182	39	Elemol	*	*		1559
19	α - terpineol		*	*	1195	40	Germacrene B		*		1572
20	Decanal	*	*	*	1205	41	α-sinensal	*	*	*	1756
21	β -citronellol	*	*		1229			26	35	19	

The oven condition, injector and detector temperatures, and column (DB-5) were the same as those given above for the Agilent 6890 N GC.

Helium was the carrier gas at a flow rate of 1.1 mL/min and a linear velocity of 38.7 cm/s. Injection volume was 1  $\mu$ L.

Table 4

Statistical analysis of variation in juice quality parameters of mandarin scions. Mean is average parameter in
% over the different scions used with three replicates. St. err = standard error. F value is accompanied by its
significance, indicated by: NS = not significant, $* =$ significant at P = 0.05, $** =$ significant at P = 0.01.

cultivars	<b>TSS (%)</b>	Total Acids (%)	TSS /TA rate	Ascorbic acid (%)	РН	Juice (%)	Total dry matter (%)	Ash (%)
Fortune(scion)	9	2.03	4.43	31.50	2.92	74.35	14.02	3
Robinson(scion)	9.8	0.61	16.06	39.95	3.75	73.88	13.50	2
Osceola(scion)	8	0.68	11.76	45.58	3.64	67.68	15.20	1
	F**	F**	F**	F**	F**	F**		

#### Identification of components

Components were identified by comparing their LRIs and also comparing their mass spectra with those of reference compounds in the data system of the Wiley library and NIST Mass Spectral Search program (Chem. SW. Inc; NIST 98 version database) connected to a Varian Saturn 2000R MS. Identification of compounds were also determined by comparing the retention time of each compound with that of known compounds (Adams, 2001; McLafferty & Stauffer, 1991).

#### Data analysis

SPSS 18 was used for analysis of the data obtained from the experiments. Analysis of variations was based on the measurements of 9 peel component and 6 juice characteristics. Variations among and within cultivars were analyzed using analysis of variance (ANOVA)-one way. The correlation between pairs of characters and altitude was evaluated using Pearson's correlation coefficient (Table 3 and 4).

#### RESULTS

#### Flavor compounds of the Fortune mandarin peel

GC-MS analysis of the flavor compounds extracted from Fortune mandarin peel using cold-press led to the identification of 26 volatile components (Table 2, Figure 1) including 11 oxygenated terpenes [6 aldehydes, 4 alcohols, 1esters] and 15 non oxygenated terpenes [8 monoterpens, 7 sesqiterpens]. Flavor compounds of the Robinson mandarin peel

GC-MS analysis of the flavor compounds extracted from Robinson mandarin peel using cold-press led to the identification of 35 volatile components (Table 2) including 14 oxygenated terpenes [9 aldehydes, 5 alcohols], 20 non oxygenated terpenes [10 monoterpens, 10 sesqiterpens] and 1 other compound..

#### Flavor compounds of the Osceola mandarin peel

GC-MS analysis of the flavor compounds extracted from Osceola mandarin peel using cold-press led to the identification of 19 volatile components (Table 2) including 10 oxygenated terpenes [7 aldehydes, 3 alcohols] and 9 non oxygenated terpenes [6 monoterpens, 3 sesqiterpens].

#### Aldehydes

Nine aldehyde components that identified in this analysis were octanal, nonanal, citronellal, decanal, geranial, perillaldehyde, undecanal, dodecanal, and  $\alpha$ sinensal (Table 3). In addition they were quantified from 0.46% to 0.58%. The concentrations of  $\alpha$ sinensal, octanal and decanal were higher in our samples. Octanal has a Citrus-like aroma, and is considered as one of the major contributors to mandarin flavor (Buettner *et al.*, 2003). Among the three scions examined, Fortune showed the highest content of aldehydes (Table 3). Since the aldehyde content of Citrus oil is considered as one of the most important indicators of high quality, scion apparently has a profound influence on this factor.

Robinson aldehydes were also compared to those of Fortune and Osceola in this study.

Undecanal and dodecanal were identified in Robinson, while they were not detected in the Fortune and Osceola. Amount of aldehydes in Fortune was 1.26 times higher than Osceola (Table 3)



#### Alcohols

Seven alcohol components identified in this analysis were linalool, trans- p-mentha-2, 8-dien-1-ol, terpinene-4-ol,  $\alpha$ -terpineol,  $\beta$ -citronellol, thymol and elemol (Table 3).

The total amount of alcohols ranged from 0.59% to 1.25%. Linalool was identified as the major component in this study and it was the most abundant. Linalool has been recognized as one of the most important components for mandarin flavor (Buettner *et al.*, 2003). Linalool has a flowery aroma (Buettner *et al.*, 2003) and its level is important to flavor characteristics of mandarin oil (Salem, 2003). Among the three scions examined, Robinson showed the highest content of alcohols (Table 3). Robinson alcohols were also compared to those of Fortune and Osceola in this study. Thymol was identified in Robinson, while it was not detected in Fortune and

Osceola. Amount of alcohols in Robinson was 2.11 times higher than Osceola (Table 3).

#### Esters

One ester component identified in this analysis was citronellyl acetate. The total amount of esters ranged from 0.00% to 0.05%. Among the three scions examined, Fortune showed the highest content of esters (Table 3).

#### Monoterpenes hydrocarbons

The total amount of monoterpene hydrocarbons ranged from 95.37% to 96.94%. Limonene was the major component among the monoterpene hydrocarbons of mandarin oil. Limonene has a weak Citrus-like aroma (Buettner *et al.*, 2003) and is considered as one of the major contributors to mandarin flavor. Among the three scions examined,

Fortune showed the highest content of monoterpene (Table 3).

#### Sesquiterpenes hydrocarbons

The total amount of sesquiterpene hydrocarbons ranged from 0.06% to 0.33%. Germacrene D and  $\delta$ -elemene were the major components among the sesquiterpen hydrocarbons of Robinson oil. Among the three scions examined, Fortune and Robinson showed the highest content of sesquiterpenes (Table, 3).

#### Juice quality parameters

Juice quality parameters are given in Table 4. The content of total acid was from 0.61% (Robinson) to 2.03% (Fortune), and Brix (total soluble solids) was from 8% (Osceola) to 9.8% (Robinson). TSS/TA rate was from 4.43 (Fortune) to 16.06 (Robinson). Ascorbic acid was from 31.50% (Fortune) to 45.58% (Osceola). The pH value was from 2.92 (Fortune) to

3.75 (Robinson). The juice yield was from 67.68% (Osceola) to 74.35% (Fortune). Ash was from 1% (Osceola) to 3% (Fortune). Total dry matter was from 13.50% (Robinson) to 15.20% (Osceola).

Among the three scions examined, Robinson showed the highest content of TSS, TSS/TA and pH. The lowest content of TSS/TA and pH were produced by Fortune. (Table 4).

#### Results of statistical analyses

Statistical analysis was performed on the peel and juice data using SPSS 18. Comparisons were made using one-way analysis of variance (ANOVA) and Duncan's multiple range tests. Differences were considered to be significant at P < 0.01. These differences on the 1% level occurred in octanal, decanal,  $\alpha$ -sinensal, linalool,  $\alpha$ -pinen, sabinene, (E)- $\beta$ -ocimene, TSS, TA, TSS/TA, ascorbic acid, pH and juice. The non affected oil components were  $\beta$ -myrcen and limonene (Table 3 and Table 4).

#### Table 5

Correlation matrix (numbers in this table correspond with main components mentioned in Table 3)

	octanal	decanal	α-sinensal	linalool	<b>α-pinene</b>	sabinene	β-myrcene	limonene
decanal	$0.92^{**}$							
α-sinensal	-0.87**	-0.87**						
linalool	-0.12	-0.41	0.25					
α-pinene	0.26	-0.04	-0.17	0.89**				
sabinene	-0.81**	-0.68*	$0.90^{**}$	-0.15	-0.56			
β-myrcene	0.16	-0.04	0.29	0.54	0.45	0.11		
limonene	-0.15	0.15	0.21	-0.71*	-0.84**	0.55	-0.13	
(E)-β-ocimene	-0.74*	-0.60	$0.79^{*}$	-0.35	-0.67*	0.94**	-0.004	0.53

\*=significant at 0.05 - \*\*=significant at 0.01

#### **Results of correlation**

Simple intercorrellations between 9 peel components are presented in a correlation matrix (Table 5). The highest positive values or r (correlation coefficient) were between [(E)- $\beta$ -ocimene and sabinene (94%)]; [decanal and octanal (92%)]; [sabinene and  $\alpha$ -sinensal (90%)]. The highest significant negative correlations were between [ $\alpha$ -sinensal and octanal (87%)]; [ $\alpha$ sinensal and decanal (87%)]; [limonene and  $\alpha$ -pinene (84%)] (Table 5). Also simple intercorrellations between 6 juice characteristics are presented in a correlation matrix (Table 6). The highest positive values or r (correlation coefficient) were between [pH and TSS /TA (96%)]. The highest significant negative correlations were between [pH and TA (98%)]; [TSS/TA and TA (92%)] (Table 6).

#### DISCUSSION

Our observation that different scions or cultivars have an effect on some of the components of mandarin oil is in accordance with previous findings (Lota *et al.*, 2000; Lota *et al.*, 2001; Fanciullino *et al.*, 2006). The compositions of the peel oils obtained by cold pressing from different scions of mandarin were quite similar. However, the relative concentration of compounds was different according to the type of scion.

Comparison of our data with those in the literatures revealed some inconsistencies with previous studies (Lota *et al.*, 2000; Fanciullino *et al.*,

2006). It may be related to rootstock and environmental factors that can influence the compositions. However, it should be noticed that the extraction methods also may influence the results. Fertilizer (Rui *et al.*, 2006) and irrigation (Al-Rousan

*et al.*, 2012) affects the content of compositions present in Citrus juice. Fertilization, irrigation, and other operations were carried out uniform in this study so we do not believe that this variability is a result of these factors.

#### Table 6

Correlation matrix (numbers in this table correspond with juice quality parameters mentioned in Table 4).

	TSS (%)	TA (%)	TSS /TA	Ascorbic acid(%)	рН
TA (%)	.009				
TSS /TA	0.30	-0.92**			
Ascorbic acid(%)	-0.45	-0.86**	$0.70^{*}$		
pH	0.06	-0.98*	0.96**	$0.86^{**}$	
Juice (%)	$0.86^{**}$	0.45	-0.21	-0.83**	-0.44

\*=significant at 0.05 - \*\*=significant at 0.01

The discovery of geranyl pyrophosphate (GPP), as an intermediate between mevalonic acid and oxygenated compounds (Alcohols and aldehyds), led to a rapid description of the oxygenated compounds biosynthetic pathway. The biosynthesis pathway of oxygenated compounds in higher plants is as below:

# Mevalonic acid $\rightarrow$ Isopentenyl Pyrophosphate $\rightarrow$ 3.3-dimethylallylpyrophosphate $\rightarrow$ geranyl pyrophosphate $\rightarrow$ Alcohols and Aldehyds

This reaction pathway catalyzed by isopentenyl pyrophosphate isomerase and geranyl pyrophosphate synthase, respectively (Baghalian and Naghdabadi, 2000). The pronounced enhancement in the amount of oxygenated compounds, when Robinson used as the scion, Indicate that either the synthesis of oxygenated compounds is enhanced or activities of both enzymes increased.

High positive correlations between pairs of terpenes suggest the presence of a genetic control (Scora *et al.*, 1976) and such dependence between pairs of terpenes is due to their derivation of one from another is not known. Similarly, high negative correlations observed between  $\alpha$ -sinensal and octanal;  $\alpha$ -sinensal and decanal; limonene and  $\alpha$ -pinene suggest that one of the two compounds is being synthesized at the expense of the other or of its precursor. Non-significant negative and positive

correlations can imply genetic and/or biosynthetic independence. However, without an extended insight into the biosynthetic pathway of each terpenoid compound, the true significance of these correlations is not clear. The highest positive value (correlation) was between [(E)- $\beta$ -ocimene and sabinene (94%)]. This result indicates that these compounds should be under the control of a single dominant gene (Scora *et al.*, 1976) (Table 4).

Considering that acetate is necessary for the synthesis of terpenes, it can be assumed that there is a specialized function for this molecule and it may be better served by Robinson. Our results showed that there was a positive correlation between pH and TSS/TA (sugars). This finding was similar to previous studies (Baldwin, 2002).

#### CONCLUSION

In the present study we found that the amount of peel and juice compositions were significantly affected by scions and there was a great variation in most measured characteristics among different scions. The present study demonstrated that volatile compounds in peel and quality parameters in juice were affected by scion. Among the three scions examined, Robinson showed the highest content of TSS, TSS/TA and pH. The lowest content of TSS/TA and pH were produced by Fortune. These results indicate that there is a positive correlation between pH and TSS/TA (sugars). Studies like this is very important

to determine the amount of chemical compositions existing in the scions that we want to use, before their fruits can be used in food industries, aromatherapy, pharmacy, cosmetics, hygienic products and other areas. Further research on the relationship between scions and quality parameters is necessary.

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