PAPER

VOLATILES AND ACCEPTABILITY OF LIQUEURS FROM KUMQUAT AND GRAPEFRUIT

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ABSTRACT

The aim of this work was to produce liqueurs from "minor" citrus fruits, such as kumquat and grapefruit, characterize their volatile fraction and evaluate their acceptability by a consumer test. A *limoncello* sample (LP) was produced under the same conditions and used for comparison. All the new liqueurs were found to be richer in limonene and poorer in oxygenated compounds than the LP. The volatile fraction was mostly represented (85%) by limonene in grapefruit liqueur. Liqueur from kumquat peel (KP) was the richest in volatile compounds, whereas the one from kumquat whole fruit (KWF) was the poorest. This latter also had the particular feature to be the richest in sesquiterpene alcohols. Octanal and decanal, and two acetals deriving from these aldehydes (1,1-diethoxyoctane and 1,1-diethoxydecane) were most prevalent in KP and LP. The consumer test showed that all liqueurs were judged to be acceptable. Nevertheless, *limoncello* remained the most preferred, while the KWF liqueur obtained the best flavour score in the group of minor citrus fruits.

Keywords: consumer acceptance, grapefruit, kumquat, liqueur, volatile compounds

1. INTRODUCTION

Citrus fruits are either consumed as fresh or processed to obtain juices, jams and, in small amounts, to produce liqueurs such as the so-called *rosolio. Rosolios* are liqueurs obtained by alcoholic maceration of flowers or fruits with the final addition of water and sugar. The most famous Italian *rosolio* made from citrus fruits, is *limoncello.* It is highly requested on the international market and it is manufactured by the alcoholic maceration of lemon (*Citrus limon* L.) peel. The composition of the volatile fraction plays a fundamental role in the development of citrus liqueurs aroma. In particular, the ratios carbonyls-to-oxygenated compounds, alcohols-to-oxygenated compounds, and esters-to-oxygenated compounds are indices of flavouring quality (POIANA *et al.*, 2006). Several investigations have been carried out on the volatile compounds of *limoncello* in order to find the molecular markers to establish quality and genuineness. VERSARI *et al.* (2003) reported that the addition of essential oils to *limoncello* causes an increase of oxygenated compounds and a loss of hydrocarbons. They also reported that compounds such as ethyl acetate, acetaldehyde, and 2-methyl-1-propanol should be related to the occurrence of microbiological activity in the sugar syrup. CRUPI *et al.* (2007) found differences in terms of type, amount, and variation range of volatile compounds in 12 commercial *limoncello* samples and in 2 types of *limoncello* produced in a laboratory. POIANA *et al.* (2006) reported variations in the volatile profiles of the alcoholic extract of lemon fruit to be a function of the geographic area and season. Besides *limoncello*, there are only a few liqueurs made from citrus fruits, such as r*osolio* from tangerine and orange, mainly produced for local markets. To our knowledge, no effort has been made for producing liqueurs from "minor" citrus fruits, such as kumquat (*Fortunella margarita* L.) and grapefruit (*Citrus paradisi* L.).

Kumquat is a vigorous and prolific small bushy tree that produces oval or round fruits with a smooth, bright orange rind (BARRECA *et al.*, 2011). Unlike other citrus fruits, kumquat fruit is eaten without discarding the peel, and this has nutritional relevance since this part is particularly rich in flavonoids (GATTUSO *et al.*, 2007; TRIPOLI *et al.*, 2007). Many citrus flavonoids exhibit antioxidant activity, inhibit angiogenesis, and slow down cancer cell migration and proliferation (BARRECA *et al.*, 2009; BENAVENTE-GARCÍA and CASTILLO, 2008). There are only a few studies on the volatile constituents of kumquat. BERNHARD and SCRUBIS (1961) found limonene to be the most abundant compound in kumquat oil extracted by steam distillation. Aldehydes, ketones, free alcohols, terpene esters, α-pinene, and myrcene were also reported in this study. KOYASAKO and BERNHARD (1983) identified 71 volatiles in oil obtained by simultaneous distillation and extraction; UMANO *et al.* (1994) reported 84 volatiles in steam-distillation extracts; CHOI (1995) identified 82 volatiles in oil extracted by cold pressing. More recently, PENG *et al.* (2013) identified a total of 43 compounds in the volatile fractions of kumquat essential oils extracted by different methods. The principal constituents of the oils were similar, and differences were only found for minor compounds such as linalool, terpinen-4-ol and α-terpineol.

Grapefruit is a citrus fruit that contributes to human health mainly thanks to its high contents of ascorbic acid and fiber (PEIRÓ *et al.*, 2006). Unfortunately, the presence of some flavonoids, such as naringin, is responsible for the bitter taste that limits acceptance by consumers. Nevertheless, fresh or processed grapefruit may be conveniently mixed with other foods to formulate desirable and wholesome products.

The present study aimed to assess the possibility of using kumquat and grapefruit for the production of innovative types of *rosolio*. The experimental liqueurs were produced on a laboratory-scale and were subjected to volatile profile characterization by headspace-solid

phase microextraction (HS-SPME) and evaluation of consumer acceptance in comparison with *limoncello*.

2. MATERIALS AND METHODS

2.1. Liqueur making

Fresh fruit peels were utilized for the preparation of kumquat (*Fortunella margarita*) (KP), grapefruit (*Marsh seedless*) (GP), and lemon (*Femminello comune*) (LP) liqueurs. For this purpose, about 500 g of each fruit was accurately peeled, and the peels, consisting of the flavedo part, were put into a jar containing 500 mL of ethanol (95% v/v) and left to steep for 2 weeks. After this period, the peels were taken out of the alcohol and syrup made with 500 mL of water plus 400 g of sugar was added to the ethanol extract. The liqueurs obtained were let to rest for 2 months in the dark at room temperature for maturation. During preparation, it was observed that peeling the kumquat was very difficult, due to the small size of the fruit (about 15 g). In order to assess the possibility of avoiding such step, a liqueur from the maceration of the whole fruit (KWF) was also prepared. In this latter preparation, 500 g of the fruit was directly put into 500 mL of ethanol (95% v/v) and left to steep for 2 weeks; then the preparation followed the same steps as described for the other liqueurs.

2.2. Volatile fraction extraction and GC/MS analysis

Headspace-solid phase microextraction (HS-SPME) was chosen as the extraction technique for the present study, since it had been successfully applied to determine the volatile composition of kumquat essential oils (PENG *et al.*, 2013) and lemon liquor (CRUPI *et al.*, 2007). Volatile compounds were extracted using a preconditioned 2-cm-long 50/30 mm divinylbenzene/carboxen/polydimethylsiloxane fiber (Supelco, Bellefonte, Pa., U.S.A.). Two mL of each liqueur were put in a 12-mL crimped vial, with 0.4 g NaCl added, and conditioned for 10 min at 37°C and stirred with a magnetic bar. Then the fiber was exposed in the headspace of the vial for 20 min. Desorption of analytes from the SPME fiber took place in a split/splitless injector set at 250°C with a split ratio of 1:25 using a 3 min desorption time. Separation of volatile compounds was performed using an Agilent 6890 gas chromatograph (GC) coupled with an Agilent 5975 mass spectrometer (MS) (Agilent, Wilmington, Del., U.S.A.) using a HP5-MS column (30 m × 0.25 mm × 0.25 mm). The chromatographic conditions were: (i) oven, 40°C (2 min) to 190°C at 5°C min^{-1}, to 230°C at 15°C min^{-1}, held 2 min; (ii) detector, source temperature 240°C; transfer line temperature 240°C; (iii) carrier gas, helium at constant flow of 1.0 mL min^{-1}. The impact energy was 70 eV. Data were acquired using full-scan mode in the range of 20-250 m/z at an acquisition rate of 5 Hz. Volatile compounds were tentatively identified by comparing the experimental spectra with those reported in the NIST Library and with those obtained by pure external standard injection when available. Each sample was analyzed in triplicate and results were reported as a mean of area counts x 10^6. The repeatability of the SPME-GC/MS method was lower than 10% in terms of relative standard deviation (RSD).

2.3. Acceptance and preference testing

The consumer test was carried out in a conference room where temporary partitions were erected to create isolated booths able to separate testers during analysis, in compliance with the Standard no. 8589 of the International Organization for Standardization (ISO

1988). Testing was performed at room temperature (20 °C) with appropriate and adequate artificial lighting, simulating daylight. A total of 75 consumers (age 19–47, mean 23.1; 45 males and 30 females) were recruited to participate in the consumer test. A 3-digit random code was assigned to the liqueurs, which were served at room temperature in 80-mL white polyethylene glasses. For each sample, about 10 mL was served. Mineral water was at each participant's disposal to cleanse mouth during testing. The evaluation form used had 3 sections: the first required information about the sex and age of the panelists; the second section required the evaluation of color, odor, and flavor using a 6-point hedonic scale (1 = extremely dislike; 6 = like extremely); the last section asked the consumers to rank the samples according to overall appreciation. The use of flavor, instead of taste, as a sensorial descriptor was chosen because our purpose was to assess the blend of taste and smell sensations evoked in the mouth.

2.4. Statistical analysis

The results of color, odor, and flavor assessment were subjected to a one-way analysis of variance (ANOVA). Moreover, differences in the preference rank sums between all possible pairs of products were considered. Should any of these (absolute) differences exceed a critical value, the preferences for that pair of products would differ from one another at the stated statistical significance level (n = 75, $P \leq 0.05$, critical value = 40.6) (BASKER, 1988).

3. RESULTS AND DISCUSSIONS

3.1. Volatile fraction

Figures 1 and 2 show the total ion current profile of volatile compounds of liqueurs obtained from kumquat peel (Fig. 1A), kumquat whole fruit (Figure 1B), grapefruit peel (Fig. 2A), and lemon peel (Fig. 2B). Clearly, the 4 liqueurs were different under a qualitative point of view.

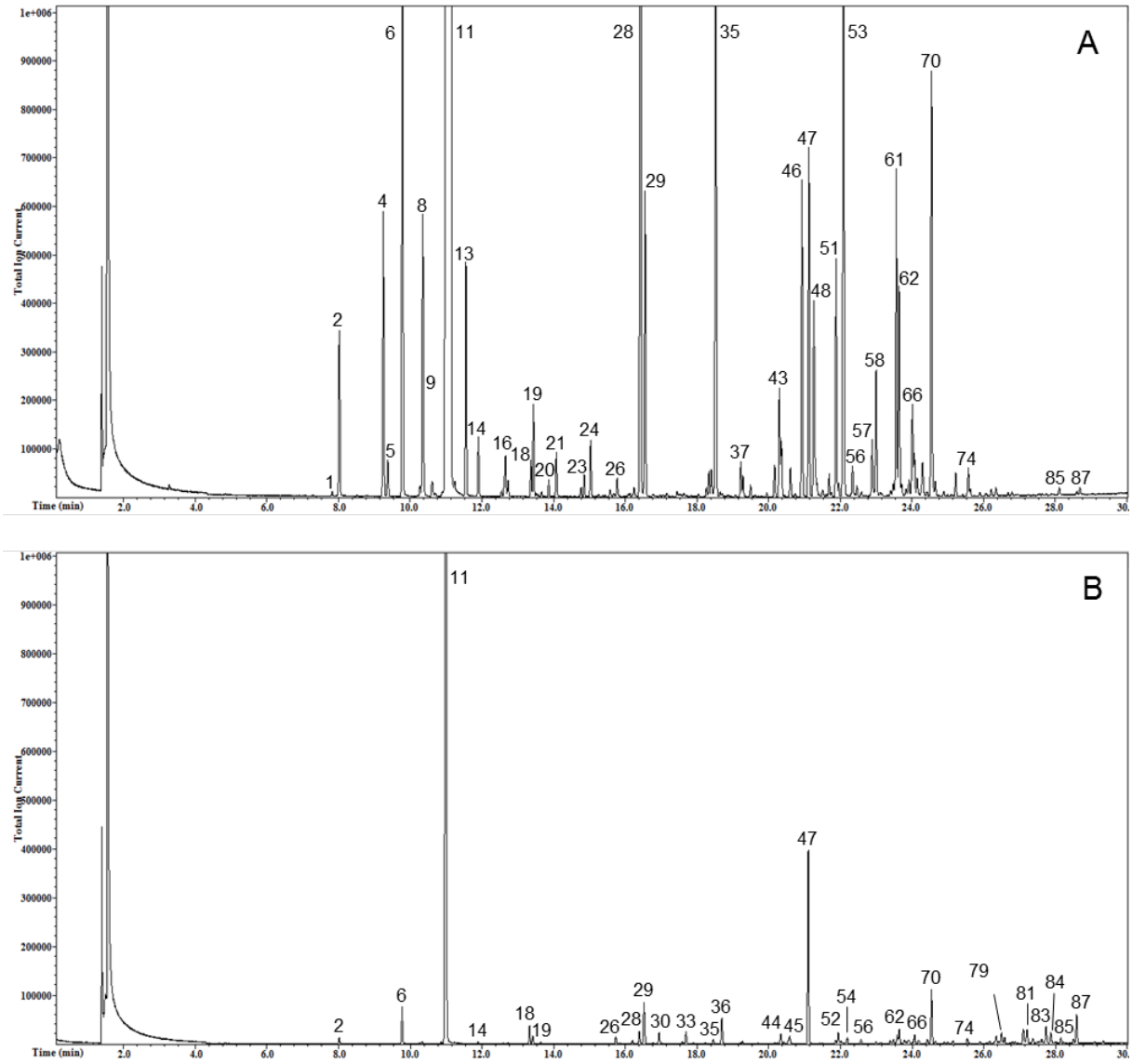

Figure 1: SPME-GC/MS profiles of kumquat peel liqueur (A) and kumquat whole fruit liqueur (B). The peak numbers refer to the compounds in Table 1.

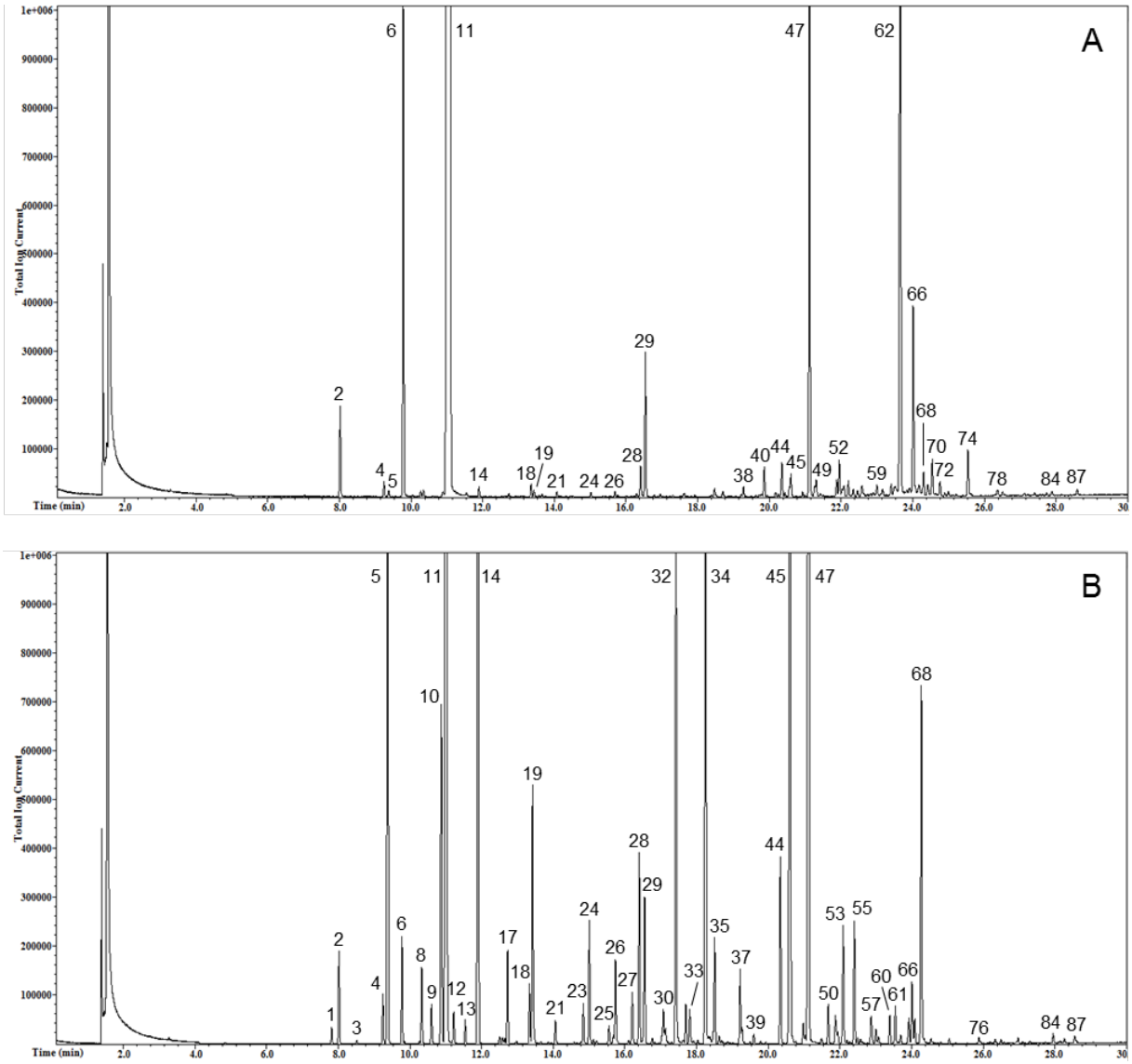

Figure 2: SPME-GC/MS profiles of grapefruit peel liqueur (A) and lemon peel liqueur (B). The peak numbers refer to the compounds in Table 1.

Table 1 summarizes the mean values for the volatile compounds expressed as both absolute and relative percentage area. The total area and the sums of the areas of monoterpenes (MTs), sesquiterpenes (STs), and oxygenated compounds (OCs) are also reported in Table 1.

Table 1: Volatile composition of liqueurs.

No.	Compound	KP		KWF		GP		LP		[b]ID
		[a]Area	%	Area	%	Area	%	Area	%	
1	α-Thujene	0.20	0.01	-	-	-	-	0.50	0.07	MS
2	α-Pinene	7.63	0.47	0.25	0.18	3.88	0.40	3.95	0.54	MS, ES
3	Camphene	-	-	-	-	-	-	0.15	0.02	MS, ES
4	β-Sabinene	12.67	0.78	-	-	0.66	0.07	2.16	0.29	MS, ES
5	β-Pinene	1.73	0.11	-	-	0.29	0.03	39.85	5.43	MS
6	β-Myrcene	36.77	2.26	1.43	1.05	20.92	2.14	4.33	0.59	MS, ES
7	α-Phellandrene	0.50	0.03	-	-	0.28	0.03	0.10	0.01	MS
8	Octanal	14.34	0.88	0.08	0.06	0.33	0.03	3.30	0.45	MS, ES
9	α-Terpinene	0.89	0.05	-	-	0.07	0.01	1.72	0.23	MS, ES
10	p-Cymene	-	-	0.08	0.06	0.22	0.02	16.43	2.24	MS, ES
11	Limonene	1239.37	76.07	104.96	76.96	833.53	85.29	231.73	31.56	MS, ES
12	β-*cis*-Ocimene	0.88	0.05	-	-	-	-	1.46	0.20	MS
13	β-*trans*-Ocimene	9.66	0.59	-	-	-	-	1.02	0.14	MS
14	γ-Terpinene	2.62	0.16	0.13	0.10	0.42	0.04	64.83	8.83	MS
15	*trans*-Sabinene hydrate	0.25	0.02	-	-	-	-	0.30	0.04	MS
16	1-Octanol	2.40	0.15	0.05	0.04	-	-	0.30	0.04	MS, ES
17	α-Terpinolene	0.76	0.05	0.06	0.04	0.15	0.02	4.07	0.55	MS
18	Linalool	1.55	0.10	0.79	0.58	0.53	0.05	2.56	0.35	MS, ES
19	Nonanal	4.02	0.25	0.37	0.27	0.30	0.03	11.73	1.60	MS, ES
20	Nonanol	0.21	0.01	0.07	0.05	0.13	0.01	-	-	MS, ES
21	γ-Terpinolene	2.06	0.13	-	-	0.22	0.02	1.00	0.14	MS
22	Camphor	0.39	0.02	-	-	-	-	0.08	0.01	MS
23	β-Citronellal	1.00	0.06	-	-	-	-	1.85	0.25	MS, ES
24	*cis*-Sabinene hydrate	2.60	0.16	-	-	-	-	6.00	0.82	MS
25	1-Decanol, 2-hexyl-	0.39	0.02	-	-	-	-	0.08	0.01	MS
26	(-)-4-Terpineol	0.93	0.06	0.36	0.26	-	-	4.14	0.56	MS
27	α-Terpineol	0.55	0.03	0.15	0.11	0.24	0.02	2.43	0.33	MS, ES
28	Decanal	53.75	3.30	0.59	0.43	1.44	0.15	8.25	1.12	MS, ES
29	Acetic acid, octyl ester	13.76	0.84	2.04	1.50	6.16	0.63	7.50	1.02	MS
30	Nerol	-	-	0.50	0.37	0.10	0.01	1.99	0.27	MS, ES
31	β-Citronellol	0.24	0.01	-	-	0.07	0.01	0.89	0.12	MS, ES

32	Z-Citral (neral)	0.24	0.01	-	-	-	-	27.04	3.68	MS
33	*trans*-Geraniol	-	-	0.60	0.44	-	-	1.78	0.24	MS, ES
34	E-Citral (geranial)	0.43	0.03	0.06	0.04	-	-	39.13	5.33	MS
35	1,1-Diethoxyoctane	39.04	2.40	0.23	0.17	0.14	0.01	5.19	0.71	MS
36	Anethol	0.21	0.01	1.26	0.92	0.31	0.03	0.36	0.05	MS, ES
37	Undecanal	1.57	0.10	0.05	0.04	0.14	0.01	3.27	0.45	MS
38	Nonyl acetate	0.96	0.06	0.09	0.07	0.47	0.05	0.79	0.11	MS
39	Methyl geranoate	0.12	0.01	-	-	-	-	0.45	0.06	MS
40	δ-Elemene	-	-	-	-	1.37	0.14	-	-	MS
41	*trans*-Carvyl acetate	0.18	0.01	-	-	-	-	-	-	MS
42	Copaene	1.48	0.09	-	-	0.24	0.02	-	-	MS
43	α-Terpinenyl acetate	5.03	0.31	-	-	0.10	0.01	-	-	MS
44	Citronellyl acetate	2.76	0.17	0.53	0.39	1.76	0.18	8.45	1.15	MS
45	Neryl acetate	1.47	0.09	0.57	0.42	1.61	0.16	87.54	11.92	MS, ES
46	Isoterpinolene	14.77	0.91	-	-	0.21	0.02	0.89	0.12	MS
47	Geranyl acetate	16.74	1.03	8.40	6.16	24.00	2.46	89.29	12.16	MS, ES
48	β-Cubebene	10.60	0.65	-	-	0.48	0.05	-	-	MS
49	β-Elemene	0.63	0.04	-	-	0.84	0.09	-	-	MS
50	Citronellal	1.00	0.06	-	-	-	-	1.86	0.25	MS, ES
51	Acetic acid, decyl ester	10.53	0.65	0.17	0.12	0.83	0.08	1.70	0.23	MS
52	Limonen-10-yl acetate	0.61	0.04	0.52	0.38	1.63	0.17	-	-	MS
53	*trans*-Caryophyllene	37.14	2.28	0.18	0.13	0.75	0.08	5.82	0.79	MS
54	α-Santalol	-	-	0.32	0.23	0.77	0.08	-	-	MS
55	α-Bergamotene	-	-	-	-	-	-	5.45	0.74	MS
56	*cis*-Caryophyllene	0.56	0.03	0.20	0.15	0.31	0.03	0.29	0.04	MS
57	Neryl propionate	2.98	0.18	-	-	0.21	0.02	1.64	0.22	MS
58	α-Humulene	6.12	0.38	0.08	0.06	0.27	0.03	0.76	0.10	MS
59	β-Santalene	-	-	-	-	0.70	0.07	0.37	0.05	MS
60	Geranyl propionate	0.30	0.02	0.19	0.14	0.74	0.08	1.27	0.17	MS, ES
61	1,1-Diethoxydecane	14.40	0.88	-	-	-	-	1.79	0.24	MS
62	Germacrene D	10.20	0.63	0.73	0.54	47.56	4.87	0.10	0.01	MS
63	*trans*-β-Farnesene	0.61	0.04	0.20	0.15	0.26	0.03	0.45	0.06	MS
64	β-Selinene	0.43	0.03	0.30	0.22	0.37	0.04	-	-	MS

65	Valencene	0.91	0.06	-	-	0.71	0.07	1.35	0.18	MS, ES
66	Bicyclogermacrene	4.93	0.30	0.53	0.39	10.03	1.03	3.06	0.42	MS
67	*cis*-α-Bisabolene	2.00	0.12	0.24	0.18	1.08	0.11	1.18	0.16	MS
68	β-Bisabolene	2.10	0.13	-	-	1.40	0.14	16.20	2.21	MS
69	γ-Cadinene	0.24	0.01	0.23	0.17	0.77	0.08	-	-	MS
70	δ-Cadinene	21.33	1.31	2.45	1.80	1.90	0.19	0.24	0.03	MS
71	Longifolene	0.81	0.05	0.16	0.12	-	-	-	-	MS
72	α-Chamigrene	-	-	-	-	0.84	0.09	-	-	MS
73	γ-Bisabolene	-	-	0.07	0.05	0.27	0.03	0.23	0.03	MS
74	Germacrene B	1.45	0.09	0.19	0.14	2.47	0.25	-	-	MS
75	Nerolidol	0.34	0.02	-	-	0.14	0.01	-	-	MS
76	Palustrol	0.24	0.01	0.10	0.07	-	-	0.25	0.03	MS
77	Caryophyllene oxide	0.36	0.02	0.15	0.11	-	-	-	-	MS
78	Dodecanoic acid, ethyl ester	0.49	0.03	0.47	0.34	0.50	0.05	0.24	0.03	MS
79	Veridiflorol	-	-	0.60	0.44	-	-	0.19	0.03	MS
80	Globulol	-	-	0.29	0.21	0.21	0.02	-	-	MS
81	Fonenol	-	-	0.81	0.59	0.15	0.02	-	-	MS
82	t-Cadinol	0.09	0.01	0.22	0.16	-	-	-	-	MS
83	Aromadendrene	0.11	0.01	0.87	0.64	0.17	0.02	-	-	MS
84	Cedrenol	0.04	0.01	0.52	0.38	0.27	0.03	0.44	0.06	MS
85	Hinesol	0.46	0.03	0.26	0.19	-	-	-	-	MS
86	Torreyol	-	-	0.21	0.15	-	-	-	-	MS
87	α-Bisabolol	0.20	0.01	1.43	1.05	0.34	0.03	0.49	0.07	MS
	Total	1629.33	-	136.39	-	977.26	-	734.25	-	
	Monoterpenes	1333.36	81.83	106.91	78.39	860.85	88.09	380.49	51.82	
	Sesquiterpenes	101.65	6.24	6.43	4.71	72.79	7.45	35.50	4.83	
	Oxygenated compounds	194.32	11.93	23.05	16.90	43.62	4.46	318.26	43.34	

KP: kumquat peel; KWF: kumquat whole fruit; GP: grapefruit peel; LP: lemon peel. ID: identification. [a]Compounds quantified as total area counts x 10^6 (mean of 3 repetitions). [b]MS: identification based on the NIST MS library; ES: identification based on authentic external standards analysed by mass spectrometry.

The KP liqueur was the richest in volatile compounds (73 molecules identified), followed by the LP (65), the GP (61), and the KWF (54). The KP also had the highest total integrated peaks area, followed by the GP, the LP, and the KWF. Even though the study was not quantitative, under our experimental conditions the area of the KP appears to be about 12-fold larger than that of the KWF, and this could be a consequence of the peeling operation due to: i) the breakage of the cells containing the essential oils that favored the better

extraction of the volatile compounds during maceration; ii) the higher contact area between the peel and alcohol since only peels had been used in the maceration. In comparison to the LP, the KP total area was about 2 times higher, the KWF was about one fifth lower, and the GP was about 30% higher. Among the volatile compounds, MTs group was the most abundant in all the samples, constituting 78-80% of the total, with the exception of the LP, where these compounds were found to be about one-half of the total. In fact, the LP was characterized by a remarkable presence of OCs, which represent about the second half of the total volatile compounds. As concerns single volatiles, limonene was the predominant compound identified, even though the peak area strongly varied among liqueurs (from about 105×10^6 in KWF to about 1239×10^6 in KP). In terms of relative abundance, this monoterpene represented about 85% of the total area in the GP and about 76% in kumquat samples (both in the KP and the KWF), which are much higher than in the LP (about 32%). The abundance of limonene was expected, since it is the principal component of the volatile fraction of various citrus fruits (VERSARI *et al.*, 2003; CRUPI *et al.*, 2007; DUGO *et al.*, 2010; ASIKIN *et al.*, 2012), including kumquat, in which it represents more than 90% of volatile compounds of the peel essential oil (UMANO *et al.*, 1994; CHOI, 2005). The low concentration of limonene detected in the LP liqueur, compared to the KP and the GP, could be explained by the different content in the corresponding essential oils. As reported by CACCIONI *et al.* (1998), the lemon essential oils were characterized by a limonene concentration of 60–71% of the total volatile compounds, while the limonene concentrations in the essential oil of other citrus, such as grapefruit, orange, and bitter orange, were always higher than 90%. This monoterpene is associated with odor descriptors such as lemon-like, lemon, and orange, but presents a high odor threshold (CHOI, 2005; POHJANHEIMO and SANDELL, 2009). As regards the other MTs, the most representative ones, with peak area > 15×10^6, were ß-myrcene, isoterpinolene, ß-sabinene, and ß-trans-ocimene in KP, and α-terpinene, ß-pinene, geranial, neral, and *p*-cymene in the LP. It is well known that neral and geranial (terpenoid isomers known as citral) are responsible for the strong lemon aroma; they were not detected or detected at only very low level in the KP, the KWF, and the GP samples. Apart from limonene, ß-myrcene was the monoterpene found in appreciable amounts in the GP and the KWF samples (20.92×10^6 and 1.43×10^6, respectively). As far as STs are concerned, the KP contained more compounds with peak area > 10×10^6, such as trans-caryophyllene, δ-cadinene, β-cubebene, and germacrene D, whereas germacrene D and β-bisabolene were found in the GP and in the LP, respectively. This suggests that the KP liqueur is characterized by greater aroma complexity compared with the other samples investigated. The KWF had the particular feature to be the richest in STs alcohols (α-bisabolol, fonenol, veridiflorol, cedrenol, and globulol). These compounds are the primary constituents of the essential oil, conferring a weak sweet floral aroma, and are used commercially in various fragrances. Among the OCs, geranyl acetate and neryl acetate were detected at the highest level in the LP (peak area value about 90×10^6). They were also found in the other liqueurs under examination, but at lower levels. These esters were associated with fresh and citrusy notes (THI MINH TU *et al.*, 2002), and are used in flavor and perfumery products to impart floral and fruity aromas. The KP liqueur also contained high levels of octanal and decanal (peak area values about 14.34×10^6 and 54×10^6, respectively). This finding does not agree with the results of previous studies carried out on the volatile fraction of kumquat essential oil, in which octanal and decanal were not detected or detected only at trace level (UMANO *et al.*, 1994; PENG *et al.*, 2013). These two aldehydes are commonly detected both in *Citrus sphaerocarpa* peel oil (THI MINH TU *et al.*, 2002) and in orange essential oil (HÖGNADÓTTIR and ROUSSEFF, 2003). At GC/Olfactometry analysis, octanal was associated to sweet, citrusy, lemon and green descriptors, whereas decanal was perceived as sour, metallic, lemon and fatty (THI MINH TU *et al.*, 2002; HÖGNADÓTTIR and

ROUSSEFF, 2003). In our study, the presence of 2 acetals corresponding to the 2 aldehydes, 1,1-diethoxyoctane, and 1,1-diethoxydecane, was ascertained. 1,1-Diethoxyoctane has an odor of fatty, oily, green citrus with woody, spicy and fruity nuances (MOSCIANO, 1994a), whereas 1,1-diethoxydecane presents an odor defined as waxy, green, aldehydic and orange with cognac and coconut nuances (MOSCIANO, 1994b). The 2 acetals were most prevalent in the KP and the LP liqueurs, and their presence was due to the high level of the aldehydes. In fact, acetals originate from the reaction between alcohols and aldehydes, giving rise to an unstable semiacetal, which evolves to a stable derivative after reacting with a second alcohol molecule (HEYDANEK and MIN, 1976). PLUTOWSKA *et al.* (2010) found acetals as minor compounds in alcoholic beverages and spirits, with a possible role in enhancing the bouquet of the product.

3.2. Acceptance and preference testing

Figure 3 reports the results of the sensory analysis. No significant difference among samples was perceived regarding color, which ranged between 3.4 and 3.9 (for the GP and the LP, respectively). The LP was the most appreciated sample as to flavor. This result could be due to the higher concentration of volatile compounds with a high olfactory impact (in particular OCs) and the greater familiarity of consumers with this traditional Italian liqueur. Regarding the liqueurs obtained from kumquat, the odor scores were 2.89 for the KP and 3.20 for the KWF, while the flavor scores were 3.01 and 3.32 highlighting a certain appreciation by consumers. This could be linked to the high amounts of sesquiterpene alcohols. The grapefruit liqueur was more significantly preferred for its odor in comparison to the two kumquat liqueurs.

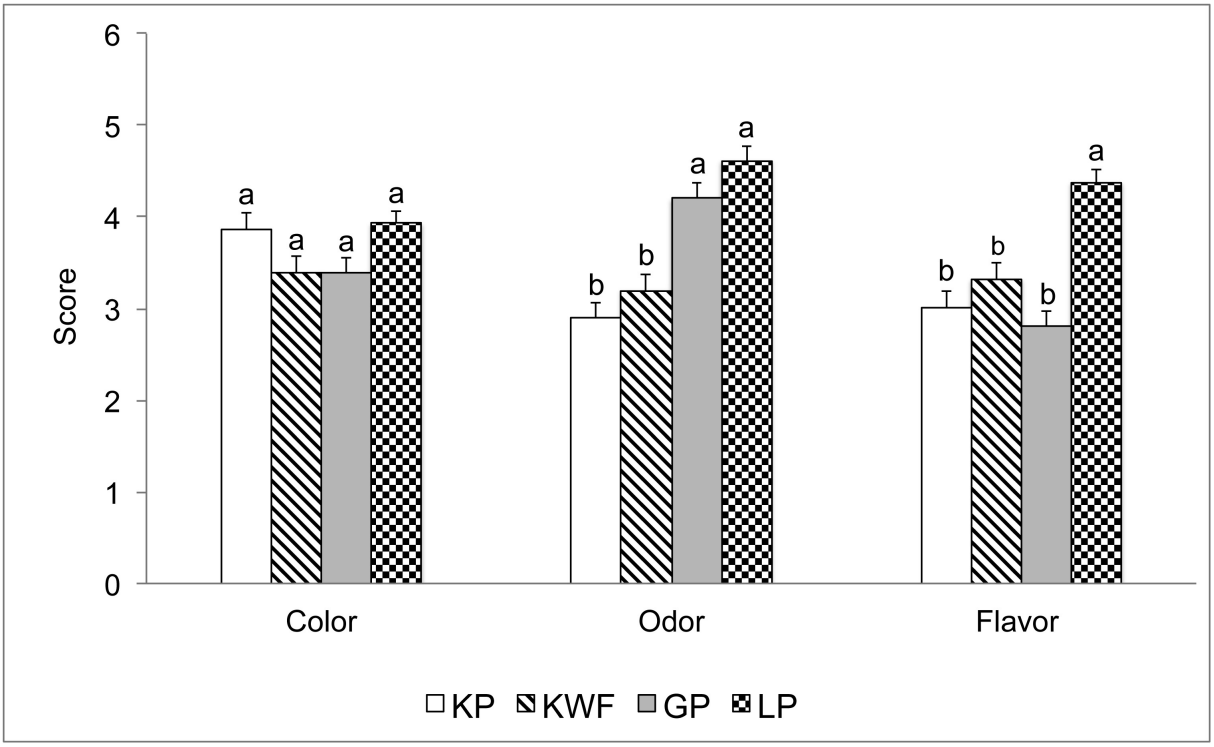

Figure 3: Mean score values and statistic analyses of the consumer acceptance of the liqueurs. KP, kumquat peel; KWF, kumquat whole fruit; GP, grapefruit peel; LP, lemon peel. Values having different subscript letters are significantly different (P<0.05).

Table 2 shows the ranking of preferences expressed by the panelists (third section of the evaluation form). In the same table the result of the statistical analysis obtained comparing the differences among the rank sums of the single liqueur with the critical value, as proposed by BASKER (1988), is reported. The rank sums were obtained by adding the preference ranking scores (from 1 to 4 starting from the most appreciated liqueur) expressed by each panelist. As expected, the LP proved to be the most appreciated liqueur, whereas the KWF and the KP were more appreciated than the GP. On the whole, the taste panel data highlighted the possibility of using kumquat for the production of *rosolio*, even though adjustments in the preparation process (fruit to ethyl alcohol ratio; duration of the maceration step) should be carried out to improve the odor and flavor perception. The use of the whole fruit instead of the peel determined an increase in the preference by the taste panel members; therefore, the peeling step could be avoided.

Table 2: Rank sums of preferences and results of the statistical analysis (BASKER, 1988) of the liqueurs.

			KP	**KWF**	**GP**	**LP**
		Rank sums	*206*	*183*	*230*	*122*
KP	BC	*206*	0	23	24	**84**
KWF	B	*183*	23	0	**47**	**61**
GP	C	*230*	24	**47**	0	**108**
LP	A	*122*	**84**	**61**	**108**	0

ABC: Different letter indicates significant differences (n = 75, $P \leq 0.05$, critical value = 40.6).
Bold font indicates values higher than critical value.

4. CONCLUSIONS

The main result of this study was the assessment of the feasibility of using minor citrus fruits for producing innovative liqueurs. With respect to *limoncello*, the kumquat and grapefruit liqueurs had greater concentrations of limonene and lower concentration of oxygenated compounds, the latter having high relative flavor activity. These differences justify the preference given to the liqueur obtained from lemon peel, even though all the innovative liqueurs were judged to be acceptable. Among them, the kumquat liqueur obtained from whole fruit seems to be the most promising, probably because it had the highest content of sesquiterpene alcohols.

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