



Original Article

The Effect of Mandarins (*Citrus* spp.) Scions on Peel Components and Juice Quality

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Abstract

The effects of mandarin scions on peel components and juice quality parameters were investigated in this study. Peel flavor components were extracted by using cold-press and eluted by using n-hexane. Then all analyzed by GC-FID and GC-MS. Total soluble solids, total acids, pH value, ascorbic acid as well as density and ash were determined in juice obtained from mandarin scions. Twenty-seven, Twenty-seven, thirty-five and forty peel components in Unshiu, Clementine, Minneola tangelo and Lee varieties respectively including: aldehydes, alcohols, esters, monoterpenes, sesquiterpenes and other components were identified and quantified. The major flavor components were linalool, limonene, γ -terpinene, (E) β -ocimene, β -myrcene, α -pinene. Among the four scions examined, Lee showed the highest content of aldehydes and Clementine showed the highest content of TSS/TA. Since the aldehyde and TSS/TA content of citrus are considered as two of the more important indicators of high quality, variety apparently has a profound influence on citrus quality.

Key words: Flavor components, Juice quality, Peel oil, Mandarin scions, *Citrus* spp.

Introduction

The citrus is an economically important crop cultivated extensively in Iran. The total annual citrus production of Iran was about 87000 tons in 2010 [1]. Mandarin hybrids are so variable as the result of hybridization between many fine-quality mandarins and *Citrus* species. Many of these varieties are now being used successfully for juice production and as fresh fruit. Minneola tangelo is a hybrid of Duncan grapefruit and Dancy tangerine produced in Florida by the U.S. Department of Agriculture and named in 1931. Lee Mandarin is a hybrid between the Clementine and Orlando tangelo. It has been regarded as a citrus fruit with potential commercial value because of its attractive and pleasant aroma [2]. Although Lee has pleasant aroma, the flavor components of Lee has not been investigated before. In *Citrus* L. species essential oils occur 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 used commercially for flavoring foods, beverages, perfumes, cosmetics, medicines, etc [3]. The quantity of oxygenated compounds present in the oil, is variable and depends upon a number of factors including: rootstock [4, 5], scions or varieties [6-8], seasonal variation [9], organ [10], method [11] and etc.

The quality of an essential oil may be calculated from the quantity of oxygenated compounds present in the oil. Branched aldehydes and alcohols are important flavor compounds in many food products [3].

Various studies have shown that the tangerine-like smell is mainly based on carbonyl compounds, such as α -sinensal, geranial, citronellal, decanal and perilaldehyde [12]. The quality of a honey may be

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calculated from the amount of oxygenated components present in the honey [13,14] and various flowers may influence the quality of volatile flavor components present in the honey. It had been recognized previously that oxygenated compounds are important factor in deceiving and attracting the pollinators. These results may have consequences for yield in agricultural [15,16].

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 juice sugar content and processes over 95% of its crop [17]. The greatest amounts of the high quality 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 concentration of composition such as TSS, acids and vitamin C [4]. In citrus, fruit juice content, TSS and TA concentration are the main internal quality parameters used all over the world [18]. 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 [19]. The quantity 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 [19].

Various studies have shown that the scion used may influence the quantity of chemical compositions (TSS, TA and vitamin C) present in the juice [20]. 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 scions in terms of quantity of compositions (TSS, acids and vitamin C).

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

Materials and Methods

Mandarin scions

In 1989, mandarin scions that grafted on sour orange rootstock, were planted at 8×4 m with three replication at Ramsar Citrus Research Institute

[Latitude 36° 54' N, longitude 50° 40' E; Caspian Sea climate, average rainfall 970 mm per year and average temperature 16.25 °C; soil was classified as loam-clay, pH range (6.9 to 7)]. Unshiu, Clementine, Tangelo and Lee were used as scions in this experiment (Table 1).

Preparation of peel sample

In the last week of January 2012, 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 2012, at least 10 mature fruit were collected from many parts of the same trees located in Ramsar research station. Juice was obtained by using the Indelicate Super Automatic, Type A2 104 extractor. After extraction, juice is 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 [21].

GC and GC-MS

An Agilent 6890N gas chromatograph (USA) equipped with a DB-5 (30 m ×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.

Table 1 Common and botanical names for *Citrus taxa* used as scions and rootstock [2].

Common name	Botanical name	Parents	Category
Satsuma mandarin (scion)	<i>Citrus unshiu</i> cv. Miyagawa	<i>Citrus sp.</i>	Mandarin
Clementine (scion)	<i>Citrus clementina</i> cv. Cadoux		Mandarin
Lee (scion)	<i>Citrus</i> sp. cv. Lee	(<i>Citrus reticulata</i> cv. Dancy × <i>Citrus paradisi</i> cv. Duncan) × (<i>Citrus clementina</i> cv. Cadoux)	Mandarin hybrid
Honeybell tangelo (scion)	<i>Citrus</i> sp. cv. Honeybell	(<i>Citrus reticulata</i> cv. Dancy × <i>Citrus paradisi</i> cv. Duncan)	Tangelo
Sour orange (Rootstock)	<i>Citrus aurantium</i>	<i>Citrus reticulata</i> × <i>Citrus grandis</i>	Sour orange

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-alkenes (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.

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 µL.

Identification of components

Components were identified by comparing their LRIs and matching 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. Identifications were also determined by comparing the retention time of each compound with that of known compounds [22,23].

Data analysis

SPSS 18 was used for analysis of the data obtained from the experiments. Analysis of variations was based on the measurements of 7 peel component and 6 juice characteristics. Variations among and within scions were analyzed using analysis of variance (ANOVA)-one way. Correlation between pairs of characters and altitude was evaluated using Pearson's correlation coefficient.

Results

Flavor compounds of the 'Unshiu' mandarin peel

GC-MS analyze of the flavor compounds extracted from 'Unshiu' mandarin peel by using cold-press allowed identification of 27 volatile components (Table 2) : 6 oxygenated terpenes [2 aldehydes, 3 alcohols, 1 esters], 21 non oxygenated terpenes [11 monoterpenes, 10 sesquiterpenes].

Flavor compounds of the 'Clementine' mandarin peel GC-MS analyze of the flavor compounds extracted from 'Clementine' mandarin peel by using cold-press allowed identification of 27 volatile components (Table 2): 12 oxygenated terpenes [9 aldehydes, 3 alcohols], 15 non oxygenated terpenes [6 monoterpenes, 9 sesquiterpenes].

Flavor compounds of the 'Minneola tangelo' peel GC-MS analyze of the flavor compounds extracted from 'Minneola tangelo' peel by using cold-press allowed identification of 35 volatile components (Table 2, Fig 1): 13 oxygenated terpenes [6 aldehydes, 4 alcohols, 3 esters], 21 non oxygenated terpenes [10 monoterpenes, 11 Sesquiterpenes] and 1 other compound.

Flavor compounds of the 'Lee' mandarin peel GC-MS analyze of the flavor compounds extracted from 'Lee' mandarin peel by using cold-press allowed identification of 40 volatile components (Table 2) : 20 oxygenated terpenes [13 aldehydes , 5 alcohols , 2 esters], 19 non oxygenated terpenes [11 monoterpenes, 8 Sesquiterpenes] and 1 other compound.

Aldehydes

Thirteen aldehyde components that identified in this analysis were octanal, nonanal, citronellal, decanal, neral , (E)-2-decanal, geranial, perillaldehyde, undecanal, (E)2,4-decadienal, dodecanal, β-sinensal and α-sinensal (Table 3). In addition they were quantified [from 0.09% to 0.81%] that it was determined and reported as relative amount of those compounds in oil. The concentrations of 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 [12]. Among the four scions examined, Lee showed the highest content of aldehydes (Table 3). Since the aldehyde content of citrus oil is considered as one of the more important indicators of high quality, scion apparently has a profound influence on mandarin oil quality.

Lee aldehydes were also compared to those of Unshiu, Clementine and Tangelo in this study. Neral, (E)-2-decanal, undecanal, (E) 2,4-decadienal were identified in Lee, while they were not detected in Unshiu, Clementine and Tangelo. Compared with Unshiu, the Lee improved and increased aldehyde components about 9 times (Table 3).

Alcohols

Six alcohol components identified in this analysis were linalool, terpinene-4-ol, α -terpineol, β -citronellol, thymol, elemol (Table 3). The total amount of alcohols ranged [from 0.36% to 1.02%] that it was determined and reported as relative amount of those compounds in oil. Linalool was 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 peel oil flavor. Linalool has a flowery aroma [12] and its level is important to flavor character in mandarin peel oil [3]. Among the four varieties examined, Lee showed the highest content of alcohols (Table 3).

Lee alcohols were also compared to those of Unshiu, Clementine and Tangelo in this study. Terpinene-4-ol and β -citronellol were identified in Lee, while they were not detected in Unshiu, Clementine and Tangelo. Compared with Unshiu, Lee improved and increased alcohol components about 3 times (Table 3).

Esters

Three ester components identified in the analysis were citronellyl acetate, neryl acetate, geranyl acetate. The total amount of esters ranged [from 0.00% to 0.08%]. Among the four scions examined, Tangelo showed the highest content of esters in oil (Table 3).

Monoterpenes hydrocarbons

The total amount of monoterpene hydrocarbons ranged [from 95.69 % to 97.91 %]. Limonene was the major component among the monoterpene hydrocarbons of mandarin peel oil. Limonene has a weak citrus-like aroma [12] and is considered as one of the major contributors to mandarin flavor [3]. Among the four scions examined, Clementine had the highest monoterpenes hydrocarbons in oil (Table 3).

Sesquiterpenes hydrocarbons

The total amount of sesquiterpene hydrocarbons ranged [from 0.13 % to 1.09 %]. Germacrene D, δ -cadinene and β -elemene were the major components among the sesquiterpen hydrocarbons of mandarin peel oil. Among the four scions examined, Unshiu had the highest sesquiterpenes content in oil (Table 3).

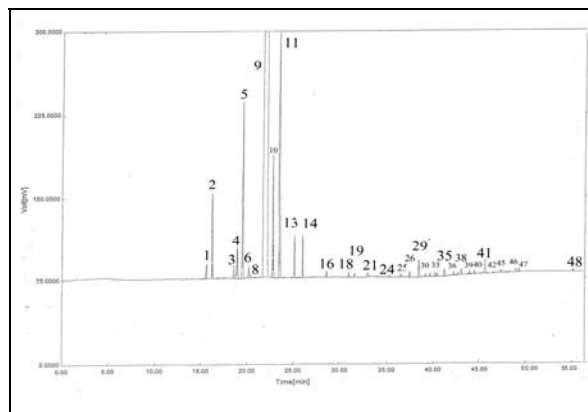


Fig 1 HRGC chromatograms of 'Minneola tangelo' peel oil.

Juice quality parameters

Juice quality parameters are given in table 4. Brix (total soluble solids) was from 9.00 % (Unshiu) to 10.00 % (Minneola tangelo) and the content of total acidity was from 0.44% (Clementine) to 1.82% (Minneola tangelo). TSS/TA rate was from 5.49% (Minneola tangelo) to 22.72% (Clementine). Ascorbic acid was from 29.57 % (Unshiu) to 53.33% (Clementine). The pH value was from 2.96 % (Minneola tangelo) to 4.02% (Clementine). The juice yield was from 60.52% (Minneola tangelo) to 79.33% (Unshiu). Total dry matter was from 12.83% (Unshiu) to 16.01% (Clementine). Ash was 3 % for all samples. Among the four scions examined, Clementine showed the highest content of TSS /TA, pH and Ascorbic acid. The lowest of TSS /TA, pH and juice content were produced by Minneola tangelo. Among scion selections, Unshiu had the highest juice content. (Table 4).

Results of statistical analyses

Statistical analysis was performed on the peel and juice data using SPSS 18. The Duncan's multiple range tests was used to separate the significant scions. Among all analyzed compounds, 12 showed statistically significant differences due to the influence of different scions. These differences on the 1% level occurred in decanal, linalool, α -pinen, sabinene, limonen, ocimene, TSS, TA, TSS /TA, ascorbic acid, pH, juice yield. The non affected oil component was β -myrcen and it is provided only for convenience of the reader (Table 3 and 4).

Table 2 Peel volatile components of mandarin scions. (*There is in oil).

	Component	Unshiu	Clementine	Tangelo	Lee	KI
1	α - thujene	*	-	*	*	928
2	α -pinene	*	*	*	*	935
3	Sabinene	*	*	*	*	975
4	β -pinene	*	*	*	*	979
5	β -myrcene	*	*	*	*	991
6	Octanal	-	*	*	*	1003
7	α -phellandrene	*	-	-	-	1006
8	α -terpinene	*	-	*	*	1012
9	Limonene	*	*	*	*	1036
10	(E)- β -ocimene	*	*	*	*	1049
11	γ - terpinene	*	-	*	*	1061
12	(E)sabinene hydrate	-	-	-	*	1065
13	α -terpinolene	*	-	*	*	1091
14	Linalool	*	*	*	*	1100
15	Nonanal	-	*	-	*	1109
16	Citronellal	*	*	*	*	1154
17	Terpinene-4-ol	-	-	-	*	1182
18	α -terpineol	*	*	*	*	1195
19	Decanal	*	*	*	*	1205
20	β -citronellol	-	-	-	*	1229
21	Thymol methyl ether	-	-	*	*	1236
22	Neral	-	-	-	*	1244
23	(E)-2-decenal	-	-	-	*	1263
24	Geranial	-	*	*	*	1275
25	Perilla aldehyde	-	*	*	*	1282
26	Thymol	-	-	*	*	1291
27	Undecanal	-	-	-	*	1307
28	(E)2,4-decadienal	-	-	-	*	1322
29	δ -elemene	*	-	*	*	1344
30	Citronellyl acetate	-	-	*	-	1350
31	Neryl acetate	-	-	*	*	1356
32	α -copaene	*	*	*	-	1373
33	Granyl acetate	*	-	*	*	1382
34	β -cubebene	-	*	-	-	1388
35	β -elemene	*	*	*	*	1399
36	Dodecanal	-	*	-	*	1409
37	(Z)- β -caryophyllene	*	-	*	-	1431
38	γ -elemene	*	-	*	*	1440
39	(Z)- β -farnesene	-	*	*	*	1458
40	α -humulene	*	*	*	-	1466
41	Germacrene D	*	*	*	*	1493
42	Valencene	-	-	*	-	1499
43	Bicyclogermacrene	*	*	-	-	1504
44	(E,E)- α -farnesene	*	*	-	*	1523
45	δ -cadinene	*	*	*	*	1532
46	Elemol	*	*	*	*	1559
47	Germacrene B	-	-	*	*	1572
48	β -sinensal	-	*	*	*	1704
49	α -sinensal	-	*	-	*	1756
-	-	27	27	35	40	-

Table 3 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	Unshiu		Clementine		Minneola tangelo		Lee		F value
	Mean	St.err	Mean	St.err	Mean	St.err	Mean	St.err	
Oxygenated compounds									
a) Aldehyds	-	-	-	-	-	-	-	-	-
1) Octanal	-	-	0.27	0.02	0.16	0.04	0.34	0.03	-
2) Nonanal	-	-	0.01	0.006	-	-	0.09	0.01	-
3) Citronellal	0.02	0	0.07	0.006	0.07	0.01	0.07	0	-
4) Decanal	0.07	0.01	0.19	0.02	0.05	0.006	0.2	0.01	F**
5) Neral	-	-	-	-	-	-	0.01	0.001	-
6) (E)-2-decanal	-	-	-	-	-	-	0.007	0.003	-
7) Geranial	-	-	0.01	0	0.01	0	0.01	0.006	-
8) Perilla aldehyde	-	-	0.01	0	0.01	0.006	0.02	0	-
9) Undecanal	-	-	-	-	-	-	0.008	0.002	-
10) (E)2,4-decadienal	-	-	-	-	-	-	0.007	0.003	-
11) Dodecanal	-	-	0.03	0.006	-	-	0.02	0.006	-
12) β -sinensal	-	-	0.01	0.006	0.01	0.006	0.01	0	-
13) α -sinensal	-	-	0.17	0.01	-	-	0.02	0.01	-
Total	0.09	0.01	0.77	0.07	0.31	0.06	0.81	0.08	-
b) Alcohols	-	-	-	-	-	-	-	-	-
1) Linalool	0.310	0.030	0.570	0.020	0.350	0.050	0.880	0.110	F**
2) Terpinen-4-ol	--	-	-	-	-	-	0.010	0.000	-
3) α -terpineol	0.040	0.006	0.030	0.000	0.070	0.010	0.090	0.006	-
4) β -citronellol	-	-	-	-	-	-	0.010	0.006	-
5) Thymol	-	-	-	-	0.040	0.000	0.030	0.006	-
6) Elemol	0.010	0.010	0.030	0.010	0.030	0.010	-	-	-
Total	0.36	0.04	0.63	0.03	0.49	0.07	1.02	0.12	-
c) Esters	-	-	-	-	-	-	-	-	-
1) Citronellyl acetate	-	-	-	-	0.02	0	-	-	-
2) Neryl acetate	-	-	-	-	0.04	0.006	0.008	0.002	-
3) Granyl acetate	0.03	0	-	-	0.02	0	0.008	0.001	-
total	0.03	0	-	-	0.08	0.006	0.01	0.003	-
Monoterpenes									
1) α -thujene	0.15	0.03	-	-	0.12	0.02	0.23	0.01	-
2) α -pinene	0.8	0.13	0.51	0.01	0.75	0.09	1.04	0.09	F**
3) Sabinene	0.14	0.006	0.6	0.09	0.13	0.006	0.46	0.07	F**
4) β -pinene	0.35	0.1	0.03	0	0.32	0.1	0.55	0.04	-
5) β -myrcene	1.44	0.29	1.72	0.07	1.53	0.17	1.75	0.15	NS
6) α -phellandrene	0.05	0	-	-	-	-	-	-	-
7) α -terpinene	0.02	0.01	-	-	0.02	0.01	0.01	0.006	-
8) Limonene	87.09	0.53	94.19	0.71	88.91	1.88	84.85	1.16	F**
9) (E)- β -ocimene	0.47	0.1	0.86	0.35	1.13	0.43	1.01	0.07	F**
10) γ -terpinene	4.97	0.97	-	-	4.47	0.85	6.8	0.72	-
11) (E)-sabinene hydrate	-	-	-	-	-	-	0.2	0.06	-
12) α -terpinolene	0.21	0.006	-	-	0.33	0.13	0.45	0.006	-
Total	95.69	2.17	97.91	1.23	97.71	3.68	97.35	2.38	-
Sesquiterpenes									
1) δ -elemene	0.17	0.02	-	-	0.15	0.01	0.04	0.006	-
2) α -copaene	0.04	0	0.04	0	0.02	0	-	-	-
3) β -cubebene	-	-	0.02	0.006	-	-	-	-	-
4) β -elemene	0.49	0.02	0.01	0.01	0.08	0.006	0.01	0.006	-
5) (Z)- β -caryophyllene	0.04	0.006	-	-	0.02	0.006	-	-	-
6) γ -elemene	0.03	0.006	-	-	0.09	0.02	0.01	0.006	-
7) α -humulene	-	-	0.01	0	0.01	0	0.01	0.006	-
8) (Z)- β -farnesene	0.05	0.006	0.01	0.006	0.01	0.006	-	-	-
9) Germacrene D	0.17	0.01	0.02	0	0.1	0.01	0.04	0	-
10) Valencene	-	-	-	-	0.003	0.001	-	-	-
11) Bicyclogermacrene	0.01	0.006	0.01	0	-	-	-	-	-
12) E,E- α -farnesene	0.06	0.006	0.01	0	-	-	0.004	0.002	-
13) δ -cadinene	0.03	0.006	0.02	0.006	0.01	0.006	0.008	0.002	-
14) Germacrene B	-	-	-	-	0.03	0.01	0.01	0	-
Total	1.09	0.08	0.15	0.02	0.52	0.07	0.13	0.02	-
Other compounds									
1)Thymol methyl ether	-	-	-	-	0.05	0.006	0.05	0.006	-
Total oxygenated compounds	0.48	0.05	1.4	0.1	0.88	0.13	1.84	0.2	-
Total	97.26	2.3	99.46	1.35	99.16	3.89	99.37	2.6	-

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.

Scion	TSS (%)	Total Acids (%)	TSS /TA rate	Ascorbic acid (%)	pH	Juice (%)	Total dry matter (%)	Ash (%)
Unshiu (scion)	9	1.05	8.57	29.57	3.23	79.33	12.83	3
Clementine (scion)	9.8	0.44	22.27	53.33	4.02	70.33	16.01	3
Minneola tangelo (scion)	10	1.82	5.49	34.85	2.96	60.52	15.53	3
Lee(scion)	9.6	0.75	12.8	39.78	3.6	74.5	15.38	3
-	F**	F**	F**	F**	F**	F**	-	-

Table 5 Correlation matrix (numbers in this table correspond with main components mentioned in Table 3).

-	Decanal	Linalool	α -pinene	Sabinene	β -myrcene	Limonene
Linalool	0.85**	-	-	-	-	-
α -pinene	0.06	0.49	-	-	-	-
Sabinene	0.92**	0.70**	-0.20	-	-	-
β -myrcene	0.69*	0.68*	0.32	0.60*	-	-
Limonene	0.15	-0.29	-0.92**	0.41	-0.007	-
(E)- β -ocimene	0.19	0.33	0.21	0.07	0.51	-0.10

*=significant at 0.05, **=significant at 0.01

Table 6 Correlation matrix (numbers in this table correspond with juice quality parameters mentioned in Table 4).

-	TSS (%)	TA (%)	TSS /TA	Ascorbic acid (%)	pH
TA (%)	0.24	-	-	-	-
TSS /TA	0.15	-0.88**	-	-	-
Ascorbic acid (%)	0.51	-0.66*	0.92**	-	-
pH	0.09	-0.92**	0.97**	0.87**	-
Juice (%)	-0.88**	-0.61*	0.20	-0.17	0.30

*=significant at 0.05, **=significant at 0.01

Results of correlation

Simple intercorrelations between 7 components are presented in a correlation matrix (Table 5). The highest positive values or r (correlation coefficient) were between [sabinene and decanal (92%)]; [linalool and decanal (85%)]; [sabinene and linalool (70%)]. The highest significant negative correlations were between [limonene and α -pinene (92%)] (Table 5).

Also simple intercorrelations 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 (97%)]; [Ascorbic acid and TSS /TA (92%)]; [pH and Ascorbic acid (87%)]. The highest significant negative correlations were between [pH and TA (92%)] ; [TSS /TA and TA (88%)] ; [Juice and TSS (88%)] (Table 6).

Discussion

Our observations that different scions/varieties have an effect on some of the components of mandarin oil are accord with other observations [6-8]. The

compositions of the peel oils obtained by cold pressing from different scions of mandarin were very similar. However, relative concentration of compounds differed according to type of scion.

A comparison of our data with those in the literatures revealed that some of the components identified in our study are not compatible with the published one for Unshiu [6]. Also comparisons of our data with those in the literatures revealed that content of the juice compositions in our study are not agree with previously published for Unshiu and Clementine [20]. It may be related to rootstock and environmental factors that can influence compositions. However, it should be kept in mind that the chemical methods also have an effect on content of the peel and juice compositions. Fertilizer [24] and irrigation [25] 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 results from these factors.

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 major pathway of oxygenated compounds biosynthesis in higher plants is as below:

Mevalonic acid → Isopentenyl Pyrophosphate → 3.3-dimethylallylpyrophosphate → geranyl pyrophosphate → Alcohols and Aldehyds

The steps in the pathway are catalyzed by isopentenyl pyrophosphate isomerase and geranyl pyrophosphate synthase, respectively [26]. The pronounced enhancement in the amount of oxygenated compounds, when Lee was used as the scion, showed that either the synthesis of geranyl pyrophosphate is enhanced or activities of both enzymes increased.

High positive correlations between two terpenes such as [sabinene and decanal (92%)]; [linalool and decanal (85%)]; [sabinene and linalool (70%)] suggest a genetic control [27]. Whether such dependence between two terpenes is due to their derivation of one from another is not known. Similarly, high negative correlations observed between [limonene and α -pinene (92%)] 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 a thorough knowledge of the Biosynthetic pathway leading to each terpenoid compound, the true significance of these observed correlations is not clear. The highest positive value (correlation) was between [sabinene and decanal (92%)]. This result indicated which these compounds were under the control of a single dominant gene [27].

Due to the fact that acetate is necessary for the synthesis of terpenes, leads us to believe that there is a specialized function for this interesting molecule and that this molecule may be better served and utilized when Lee is used as the scion. Our results show that there is a positive correlation between TSS/TA and pH. These doses agree with previously published [28].

Conclusion

In the present study we found that the amount of peel and juice compositions were significantly affected by scions and there is a great variation in most of the measured characters among different scions. The present study demonstrated that volatile compounds in peel and quality parameters in juice can vary when different scions are utilized. Among the four scions examined, Clementine showed the highest content of TSS /TA, pH and ascorbic acid. The lowest of TSS

/TA, pH and juice content were produced by Minneola tangelo. These results show that there is a positive correlation between TSS/TA and pH. Many studies, such as this study is very crucial in order to determine the amount of chemical compositions existing in the scions that we want to use, before their fruits can be utilized 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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References

1. FAO. Statistical Database. Available from <<http://www.fao.org>> Accessed 23 February 2012.
2. Fotouhi- Ghazvini R, Fattahi- moghadam J. Citrus growing in Iran, Guilan University. 2007
3. Salem A. Extraction and identification of essential oil components of the peel, leaf and flower of tangerine "Citrus nobilis loureior var deliciosa swingle" cultivated at the north of Iran. Master of science thesis, Islamic Azad University, Pharmaceutical Sciences Branch, 2003.
4. Babazadeh- Darjazi B, Rustaiyan A, Talaei A, Khalighi A, Larijani K, Golein B, Taghizad R. The effects of rootstock on the volatile flavor components of page mandarin juice and peel. Iranian J Chem Chem Eng. 2009;28:99-111.
5. Babazadeh- Darjazi B. The effects of rootstock on the volatile flavour components of page mandarin flower and leaf. Afr J Agric Res. 2011;6:1884-1896.
6. Lota ML, Serra D, Tomi F, Casanova J. Chemical variability of peel and leaf essential oils of 15 species of mandarins. Biochem Syst Ecol. 2001;29:77-104.
7. Lota ML, Serra D, Tomi F, Casanova J. Chemical variability of peel and leaf essential oils of mandarins from *Citrus reticulata* Blanco. Biochem Syst Ecol. 2000;28:61-78.
8. Fanciullino AL, Tomi F, Luro F, Desjobert JM, Casanova J. Chemical variability of peel and leaf oils of mandarins. Flavour Fragr J. 2006;21:359-367.
9. Babazadeh- Darjazi B, Rustaiyan A, Taghizad R, Golein B. A study on oxygenated constituent's percentage existed in page mandarine peel oil during a special season. J Med Plant. 2011; 4:87-93.

10. Babazadeh- Darjazi B. Comparison of volatile components of flower, leaf, peel and juice of 'Page' mandarin. *Afr J Biotechnol.* 2011;10:10437-10446.
11. Babazadeh -Darjazi B. A comparison of volatile components of flower of page mandarin obtained by ultrasound-assisted extraction and hydrodistillation. *J Med Plant Res.* 2011;5:2840-2847.
12. Buettner A, Mestres M, Fischer A, Guasch J, Schieberie P. Evaluation of the most odor-active compounds in the peel oil of clementines (*Citrus reticulata* blanco cv. Clementine). *Eur Food Res Technol.* 2003;216:11-14.
13. Alissandrakis E, Daferera D, Tarantilis PA, Polissiou M, Harizanis PC. Ultrasound assisted extraction of volatile compounds from *Citrus* flowers and *Citrus* honey. *Food Chem.* 2003;82:575-582.
14. Alistair LW, Yinrong LU, Seng-To T. Extractives from New Zealand honey 4.linalool derivatives and other components from nodding thistle (*Corduus nutans*) honey. *J Agric Food Chem.* 1993;41:873-878.
15. Kite G, Reynolds T, Prance T. Potential pollinator – attracting chemicals from Victoria (Nymphaeaceae) .*Biochem syst Ecol.* 1991;19:535-539.
16. Andrews ES, Theis N, Alder LS. Pollinator and herbivore attraction to cucurbita floral volatiles. *J Chem Ecol.* 2007;33:1682-1691.
17. Rouse RE. *Citrus* fruit quality and yield of six Valencia clones on 16 rootstocks in the Immokalee foundation grove. *Proc Fla State Hort Soc.* 2000;113:112-114.
18. Antonucci F, Pallottino F, Paglia G, Palma A, Aquino SD, Menesatti P. Non-destructive estimation of mandarin maturity status through portable VIS-NIR spectrophotometer. *Food Bioprocess Technol.* 2011;4:809–813.
19. Hardy S, Sanderson G. Citrus maturity testing. *Primefact.* 2010; 980:1-6.
20. Nematollahi C. Evaluation the effect of Citrumelo Swingle rootstock on quantitative and qualitative characteristics in mandarins and orange varieties. Iran Citrus Research Institute, Final Report of Project, 2005.
21. Majedi M. Food chemical analysis methods, University Jihad, 1994.
22. Adams RP. Identification of essential oil components by gas chromatography/mass spectrometry, Allured Publishing Corporation, Carol Stream, Illinois, USA, 2001.
23. McLafferty FW, Stauffer DB. The important peak index of the registry of mass spectral data, Wiley, 1991.
24. Rui W, Xue-gen S, You-zhangl W, Xiao-ei Y, Juhani U. Yield and quality responses of citrus (*Citrus reticulata*) and tea (*Podocarpus fleuryi* Hickel) to compound fertilizers. *J Zhejiang Uni Sci B.* 2006; 7:696-701.
25. Al-Rousan WMM, Ajo RY, Angor MM, Osaili T, Bani-Hani NM. Impact of different irrigation levels and harvesting periods on the quantity and quality of Navel oranges (*Citrus sinensis*) and fruit juice. *J Food Agric Environ.* 2012;10:115-119.
26. Hay RKM, Waterman P. Volatile oil crops; their biology, biochemistry and production, Wiley-Blackwell. 1995.
27. Scora RW, Esen A, Kumamoto J. Distribution of essential oils in leaf tissue of an F2 population of Citrus. *Euphytica* 1976;25:201-209.
28. Baldwin E A, Fruit flavor, volatile metabolism and consumer perceptions. In: Knee M (eds.) Fruit quality and its biological basis, CRC Press LLC Publication, 2002;89–106.