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Characterisation of the Volatile Compounds and Key Odourants in Japanese Mandarins by Gas Chromatography–Mass Spectrometry and Gas Chromatography–Olfactometry

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Abstract: Japanese mandarins are becoming increasingly popular due to their pleasant aroma. The volatiles in four varieties of Japanese mandarins (Iyokan, Ponkan, Shiranui, and Unshiu mikan) were extracted by headspace solid-phase microextraction (HS-SPME) and solvent extraction, then analysed by gas chromatography–mass spectrometry (GC-MS). Principal component analysis (PCA) of the GC-MS data demonstrated distinct segregation of all four Japanese mandarin varieties. Esters, such as neryl acetate, distinguished Iyokan. Methylthymol uniquely characterised Ponkan, valencene was exclusive to Shiranui, and acids like hexanoic acid and heptanoic acid differentiated Unshiu mikan from the other three varieties. Aroma extract dilution analysis (AEDA) revealed 131 key odourants across four Japanese mandarins, including myrcene (peppery, terpenic), perillyl alcohol (green, spicy, floral), *trans*-nerolidol (sweet, floral), and *trans*-farnesol (woody, floral, green). Finally, sensory evaluation was conducted on the four Japanese mandarin peel extracts to describe the distinct aroma profile of each variety of Japanese mandarin: Iyokan had higher floral and juicy notes, Ponkan showed higher sulphury notes, Shiranui was perceived to have more albedo notes, and Unshiu mikan exhibited higher peely, green, and woody notes.

Keywords: Japanese mandarin; volatile; odourant; GC-MS; HS-SPME; GC-O; AEDA

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1. Introduction

Owing to their economic importance and wide applications, *Citrus* flavours are among the most desirable natural flavours, explaining various reports on the composition of volatile compounds from various *Citrus* fruits [1,2]. Within *Citrus*, mandarin fruits are increasingly attracting attention because of their nutritional importance and enticing flavour [3]. Recently, there has been a growing global interest in Japanese mandarins, predominantly due to their immaculate fruits, attractive aroma, limited supply, and purported health benefits [4–6]. In contrast to mandarins produced in other regions [7,8], despite previous research on the volatile compounds of Japanese mandarins, there is a notable lack of systematic aroma analysis and comparative studies among the varieties of Japanese mandarin fruits [9–11]. This leaves a gap in understanding the unique characteristics that distinguish one variety from another, necessitating a systematic investigation into the aroma of Japanese mandarins.

The inherent complexity of *Citrus* matrix, along with the presence of potent volatile compounds at trace levels, presents a substantial challenge to the analysis of *Citrus* aroma [12]. To effectively navigate this complexity, thorough sample preparation is necessary, which includes the extraction and concentration of volatiles to detectable levels. Among the various sample preparation methods available, solvent extraction and headspace solid-phase microextraction (HS-SPME) have been commonly employed for

capturing the aroma compounds of *Citrus* juices and peels due to their broad applicability and efficacy [13–16]. Despite their widespread utilisation, there is a lack of complementary analysis combining the benefits of HS-SPME and solvent extraction to characterise the volatile profiles of specific popular Japanese mandarins. HS-SPME provides a convenient and efficient method for analysing volatile compounds without altering their composition or introducing solvent-related biases. This technique requires minimal sample volume and enhances sensitivity while minimising matrix effects [17–19]. These advantages make HS-SPME highly suitable for analysing the volatile compounds of *Citrus* fruits. For example, Goh et al. [13] utilised HS-SPME to compare the volatile profiles of different parts (flower, leaf, peel and juice) of Malaysian pomelo. Hou et al. [14] explored the volatile composition changes in navel orange at different growth stages by HS-SPME. On the other hand, the solvent extraction technique is a widely employed and conventional method for extracting *Citrus* volatile compounds due to its simplicity, broad applicability, and cost-effectiveness [20]. Goh et al. [21] characterised the volatile profiles of several kinds of kumquat and calamansi peel oils extracted by solvent extraction with dichloromethane (DCM). Additionally, the solvent extraction technique is well-suited for capturing low-volatility and oil-soluble compounds in *Citrus* that might be overlooked by HS procedures [22]. The complementary extraction strategies underscore the importance of a combined approach in characterising the volatile profiles of popular Japanese mandarin varieties, thereby facilitating a better comparison among these varieties.

The diverse range of volatile compounds revealed in the extracts through HS-SPME and solvent extraction highlights the complexity of volatile composition in *Citrus*. While the unique aroma characteristic of each *Citrus* variety is the result of a specifically proportioned and complex mixture of volatiles [2], it is important to note that concentration does not necessarily equate to odour threshold [23]. To unravel the key odourants responsible for the distinctive aroma of Japanese mandarins, aroma extract dilution analysis (AEDA) coupled with gas chromatography–olfactometry (GC-O) offers a powerful approach. GC-O is a technique that combines the separation capabilities of gas chromatography with the sensitivity of the human nose as a detector [24]. AEDA, a well-known dilution analytical approaches, is one of the most sophisticated GC-O techniques that have been widely employed for identifying and ranking the contribution and potency of the odourant to the *Citrus* aroma [23,25]. AEDA applies a series of dilutions (n^0, n^1, n^2, n^3, etc.) to determine the flavour dilution (FD) factor of a compound at one dilution, in which none of the well-trained panellists could detect the smell of the compound in a glass sniffing port. The FD factor is one of the main parameters used to elucidate the role of each compound in *Citrus* aroma [20]. By leveraging AEDA through gas chromatography–olfactometry/mass spectrometry (GC-O/MS), this study aimed to bridge the knowledge gap in understanding the key odourants responsible for the characteristic aroma of Japanese mandarin varieties. In addition, sensory evaluation further enhances this understanding by systematically assessing aroma perception through human senses, combining subjective and objective characterization with instrumental analyses [26].

Therefore, the objective of this study was to understand the contribution of volatile compounds to the aroma of Japanese mandarins. This was achieved by investigating the volatile profile of juice and peel of four varieties of Japanese mandarins (Iyokan, Ponkan, Shiranui, and Unshiu mikan) using HS-SPME and analysed by gas chromatography–mass spectrometry/flame ionisation detector (GC-MS/FID). Additionally, the volatile extracts from mandarin peels obtained via solvent extraction were also analysed. Then, to interpret the differences among the four mandarin varieties, principal component analysis (PCA) was applied to the GC-MS data. The key aroma compounds of the four Japanese mandarin peel extracts were characterised using GC-O/MS, and a heatmap analysis was applied to interpret the resulting data sets. Finally, a sensory evaluation of the peel extracts was conducted to better understand their aroma profile.

2. Materials and Methods

2.1. Plant Materials and Sample Preparation

This study benefited from collaborative expertise provided by Ehime Beverage Inc. (Ehime, Tokyo, Japan) and Mane SEA Pte Ltd. (Singapore). Following a preliminary sensory evaluation of several Japanese mandarins, four varieties of Iyokan, Ponkan, Shiranui, and Unshiu mikan were selected and analysed in this work. The Japanese mandarins were sourced from local orchards in Ehime and Wakayama prefectures in Japan and were harvested by professional fruit growers at their commercial maturity stage. Approximately 6 kg of each variety of mature fruits were carefully collected, with any blemished or defective fruits being excluded. The selected fruits underwent a careful washing, drying, and storage process in refrigerated conditions (4 °C) prior to use, and were extracted within one week of collection. The mandarin peel was manually separated from the flesh, with a 180 g portion randomly selected for each solvent extraction procedure. Additionally, a fraction of the peels was sliced into small fragments measuring approximately 1 cm × 1 cm for the HS-SPME procedure. Mandarin juice was extracted manually by squeezing the pulp after peel removal to prevent any contamination from the substances presented in the flavedo and albedo. The freshly extracted juice was utilised immediately.

2.2. Chemicals and Reagents

High-performance liquid chromatography (HPLC)-grade DCM and anhydrous sodium sulphate (Na_2SO_4) for solvent extraction were obtained from VWR (Radnor, PA, USA). The internal standard, 2-octanol, and the C_7–C_{40} alkane standards were procured from Sigma Aldrich (St. Louis, MO, USA). The standards for GC-MS/FID analysis were supplied by Mane SEA Pte Ltd. (Singapore).

2.3. HS-SPME Procedure

The HS-SPME protocol was modified from Goh et al. [27]. A sample of 2.000 g of mandarin peel or mandarin juice was placed in a 20 mL vial, which was then sealed with a PTFE-coated silicone septum (Agilent, Santa Clara, CA, USA). The sample was extracted using a Carboxen/Polydimethylsiloxane (CAR/PDMS) fibre from Supelco (Bellefonte, PA, USA) with the following conditions: temperature of 40 °C, agitation speed of 250 rpm, and extraction time of 30 min. The fibre was then thermally desorbed into the GC injector at 250 °C for 5 min. For both the mandarin peel and the mandarin juice, five replicates were conducted.

2.4. Solvent Extraction

Extensive studies on *Citrus* aroma analysis have demonstrated that 2-octanol is chemically stable and does not interfere with the volatile compounds of interest. Its retention time and peak do not overlap with those of the target compounds, ensuring accurate and reliable quantification. Therefore, 2-octanol was selected as the internal standard in this study [7,13,27]. A volume of 360.0 mL of DCM was combined with 2.0 µL of 2-octanol internal standard and added to the peel. The mixture was shaken at 250 rpm for 120 min using a Stuart SSL2 Reciprocating Shaker (Bibby Scientific Ltd., Stone, UK). Subsequently, 80.0 g of Na_2SO_4 was added to eliminate moisture. The mixture was then filtered through Whatman grade 1 qualitative filter paper (Cat No. 1001-150, 150 mm, Whatman, Kent, UK) to remove the Na_2SO_4 and spent peels. The resulting peel oil extract was concentrated using a Buchi rotary evaporator (Flawil, Switzerland) with the following settings: 150 rpm, water bath at 25 °C, condenser at 5 °C, and a vacuum pressure of 500 mbar. After 60 min, the concentrated peel oil extracts were transferred and stored at −18 °C for further analysis. Each extraction was subjected to three replicates, and all extracts were stored at 4 °C for subsequent analyses.

2.5. GC-MS/FID Analysis

The GC-MS/FID procedure was adapted from Goh et al. [13]. The analysis was performed using an Agilent 7890B GC system with a MS and FID (Agilent Technologies, Santa Clara, CA, USA). Separation of compounds or standards was carried out on an Agilent HP-INNOWax column with specifications of 60 mm × 250 µm × 0.25 µm (Woodbridge, VA, USA). Semi-quantification of compounds using solvent extraction was achieved by comparing the FID peak area of each compound to that of the internal standard, with results expressed in ng/mL. All experiments were performed in triplicate (three repeated samplings with three different injections in GC), and the mean values along with standard deviations are presented.

2.6. GC-O/MS and AEDA Analysis

An Agilent 8890 GC coupled with an Agilent 5977B mass selective detector (MSD) system (Agilent Technologies, Santa Clara, CA, USA) was utilised in this protocol. The column used was the HP-INNOWax (30 m × 250 µm × 0.25 µm) (Agilent, Woodbridge, VA, USA), with helium serving as the carrier gas, maintained at a flow rate of 1.2 mL/min. The injector was operated in splitless mode with an injection volume of 1 µL, and the GC flow was split equally between the olfactory detection port (ODP3, Gerstel GmbH & Co., Mülheim an der Ruhr, Germany) and the MSD. The temperature gradient was optimised to minimise the coelution of odourants. The oven temperature program consisted of an initial 50 °C for 3.5 min, followed by a series of linear temperature ramps and increments (increased at 5 °C/min to 85 °C; at 7 °C/min to 120 °C; at 5 °C/min to 155 °C; at 7 °C/min to 190 °C; and at 10 °C/min to 240 °C) to reach a final temperature of 240 °C, held for 5 min (37.5 min). A continuous flow of moist air at 30 mL/min was maintained to prevent nasal membrane dehydration and to clear the eluted compounds from the sniffing port. C_7–C_{30} alkane standards and individual compound standards were analysed under the same conditions to determine the linear retention indices (LRI) of the eluted compounds. It should be noted that the temperature ramping steps employed in this study could contribute to variability in experimental LRI values compared to the NIST library values [28]. AEDA for four Japanese mandarin peel oil extracts was conducted by five experienced flavourists (as panellists; 2 males and 3 females; aged 26–50), employing the stepwise 5-fold dilutions, starting from the lowest dilution factor (0) (a dilution factor of 0 corresponds to a FD value of $5^0 = 1$; a dilution factor of 1 corresponds to a FD value of $5^1 = 5$; and so forth). Each panellist recorded the time and descriptors of perceived compounds independently during the GC-O/MS run. The sniffed compounds were identified by matching their LRI with in-house standards and comparing the descriptors provided by the panellists with literature descriptions. The FD values were then assigned to each compound based on the highest dilution at which the panellists could detect them.

2.7. Sensory Profiling

The sensory evaluation method was modified from Goh et al. [21]. Four undiluted Japanese mandarin peel oil extracts were evaluated by seven experienced flavourists serving as panellists (2 males and 5 females; aged 26–50) and a total of seven aroma attributes (albedo, floral, green, juicy, peely, sulphury, woody) were assessed by all panellists.

2.8. Data Analysis

All experiments were conducted in at least triplicate and the results were presented as mean values ± standard deviations. GC-MS/FID data was processed using MSD Chemstation (Agilent, Santa Clara, CA, USA, version F.01.03.2357) and then imported into Mass Profiler Professional (MPP) (Agilent, Santa Clara, CA, USA, version 14.9.1). The MPP processing was adapted from Pua et al. [29]. The fold-change set at 10.0. The resulting filtered compounds were used to generate PCA scores and loadings plots with Origin 2022 SR1 (OriginLab, Northampton, MA, USA). Heatmap analysis was performed RStudio (Posit, Boston, MA, USA, version 2023.03.0+386 (R Core Team 4.3.0)) with the data.table and magrittr packages, then implemented circular visualisation with ComplexHeatmap and circlize packages.

3. Results and Discussion

3.1. Extraction of Volatile Compounds in Japanese Mandarin Juices and Peels by HS-SPME

In this study, four varieties of Japanese mandarins were selected: Iyokan (*Citrus iyo* hort. ex Tanaka) produced in Ehime, a typical edible *Citrus* fruit frequently consumed in Japan [30]; Ponkan (*Citrus reticulata* Blanco) produced in Ehime, widely used as a breeding parent for developing economically significant varieties in Japan [30,31]; Shiranui (also known as Dekopon, *Citrus unshiu* Marc. × *Citrus sinensis* Osbeck × *Citrus reticulata* Blanco) produced in Ehime, currently one of the most popular Japanese mandarin varieties internationally, especially in North America as a commercial product under the name of 'Sumo Citrus' [32,33]; and Unshiu mikan (*Citrus unshiu* Marc.) produced in Wakayama, a predominant variety of *Citrus* cultivated in Japan [34].

Among the techniques used for the extraction of aromas from fresh *Citrus* juice and peel, the pre-concentration of volatile compounds by HS-SPME is a sensitive and fast method that reduces the complex *Citrus* fruit matrix effects [17,18]. Here, HS-SPME was applied to extract the volatiles from both fresh Japanese mandarin juices and peels. Based on HS-SPME extraction, 83 compounds were identified in the four Japanese mandarin juices (Table 1). In general, the volatiles of these four mandarin juices could be categorised into terpenes, alcohols, aldehydes, esters, acids, ketones, phenols, and others. As expected of *Citrus* samples, across all four Japanese mandarin juices, terpenes were the most abundant volatile compounds, with limonene representing the bulk of mandarin juices. Other major terpenes, such as γ-terpinene, *p*-cymene, myrcene, and terpinolene, were consistent with the characterisation of mandarin (*Citrus reticulata* Blanco var. Willow Leaf) juice extracted using HS-SPME [35]. Aldehydes were found in relatively high abundance in the four Japanese mandarin juices, with acetaldehyde being the most abundant, which might contribute pungent and alcoholic notes [36]. All four mandarin juices contained similar alcohol compounds; however, the major alcohol present in each mandarin juice was different. Specifically, linalool was the predominant alcohol in Iyokan juice, whereas terpinen-4-ol was most prominent in Ponkan juice. In contrast, Shiranui juice was characterised by a high presence of *cis*-3-hexenol, and hexanol was the most notable alcohol in Unshiu mikan juice. Octanoic acid and nonanoic acid were common acids found in all juices, and three ketones (6-methyl-5-hepten-2-one, geranyl acetone, and β-ionone) were also detected.

Despite these similarities among the four Japanese mandarin juices, distinct characteristics existed in the volatile composition of each variety. For instance, although exhibiting the lowest abundance of total volatile content, Iyokan juice displayed a relatively high proportion of aldehydes and alcohols. Notably, *trans*-*trans*-2,4-nonadienal was exclusively detected in Iyokan juice, and linalool, the most abundant alcohol in Iyokan juice, demonstrated a significantly higher abundance as compared to the other three Japanese mandarin juices. The presence of *trans*-*trans*-2,4-nonadienal may contribute to floral, green, or fatty nuances for Iyokan juice [37]. As a terpene alcohol, linalool was previously identified as a potent volatile compound in Satsuma mandarin fruit with a distinctive sweet floral aroma [23]. Ponkan juice had the highest total volatile content, with leading abundances of terpenes, aldehydes, and volatile phenol. Thymol, the only volatile phenol detected in the four Japanese mandarin juices, was found in Ponkan and Unshiu mikan juices, and had been reported as the only odour-active phenol found in Ponkan mandarin juice in a previous study [1]. The presence of thymol and abundant terpenes might contribute spicy and fresh notes to the Ponkan mandarin juice profile [37,38]. Notably, Shiranui juice contained more types of sesquiterpenes with relatively higher abundances, such as δ-elemene, α-copaene, β-caryophyllene, valencene, and α-selinene, which potentially contribute a woody and spicy aroma to Shiranui juice with a hint of fresh notes [38]. Unshiu mikan juice contained the highest abundance of alcohols, ketones, and acids, with a relatively higher abundance of hexanol, *cis*-3-hexenol, 6-methyl-5-hepten-2-one, and hexanoic acid. These characteristics indicate a unique green and fresh profile in Unshiu mikan juice [23].

Table 1. Identification of volatile compounds in juices of four varieties of Japanese mandarin (Iyokan, Ponkan, Shiranui, and Unshiu mikan) extracted by HS-SPME (40 °C, 30 min).

No.	Compound	LRI [I]	CAS Number	Abundance (FID Peak Area)				Identification [II]
				Iyokan	Ponkan	Shiranui	Unshiu Mikan	
1	Acetaldehyde [1,2]	671	75-07-0	355,475 ± 42,481 [c]	1,481,261 ± 126,612 [a]	1,189,841 ± 74,013 [b]	1,263,030 ± 115,588 [b]	LRI, MS, STD
2	Ethyl acetate [1,3,4,5]	917	141-78-6	-	2,463,085 ± 156,200 [b]	9,149,139 ± 392,714 [a]	480,006 ± 22,211 [c]	LRI, MS, STD
3	Methyl butanoate [2]	1001	623-42-7	119,024 ± 8693	Trace	-	-	LRI, MS, STD
4	*α*-Pinene [1,2,3,4,5,6]	1038	80-56-8	177,964 ± 15,502 [c]	270,643 ± 16,738 [b]	151,267 ± 5409 [d]	415,268 ± 4364 [a]	LRI, MS, STD
5	*α*-Thujene [1,3,4]	1042	2867-05-2	98,181 ± 2933 [a]	43,115 ± 2641 [b]	27,773 ± 1533 [d]	32,976 ± 1827 [c]	LRI, MS
6	Ethyl butanoate [1,2]	1049	105-54-4	-	103,026 ± 6719 [a]	83,154 ± 6541 [b]	-	LRI, MS, STD
7	Hexanal [1,2,3,5]	1099	66-25-1	330,073 ± 30,116 [b]	606,791 ± 51,092 [a]	319,481 ± 25,169 [b]	163,403 ± 13,566 [c]	LRI, MS, STD
8	*β*-Pinene [1,3,4,5,6]	1123	127-91-3	98,609 ± 7584 [b]	125,393 ± 14,584 [a]	22,518 ± 479 [c]	120,178 ± 5268 [a]	LRI, MS, STD
9	Sabinene [1,3,4,5,6]	1135	3387-41-5	43,530 ± 4574 [b]	120,328 ± 12,367 [a]	-	41,604 ± 2843 [b]	LRI, MS, STD
10	1-Penten-3-ol [1,6]	1165	616-25-1	55,399 ± 3051 [b]	-	-	63,702 ± 3674 [a]	LRI, MS
11	Myrcene [1,2,3,4,5,6]	1175	123-35-3	236,666 ± 25,932 [c]	918,697 ± 14,419 [b]	1,219,188 ± 84,847 [a]	1,176,388 ± 93,611 [a]	LRI, MS, STD
12	*α*-Phellandrene [1,2,3,4]	1182	99-83-2	34,869 ± 3153 [d]	300,799 ± 20,009 [a]	150,857 ± 8420 [b]	119,937 ± 1400 [c]	LRI, MS, STD
13	*α*-Terpinene [1,2,3,4]	1195	99-86-5	115,489 ± 11,657 [c]	1,296,352 ± 37,576 [a]	364,443 ± 32,125 [b]	417,156 ± 19,230 [b]	LRI, MS
14	Methyl hexanoate [2]	1197	106-70-7	75,220 ± 1034	-	-	-	LRI, MS, STD
15	Heptanal [1,2,3]	1198	111-71-7	-	69,281 ± 4591 [a]	43,456 ± 1875 [b]	-	LRI, MS, STD
16	Limonene [1,2,3,4,5,6]	1229	138-86-3	14,758,307 ± 1,002,304 [c]	118,087,550 ± 4,893,815 [a]	65,070,290 ± 7,801,430 [b]	59,520,248 ± 6,412,533 [b]	LRI, MS, STD
17	*β*-Phellandrene [1,3,4,5,6]	1233	555-10-2	98,257 ± 5297 [c]	526,885 ± 26,504 [a]	277,990 ± 10,190 [b]	285,054 ± 16,632 [b]	LRI, MS
18	*trans*-2-Hexenal [1,2,3]	1239	6728-26-3	44,549 ± 4045 [b]	46,299 ± 3855 [b]	261,696 ± 26,963 [a]	245,374 ± 12,800 [a]	LRI, MS, STD
19	*cis*-*β*-Ocimene [1,3,4,5]	1254	3338-55-4	46,912 ± 2888 [b]	16,193 ± 1296 [d]	76,751 ± 2538 [a]	26,159 ± 2379 [c]	LRI, MS, STD
20	Pentanol [1,3]	1259	71-41-0	31,067 ± 2067 [b]	-	-	63,300 ± 6002 [a]	LRI, MS, STD
21	*γ*-Terpinene [1,2,3,4,5,6]	1265	99-85-4	756,879 ± 37,299 [c]	6,955,973 ± 270,481 [a]	258,010 ± 26,985 [d]	2,637,181 ± 250,490 [b]	LRI, MS, STD
22	*trans*-*β*-Ocimene [1,3,4,5]	1267	3779-61-1	48,591 ± 4735 [ab]	Trace	51,405 ± 3879 [a]	43,507 ± 2693 [b]	LRI, MS, STD
23	*p*-Mentha-3,8-diene [1]	1280	586-67-4	-	34,763 ± 3335 [a]	17,783 ± 1703 [b]	-	LRI, MS
24	*p*-Cymene [1,2,3,4,5,6]	1294	99-87-6	736,422 ± 54,143 [c]	6,257,423 ± 238,852 [a]	535,553 ± 15,422 [c]	1,754,855 ± 187,714 [b]	LRI, MS, STD
25	Terpinolene [1,2,3,4,5,6]	1304	586-62-9	196,568 ± 13,512 [c]	2,205,629 ± 84,146 [a]	737,783 ± 57,846 [b]	808,365 ± 121,744 [b]	LRI, MS, STD
26	Acetoin [1]	1305	513-86-0	-	-	-	756,403 ± 65,559	LRI, MS, STD
27	Isoterpinolene [1,4]	1310	586-63-0	25,896 ± 1510 [b]	-	100,128 ± 9100 [a]	-	LRI, MS
28	*cis*-2-Pentenol [1,6]	1327	1576-95-0	19,815 ± 1482 [b]	31,352 ± 2402 [a]	-	-	LRI, MS
29	*trans*-2-Heptenal [1]	1331	18829-55-5	-	38,634 ± 3120	-	-	LRI, MS, STD
30	6-Methyl-5-hepten-2-one [1,3,4]	1351	110-93-0	28,623 ± 864 [c]	33,268 ± 1843 [b]	25,640 ± 1717 [c]	64,389 ± 3462 [a]	LRI, MS, STD

Table 1. *Cont.*

No.	Compound	LRI [I]	CAS Number	Abundance (FID Peak Area)				Identification [II]
				Iyokan	Ponkan	Shiranui	Unshiu mikan	
31	Hexanol [1,2,3,5,6]	1357	111-27-3	164,779 ± 12,132 [b]	94,543 ± 4379 [c]	47,972 ± 5501 [c]	759,679 ± 66,784 [a]	LRI, MS, STD
32	*cis*-Alloocimene [1,4,5]	1379	673-84-7	16,464 ± 1658 [b]	-	20,509 ± 2266 [a]	-	LRI, MS, STD
33	*cis*-3-Hexenol [1,3,5,6]	1392	928-96-1	111,666 ± 2265 [b]	44,045 ± 2834 [d]	62,168 ± 2074 [c]	261,090 ± 9818 [a]	LRI, MS, STD
34	Methyl octanoate [1,2]	1395	111-11-5	17,354 ± 1571	-	-	-	LRI, MS, STD
35	Nonanal [1,2,3,4,5,6]	1407	124-19-6	-	38,026 ± 540 [a]	-	34,931 ± 459 [b]	LRI, MS, STD
36	*trans*-2-Hexenol [1,2,3,6]	1410	928-95-0	27,407 ± 2534 [b]	-	35,615 ± 2096 [b]	125,055 ± 8855 [a]	LRI, MS, STD
37	*p*-Mentha-1,3,8-triene [1,3,4]	1413	18368-95-1	-	29,461 ± 922	-	-	LRI, MS
38	*trans*-2-Octenal [1]	1433	2548-87-0	-	80,771 ± 8385	-	-	LRI, MS, STD
39	Ethyl octanoate [1,2,5]	1438	106-32-1	11,923 ± 1142	-	-	-	LRI, MS, STD
40	*p*-Cymenene [3]	1457	1195-32-0	54,839 ± 1755 [d]	326,135 ± 15,218 [a]	181,567 ± 4767 [b]	106,258 ± 6924 [c]	LRI, MS
41	Heptanol [1,2,3,6]	1460	111-70-6	32,725 ± 2726 [b]	50,075 ± 5515 [a]	-	53,777 ± 601 [a]	LRI, MS, STD
42	Acetic acid [1,3,4,5,6]	1465	64-19-7	-	-	21,066 ± 2144 [b]	38,735 ± 2687 [a]	LRI, MS, STD
43	*cis*-Limonene oxide [1,3,4,6]	1468	13837-75-7	-	Trace	-	-	LRI, MS
44	*α*-Cubebene [1,2,3,5]	1473	17699-14-8	-	-	-	24,606 ± 668	LRI, MS
45	*trans*-Limonene oxide [3,4]	1481	4959-35-7	-	45,880 ± 2321	-	-	LRI, MS
46	*δ*-Elemene [1,3,5,6]	1487	20307-84-0	18,083 ± 526 [b]	-	36,304 ± 2783 [a]	-	LRI, MS
47	2-Ethylhexanol [3]	1500	104-76-7	29,728 ± 3204 [b]	35,732 ± 1743 [a]	31,297 ± 2398 [b]	-	LRI, MS, STD
48	*α*-Copaene [1,2,3,4,5,6]	1513	3856-25-5	-	-	16,648 ± 1234	-	LRI, MS
49	*trans*-2-Heptenol [1]	1520	33467-76-4	11,027 ± 740	-	-	-	LRI, MS
50	Ethyl nonanoate [1]	1544	123-29-5	-	-	-	22,281 ± 2145	LRI, MS, STD
51	Linalool [1,2,3,4,5,6]	1552	78-70-6	168,557 ± 9898 [a]	66,715 ± 855 [b]	32,790 ± 2499 [c]	42,386 ± 2325 [c]	LRI, MS, STD
52	Octanol [1,2,3,4,5,6]	1567	111-87-5	30,638 ± 3224 [b]	54,564 ± 1669 [a]	56,588 ± 1463 [a]	33,413 ± 530 [b]	LRI, MS, STD
53	Methylthymol [3,4]	1602	1076-56-8	-	178,301 ± 5016	-	-	LRI, MS
54	*β*-Elemene [1,3,4,5,6]	1611	515-13-9	-	-	29,338 ± 2679 [b]	88,288 ± 5858 [a]	LRI, MS
55	Terpinen-4-ol [1,2,3,4,6]	1618	562-74-3	-	106,146 ± 5719 [a]	35,464 ± 3323 [b]	22,148 ± 2571 [c]	LRI, MS, STD
56	*β*-Caryophyllene [1,3,4,5]	1624	87-44-5	-	-	49,205 ± 4560	-	LRI, MS, STD
57	*p*-Menth-1-en-9-al [3]	1635	29548-14-9	-	17,407 ± 2037	-	-	LRI, MS
58	Nonanol [1,3,4,5,6]	1662	143-08-8	19,302 ± 1450 [b]	34,318 ± 3526 [a]	22,458 ± 2048 [b]	35,654 ± 2020 [a]	LRI, MS, STD
59	Alloaromadendrene [3,4]	1671	25246-27-9	-	-	82,652 ± 8966 [a]	32,436 ± 2132 [b]	LRI, MS
60	Citronellyl acetate [1,3,4,5,6]	1671	150-84-5	-	-	35,537 ± 3362	-	LRI, MS, STD
61	*α*-Humulene [3,4,5,6]	1699	6753-98-6	-	-	18,615 ± 1885 [b]	34,186 ± 3438 [a]	LRI, MS
62	*α*-Terpineol [1,2,3,4,5,6]	1710	98-55-5	86,918 ± 2007 [a]	29,838 ± 1710 [b]	18,280 ± 1213 [c]	-	LRI, MS, STD
63	*trans-trans*-2,4-Nonadienal [1,3]	1718	5910-87-2	26,636 ± 1626	-	-	-	LRI, MS
64	Dodecanal [3,4]	1723	112-54-9	25,070 ± 642	-	-	-	LRI, MS, STD
65	*β*-Selinene [1,4,5,6]	1725	17066-67-0	-	-	75,720 ± 4007 [a]	72,054 ± 5407 [a]	LRI, MS
66	Germacrene D [1,3,4,5,6]	1739	23986-74-5	-	-	-	16,146 ± 627	LRI, MS, STD

Table 1. *Cont.*

No.	Compound	LRI [I]	CAS Number	Abundance (FID Peak Area)				Identification [II]
				Iyokan	Ponkan	Shiranui	Unshiu mikan	
67	Neryl acetate [1,3,4,6]	1741	141-12-8	21,898 ± 1699	-	-	Trace	LRI, MS, STD
68	Valencene [1,2,3,4]	1744	4630-07-3	-	-	1,814,673 ± 135,772 [a]	816,674 ± 34,213 [b]	LRI, MS, STD
69	*α*-Selinene [1,5]	1753	473-13-2	-	-	90,580 ± 5318 [a]	45,375 ± 4649 [b]	LRI, MS
70	*α*-Farnesene [1,3,4,5,6]	1761	502-61-4	-	-	25,118 ± 1716 [a]	22,744 ± 1662 [a]	LRI, MS, STD
71	Decanol [3,4]	1767	112-30-1	Trace	24,327 ± 1835 [b]	55,265 ± 4087 [a]	-	LRI, MS, STD
72	Citronellol [1,2,3,4,5,6]	1768	106-22-9	-	15,891 ± 1034 [b]	24,504 ± 2087 [a]	-	LRI, MS, STD
73	*δ*-Cadinene [1,3,4,6]	1780	483-76-1	22,324 ± 1343 [c]	-	33,587 ± 822 [a]	30,342 ± 991 [b]	LRI, MS
74	*trans*-*trans*-2,4-Decadienal [1,3,5,6]	1833	25152-84-5	10,661 ± 987 [b]	13,234 ± 917 [a]	-	-	LRI, MS, STD
75	Hexanoic acid [1,3,4,6]	1855	142-62-1	-	-	-	15,390 ± 989	LRI, MS, STD
76	Geranyl acetone [1,6]	1871	3796-70-1	29,679 ± 2190 [c]	45,827 ± 3877 [b]	38,750 ± 1213 [b]	65,161 ± 5630 [a]	LRI, MS, STD
77	Heptanoic acid [1]	1964	111-14-8	-	-	-	15,899 ± 406	LRI, MS, STD
78	*β*-Ionone [1,2,3]	1965	14901-07-6	13,113 ± 1145 [b]	15,134 ± 1570 [b]	-	42,300 ± 2247 [a]	LRI, MS, STD
79	Dodecanol [3]	1972	112-53-8	-	8952 ± 455	-	-	LRI, MS, STD
80	Octanoic acid [1,3,4,5,6]	2064	124-07-2	16,593 ± 252 [d]	19,187 ± 532 [c]	42,068 ± 2523 [b]	82,148 ± 4344 [a]	LRI, MS, STD
81	Nonanoic acid [1,3,4,5,6]	2171	112-05-0	Trace	Trace	26,792 ± 2109 [b]	89,453 ± 7917 [a]	LRI, MS, STD
82	Thymol [3]	2177	89-83-8	-	11,779 ± 342	-	Trace	LRI, MS, STD
83	*p*-Menth-8-ene-1,2-diol [3,5]	2288	1946-00-5	Trace	45,352 ± 1248	Trace	Trace	LRI, MS
Total peak area				19,489,768 ± 1,099,266 [c]	143,464,378 ± 5,751,127 [a]	83,195,275 ± 7,855,946 [b]	73,527,094 ± 7,195,905 [b]	

'-' means that the compound was not detected. 'Trace' means that the FID peak area of the compound was unquantifiable, either due to matrix noise or a peak area < 8000. [I] LRI: Experimental linear retention index on an HP-INNOWax column relative to C_7–C_{40} alkane standards. [II] Identification methods: "LRI", comparison of experimental to reference retention indices; "MS", comparison with mass spectrum of the compound in the NIST library version 2.2; and "STD", comparison with authentic standards. [a,b,c,d] Within a row, different superscript letters indicate statistical significance difference at $p < 0.05$. Compounds reported in [1] Goh et al. [13]; [2] Sun et al. [39]; [3] Uehara and Baldovini [40]; [4] B'chir and Arnaud [41]; [5] Cheong et al. [42]; [6] Goh et al. [21].

Table 2 lists 131 volatile compounds identified in four varieties of Japanese mandarin peels extracted by HS-SPME. Similar to the result above, terpenes, mainly consisting of limonene, γ-terpinene, myrcene, and *trans*-β-ocimene, were the major volatile groups found in all four Japanese mandarin peels, but compared to juices, mandarin peels contained more varieties of sesquiterpenes. Compared to the alcohols identified in juices, the analysis of four Japanese mandarin peels found more kinds of alcohols and terpene alcohols with varying abundances. While several alcohol compounds or terpene alcohol derivatives were present in all four types of Japanese mandarin peels, a distinct variation in their abundance was observed. Notably, the esters composition among the peels was significantly different. Iyokan peel was characterised by the presence of several distinct esters, such as ethyl butanoate and ethyl hexanoate. In contrast, Unshiu mikan peel only contained three types of esters with minimal abundance. Three volatile phenols (thymol, eugenol, and carvacrol) were found in four mandarin peels. Indole was also present in all four Japanese mandarin peels.

The unique combination and abundance of volatile compounds in each mandarin variety resulted in distinct differences in their aroma profiles. There were significant differences in the volatile compositions of the four Japanese mandarin peels. Iyokan peel had the highest abundance of alcohols, and linalool was its most abundant alcohol. It contained the highest abundance of esters among the four Japanese mandarins with several terpene esters, such as hexyl hexanoate, neryl acetate, and perillyl acetate. The presence of these alcohols and esters in Iyokan peel has the potential to contribute a complex fragrance profile combining floral, citrusy, and sweet nuances [2,22]. Ponkan peel exhibited the highest abundance of aldehydes, especially β-sinensal and α-sinensal, which have been identified in mandarin oil and are known for their pleasant citrusy scent with green notes [2,22]. Additionally, Ponkan peel contained the highest abundance of terpenes, which could contribute to the woody and peely aroma profiles. Shiranui peel contained many sesquiterpenes with relatively higher abundances, such as valencene and α-farnesene. Its most abundant alcohol was decanol, which has been identified as a key odourant in many mandarin species [22,43]. In addition, nootkatone was only detected in Shiranui peel. The presence of these compounds could have resulted in the green, citrusy and peely impression of Shiranui peel. In comparison to the other three Japanese mandarin peels, notable differences in Unshiu mikan peel were demonstrated by the apparent absence of many kinds of aldehydes, alcohols, and esters, such as *trans*-2-decenol, benzyl alcohol, and octyl acetate. Particularly, the abundance of aldehydes in Unshiu mikan peel was significantly lower than that in other three Japanese mandarin peels, with a lack of *trans-trans*-2,4-decadienal and *trans-cis*-2,6-dodecadienal. Some aldehydes that have been recognised as important contributors to mandarin aroma, such as decanal, neral, β-sinensal, and α-sinensal, were present at only trace levels in Unshiu mikan peel [2,22]. Conversely, Unshiu mikan exhibited a remarkably high abundance of terpenes, which may impart a characteristic green and woody aroma to Unshiu mikan peel [2].

The volatile compounds extracted from Japanese mandarin juices and peels by HS-SPME showed distinct differences in terms of composition and abundance. While both juices and peels contained terpenes, aldehydes, alcohols, esters, ketones, and others, the peels exhibited a more diverse and abundant of volatile compounds. Therefore, a complementary solvent extraction method was subsequently chosen to extract volatiles from these four Japanese mandarin peels (Section 3.2). In general, the application of HS-SPME analysis revealed intricate volatile profiles in both Japanese mandarin juices and peels, elucidating the distinctive volatile compositions that enable the differentiation of these four Japanese mandarin varieties from other mandarin varieties.

Table 2. Identification of volatile compounds in four varieties of Japanese mandarin (Iyokan, Ponkan, Shiranui, and Unshiu mikan) peels extracted by HS-SPME (40 °C, 30 min).

No.	Compound	LRI [I]	CAS Number	Abundance (FID Peak Area)				Identification [II]
				Iyokan	Ponkan	Shiranui	Unshiu Mikan	
1	Acetaldehyde [1,2]	671	75-07-0	3,021,814 ± 113,450 [b]	2,379,431 ± 66,713 [c]	8,209,625 ± 229,458 [a]	-	LRI, MS, STD
2	Ethyl acetate [1,3,4,5]	917	141-78-6	2,412,262 ± 223,644 [a]	Trace	Trace	117,903 ± 10,373 [b]	LRI, MS, STD
3	Methyl butanoate [2]	1001	623-42-7	494,504 ± 50,478	Trace	Trace	-	LRI, MS, STD
4	α-Pinene [1,2,3,4,5,6]	1038	80-56-8	72,767,898 ± 3,542,614 [b]	84,955,972 ± 2,536,220 [a]	37,673,143 ± 1,839,905 [c]	7,405,861 ± 254,832 [d]	LRI, MS, STD
5	α-Thujene [1,3,4]	1042	2867-05-2	33,907,447 ± 2,516,927 [b]	48,208,167 ± 933,902 [a]	14,676,075 ± 534,126 [c]	364,519 ± 22,485 [d]	LRI, MS
6	Ethyl butanoate [1,2]	1049	105-54-4	403,512 ± 41,054	-	-	-	LRI, MS, STD
7	Fenchene [1,4]	1077	471-84-1	251,486 ± 24,760 [a]	218,369 ± 9024 [ab]	235,149 ± 22,513 [a]	190,388 ± 10,381 [b]	LRI, MS
8	Camphene [1,3,4,5]	1082	79-92-5	1,118,843 ± 106,451 [b]	1,311,309 ± 80,790 [a]	253,555 ± 1996 [c]	78,621 ± 6696 [d]	LRI, MS, STD
9	Hexanal [1,2,3,5]	1099	66-25-1	Trace	Trace	90,117 ± 3010	Trace	LRI, MS, STD
10	β-Pinene [1,3,4,5,6]	1123	127-91-3	48,161,195 ± 3,394,260 [a]	28,873,180 ± 869,334 [b]	1,742,254 ± 75,939 [c]	3,046,957 ± 164,865 [c]	LRI, MS, STD
11	Sabinene [1,3,4,5,6]	1135	3387-41-5	4,186,389 ± 29,334 [c]	52,753,832 ± 4,187,512 [a]	19,442,711 ± 346,792 [b]	487,989 ± 23,800 [c]	LRI, MS, STD
12	Myrcene [1,2,3,4,5,6]	1175	123-35-3	181,746,657 ± 3,133,756 [b]	223,400,905 ± 7,438,213 [a]	185,541,609 ± 6,318,947 [b]	35,207,496 ± 755,294 [c]	LRI, MS, STD
13	α-Phellandrene [1,2,3,4]	1182	99-83-2	971,304 ± 135,772 [c]	234,917 ± 28,355 [d]	2,463,630 ± 62,843 [a]	1,265,627 ± 40,262 [b]	LRI, MS, STD
14	α-Terpinene [1,2,3,4]	1195	99-86-5	425,859 ± 20,341 [b]	274,139 ± 23,765 [b]	477,566 ± 2719 [b]	5,378,465 ± 320,862 [a]	LRI, MS
15	Limonene [1,2,3,4,5,6]	1229	138-86-3	7,794,558,186 ± 171,677,992 [b]	9,003,005,342 ± 112,992,466 [a]	8,066,891,387 ± 325,705,414 [b]	1,135,791,679 ± 63,421,763 [c]	LRI, MS, STD
16	β-Phellandrene [1,3,4,5,6]	1233	555-10-2	13,226,859 ± 1,327,534 [c]	18,751,198 ± 426,585 [a]	15,970,718 ± 524,327 [b]	3,848,447 ± 10,554 [d]	LRI, MS
17	Ethyl hexanoate [1,2,3]	1246	123-66-0	1,420,023 ± 161,014	-	-	-	LRI, MS, STD
18	*cis*-β-Ocimene [1,3,4,5]	1254	3338-55-4	1,501,939 ± 75,692 [a]	1,208,799 ± 72,438 [b]	674,214 ± 56,472 [c]	214,089 ± 11,659 [d]	LRI, MS, STD
19	γ-Terpinene [1,2,3,4,5,6]	1265	99-85-4	335,256,197 ± 27,081,641 [b]	383,400,732 ± 8,802,941 [a]	11,978,659 ± 292,078 [d]	62,312,158 ± 604,708 [c]	LRI, MS, STD
20	*trans*-β-Ocimene [1,3,4,5]	1267	3779-61-1	226,416,538 ± 13,752,207 [a]	138,154,783 ± 17,504,308 [b]	13,259,873 ± 1,075,416 [c]	3,220,802 ± 250,457 [c]	LRI, MS, STD
21	*p*-Mentha-3,8-diene [1]	1280	586-67-4	202,373 ± 8356 [b]	341,690 ± 13,408 [a]	167,391 ± 12,674 [c]	84,575 ± 5882 [d]	LRI, MS
22	Hexyl acetate [1,3,4]	1288	142-92-7	357,655 ± 25,769 [a]	-	-	27,363 ± 523 [b]	LRI, MS, STD
23	*p*-Cymene [1,2,3,4,5,6]	1294	99-87-6	34,255,941 ± 1,493,829 [a]	33,859,784 ± 1,941,883 [a]	2,807,393 ± 212,707 [c]	14,139,510 ± 1,068,535 [b]	LRI, MS, STD
24	Terpinolene [1,2,3,4,5,6]	1304	586-62-9	50,351,353 ± 2,521,776 [b]	63,825,352 ± 2,750,559 [a]	25,708,236 ± 1,030,117 [c]	1,1878,259 ± 930,233 [d]	LRI, MS, STD
25	Octanal [1,2,3,4,5,6]	1306	124-13-0	-	282,649 ± 12,185 [b]	391,863 ± 29,293 [a]	-	LRI, MS, STD
26	Isoterpinolene [1,4]	1310	586-63-0	1,139,956 ± 71,812 [b]	1,881,552 ± 179,005 [a]	975,303 ± 80,256 [b]	439,599 ± 48,054 [c]	LRI, MS
27	*cis*-2-Pentenol [1,6]	1327	1576-95-0	59,984 ± 4403	-	-	-	LRI, MS
28	*cis*-3-Hexenyl acetate [1,3,5]	1328	3681-71-8	724,286 ± 31,438 [a]	-	-	54,471 ± 2973 [b]	LRI, MS, STD
29	6-Methyl-5-hepten-2-one [1,3,4]	1351	110-93-0	20,061 ± 1708 [b]	-	21,736 ± 2068 [b]	33,168 ± 2662 [a]	LRI, MS, STD
30	Hexanol [1,2,3,5,6]	1357	111-27-3	1,141,555 ± 71,011 [a]	176,255 ± 9873 [c]	629,718 ± 14,528 [b]	245,510 ± 30,423 [c]	LRI, MS, STD
31	*cis*-Alloocimene [1,4,5]	1379	673-84-7	1,674,019 ± 101,035 [a]	846,605 ± 47,359 [b]	498,268 ± 51,697 [c]	232,381 ± 4693 [d]	LRI, MS, STD
32	*cis*-3-Hexenol [1,3,5,6]	1392	928-96-1	1,560,263 ± 109,543 [a]	807,807 ± 75,632 [b]	935,481 ± 11,045 [b]	67,410 ± 4843 [c]	LRI, MS, STD

Table 2. *Cont.*

No.	Compound	LRI [I]	CAS Number	Abundance (FID Peak Area)				Identification [II]
				Iyokan	Ponkan	Shiranui	Unshiu Mikan	
33	Methyl octanoate [1,2]	1395	111-11-5	165,456 ± 15,096	-	-	-	LRI, MS, STD
34	*trans*-Alloocimene [1]	1402	14947-20-7	893,954 ± 40,097 [a]	531,250 ± 58,378 [b]	360,579 ± 34,087 [c]	207,150 ± 19,239 [d]	LRI, MS
35	*trans*-2-Hexenol [1,2,3,6]	1410	928-95-0	125,465 ± 5396	-	-	-	LRI, MS, STD
36	*p*-Mentha-1,3,8-triene [1,3,4]	1413	18368-95-1	210,801 ± 20,445 [a]	195,113 ± 7165 [a]	213,968 ± 20,664 [a]	66,809 ± 9454 [b]	LRI, MS
37	Hexyl butanoate [1,2,3]	1421	2639-63-6	1,107,410 ± 103,495	-	-	-	LRI, MS, STD
38	Ethyl octanoate [1,2,5]	1438	106-32-1	395,035 ± 43,480 [a]	-	24,480 ± 2627 [b]	-	LRI, MS, STD
39	*p*-Mentha-1,5,8-triene [2]	1440	21195-59-5	120,366 ± 9076 [a]	110,244 ± 6032 [ab]	98,940 ± 8028 [b]	48,492 ± 4867 [c]	LRI, MS
40	*p*-Cymenene [3]	1457	1195-32-0	2,948,285 ± 207,196 [a]	3,097,667 ± 204,365 [a]	1,338,095 ± 130,297 [b]	1,631,156 ± 111,077 [b]	LRI, MS
41	*cis*-Limonene oxide [1,3,4,6]	1468	13837-75-7	Trace	118,353 ± 12,087 [a]	95,713 ± 1556 [b]	Trace	LRI, MS
42	*cis*-3-Hexenyl butanoate [1,3]	1471	16491-36-4	437,567 ± 41,062	-	-	-	LRI, MS, STD
43	*α*-Cubebene [1,2,3,5]	1473	17699-14-8	901,160 ± 54,638 [a]	127,939 ± 5198 [c]	266,232 ± 8816 [d]	361,791 ± 29,736 [b]	LRI, MS
44	*trans*-Limonene oxide [3,4]	1481	4959-35-7	132,628 ± 11,778 [c]	1,524,017 ± 88,197 [a]	1,343,757 ± 131,036 [b]	54,539 ± 2665 [c]	LRI, MS
45	Octyl acetate [1,3,4,5]	1483	112-14-1	1,041,047 ± 48,326 [a]	435,829 ± 12,954 [b]	205,589 ± 13,573 [c]	-	LRI, MS, STD
46	*δ*-Elemene [1,3,5,6]	1487	20307-84-0	14,570,016 ± 778,325 [a]	1,377,078 ± 95,264 [b]	698,139 ± 36,489 [b]	1,149,042 ± 28,839 [b]	LRI, MS
47	Citronellal [1,3,4]	1493	106-23-0	-	183,173 ± 9278 [a]	90,924 ± 6271 [b]	-	LRI, MS, STD
48	*α*-Ylangene [3,6]	1503	14912-44-8	618,142 ± 28,949 [a]	91,961 ± 6194 [b]	78,245 ± 6377 [b]	82,568 ± 5267 [b]	LRI, MS
49	*α*-Copaene [1,2,3,4,5,6]	1513	3856-25-5	3,402,465 ± 500,759 [a]	-	3,387,074 ± 254,593 [b]	1,380,120 ± 151,456 [b]	LRI, MS
50	Decanal [1,2,3,4,5,6]	1515	112-31-2	1,251,121 ± 65,784 [b]	7,168,137 ± 497,569 [a]	1,236,357 ± 121,466 [b]	Trace	LRI, MS, STD
51	Linalool [1,2,3,4,5,6]	1552	78-70-6	19,839,139 ± 1,716,833 [a]	7,061,014 ± 611,543 [b]	2,156,911 ± 237,030 [c]	122,394 ± 5602 [d]	LRI, MS, STD
52	*cis*-4-Decenal [3]	1555	21662-09-9	-	66,948 ± 2022	-	-	LRI, MS, STD
53	*β*-Cubebene [1,2,3]	1557	13744-15-5	463,836 ± 22,840 [a]	-	115,995 ± 10,154 [b]	103,283 ± 1237 [b]	LRI, MS
54	Linalyl acetate [3,4]	1566	115-95-7	48,017 ± 3747	-	-	-	LRI, MS, STD
55	Octanol [1,2,3,4,5,6]	1567	111-87-5	187,148 ± 10,299 [c]	2,825,984 ± 268,182 [a]	1,757,499 ± 186,038 [b]	55,432 ± 5639 [c]	LRI, MS, STD
56	*trans*-*α*-Bergamotene [3,4]	1576	13474-59-4	173,673 ± 5351 [a]	130,315 ± 6438 [b]	-	-	LRI, MS
57	Nonyl acetate [4]	1584	143-13-5	135,996 ± 8557 [a]	51,267 ± 1102 [b]	33,249 ± 3525 [c]	-	LRI, MS, STD
58	Methyl decanoate [1]	1591	110-42-9	-	-	32,015 ± 2545	-	LRI, MS
59	*β*-Copaene [1,2,3,4]	1595	18252-44-3	770,008 ± 73,148 [a]	-	140,828 ± 9270 [b]	125,276 ± 3185 [b]	LRI, MS
60	Methylthymol [3,4]	1602	1076-56-8	-	7,416,428 ± 577,654	-	-	LRI, MS
61	*β*-Elemene [1,3,4,5,6]	1611	515-13-9	4,396,452 ± 417,605 [b]	-	876,753 ± 60,868 [c]	4,979,190 ± 391,615 [a]	LRI, MS
62	Hexyl hexanoate [1]	1615	6378-65-0	1,351,623 ± 100,303	-	-	-	LRI, MS, STD
63	Undecanal [3,4,5,6]	1617	112-44-7	-	566,099 ± 27,765 [a]	488,674 ± 45,944 [b]	-	LRI, MS, STD
64	Terpinen-4-ol [1,2,3,4,6]	1618	562-74-3	-	418,702 ± 19,007 [a]	-	83,869 ± 6973 [b]	LRI, MS, STD
65	*β*-Caryophyllene [1,3,4,5]	1624	87-44-5	3,932,499 ± 207,687 [a]	353,044 ± 35,252 [d]	764,800 ± 6263 [c]	2,024,648 ± 183,248 [b]	LRI, MS, STD
66	*β*-Gurjunene	1625	17334-55-3	-	-	-	192,441 ± 17,451	LRI, MS
67	*trans*-Dihydrocarvone [2,3]	1626	5948-04-9	532,126 ± 75,746 [a]	169,144 ± 5807 [b]	116,528 ± 15,675 [bc]	69,907 ± 4068 [c]	LRI, MS
68	*γ*-Elemene [1,3,4,5,6]	1656	29873-99-2	4,248,781 ± 146,454 [a]	1,739,293 ± 95,084 [b]	-	329,240 ± 25,738 [c]	LRI, MS

Table 2. *Cont.*

No.	Compound	LRI [I]	CAS Number	Abundance (FID Peak Area)				Identification [II]
				Iyokan	Ponkan	Shiranui	Unshiu Mikan	
69	*cis*-3-Hexenyl hexanoate [1]	1659	31501-11-8	565,004 ± 29,440	-	-	-	LRI, MS, STD
70	*trans*-2-Decenal [1,3,5]	1661	3913-81-3	-	1,248,632 ± 123,764	-	-	LRI, MS, STD
71	Nonanol [1,3,4,5,6]	1662	143-08-8	41,061 ± 2908 [c]	332,089 ± 29,052 [b]	659,399 ± 48,236 [a]	Trace	LRI, MS, STD
72	Citronellyl acetate [1,3,4,5,6]	1671	150-84-5	-	705,591 ± 20,817 [b]	1,353,091 ± 106,793 [a]	-	LRI, MS, STD
73	*trans*-*β*-Farnesene [1,3,4,6]	1676	18794-84-8	4,342,285 ± 443,666 [a]	2,665,085 ± 54,910 [b]	347,988 ± 32,701 [c]	134,819 ± 10,243 [c]	LRI, MS
74	Decyl acetate [3,4,5,6]	1689	112-17-4	-	763,481 ± 72,735 [a]	415,566 ± 15,990 [b]	-	LRI, MS, STD
75	*γ*-Muurolene [1,3,4,6]	1693	30021-74-0	4,273,643 ± 306,833 [a]	123,575 ± 8632 [b]	-	235,926 ± 19,014 [b]	LRI, MS
76	*α*-Humulene [3,4,5,6]	1699	6753-98-6	3,448,333 ± 286,530 [a]	509,886 ± 30,877 [c]	770,864 ± 47,609 [c]	2,265,701 ± 232,056 [b]	LRI, MS
77	Neral [1,3,4,5]	1704	106-26-3	232,615 ± 15,937 [a]	70,784 ± 6092 [b]	37,846 ± 1303 [c]	Trace	LRI, MS, STD
78	*α*-Terpineol [1,2,3,4,5,6]	1710	98-55-5	-	1,510,068 ± 112,107 [a]	893,486 ± 62,724 [c]	972,896 ± 108,044 [b]	LRI, MS, STD
79	Dodecanal [3,4]	1723	112-54-9	611,380 ± 15,376 [b]	4,621,407 ± 273,589 [a]	4,207,331 ± 331,690 [a]	-	LRI, MS, STD
80	*β*-Selinene [1,4,5,6]	1725	17066-67-0	1,396,586 ± 167,426 [b]	141,199 ± 16,442 [c]	276,085 ± 24,848 [c]	1,720,951 ± 131,977 [a]	LRI, MS
81	Germacrene D [1,3,4,5,6]	1739	23986-74-5	2,604,458 ± 215,011	-	-	-	LRI, MS, STD
82	Neryl acetate [1,3,4,6]	1741	141-12-8	3,906,687 ± 322,516 [a]	1,043,472 ± 120,990 [b]	1,106,805 ± 63,115 [b]	-	LRI, MS, STD
83	*δ*-Selinene [1]	1743	28624-23-9	2,923,547 ± 225,794 [a]	472,730 ± 22,823 [c]	1,110,507 ± 106,279 [b]	999,774 ± 107,057 [b]	LRI, MS
84	Valencene [1,2,3,4]	1744	4630-07-3	946,351 ± 73,168 [c]	-	18,201,327 ± 1,406,097 [a]	8,511,199 ± 755,215 [b]	LRI, MS, STD
85	*α*-Muurolene [1,3,4]	1747	10208-80-7	2,139,599 ± 87,154 [a]	156,714 ± 6062 [b]	-	-	LRI, MS
86	Geranial [1,3,4,5,6]	1748	141-27-5	68,557 ± 5015 [b]	239,032 ± 33,071 [a]	Trace	2936 ± 147 [c]	LRI, MS, STD
87	*α*-Selinene [1,5]	1753	473-13-2	1,601,701 ± 80,894 [b]	-	1,222,031 ± 102,210 [c]	2,854,491 ± 214,256 [a]	LRI, MS
88	*α*-Farnesene [1,3,4,5,6]	1761	502-61-4	3,682,771 ± 215,845 [b]	2,027,817 ± 105,590 [c]	18,592,435 ± 1,527,910 [a]	3,379,537 ± 78,648 [bc]	LRI, MS, STD
89	Geranyl acetate [1,3,4,5,6]	1765	105-87-3	3,349,148 ± 188,570	-	-	-	LRI, MS, STD
90	Decanol [3,4]	1767	112-30-1	2,145,521 ± 196,674 [c]	4,573,607 ± 334,157 [b]	6,191,909 ± 580,822 [a]	Trace	LRI, MS, STD
91	Citronellol [1,2,3,4,5,6]	1768	106-22-9	296,728 ± 24,666 [c]	2,431,748 ± 247,414 [a]	1,798,873 ± 182,943 [b]	Trace	LRI, MS, STD
92	*δ*-Cadinene [1,3,4,6]	1780	483-76-1	7,045,004 ± 196,134 [a]	835,474 ± 44,285 [d]	1,542,340 ± 139,745 [c]	1,940,735 ± 128,660 [b]	LRI, MS
93	*γ*-Cadinene [1,3,6]	1784	39029-41-9	2,394,928 ± 186,049 [a]	347,242 ± 33,169 [b]	-	303,859 ± 26,715 [b]	LRI, MS
94	*β*-Sesquiphellandrene [3,4]	1789	20307-83-9	257,824 ± 13,964 [a]	202,586 ± 7225 [b]	-	-	LRI, MS
95	*cis*-4-Decenol	1799	57074-37-0	-	56,380 ± 3687 [b]	61,942 ± 3662 [a]	-	LRI, MS
96	Perillyl aldehyde [1,3,4,5,6]	1818	2111-75-3	Trace	1,085,479 ± 100,983 [a]	495,968 ± 34,962 [b]	-	LRI, MS, STD
97	*α*-Cadinene [3]	1826	24406-05-1	1,467,487 ± 122,452 [a]	-	-	145,415 ± 13,270 [b]	LRI, MS
98	*trans*-2-Decenol [5,6]	1830	18409-18-2	238,075 ± 15,624 [a]	145,406 ± 13,141 [b]	117,321 ± 11,457 [c]	-	LRI, MS
99	*trans*-*trans*-2,4-Decadienal [1,3,5,6]	1833	25152-84-5	290,521 ± 30,168 [b]	542,977 ± 21,873 [a]	108,927 ± 9438 [c]	-	LRI, MS, STD
100	*trans*-Carveol [1,3,4,6]	1848	1197-07-5	-	54,800 ± 3675 [b]	109,216 ± 9358 [a]	-	LRI, MS, STD
101	Calamenene [1,3]	1850	483-77-2	795,574 ± 73,127 [a]	101,296 ± 4162 [c]	207,106 ± 11,690 [d]	312,129 ± 24,238 [b]	LRI, MS
102	Undecanol [3,4]	1852	112-42-5	84,785 ± 3126 [a]	61,928 ± 2808 [b]	-	-	LRI, MS
103	*cis*-Carveol [1,3,4,6]	1884	1197-06-4	-	250,251 ± 25,009 [a]	157,451 ± 13,436 [b]	-	LRI, MS, STD
104	*trans*-2-Dodecenal [1,3,5]	1885	20407-84-5	142,673 ± 14,121 [a]	34,987 ± 3199 [b]	Trace	-	LRI, MS, STD

Table 2. *Cont.*

No.	Compound	LRI [I]	CAS Number	Abundance (FID Peak Area)				Identification [II]
				Iyokan	Ponkan	Shiranui	Unshiu Mikan	
105	Benzyl alcohol [1,3,4,6]	1898	100-51-6	77,059 ± 3097 [a]	72,336 ± 6248 [a]	71,040 ± 6005 [a]	-	LRI, MS, STD
106	*trans-cis*-2,6-Dodecadienal [5]	1911	21662-13-5	93,919 ± 1358 [b]	102,340 ± 1527 [a]	31,910 ± 3351 [c]	-	LRI, MS, STD
107	Perillyl acetate [1,3,4,5,6]	1925	15111-96-3	362,777 ± 14,110 [a]	27,093 ± 1526 [b]	-	-	LRI, MS
108	Tetradecanal [3,4]	1935	124-25-4	-	201,756 ± 20,358	-	-	LRI, MS
109	*α*-Calacorene [4]	1951	21391-99-1	460,545 ± 14,248 [a]	58,725 ± 5455 [c]	75,623 ± 3759 [b]	92,329 ± 6458 [b]	LRI, MS
110	*p*-Menth-1-en-9-ol [3,6]	1952	18479-68-0	-	71,104 ± 7850 [a]	42,944 ± 3627 [b]	-	LRI, MS
111	Heptanoic acid [1]	1964	111-14-8	-	-	-	26,743 ± 1102	LRI, MS, STD
112	Dodecanol [3]	1972	112-53-8	-	55,051 ± 5365 [b]	147,603 ± 10,680 [a]	-	LRI, MS, STD
113	*cis*-Nerolidol [3]	2010	142-50-7	Trace	Trace	-	-	LRI, MS, STD
114	Perillyl alcohol [1,2,3,4,5,6]	2012	536-59-4	291,604 ± 28,313 [a]	185,643 ± 12,165 [b]	112,364 ± 4774 [c]	37,207 ± 3229 [d]	LRI, MS, STD
115	Methyleugenol [1]	2029	93-15-2	288,659 ± 26,281 [a]	-	44,808 ± 3267 [b]	-	LRI, MS, STD
116	*trans*-Nerolidol [3,5]	2044	40716-66-3	132,973 ± 2854 [a]	44,950 ± 4797 [b]	-	-	LRI, MS, STD
117	Octanoic acid [1,3,4,5,6]	2064	124-07-2	Trace	38,430 ± 2295 [b]	31,011 ± 3097 [c]	55,451 ± 6204 [a]	LRI, MS, STD
118	Elemol [1,4,5,6]	2098	639-99-6	129,980 ± 12,453 [a]	-	48,784 ± 1458 [b]	-	LRI, MS
119	Methyl *N*-methylanthranilate [3,5]	2107	85-91-6	Trace	24,816 ± 2151	Trace	-	LRI, MS, STD
120	Globulol [3,4]	2108	489-41-8	55,438 ± 5066	-	-	-	LRI, MS
121	Nonanoic acid [1,3,4,5,6]	2171	112-05-0	34,088 ± 2430 [c]	13,818 ± 325 [d]	38,801 ± 1404 [b]	45,093 ± 3195 [a]	LRI, MS, STD
122	Thymol [3]	2177	89-83-8	52,858 ± 1832 [b]	1,168,809 ± 44,593 [a]	20,512 ± 1747 [b]	26,514 ± 2400 [b]	LRI, MS, STD
123	Eugenol [3]	2194	97-53-0	411,866 ± 17,797	-	Trace	-	LRI, MS, STD
124	Carvacrol [3,4]	2231	499-75-2	37,632 ± 3220 [b]	95,715 ± 8702 [a]	14,500 ± 1335 [c]	19,723 ± 1394 [c]	LRI, MS, STD
125	*β*-Sinensal [3]	2255	60066-88-8	355,351 ± 4653 [a]	243,727 ± 12,764 [b]	19,655 ± 567 [c]	Trace	LRI, MS, STD
126	Isospathulenol [6]	2272	88395-46-4	52,658 ± 2436	-	-	-	LRI, MS
127	Decanoic acid [1,3,4,5,6]	2277	334-48-5	28,821 ± 1238	Trace	Trace	Trace	LRI, MS, STD
128	*p*-Menth-8-ene-1,2-diol [3,5]	2288	1946-00-5	279,513 ± 26,598 [b]	563,909 ± 48,359 [a]	536,560 ± 24,663 [a]	317,897 ± 19,309 [b]	LRI, MS
129	*α*-Sinensal [3]	2360	17909-77-2	195,811 ± 7979 [b]	293,104 ± 17,654 [a]	Trace	Trace	LRI, MS, STD
130	Indole [1,6]	2488	120-72-9	65,046 ± 3222	Trace	Trace	Trace	LRI, MS, STD
131	Nootkatone [1,2,3,4]	2580	4674-50-4	-	-	111,415 ± 8811	-	LRI, MS, STD
	Total peak area			8,932,836,018 ± 176,904,541 [b]	10,155,518,812 ± 121,237,952 [a]	8,488,970,363 ± 326,245,173 [c]	1,323,601,924 ± 65,326,925 [d]	

'-' means that the compound was not detected. 'Trace' means that the FID peak area of the compound was unquantifiable, either due to matrix noise or a peak area < 8000. [I] LRI: Experimental linear retention index on an HP-INNOWax column relative to C_7–C_{40} alkane standards. [II] Identification methods: "LRI", comparison of experimental to reference retention indices; "MS", comparison with mass spectrum of the compound in the NIST library version 2.2; and "STD", comparison with authentic standards. [a,b,c,d] Within a row, different superscript letters indicate statistical significance difference at $p < 0.05$. Compounds reported in [1] Goh et al. [13]; [2] Sun et al. [39]; [3] Uehara and Baldovini [40]; [4] B'chir and Arnaud [41]; [5] Cheong et al. [42]; [6] Goh et al. [21].

3.2. Extraction of Volatile Compounds in Japanese Mandarin Peels by Solvent Extraction

A total of 164 volatile compounds were identified in the DCM extracts of the four Japanese mandarin peels (Table 3). In all four Japanese mandarin peel extracts, the most abundant compound was limonene, and terpenes represented the most common class of compounds identified in this study. Alcohols comprised the second most abundant volatile group with linalool found to be the main alcohol in all four Japanese mandarin peel extracts. As shown in Table 3, all four Japanese mandarin peel extracts demonstrated similar volatile compound compositions but differed in their quantitative profiles. For instance, Iyokan peel extract contained significantly higher concentrations of alcohols, esters, and acids, with distinct higher concentrations of linalool, geraniol, *trans*-nerolidol, neryl acetate, perillyl acetate, and octanoic acid. The main aldehydes were α-sinensal and β-sinensal, with a notable higher abundance than the other three Japanese mandarin peel extracts. Notably, neral was detected in all Japanese mandarin peel extracts except for Iyokan. The high abundances of these compounds could potentially characterise Iyokan with floral and sweet profiles [2]. Interestingly, Ponkan contained the highest amount of volatile phenols, with thymol and 4-vinylguaiacol found in significantly higher concentrations than the other three analysed Japanese mandarin peel extracts. The existence of these compounds imply that Ponkan could be distinguishable with spicy, phenolic, and woody aroma [44]. γ-Terpinene was the next most abundant terpene found in the other three peel extracts. In Shiranui, the second most abundant terpene was myrcene, followed by sabinene, α-farnesene, *trans*-β-ocimene, and valencene, which was generally consistent with the results of Umano et al. [33]. The higher amounts of these terpenes may impart herbal and citrusy characteristics to Shiranui [38]. In addition, Shiranui peel extract had the highest amount of nootkatone, which might contribute peely and citrusy profiles in Shiranui peel [45]. Unshiu mikan peel extract had the lowest amounts of volatiles, and in particular, it lacked common citrus aldehydes such as citronellal, *cis*-4-decenal, and *trans*-2-decenal. However, the proportions of alcohols were remarkably high, which may contribute to the distinct green and woody characteristic of Unshiu mikan peel extract [38].

While solvent extraction facilitates semi-quantitative analysis, the combination of HS-SPME and solvent extraction provided a complementary extraction of volatile compounds from four Japanese mandarin fruits in this study. For instance, acetaldehyde, ethyl acetate, and methyl butanoate were only extracted by HS-SPME. Butanoic acid, *cis*-carvyl acetate, *trans*-carvyl acetate, and carvone were only detected in the solvent extracts of the four Japanese mandarin varieties and might play a crucial role in shaping their distinctive green and spicy aroma profiles [45]. Additionally, nerol, geraniol, *trans-trans*-farnesol, and vanillin were also only detected in the solvent extracts and may impart sweet and floral characteristics to these Japanese mandarins [38]. Each variety displayed distinctive characteristics, including varying concentrations of specific compounds or the absence of certain compounds, highlighting the unique volatile profiles of the four Japanese mandarins. These results enhance our comprehension of the volatile composition of Japanese mandarin peels and offer valuable insights into their distinct aroma attributes.

Table 3. Identification of volatile compounds and their concentration (ng/mL) in four varieties of Japanese mandarin (Iyokan, Ponkan, Shiranui, and Unshiu mikan) peel extracts using solvent extraction.

No.	Compound	LRI [I]	CAS Number	Iyokan	Ponkan	Shiranui	Unshiu Mikan	Identification [II]
1	*α*-Pinene [1,2,3,4,5,6]	1038	80-56-8	1546.03 ± 42.22 [b]	1027.75 ± 19.21 [c]	2847.14 ± 43.34 [a]	352.98 ± 8.61 [d]	LRI, MS, STD
2	*α*-Thujene [1,3,4]	1042	2867-05-2	2562.59 ± 27.55 [b]	897.25 ± 34.33 [c]	2721.30 ± 9.81 [a]	135.32 ± 3.74 [d]	LRI, MS
3	Camphene [1,3,4,6]	1082	79-92-5	17.27 ± 0.39 [a]	10.25 ± 0.58 [b]	3.26 ± 0.29 [d]	4.62 ± 0.12 [c]	LRI, MS, STD
4	Hexanal [1,2,3,6]	1099	66-25-1	21.36 ± 0.63 [a]	11.69 ± 0.37 [c]	18.77 ± 1.76 [b]	19.04 ± 0.92 [b]	LRI, MS, STD
5	*β*-Pinene [1,3,4,5,6]	1123	127-91-3	1666.40 ± 4.81 [a]	738.89 ± 30.38 [b]	238.43 ± 4.22 [c]	191.32 ± 7.29 [d]	LRI, MS, STD
6	Sabinene [1,3,4,5,6]	1135	3387-41-5	1354.84 ± 12.66 [c]	2416.02 ± 46.50 [b]	12,553.31 ± 258.90 [a]	77.80 ± 2.45 [d]	LRI, MS, STD
7	1-Penten-3-ol [1,5]	1165	616-25-1	16.59 ± 0.43 [b]	-	-	20.11 ± 0.57 [a]	LRI, MS
8	Myrcene [1,2,3,4,5,6]	1175	123-35-3	8660.65 ± 69.73 [b]	4064.46 ± 45.72 [c]	13,831.64 ± 102.60 [a]	926.11 ± 39.92 [d]	LRI, MS, STD
9	*α*-Phellandrene [1,2,3,4]	1182	99-83-2	15.88 ± 0.32 [a]	3.88 ± 0.25 [b]	Trace	15.88 ± 0.64 [a]	LRI, MS, STD
10	*α*-Terpinene [1,2,3,4]	1195	99-86-5	Trace	Trace	Trace	72.49 ± 1.37	LRI, MS
11	Limonene [1,2,3,4,5,6]	1229	138-86-3	421,726.10 ± 2687.60 [b]	194,306.44 ± 3782.63 [c]	972,976.48 ± 8890.99 [a]	44,510.21 ± 2182.40 [d]	LRI, MS, STD
12	*β*-Phellandrene [1,3,4,5,6]	1233	555-10-2	524.16 ± 1.01 [b]	355.07 ± 6.98 [c]	883.25 ± 65.27 [a]	182.37 ± 7.03 [d]	LRI, MS
13	*trans*-2-Hexenal [1,2,3]	1239	6728-26-3	-	-	-	7.75 ± 0.32	LRI, MS, STD
14	*cis*-*β*-Ocimene [1,3,4,6]	1254	3338-55-4	89.24 ± 3.34 [a]	13.33 ± 0.86 [b]	Trace	Trace	LRI, MS, STD
15	Pentanol [1,3]	1259	71-41-0	-	-	-	11.17 ± 0.31	LRI, MS, STD
16	*γ*-Terpinene [1,2,3,4,5,6]	1265	99-85-4	31,682.10 ± 197.90 [a]	11,476.35 ± 326.57 [b]	223.70 ± 2.26 [d]	2789.72 ± 83.74 [c]	LRI, MS, STD
17	*trans*-*β*-Ocimene [1,3,4,6]	1267	3779-61-1	Trace	14.03 ± 0.70 [b]	5368.88 ± 54.14 [a]	Trace	LRI, MS, STD
18	Hexyl acetate [1,3,4]	1288	142-92-7	13.26 ± 0.34	-	-	-	LRI, MS, STD
19	*p*-Cymene [1,2,3,4,5,6]	1294	99-87-6	1219.77 ± 7.69 [a]	358.64 ± 23.87 [b]	32.93 ± 1.52 [d]	132.26 ± 5.62 [c]	LRI, MS, STD
20	Terpinolene [1,2,3,4,5,6]	1304	586-62-9	1046.39 ± 120.46 [a]	1053.84 ± 22.78 [a]	311.17 ± 8.69 [b]	Trace	LRI, MS, STD
21	Octanal [1,2,3,4,5,6]	1306	124-13-0	29.08 ± 2.05 [c]	415.92 ± 45.24 [a]	350.37 ± 20.03 [b]	53.78 ± 1.83 [c]	LRI, MS, STD
22	*cis*-2-Pentenol [1,5]	1327	1576-95-0	-	-	-	19.73 ± 0.95	LRI, MS
23	*cis*-3-Hexenyl acetate [1,3,6]	1328	3681-71-8	13.18 ± 0.30	-	-	-	LRI, MS, STD
24	Prenol [1,3,5]	1328	556-82-1	43.75 ± 1.79 [a]	14.16 ± 0.91 [c]	19.95 ± 2.09 [b]	22.81 ± 1.05 [b]	LRI, MS, STD
25	6-Methyl-5-hepten-2-one [1,3,4]	1351	110-93-0	8.04 ± 0.42 [a]	2.67 ± 0.17 [c]	-	3.26 ± 0.05 [b]	LRI, MS, STD
26	Hexanol [1,2,3,5,6]	1357	111-27-3	192.86 ± 1.30 [a]	26.77 ± 0.99 [c]	96.13 ± 2.04 [d]	69.85 ± 1.13 [b]	LRI, MS, STD
27	*cis*-Alloocimene [1,4,6]	1379	673-84-7	23.17 ± 0.94 [a]	7.15 ± 0.43 [b]	-	-	LRI, MS, STD
28	*cis*-3-Hexenol [1,3,5,6]	1392	928-96-1	172.16 ± 3.78 [b]	33.25 ± 0.73 [c]	344.19 ± 2.67 [a]	175.24 ± 2.04 [b]	LRI, MS, STD
29	Methyl octanoate [1,2]	1395	111-11-5	2.44 ± 0.04	-	-	-	LRI, MS, STD
30	Nonanal [1,2,3,4,5,6]	1407	124-19-6	46.67 ± 3.46 [b]	38.19 ± 3.76 [b]	259.41 ± 18.56 [a]	11.69 ± 0.13 [c]	LRI, MS, STD
31	*p*-Mentha-1,3,8-triene [1,3,4]	1413	18368-95-1	18.02 ± 0.67 [b]	20.45 ± 1.56 [b]	23.88 ± 2.75 [a]	11.74 ± 0.49 [c]	LRI, MS
32	Hexyl butanoate [1,2,3]	1421	2639-63-6	19.49 ± 0.57	-	-	-	LRI, MS, STD
33	*p*-Mentha-1,5,8-triene [2]	1440	21195-59-5	14.04 ± 0.22 [a]	13.95 ± 0.40 [a]	7.11 ± 0.28 [c]	11.86 ± 0.96 [b]	LRI, MS
34	*p*-Cymenene [3]	1457	1195-32-0	-	22.13 ± 1.47 [a]	-	21.33 ± 0.91 [a]	LRI, MS

Table 3. *Cont.*

No.	Compound	LRI [I]	CAS Number	Iyokan	Ponkan	Shiranui	Unshiu Mikan	Identification [II]
35	Heptanol [1,2,3,5]	1460	111-70-6	-	-	33.46 ± 2.78 [a]	15.43 ± 0.51 [b]	LRI, MS, STD
36	*cis*-Linalool oxide [1,3]	1464	5989-33-3	Trace	91.27 ± 9.03	Trace	Trace	LRI, MS, STD
37	Acetic acid [1,3,4,5,6]	1465	64-19-7	-	-	52.73 ± 4.84 [b]	67.73 ± 2.85 [a]	LRI, MS, STD
38	*cis*-Limonene oxide [1,3,4,5]	1468	13837-75-7	30.54 ± 0.50 [b]	26.14 ± 1.44 [c]	160.10 ± 1.23 [a]	11.18 ± 0.54 [d]	LRI, MS
39	*cis*-3-Hexenyl butanoate [1,3]	1471	16491-36-4	6.86 ± 0.37	-	-	-	LRI, MS, STD
40	*trans*-Sabinene hydrate [3,4]	1476	17699-16-0	176.89 ± 2.25 [c]	693.19 ± 35.08 [a]	429.44 ± 2.85 [b]	199.96 ± 8.79 [c]	LRI, MS
41	*trans*-Limonene oxide [3,4]	1481	4959-35-7	39.86 ± 1.87 [d]	89.40 ± 2.13 [b]	272.71 ± 2.32 [a]	47.57 ± 1.56 [c]	LRI, MS
42	*trans*-Linalool oxide [1,3]	1482	34995-77-2	Trace	Trace	Trace	44.67 ± 3.79	LRI, MS, STD
43	Octyl acetate [1,3,4,6]	1483	112-14-1	-	21.48 ± 1.93 [b]	43.52 ± 2.07 [a]	-	LRI, MS, STD
44	*δ*-Elemene [1,3,5,6]	1487	20307-84-0	3610.47 ± 323.05 [a]	176.09 ± 3.21 [b]	104.63 ± 3.73 [b]	262.67 ± 9.59 [b]	LRI, MS
45	Citronellal [1,3,4]	1493	106-23-0	8.23 ± 0.49 [c]	85.57 ± 3.09 [b]	1049.29 ± 8.39 [a]	-	LRI, MS, STD
46	2-Ethylhexanol [3]	1500	104-76-7	-	Trace	-	12.60 ± 0.77	LRI, MS, STD
47	*α*-Ylangene [3,5]	1503	14912-44-8	21.67 ± 0.27	-	-	-	LRI, MS
48	*α*-Copaene [1,2,3,4,5,6]	1513	3856-25-5	322.48 ± 12.79 [b]	26.50 ± 2.04 [c]	2898.51 ± 132.15 [a]	103.83 ± 1.33 [c]	LRI, MS
49	Decanal [1,2,3,4,5,6]	1515	112-31-2	335.47 ± 8.28 [c]	583.00 ± 44.89 [b]	1419.40 ± 128.08 [a]	4.59 ± 0.26 [d]	LRI, MS, STD
50	Camphor [3,4,6]	1532	76-22-2	-	6.35 ± 0.49	-	-	LRI, MS, STD
51	Linalool [1,2,3,4,5,6]	1552	78-70-6	14,830.16 ± 89.11 [a]	10,414.26 ± 251.76 [b]	4571.26 ± 31.33 [c]	3138.83 ± 151.14 [d]	LRI, MS, STD
52	*cis*-4-Decenal [3]	1555	21662-09-9	Trace	Trace	16.78 ± 1.77	-	LRI, MS, STD
53	*β*-Cubebene [1,2,3]	1557	13744-15-5	88.60 ± 5.80 [a]	-	76.34 ± 9.02 [b]	50.90 ± 0.71 [c]	LRI, MS
54	Linalyl acetate [3,4]	1566	115-95-7	3.56 ± 0.21 [b]	163.55 ± 4.65 [a]	-	Trace	LRI, MS, STD
55	Octanol [1,2,3,4,5,6]	1567	111-87-5	134.70 ± 1.12 [c]	637.51 ± 20.88 [b]	764.67 ± 17.89 [a]	126.74 ± 1.53 [c]	LRI, MS, STD
56	Isopulegol	1568	89-79-2	-	233.34 ± 15.78 [a]	8.86 ± 0.88 [b]	-	LRI, MS, STD
57	*trans*-*α*-Bergamotene [3,4]	1576	13474-59-4	23.94 ± 0.80 [a]	7.09 ± 0.12 [b]	-	-	LRI, MS
58	Nonyl acetate [4]	1584	143-13-5	27.21 ± 0.26 [a]	-	-	1.80 ± 0.18 [b]	LRI, MS, STD
59	*β*-Copaene [1,2,3,4]	1595	18252-44-3	260.38 ± 3.28 [a]	21.37 ± 0.17 [b]	15.81 ± 0.45 [c]	23.75 ± 1.03 [b]	LRI, MS
60	Methylthymol [3,4]	1602	1076-56-8	86.03 ± 2.76 [b]	245.82 ± 16.28 [a]	17.46 ± 0.55 [c]	Trace	LRI, MS
61	*β*-Elemene [1,3,4,5,6]	1611	515-13-9	1081.83 ± 6.25 [a]	47.80 ± 2.62 [d]	249.55 ± 1.62 [c]	826.68 ± 8.86 [b]	LRI, MS
62	Undecanal [3,4,5,6]	1617	112-44-7	-	25.52 ± 1.08 [b]	232.09 ± 2.47 [a]	-	LRI, MS, STD
63	Terpinen-4-ol [1,2,3,4,5]	1618	562-74-3	506.49 ± 11.96 [a]	361.16 ± 10.69 [b]	93.98 ± 2.38 [d]	141.41 ± 2.38 [c]	LRI, MS, STD
64	*β*-Caryophyllene [1,3,4,6]	1624	87-44-5	319.12 ± 17.49 [a]	16.81 ± 1.46 [d]	144.07 ± 0.83 [b]	98.54 ± 1.39 [c]	LRI, MS, STD
65	Butanoic acid [1,3]	1626	107-92-6	170.96 ± 3.10	Trace	-	-	LRI, MS, STD
66	*trans*-*p*-Mentha-2,8-dien-1-ol [3,4,5]	1640	7212-40-0	42.56 ± 2.56 [c]	69.65 ± 4.11 [b]	229.51 ± 2.49 [a]	31.79 ± 0.99 [d]	LRI, MS
67	*γ*-Elemene [1,3,4,5,6]	1656	29873-99-2	1088.56 ± 6.51 [a]	171.83 ± 1.46 [b]	65.52 ± 1.18 [c]	59.06 ± 0.76 [c]	LRI, MS
68	*trans*-2-Decenal [1,3,6]	1661	3913-81-3	49.56 ± 3.24 [b]	27.40 ± 0.50 [c]	150.85 ± 4.72 [a]	-	LRI, MS, STD
69	Nonanol [1,3,4,5,6]	1662	143-08-8	48.60 ± 3.24 [b]	30.49 ± 1.73 [c]	148.49 ± 1.87 [a]	17.84 ± 0.99 [d]	LRI, MS, STD
70	Alloaromadendrene [3,4]	1671	25246-27-9	-	-	21.18 ± 0.42 [a]	7.89 ± 0.31 [b]	LRI, MS
71	Citronellyl acetate [1,3,4,5,6]	1671	150-84-5	50.12 ± 1.70 [b]	31.31 ± 2.63 [c]	503.32 ± 26.13 [a]	6.00 ± 0.22 [c]	LRI, MS, STD
72	2-Methylbutanoic acid [3]	1675	116-53-0	13.22 ± 0.18 [a]	6.58 ± 0.21 [b]	Trace	1.53 ± 0.08 [c]	LRI, MS, STD

Table 3. *Cont.*

No.	Compound	LRI [I]	CAS Number	Iyokan	Ponkan	Shiranui	Unshiu Mikan	Identification [II]
73	*trans*-*β*-Farnesene [1,3,4,5]	1676	18794-84-8	647.95 ± 8.61 [a]	210.45 ± 6.81 [b]	-	2.09 ± 0.03 [c]	LRI, MS
74	*cis*-*p*-Mentha-2,8-dien-1-ol [3,5]	1686	3886-78-0	29.24 ± 0.94 [c]	43.98 ± 1.26 [b]	219.54 ± 2.62 [a]	6.31 ± 0.10 [d]	LRI, MS
75	Decyl acetate [3,4,5,6]	1689	112-17-4	271.03 ± 2.20 [a]	24.02 ± 0.62 [c]	47.72 ± 1.43 [b]	4.48 ± 0.07 [d]	LRI, MS, STD
76	*γ*-Muurolene [1,3,4,5]	1693	30021-74-0	-	-	7.04 ± 0.58 [a]	7.56 ± 0.34 [a]	LRI, MS
77	*α*-Humulene [3,4,5,6]	1699	6753-98-6	233.95 ± 4.58 [a]	15.04 ± 1.06 [c]	88.20 ± 1.44 [b]	91.18 ± 2.86 [b]	LRI, MS
78	Neral [1,3,4,6]	1704	106-26-3	-	119.40 ± 3.18 [a]	113.92 ± 1.66 [b]	46.30 ± 2.14 [c]	LRI, MS, STD
79	*α*-Terpineol [1,2,3,4,5,6]	1710	98-55-5	1418.51 ± 8.53 [c]	3096.50 ± 118.53 [a]	1161.46 ± 6.29 [d]	1735.62 ± 78.57 [b]	LRI, MS, STD
80	*trans*-*trans*-2,4-Nonadienal [1,3]	1718	5910-87-2	58.59 ± 0.54 [b]	69.32 ± 4.05 [b]	422.66 ± 13.79 [a]	3.57 ± 0.04 [c]	LRI, MS
81	Dodecanal [3,4]	1723	112-54-9	117.17 ± 1.08 [b]	138.65 ± 8.09 [b]	845.33 ± 27.57 [a]	10.72 ± 0.11 [c]	LRI, MS, STD
82	Germacrene D [1,3,4,5,6]	1739	23986-74-5	2981.07 ± 22.58 [a]	130.87 ± 4.58 [c]	91.65 ± 12.29 [d]	256.30 ± 4.09 [b]	LRI, MS, STD
83	Neryl acetate [1,3,4,5]	1741	141-12-8	585.07 ± 15.97 [a]	46.35 ± 3.96 [c]	519.50 ± 10.06 [b]	-	LRI, MS, STD
84	Valencene [1,2,3,4]	1744	4630-07-3	Trace	Trace	3189.66 ± 94.74 [a]	433.32 ± 20.27 [b]	LRI, MS, STD
85	*cis*-Carvyl acetate [1,4]	1746	1205-42-1	Trace	-	-	Trace	LRI, MS, STD
86	*α*-Muurolene [1,3,4]	1747	10208-80-7	34.42 ± 2.49 [a]	3.75 ± 0.12 [b]	-	-	LRI, MS
87	Geranial [1,3,4,5,6]	1748	141-27-5	24.27 ± 0.75 [b]	37.33 ± 2.08 [a]	7.47 ± 0.73 [c]	0.46 ± 0.01 [d]	LRI, MS, STD
88	*trans*-Carvyl acetate [5]	1750	1134-95-8	118.93 ± 3.69 [a]	-	-	9.92 ± 0.51 [b]	LRI, MS, STD
89	*α*-Selinene [1,6]	1753	473-13-2	-	-	301.59 ± 15.00 [a]	19.59 ± 0.74 [b]	LRI, MS
90	*α*-Farnesene [1,3,4,5,6]	1761	502-61-4	869.01 ± 19.08 [b]	220.12 ± 12.40 [c]	7344.18 ± 81.10 [a]	854.32 ± 15.50 [b]	LRI, MS, STD
91	Bicyclogermacrene [3,4,6]	1763	24703-35-3	207.10 ± 21.72 [a]	22.81 ± 1.04 [b]	-	-	LRI, MS
92	Carvone [1,3,4,5,6]	1764	99-49-0	13.96 ± 0.29 [b]	10.76 ± 0.59 [b]	287.92 ± 14.47 [a]	5.04 ± 0.03 [b]	LRI, MS, STD
93	Geranyl acetate [1,3,4,5,6]	1765	105-87-3	639.92 ± 17.29 [a]	-	-	8.49 ± 0.13 [b]	LRI, MS, STD
94	Decanol [3,4]	1767	112-30-1	237.25 ± 4.88 [b]	236.61 ± 13.02 [b]	765.29 ± 18.08 [a]	75.53 ± 0.51 [c]	LRI, MS, STD
95	Citronellol [1,2,3,4,5,6]	1768	106-22-9	42.72 ± 2.35 [c]	356.28 ± 5.81 [b]	1825.12 ± 12.90 [a]	Trace	LRI, MS, STD
96	*δ*-Cadinene [1,3,4,5]	1780	483-76-1	364.00 ± 4.92 [a]	21.87 ± 1.71 [d]	185.70 ± 15.41 [b]	95.85 ± 2.95 [c]	LRI, MS
97	*trans*-*cis*-2,4-Decadienal [1,5,6]	1784	25152-83-4	21.02 ± 0.75 [a]	8.10 ± 0.60 [b]	7.59 ± 0.64 [b]	-	LRI, MS
98	*β*-Sesquiphellandrene [3,4]	1789	20307-83-9	100.14 ± 2.57 [a]	28.71 ± 1.52 [b]	-	-	LRI, MS
99	Nerol [1,3,4,5]	1807	106-25-2	127.81 ± 3.15 [a]	77.23 ± 3.80 [c]	106.79 ± 5.99 [b]	52.84 ± 1.88 [d]	LRI, MS, STD
100	Perillyl aldehyde [1,3,4,5,6]	1818	2111-75-3	Trace	132.64 ± 1.59 [b]	245.25 ± 24.98 [a]	47.38 ± 0.22 [c]	LRI, MS, STD
101	Hexyl octanoate [3]	1820	1117-55-1	241.35 ± 5.11	-	-	-	LRI, MS
102	*trans*-2-Decenol [5,6]	1830	18409-18-2	43.72 ± 0.72 [b]	20.23 ± 1.45 [c]	68.05 ± 5.17 [a]	-	LRI, MS
103	*trans*-*trans*-2,4-Decadienal [1,3,5,6]	1833	25152-84-5	41.99 ± 3.76 [b]	28.21 ± 1.10 [c]	83.79 ± 1.02 [a]	0.96 ± 0.04 [d]	LRI, MS, STD
104	*trans*-Carveol [1,3,4,5]	1848	1197-07-5	Trace	101.32 ± 1.49 [b]	256.05 ± 4.79 [a]	81.54 ± 3.18 [c]	LRI, MS, STD
105	Undecanol [3,4]	1852	112-42-5	10.68 ± 0.85 [b]	-	26.66 ± 1.37 [a]	-	LRI, MS
106	Hexanoic acid [1,3,4,5]	1855	142-62-1	1292.19 ± 11.72 [a]	Trace	5.26 ± 0.42 [b]	4.79 ± 0.07 [b]	LRI, MS, STD
107	Geraniol [1,2,3,4,5]	1858	106-24-1	88.38 ± 5.03 [a]	36.98 ± 0.90 [b]	23.06 ± 1.87 [c]	10.09 ± 0.20 [d]	LRI, MS, STD
108	Germacrene B [3,4,5,6]	1863	15423-57-1	106.39 ± 3.04	-	-	-	LRI, MS
109	*p*-Cymen-8-ol [3,4]	1867	1197-01-9	-	26.07 ± 0.82 [a]	14.24 ± 1.21 [b]	10.87 ± 0.34 [c]	LRI, MS
110	Geranyl acetone [1,5]	1871	3796-70-1	21.53 ± 1.81 [a]	2.44 ± 0.10 [b]	3.94 ± 0.18 [b]	-	LRI, MS, STD

Table 3. *Cont.*

No.	Compound	LRI [I]	CAS Number	Iyokan	Ponkan	Shiranui	Unshiu Mikan	Identification [II]
111	Isopiperitenone [3,5,6]	1877	529-01-1	4.72 ± 0.18 [c]	136.22 ± 2.10 [a]	124.74 ± 1.09 [b]	2.66 ± 0.09 [c]	LRI, MS
112	*cis*-Carveol [1,3,4,5]	1884	1197-06-4	28.87 ± 1.89 [b]	32.73 ± 0.78 [b]	127.55 ± 8.54 [a]	10.65 ± 0.26 [c]	LRI, MS, STD
113	*trans*-2-Dodecenal [1,3,6]	1885	20407-84-5	17.22 ± 0.88 [a]	12.32 ± 0.36 [b]	-	-	LRI, MS, STD
114	Lauryl acetate [5]	1893	112-66-3	19.39 ± 0.54 [a]	2.35 ± 0.06 [c]	3.03 ± 0.29 [b]	1.59 ± 0.02 [d]	LRI, MS
115	Benzyl alcohol [1,3,4,5]	1898	100-51-6	12.94 ± 0.29 [a]	4.35 ± 0.14 [b]	12.54 ± 0.94 [a]	5.13 ± 0.75 [b]	LRI, MS, STD
116	*trans-cis*-2,6-Dodecadienal [6]	1911	21662-13-5	19.21 ± 0.12 [b]	5.28 ± 0.44 [c]	30.54 ± 0.07 [a]	-	LRI, MS, STD
117	Perillyl acetate [1,3,4,5,6]	1925	15111-96-3	105.69 ± 0.85 [a]	-	6.53 ± 0.50 [b]	5.89 ± 0.32 [b]	LRI, MS
118	Tetradecanal [3,4]	1935	124-25-4	13.14 ± 0.32 [c]	33.67 ± 0.55 [b]	38.95 ± 1.17 [a]	1.41 ± 0.08 [d]	LRI, MS
119	*p*-Menth-1-en-9-ol [3,5]	1952	18479-68-0	27.65 ± 1.29 [c]	35.15 ± 0.74 [b]	53.80 ± 4.26 [a]	19.47 ± 0.67 [d]	LRI, MS
120	Heptanoic acid [1]	1960	111-14-8	13.48 ± 0.60 [a]	1.96 ± 0.18 [d]	6.19 ± 0.06 [b]	4.72 ± 0.15 [c]	LRI, MS, STD
121	Cubebol [3]	1964	23445-02-5	37.79 ± 0.40 [b]	-	52.90 ± 0.53 [a]	8.62 ± 0.14 [c]	LRI, MS
122	*β*-Ionone [1,2,3]	1965	14901-07-6	9.29 ± 0.11 [a]	2.46 ± 0.14 [b]	1.64 ± 0.01 [c]	0.91 ± 0.03 [d]	LRI, MS, STD
123	Dodecanol [3]	1972	112-53-8	46.43 ± 0.57 [b]	41.85 ± 2.33 [c]	63.29 ± 0.47 [a]	11.83 ± 0.40 [d]	LRI, MS, STD
124	Caryophyllene oxide [1,4]	2000	1139-30-6	-	Trace	8.52 ± 0.68	Trace	LRI, MS, STD
125	*trans-trans*-2,4-Decadienol [5]	2005	18409-21-7	81.89 ± 3.48 [b]	16.29 ± 0.76 [c]	124.09 ± 5.34 [a]	3.02 ± 0.22 [d]	LRI, MS
126	*cis*-Nerolidol [3]	2010	142-50-7	9.57 ± 0.07 [a]	3.22 ± 0.06 [c]	6.90 ± 0.06 [b]	Trace	LRI, MS, STD
127	Perillyl alcohol [1,2,3,4,5,6]	2012	536-59-4	239.36 ± 1.75 [a]	115.90 ± 2.03 [c]	172.59 ± 1.43 [b]	113.32 ± 3.94 [c]	LRI, MS, STD
128	Methyleugenol [1]	2029	93-15-2	42.23 ± 2.02	-	-	-	LRI, MS, STD
129	*trans*-Nerolidol [3,6]	2044	40716-66-3	233.52 ± 1.06 [a]	25.13 ± 1.04 [c]	130.59 ± 8.90 [b]	Trace	LRI, MS, STD
130	Octanoic acid [1,3,4,5,6]	2064	124-07-2	839.13 ± 5.04 [a]	125.11 ± 4.79 [c]	180.19 ± 4.60 [b]	34.44 ± 1.62 [d]	LRI, MS, STD
131	Germacrene D-4-ol [3,4,5]	2076	198,991-79-6	74.18 ± 5.06 [b]	10.44 ± 0.92 [c]	89.44 ± 1.48 [a]	14.71 ± 0.21 [c]	LRI, MS
132	Elemol [1,4,5,6]	2098	639-99-6	373.36 ± 29.69 [a]	34.47 ± 2.25 [c]	167.76 ± 2.48 [b]	42.68 ± 1.29 [c]	LRI, MS
133	Methyl *N*-methylanthranilate [3,6]	2107	85-91-6	8.27 ± 0.60 [a]	0.56 ± 0.02 [b]	8.10 ± 0.25 [a]	-	LRI, MS, STD
134	Globulol [3,4]	2108	489-41-8	14.32 ± 0.36 [a]	-	13.29 ± 0.89 [b]	8.06 ± 0.17 [c]	LRI, MS
135	Cumin alcohol [3]	2117	536-60-7	9.61 ± 0.68 [a]	4.36 ± 0.35 [b]	Trace	2.34 ± 0.22 [c]	LRI, MS
136	Hexadecanal [5]	2148	629-80-1	89.14 ± 1.10 [a]	68.61 ± 1.97 [b]	33.67 ± 0.82 [c]	8.36 ± 0.18 [d]	LRI, MS
137	Nonanoic acid [1,3,4,5,6]	2171	112-05-0	19.75 ± 1.03 [b]	22.01 ± 2.16 [b]	69.78 ± 1.75 [a]	15.75 ± 0.61 [c]	LRI, MS, STD
138	Thymol [3]	2177	89-83-8	13.83 ± 1.11 [b]	260.88 ± 2.35 [a]	7.48 ± 0.27 [c]	8.05 ± 0.16 [c]	LRI, MS, STD
139	Eugenol [3]	2194	97-53-0	70.78 ± 2.75 [a]	0.94 ± 0.01 [b]	Trace	-	LRI, MS, STD
140	Viridiflorol [3,4]	2220	552-02-3	-	-	Trace	1.32 ± 0.02	LRI, MS
141	Methyl palmitate [1,3,5]	2226	112-39-0	10.09 ± 0.20 [b]	43.66 ± 0.88 [a]	-	6.56 ± 0.05 [c]	LRI, MS
142	Carvacrol [3,4]	2231	499-75-2	19.63 ± 0.14 [c]	52.40 ± 1.05 [a]	21.20 ± 0.42 [b]	Trace	LRI, MS, STD
143	4-Vinylguaiacol [1,4]	2236	7786-61-0	438.96 ± 4.15 [b]	2041.59 ± 9.36 [a]	383.24 ± 1.96 [c]	200.05 ± 5.91 [d]	LRI, MS, STD
144	Citronellic acid	2254	502-47-6	14.12 ± 0.14 [c]	36.58 ± 0.85 [b]	91.26 ± 1.87 [a]	10.86 ± 0.46 [d]	LRI, MS
145	*β*-Sinensal [3]	2255	60066-88-8	559.29 ± 5.18 [a]	203.25 ± 16.71 [b]	Trace	Trace	LRI, MS, STD
146	Isospathulenol [5]	2272	88395-46-4	25.12 ± 1.90	-	Trace	-	LRI, MS
147	2,3-Dihydrofarnesol	2275	51411-24-6	21.38 ± 1.54 [b]	Trace	76.48 ± 6.84 [a]	9.17 ± 0.58 [c]	LRI, MS

Table 3. *Cont.*

No.	Compound	LRI [I]	CAS Number	Iyokan	Ponkan	Shiranui	Unshiu Mikan	Identification [II]
148	Decanoic acid [1,3,4,5,6]	2277	334-48-5	74.83 ± 5.39 [c]	108.21 ± 0.86 [b]	635.75 ± 5.00 [a]	17.43 ± 0.65 [d]	LRI, MS, STD
149	*p*-Menth-8-ene-1,2-diol [3,6]	2288	1946-00-5	64.54 ± 3.59 [a]	16.48 ± 1.51 [c]	40.69 ± 1.12 [b]	8.71 ± 0.32 [d]	LRI, MS
150	*trans*-*trans*-Farnesol [1]	2289	502-67-0	30.59 ± 0.86 [a]	1.55 ± 0.12 [d]	21.47 ± 0.64 [b]	8.07 ± 0.27 [c]	LRI, MS
151	*trans*-8-Hydroxylinalool [3]	2311	75991-61-6	1770.52 ± 86.59 [a]	238.71 ± 6.94 [c]	500.81 ± 13.63 [b]	421.04 ± 19.21 [b]	LRI, MS
152	*cis*-*trans*-Farnesol [3]	2333	3790-71-4	295.09 ± 14.43 [a]	32.70 ± 0.95 [d]	51.63 ± 1.82 [c]	70.17 ± 3.20 [b]	LRI, MS, STD
153	*α*-Sinensal [3]	2360	17909-77-2	825.85 ± 7.70 [a]	520.53 ± 7.31 [b]	21.51 ± 0.90 [c]	0.70 ± 0.02 [d]	LRI, MS, STD
154	*trans*-*trans*-Farnesol [5]	2380	106-28-5	481.36 ± 18.88 [a]	32.53 ± 0.46 [c]	402.77 ± 19.07 [b]	1.59 ± 0.10 [d]	LRI, MS, STD
155	Isoeugenol [3,5]	2385	97-54-1	99.50 ± 3.54 [a]	10.32 ± 0.37 [b]	7.53 ± 0.51 [b]	9.38 ± 0.10 [b]	LRI, MS, STD
156	Isoelemicin	2416	5273-85-8	1.83 ± 0.17 [b]	1.85 ± 0.10 [b]	1.86 ± 0.07 [b]	2.48 ± 0.06 [a]	LRI, MS
157	Indole [1,5]	2488	120-72-9	174.90 ± 0.68 [a]	17.79 ± 0.87 [b]	-	Trace	LRI, MS, STD
158	Lauric acid [1,5]	2489	143-07-7	175.75 ± 2.00 [c]	329.07 ± 16.07 [a]	241.77 ± 2.18 [b]	28.93 ± 0.47 [d]	LRI, MS, STD
159	Nootkatone [1,2,3,4]	2580	4674-50-4	-	-	671.70 ± 16.03 [a]	34.55 ± 0.87 [b]	LRI, MS, STD
160	Vanillin [3,5]	2591	121-33-5	43.56 ± 3.62 [a]	16.29 ± 0.94 [c]	36.53 ± 0.52 [b]	11.42 ± 0.87 [d]	LRI, MS, STD
161	Perillic acid	2594	7694-45-3	324.83 ± 9.08 [c]	446.45 ± 41.12 [b]	617.22 ± 27.09 [a]	68.24 ± 5.91 [d]	LRI, MS
162	3-Oxo-*α*-ionol	2673	34318-21-3	31.83 ± 1.49 [a]	23.51 ± 0.46 [b]	7.80 ± 0.75 [d]	10.31 ± 0.40 [c]	LRI, MS
163	Myristic acid [1,3,5,6]	2708	544-63-8	132.07 ± 3.05 [a]	52.98 ± 4.25 [c]	118.09 ± 2.31 [b]	35.50 ± 0.93 [d]	LRI, MS, STD
164	Palmitic acid [1,3,4,5,6]	2921	57-10-3	1169.99 ± 6.73 [a]	318.77 ± 29.03 [c]	552.40 ± 14.57 [b]	540.39 ± 14.60 [b]	LRI, MS, STD
	Total concentration			516,373.36 ± 3164.30 [b]	242,460.52 ± 3667.19 [c]	1,051,185.35 ± 8702.54 [a]	60,849.01 ± 2289.68 [d]	

'-' means that the compound was not detected. 'Trace' means that the FID peak area of the compound was unquantifiable. [I] LRI: Experimental linear retention index on an HP-Innowax column relative to C_7–C_{40} alkane standards. [II] Identification methods: "LRI", comparison of experimental to reference retention indices; "MS", comparison with mass spectrum of the compound in the NIST library version 2.2; and "STD", comparison with authentic standards. [a,b,c,d] Within a row, different superscript letters indicate statistical significance difference at $p < 0.05$. Compounds reported in [1] Goh et al. [13]; [2] Sun et al. [39]; [3] Uehara and Baldovini [40]; [4] B'chir and Arnaud [41]; [5] Goh et al. [21]; [6] Cheong et al. [42].

3.3. PCA of Japanese Mandarin

PCA has become the leading unsupervised technique for reducing data dimensionality and identifying key volatile compounds that most effectively account for variations among *Citrus* samples [46,47]. Utilising the volatile composition data obtained, discrimination of the four Japanese mandarins was done by PCA, as depicted in Figure 1. The PCA scores plots revealed the clustering of the four Japanese mandarins extracted by HS-SPME (Figure 1a,c) and solvent extraction (Figure 1e), showing that both methods were sufficient to differentiate the Japanese mandarins.

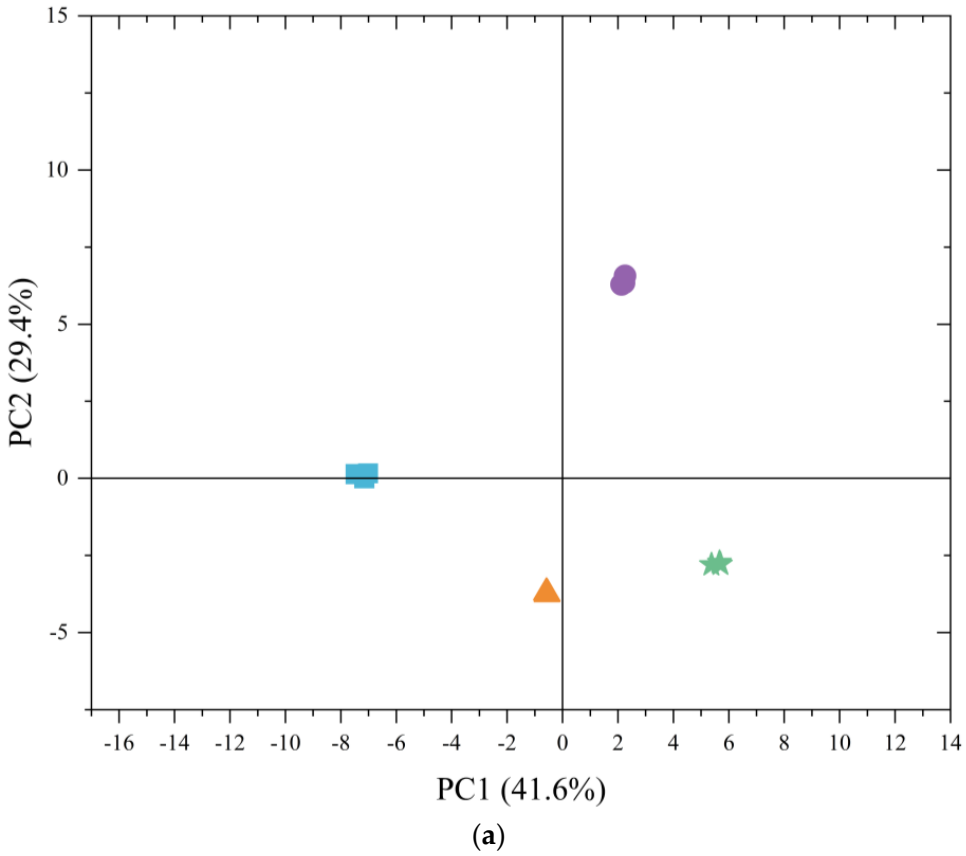
For the Japanese mandarin juices extracted by HS-SPME, PC 1 and 2 accounted for 41.6% and 29.4% of the variation, respectively (Figure 1a). Regarding the loadings plot in Figure 1b and combining the data of Table 1, many esters that were only found or with significant higher abundances in Iyokan juice, such as methyl butanoate (3; numbering with reference to Table 1), methyl hexanoate (14), methyl octanoate (34), ethyl octanoate (39), and neryl acetate (67). These esters contributed to differentiate Iyokan from the other three Japanese mandarins, which is also consistent with the discussion in Section 3.1. Moreover, these compounds may also be responsible for imparting floral characteristics that distinguish Iyokan from the other three Japanese mandarins [2,17]. *trans*-2-Heptenal (29), *trans*-2-octenal (38), *trans*-limonene oxide (45), methylthymol (53), *p*-menth-1-en-9-al (57), and dodecanol (79) were only detected in Ponkan juice. The abundances of sabinene (9), thymol (82), and *p*-menth-8-ene-1,2-diol (83) in Ponkan juice were the highest. All of these compounds dominated the Ponkan juice's position. Shiranui juice was marked by many types of sesquiterpenes with relatively high levels of δ-elemene (46), α-copaene (48), β-caryophyllene (56), and valencene (68). The abundance of ethyl acetate (2) was significantly higher than the other three mandarin juices, and citronellyl acetate (60) was only detected in Shiranui juice. All of these compounds contributed to the position of Shiranui juice in that quadrant. For Unshiu mikan juice, it was the only juice which contained germacrene D (66), hexanoic acid (75), and heptanoic acid (77). The abundance of *trans*-2-hexenol was significantly higher than other three juices. These compounds determined the scores on the positive area of PC 1 and the negative area of PC 2, and contributed to the Unshiu mikan juice's position in that quadrant.

For the Japanese mandarin peels extracted by HS-SPME, PC 1 and 2 accounted for 55.3% and 29.6% of the variation, respectively (Figure 1c). With reference to the loadings plot in Figure 1d combined with the data from Table 2, similar to the juice results of the above-mentioned, many esters, including ethyl acetate (2; numbering with reference to Table 2), methyl butanoate (3), ethyl butanoate (6), ethyl hexanoate (17), hexyl butanoate (37), and geranyl acetate (89) were only found in Iyokan peel or with significantly higher abundances, contributed to the position of Iyokan peel and separated Iyokan from the other three Japanese mandarins. *cis*-4-Decenal (52) and *trans*-2-decenal (70) were only found in Ponkan peel. The highest abundances of terpinen-4-ol (64) and methyl *N*-methylanthranilate (119) in Ponkan peel were found to determine the scores on the negative area of PC 1 and the positive area of PC 2, and contribute to the position of Ponkan peel in that quadrant. In addition, these compounds might contribute woody, musty, and waxy notes to Ponkan [45]. Methyl decanoate (58) was only detected in Shiranui peel, and certain compounds such as hexanal (9), valencene (84), and nootkatone (131) with the highest abundances in Shiranui peel determined the scores on the negative area of PC 1 and 2, affecting the position of Shiranui peel in that quadrant. Unshiu mikan peel contained the highest abundance of acids, such as heptanoic acid (111), making it distinguishable from the other three Japanese mandarin peels.

For the Japanese mandarin peels extracted by solvent extraction, PC 1 and 2 accounted for 52.8% and 25.4% of the variation respectively (Figure 1e). As shown in the loadings plot in Figure 1f and combined with the data of Table 3, strong influences were visually observed in PC 2, among which the Iyokan peel extract showed significant discrimination. In addition to many esters similar to the above-mentioned results, *cis*-β-ocimene (14; numbering with reference to Table 3), γ-terpinene (16), *p*-cymene (19), butanoic acid (65), germacrene D (82),

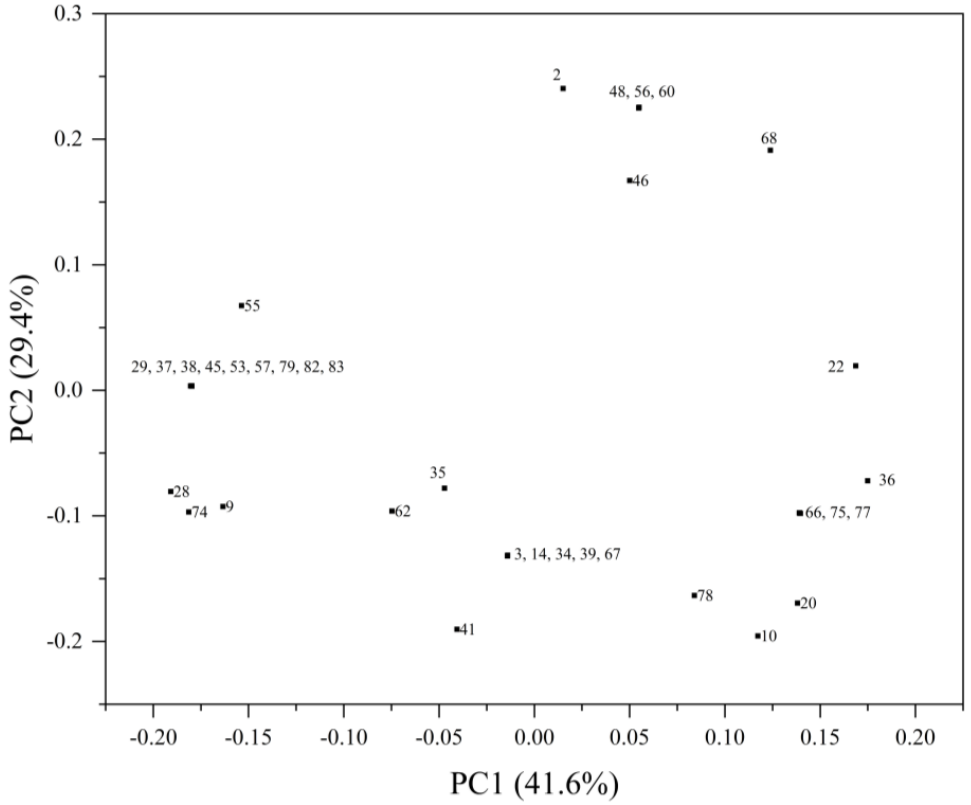
and *β*-sinensal (145) were found to determine the scores on the positive area of PC 1 and 2. Iyokan peel extract contained higher concentrations of these compounds, and thus dominated the positive axis of PC 1 and 2 in the scores plot. *cis*-Linalool oxide (36), linalyl acetate (54), isopulegol (56), and thymol (138) mainly impacted the Ponkan peel extract's position in the negative area of PC 1 and 2 owing to their high concentration in Ponkan. *trans*-*β*-Ocimene (17), valencene (84), and citronellol (95) were found to contribute to the scores on the negative area of PC 1 and positive area of PC 2, thus influencing the position of Shiranui peel extract in the scores plot. Furthermore, these compounds might be responsible for the distinctive albedo scent of Shiranui [2,38]. In Unshiu mikan, *α*-terpinene (10), *trans*-linalool oxide (42), and 2-ethylhexanol (46) were exhibited in relatively higher concentration, which were found to dominate the position of Unshiu mikan peel extract in the scores plot.

These observations revealed that the compounds influencing scores in the loadings plots varied among four Japanese mandarin varieties. Notably, comparative analysis across plots identified specific compounds contributing to the differentiation of each variety from the others. For example, esters such as neryl acetate distinguished Iyokan from the other three Japanese mandarins, and these compounds likely contribute to the distinctive floral notes of Iyokan. In contrast, methylthymol uniquely characterised Ponkan, whereas valencene was exclusive to Shiranui. Acids like hexanoic acid and heptanoic acid differentiated Unshiu mikan from the other three varieties. These findings provide valuable insights into the unique characteristics of each variety, laying the groundwork for further aroma analysis.

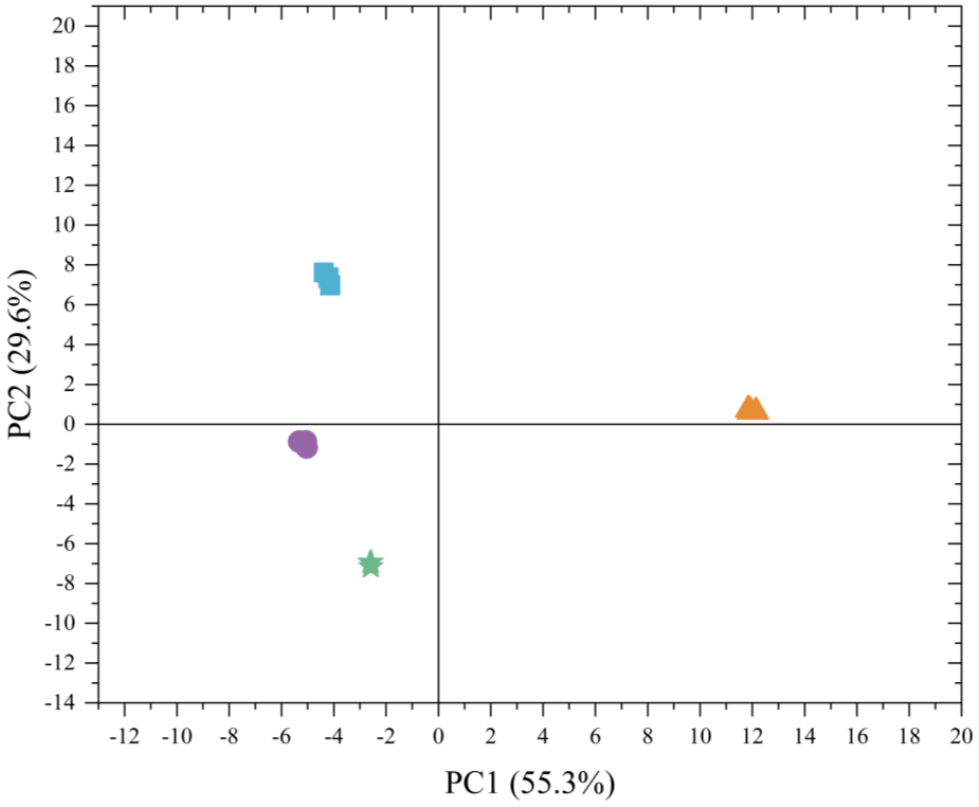


(**a**)

Figure 1. *Cont.*

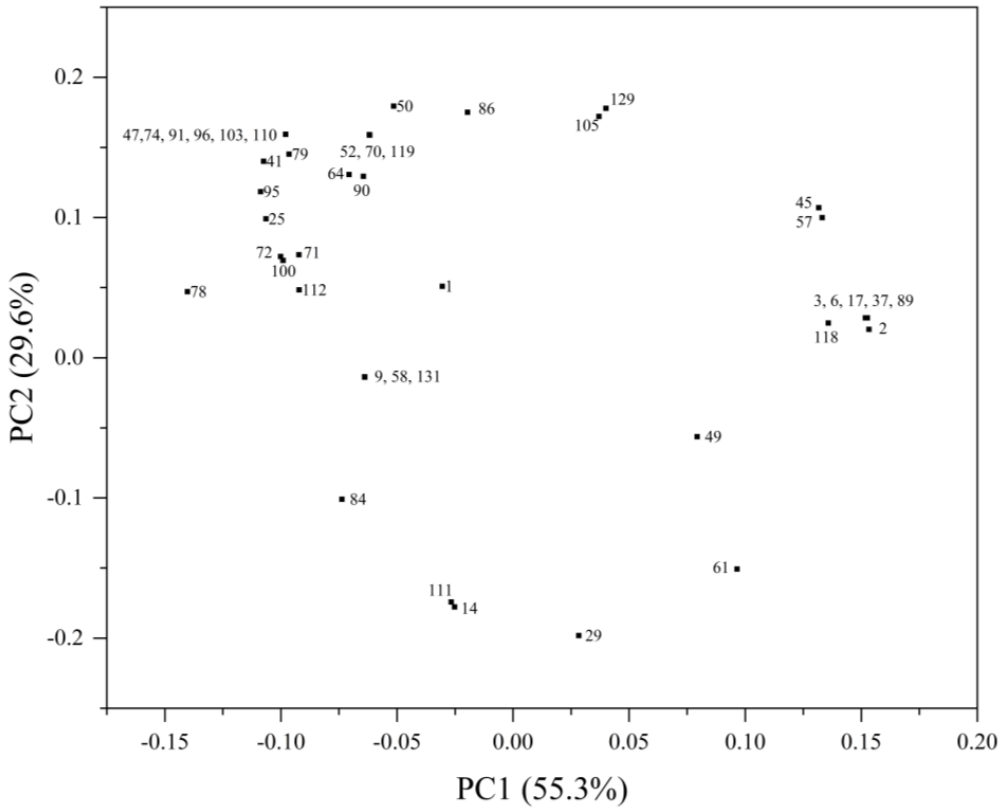


(**b**)

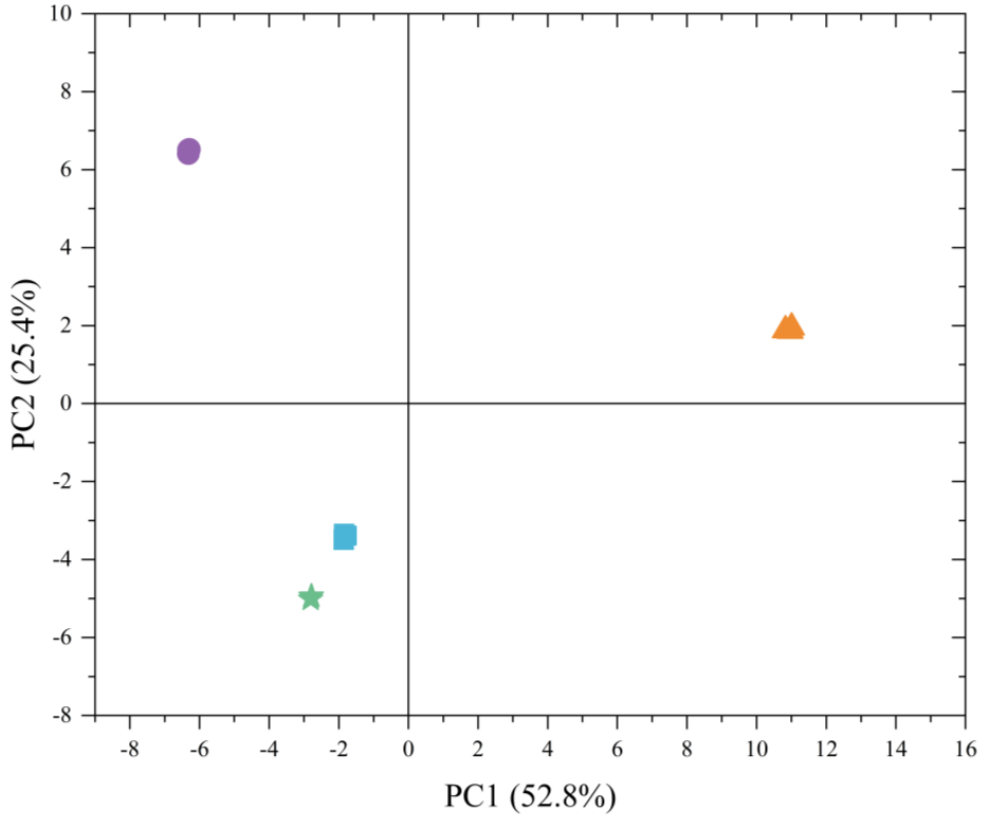


(**c**)

Figure 1. *Cont.*



(**d**)



(**e**)

Figure 1. *Cont.*

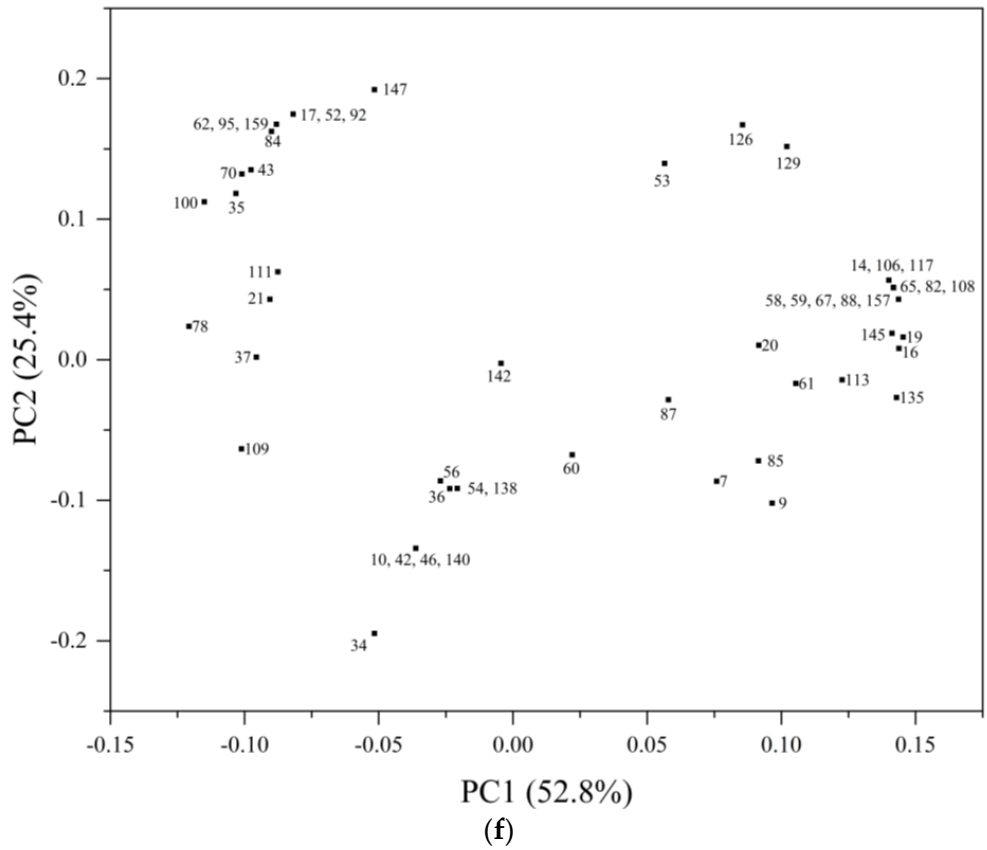


Figure 1. PCA scores and loadings plots of volatile compounds in four varieties of Japanese Mandarin (Iyokan (▲), Ponkan (■), Shiranui (●), and Unshiu mikan (★)): (**a**) Scores plot of volatiles in juices extracted by HS-SPME; (**b**) Loadings plot of volatiles in juices extracted by HS-SPME; (**c**) Scores plot of volatiles in peels extracted by HS-SPME; (**d**) Loadings plot of volatiles in peels extracted by HS-SPME; (**e**) Scores plot of volatiles in peels extracted by solvent extraction; (**f**) Loadings plot of volatiles in peels extracted by solvent extraction. The numbers denote the corresponding volatiles reported in Table 1 (juice HS-SPME plots), Table 2 (peel HS-SPME plots), and Table 3 (solvent extraction plots). The black squares indicate the contribution magnitude and direction of variables to the principal components, with their position reflecting the loading value.

3.4. Key Odourants of Japanese Mandarin Peel Extracts and Heatmap Analysis

Among the list of volatiles identified and quantified by GC-MS/FID, not all are odour-active and contribute to the aroma profile of each type of Japanese mandarin. Hence, GC-O/MS, involving the human nose as the detector, was employed to screen for the odour-active compounds. Coupled with AEDA, the potency and contribution of these compounds can be studied [48]. Referring to Table 4, 77, 63, 90, and 74 aroma-active volatiles with FD factors ranging from 1 to 3125 were detected in Iyokan, Ponkan, Shiranui, and Unshiu mikan, respectively.

Table 4. Key odourants (flavour dilution factor ≥ 1) and their respective flavour dilution factors in four varieties of Japanese mandarin (Iyokan, Ponkan, Shiranui, and Unshiu mikan) peel extracts.

No.	Compound	LRI [a]	Ref. LRI [b]	Odour Quality [c]	Flavour Dilution Factor [d]			
					Iyokan	Ponkan	Shiranui	Unshiu Mikan
1	*α*-Pinene	1045	1028 [I]	piney, green, fresh	125	125	625	5
2	*α*-Thujene	1062	1028 [I]	woody, green, fresh	5	125	625	5
3	Camphene	1088	1071 [I]	woody, herbal, terpenic	-	-	625	5
4	Unknown	1095	-	creamy, sweet, cooked	1	-	-	-
5	Hexanal	1105	1083 [I]	fresh, green, fatty	25	25	1	1
6	*β*-Pinene	1121	1112 [I]	woody, pine, green	25	25	5	125
7	Myrcene	1180	1161 [I]	peppery, terpenic	1	625	3125	125
8	Unknown	1189	-	floral, aldehydic, waxy	1	-	1	625
9	Limonene	1218	1200 [I]	citrusy, fresh, sweet	125	125	3125	625
10	*β*-Phellandrene	1230	1211 [I]	minty, terpenic	1	625	125	-
11	*cis*-*β*-Ocimene	1249	1235 [I]	herbal, floral	1	-	-	-
12	*γ*-Terpinene	1259	1246 [I]	oily, woody, citrusy	25	125	-	1
13	*trans*-*β*-Ocimene	1266	1250 [I]	citrusy, green, woody	-	-	125	-
14	Unknown	1279	-	indole, animalic, phenolic	1	-	-	-
15	*p*-Cymene	1284	1272 [I]	woody, fresh, citrusy	-	1	-	1
16	Terpinolene	1296	1283 [I]	fresh, sweet, fruity	-	1	-	1
17	Octanal	1303	1289 [I]	green, waxy, citrusy	1	5	125	1
18	Unknown	1316	-	fatty, metallic	-	1	-	-
19	Unknown	1332	-	sweet, floral	1	-	-	-
20	Prenol	1337	1320 [I]	fruity, green, floral	25	-	-	25
21	Unknown	1343	-	juicy, sweet, terpenic	-	625	-	-
22	Unknown	1352	-	floral	-	5	-	-
23	Unknown	1355	-	buttery, creamy	1	-	-	-
24	Hexanol	1369	1355 [I]	fruity, sweet, green	25	5	5	125
25	*cis*-3-Hexenol	1394	1382 [I]	fresh, green, herbal	25	1	25	5
26	Unknown	1390	-	sulphury, tropical	-	25	-	-
27	Nonanal	1404	1391 [I]	fresh, floral, citrusy	5	5	125	625
28	Unknown	1412	-	albedo, floral, green	1	-	-	-
29	*cis*-Linalool oxide	1452	1444 [I]	floral, woody, sweet	-	5	-	-
30	*cis*-Limonene oxide	1458	1452 [I]	fresh, citrusy	5	5	25	5
31	*trans*-Limonene oxide	1465	1462 [I]	fresh, citrusy	-	5	125	1
32	Unknown	1470	-	cooked, fermented, earthy	5	-	125	5
33	Acetic acid	1478	1449 [I]	sharp, pungent, sour	1	5	-	-

Table 4. *Cont.*

No.	Compound	LRI [a]	Ref. LRI [b]	Odour Quality [c]	Flavour Dilution Factor [d]			
					Iyokan	Ponkan	Shiranui	Unshiu Mikan
34	Citronellal	1490	1478 [I]	sweet, herbal, waxy	-	25	5	-
35	*α*-Copaene	1499	1492 [I]	woody, spicy	-	1	5	-
36	Decanal	1508	1498 [I]	floral, waxy, citrusy	1	125	625	125
37	2-Ethylhexanol	1527	1491 [I]	citrusy, fresh, sweet	-	5	-	1
38	*β*-Cubebene	1542	1545 [I]	citrusy, fruity, radish	25	-	5	5
39	*cis*-4-Decenal	1550	1544 [I]	citrusy, aldehydic, cardamom	25	-	125	-
40	Linalool	1567	1547 [I]	citrusy, floral, woody	125	125	25	3125
41	Octanol	1572	1557 [I]	green, citrusy, waxy	5	5	125	-
42	Unknown	1575	-	terpenic	-	5	-	-
43	*β*-Elemene	1595	1591 [I]	sweet, herbal, fresh	-	5	125	-
44	Methylthymol	1603	1590 [I]	woody, smoky, burnt	-	5	-	5
45	Terpinen-4-ol	1614	1602 [I]	woody, peppery, sweet	-	5	1	125
46	Unknown	1625	-	sulphury, grapefruit, woody	-	-	1	-
47	Undecanal	1628	1604 [I]	waxy, soapy, floral	-	-	125	-
48	Unknown	1636	-	woody, earthy	1	-	-	-
49	Unknown	1650	-	floral	-	25	-	-
50	*trans*-2-Decenal	1657	1644 [I]	waxy, fatty, cilantro	-	5	5	-
51	Butanoic acid	1660	1625 [I]	sharp, acetic, cheese	5	5	-	-
52	Nonanol	1669	1660 [I]	fatty, floral, citrusy	-	-	1	5
53	*trans*-*β*-Farnesene	1680	1664 [I]	woody, citrusy, sweet	-	5	-	-
54	Unknown	1695	-	juicy, sweet, vanilla	-	5	-	5
55	2-Methylbutanoic acid	1702	1662 [I]	acidic, fruity, cheesy	5	-	-	-
56	*α*-Terpineol	1713	1697 [I]	citrusy, woody, floral	5	3125	5	125
57	*trans*-*trans*-2,4-Nonadienal	1714	1700 [I]	fatty, green, floral	1	-	5	1
58	Germacrene D	1720	1710 [I]	woody, spicy	5	-	5	5
59	Dodecanal	1728	1711 [I]	waxy, citrusy, floral	5	25	5	-
60	Valencene	1730	1730 [I]	sweet, fresh, oily	-	1	-	-
61	Neryl acetate	1736	1724 [I]	floral, soapy, citrusy	5	-	-	5
62	*cis*-Carvyl acetate	1746	1731 [I]	green, herbaceous	1	-	-	1
63	Carvone	1751	1740 [I]	minty, spicy, caraway	1	1	5	-
64	*α*-Farnesene	1763	1746 [I]	citrusy, floral, green	5	25	5	1
65	Unknown	1767	-	green, spicy, mango	-	125	-	-
66	Geranyl acetate	1772	1752 [I]	floral, green	1	-	-	-

Table 4. *Cont.*

No.	Compound	LRI [a]	Ref. LRI [b]	Odour Quality [c]	Flavour Dilution Factor [d]			
					Iyokan	Ponkan	Shiranui	Unshiu Mikan
67	Decanol	1781	1760 [I]	fatty, waxy, citrusy	-	-	5	1
68	Citronellol	1787	1765 [I]	floral, waxy, citrusy	1	125	25	1
69	Perillyl aldehyde	1790	1793 [I]	fresh, green, cirtusy	-	625	25	-
70	Nerol	1815	1797 [I]	sweet, floral, citrusy	-	-	-	5
71	*trans*-*trans*-2,4-Decadienal	1825	1811 [I]	aldehydic, citrusy	1	-	1	1
72	Unknown	1838	-	nutty, beany	-	-	5	-
73	*trans*-Carveol	1846	1845 [I]	caraway, green, floral	-	625	5	-
74	Geraniol	1862	1847 [I]	floral, waxy, citrusy	25	5	1	-
75	*trans*-2-Dodecenal	1867	1867 [I]	metallic, mandarin, waxy	-	625	1	-
76	Hexanoic acid	1877	1846 [I]	fatty, fruity	125	5	25	-
77	*cis*-Carveol	1882	1861 [I]	caraway, green, herbal	125	5	25	125
78	Benzyl alcohol	1895	1870 [I]	floral, phenolic	-	1	1	5
79	Lauryl acetate	1898	1892 [I]	sweet, fresh, waxy	-	1	1	5
80	*trans*-*cis*-2,6-Dodecadienal	1906	1894 [I]	waxy, green, mandarin	-	5	3125	-
81	Perillyl acetate	1918	1902 [I]	spicy, phenolic, fruity	5	-	-	5
82	*p*-Menth-1-en-9-ol	1940	1933 [I]	fruity, herbal	1	5	-	5
83	Unknown	1970	-	pith, sweet, floral	1	-	-	-
84	Dodecanol	1979	1966 [I]	earthy, soapy, waxy	5	25	5	-
85	Unknown	1992	-	fresh, juicy, floral	5	-	1	625
86	*trans*-*trans*-2,4-Decadienol	2002	1994 [II]	fatty, waxy, fruity	-	1	5	5
87	Perillyl alcohol	2044	2016 [I]	green, spicy, floral	5	3125	25	5
88	*trans*-Nerolidol	2053	2042 [I]	sweet, floral	25	25	-	5
89	Germacrene D-4-ol	2055	2069 [I]	citrusy, sweet	-	5	1	-
90	Unknown	2067	-	floral, citrusy, albedo	25	-	25	-
91	Unknown	2078	-	sulphury, spicy, grapefruit	25	25	5	-
92	Methyl *N*-methylanthranilate	2091	2077 [I]	sweet, musty, phenolic	1	5	1	-
93	Octanoic acid	2093	2060 [I]	fatty, waxy, cheesy	-	25	25	-
94	Elemol	2096	2080 [I]	woody, spicy, floral	5	5	-	5
95	Unknown	2104	-	sweet, juicy, floral	1	-	125	-
96	Cumin alcohol	2116	2113 [I]	cumin, spicy, leathery	-	25	-	1
97	Unknown	2126	-	green, juicy, sweet	5	5	25	5
98	Hexadecanal	2158	2135 [I]	woody	25	-	-	-
99	Unknown	2160	-	sweet, mandarin, juicy	-	5	-	5
100	Unknown	2191	-	spicy, peely	-	25	-	-

Table 4. *Cont.*

No.	Compound	LRI [a]	Ref. LRI [b]	Odour Quality [c]	Flavour Dilution Factor [d]			
					Iyokan	Ponkan	Shiranui	Unshiu Mikan
101	Thymol	2213	2189 [I]	herbal, spicy, phenolic	5	25	-	-
102	4-Vinylguaiacol	2221	2188 [I]	spicy, clove, smoky	-	5	-	5
103	Carvacrol	2242	2236 [I]	spicy, woody, smoky	5	5	125	-
104	*β*-Sinensal	2244	2238 [I]	fresh, citrusy, waxy	5	625	-	-
105	Unknown	2252	-	meaty, sulphury	1	-	-	-
106	Isospathulenol	2267	2227 [I]	woody	125	-	5	-
107	Unknown	2276	-	vanilla, spicy, phenolic	-	25	-	-
108	2,3-Dihydrofarnesol	2283	2262 [III]	floral, fruity	625	5	125	25
109	Decanoic acid	2294	2276 [I]	sour, fatty, citrusy	-	25	1	-
110	Unknown	2307	-	sweet, phenolic, spicy	-	3125	-	-
111	*trans*-8-Hydroxylinalool	2334	2284 [I]	citrusy, lemon, alcoholic	1	5	1	25
112	*α*-Sinensal	2345	2304 [I]	citrusy, powdery, sour	1	125	-	25
113	Isoeugenol	2358	2318 [I]	spicy, woody, floral	-	625	3125	1
114	*trans*-*trans*-Farnesol	2374	2356 [I]	woody, floral, green	-	-	3125	-
115	Isoelemicin	2387	2389 [IV]	spicy, floral	5	1	-	-
116	Indole	2460	2445 [I]	animalic, floral	1	1	-	-
117	Unknown	2472	-	green, floral, peely	1	-	5	-
118	Unknown	2489	-	sweet, woody, powdery	1	125	5	-
119	Unknown	2529	-	peely, earthy, herbal	-	1	-	-
120	Nootkatone	2548	2530 [I]	grapefruit, peely, floral	-	-	5	5
121	Unknown	2551	-	woody, earthy, green	5	1	-	-
122	Vanillin	2581	2568 [I]	sweet, vanilla, phenolic	25	-	25	125
123	Unknown	2606	-	sweet, coumaric	-	25	-	-
124	Unknown	2612	-	green, sour	-	25	-	-
125	Perillic acid	2649	2640 [I]	floral, sweet	1	125	-	625
126	3-Oxo-*α*-ionol	2667	2639 [I]	spicy	1	-	-	-
127	Unknown	2722	-	spicy, woody, clove	-	25	-	1
128	Unknown	2737	-	phenolic, spicy, vanilla	-	125	5	5
129	Unknown	2824	-	woody, spicy, phenolic	625	-	5	5
130	Unknown	2901	-	spicy, clove, phenolic	-	625	5	5
131	Unknown	2922	-	green, woody, sweet	25	3125	-	5

'-' refers to compound not detected. [a] LRI: Experimental linear retention index on an HP-INNOWax column relative to C_7–C_{40} alkane standards. [b] Ref. LRI: Reference retention index values from literature: [I] NIST library version 2.2; [II] Paraskevopoulou et al. [49]; [III] Ledauphin et al. [50]; [IV] Bélanger et al. [51]. [c] Odour quality of compounds described by flavourists. [d] Flavour dilution factor refers to the highest dilution at which the compound can be detected by at least three flavourists.

Similar to the results of previous studies [22,52], mandarins of different varieties were observed to have different key odourants and/or FD factors. In Iyokan peel extract, 2,3-dihydrofarnesol (floral, fruity) exhibited the highest FD factor of 625. Moreover, Iyokan contained some unique odourants, such as cis-β-ocimene (herbal, floral), 2-methylbutanoic acid (acidic, fruity, cheesy), geranyl acetate (floral, green), hexadecanal (woody), 3-oxo-α-ionol (spicy), and some unknown compounds with sweet, floral, and albedo notes, which added intriguing complexity to its distinct fragrance. For Ponkan peel extract, perillyl alcohol (green, spicy, floral) had the highest FD factor of 3125. Additionally, Ponkan demonstrated significantly higher FD factors of the key odourants myrcene (peppery, terpenic), perillyl aldehyde (fresh, green, citrusy), trans-carveol (caraway, green, floral), trans-2-dodecenal (metallic, mandarin, waxy), and β-sinensal (fresh, citrusy, waxy). Complementing these, Ponkan also featured citronellol and α-sinensal (citrusy, powdery, sour). Additionally, Ponkan contained some special odourants, including trans-β-farnesene (woody, citrusy, sweet), valencene (sweet, fresh, oily), and some unknown compounds with spicy, sulphury, and terpenic notes. In Shiranui peel extract, myrcene, limonene, trans-cis-2,6-dodecadienal (waxy, green, mandarin), isoeugenol (spicy, woody, floral), and trans-trans-farnesol (fresh, sweet, floral) demonstrated the highest FD factors of 3125. Furthermore, Shiranui distinguished itself due to the presence of unique odourants, trans-β-ocimene (citrusy, green, woody), and undecanal (waxy, soapy, floral) with significantly higher FD factors. In Unshiu mikan, linalool (citrusy, floral, woody) had the highest FD factor of 3125 followed by limonene (citrusy, fresh, sweet), nonanal (fresh, floral, citrusy), and perillic acid (floral, sweet), which had the second highest FD factor of 625. Alongside these odourants, Unshiu mikan featured other key odourants including β-pinene (woody, pine, green), hexanol (fruity, sweet, green), terpinen-4-ol (woody, peppery, sweet), and cis-carveol (caraway, green, herbal). All these odourants might play a role in characterising the unique aroma of Unshiu mikan with woody, herbal, and floral profiles. Particularly, nerol (sweet, floral, citrusy) was identified as the key odourant only in Unshiu mikan.

Meanwhile, to get a deeper comprehension of the distinct qualitative variations in the key odourants across the four Japanese mandarins, as well as the individual odour activity of each odourant in these four species, heatmaps were generated to show the variations in the concentrations and FD factors of each key odourant in four different Japanese mandarin peel extracts (Figure 2). For the concentration, a colour code was devised based on the scale from red to blue, with their concentrations of compounds decreasing from high to low, which made it possible to make distinctions among the samples. For the FD factor of each key odourant, seven colour blocks were developed from red to blue, with the FD factors of the odourants decreasing from 3125 to the absence.

The heatmap analysis provided the opportunity to visualise the differences in the concentration of key odourants of each Japanese mandarin peel extract. In this section, the heatmap analysis combined the concentrations with FD factors of each odourant in four Japanese mandarins. In the context of aroma perception, the odour detection threshold refers to the minimum concentration required for a compound to be detectable by the human sense of smell [53]. This integrated approach enabled us to visualise the potential odour activity of each key odourant in four Japanese mandarins, by considering both concentrations and FD factors. The differences in the potential odour activity of each key odourant in four Japanese mandarins could also be visualised. Some compounds that were detected in relatively low amounts possessed relatively high FD factors in AEDA, and vice versa. For instance, *cis*-4-decenal was elucidated as a key odourant in Iyokan with a FD factor of 25 via AEDA despite being present at trace levels in Iyokan peel extract, indicating a significant contribution to the overall aroma, which was probably due to its low odour detection threshold [54]. Similarly, although 2-ethylhexanol was only present at trace levels in Ponkan peel extract, it was elucidated as a key odourant in Ponkan with a FD factor of 5 via AEDA. Interestingly, neryl acetate was not detected in Unshiu mikan GC-MS analysis, it was identified as a key odourant in Unshiu mikan with a FD factor of

5 via AEDA, highlighting the importance of considering both concentration and odour detection threshold in aroma profiling.

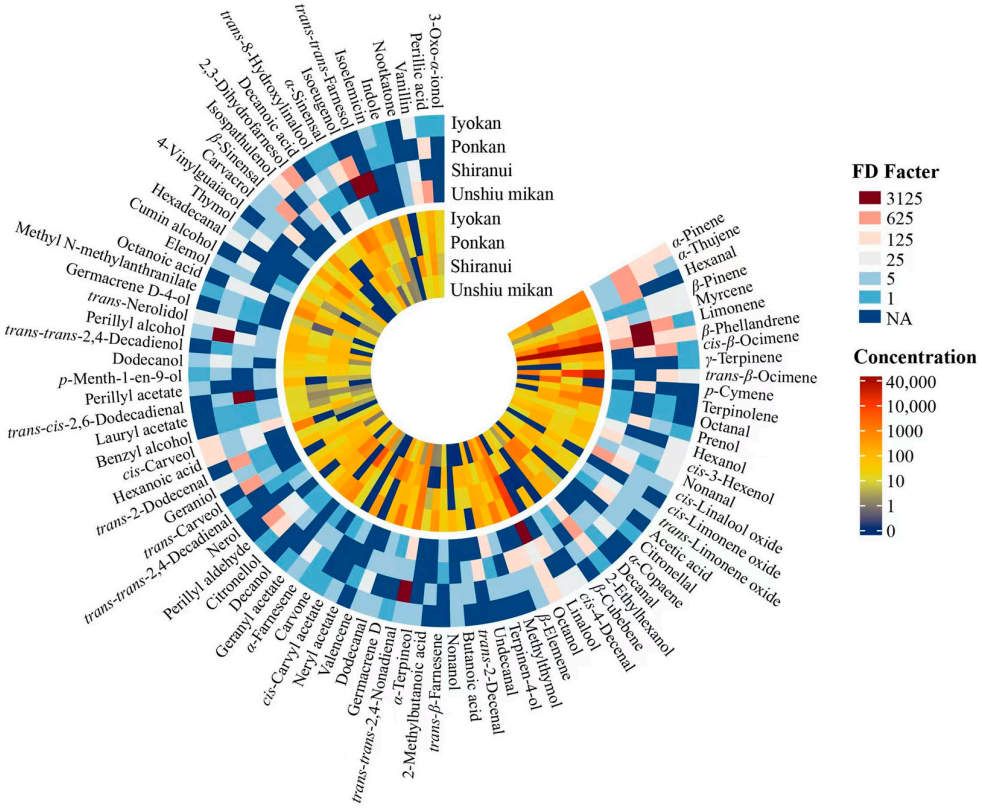


Figure 2. Heatmap of the concentrations and FD factors of the key odourants of four Japanese mandarin peel extracts. "NA" means the odourant was not detected by AEDA via GC-O/MS. For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.

3.5. Sensory Evaluation of Japanese Mandarin Peel Extracts

With the added understanding from the above analyses, sensory evaluation was conducted on the four Japanese mandarin peel extracts to understand the overall aroma profiles and to compare variances in aroma attributes amongst the Japanese mandarins. The average rating of each attribute was computed and plotted on a spider web diagram shown in Figure 3.

Distinct sensory profiles were observed for each Japanese mandarin peel extract, reflecting the variability depicted in the PCA score plot in Figure 1e and the heatmaps in Figure 2. Iyokan peel extract was perceived to be predominantly floral (3.5) and juicy (3.0) compared to the other descriptors, probably due to its high FD factor of geraniol and 2,3-dihydrofarnesol compared to the other extracts, and contained some unique compounds, including *cis*-*β*-ocimene, geranyl acetate, and some exceptional unknown compounds with floral and juicy notes (Table 4). Ponkan peel extract was perceived to be the most sulphury (3.0) and peely (3.0). These profiles might be contributed by volatiles like myrcene, perillyl alcohol, *trans*-2-dodecenal, and *β*-sinensal, which could provide a spicy and herbal note with a hint of freshness. Moreover, the specific compounds responsible for the distinct sulphury odour remain to be determined due to the complexity of key odourants in Ponkan, and the presence of some unique unknown compounds with sulphury notes. Shiranui peel extract was the most albedo-like (3.0) of the four Japanese mandarins and was characterised as juicy (2.8). Aldehydes and alcohols including undecanal, *trans*-*cis*-2,6-dodecadienal, isoeugenol, and *trans*-*trans*-farnesol could account for the waxy, herbaceous, and citrusy notes. Unshiu mikan peel extract was mainly characterised by peely (3.1), green (3.0),

woody (3.0), and floral (3.0), which could be related to alcohols and terpenes that could characterise woody, green, and herbal odour qualities, with nuances of floral notes, including limonene, *β*-pinene, linalool, terpinen-4-ol, hexanol, and *cis*-carveol. Overall, distinctions in sensory profiles amongst the Japanese mandarins were observed and could partially be explained by differences in their chemical compositions. The sensory data combined with the heatmap analysis also highlighted the likely presence of flavour interactions among the volatile compounds. Therefore, this study further illustrates the complicated nature of aroma perception and analysis in natural matrices like Japanese mandarins.

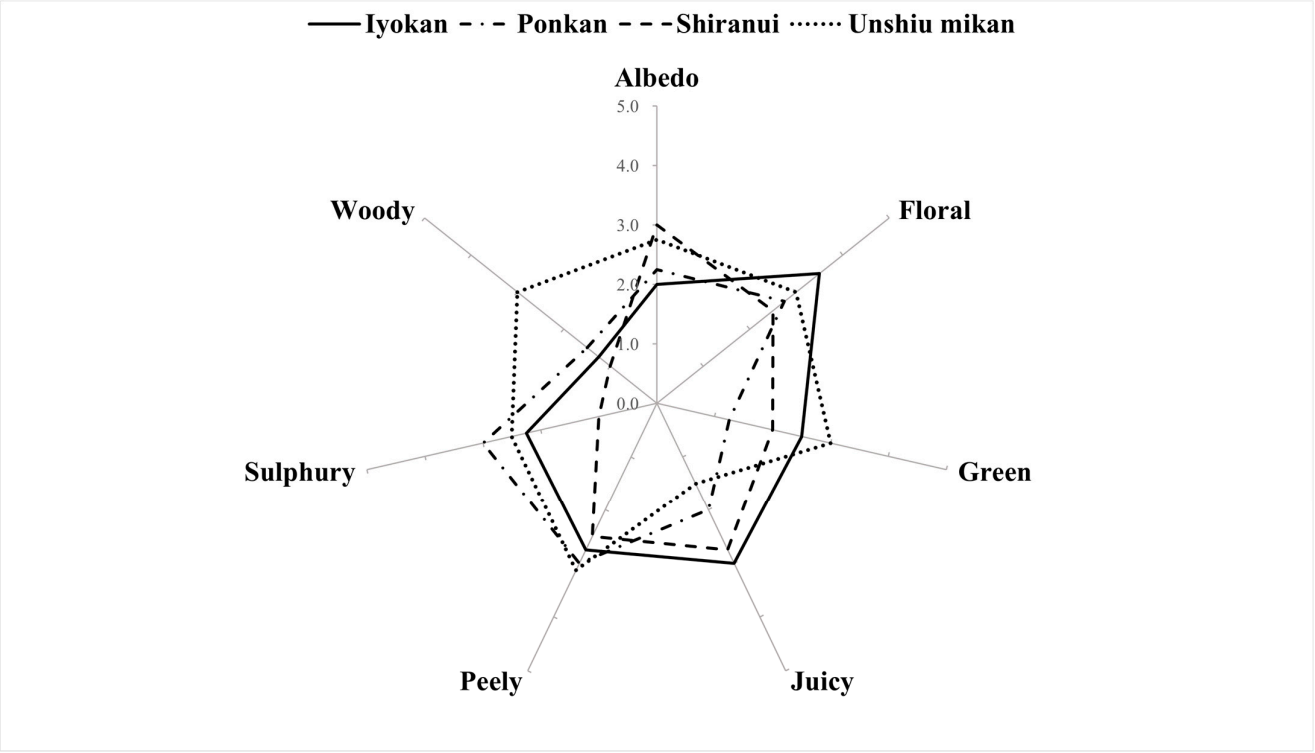


Figure 3. Sensory profiles of four varieties of Japanese mandarin (Iyokan, Ponkan, Shiranui, and Unshiu mikan) peel extracts.

4. Conclusions

Volatile compounds in four varieties of Japanese mandarins (Iyokan, Ponkan, Shiranui, and Unshiu mikan) were extracted by HS-SPME and solvent extraction, and then identified by GC-MS/FID. Based on data obtained by GC-MS analysis, distinct segregation of the four Japanese mandarins by PCA was possible. Furthermore, key odourants of four Japanese mandarin peel extracts were identified using AEDA and combined with the heatmap analysis of these key odourants, allowing for further discrimination of the Japanese mandarins based on variations in their key odourants and FD factors. Finally, distinctions in sensory profiles among the four Japanese mandarin peel extracts were observed. Iyokan had higher floral and juicy ratings, and Unshiu mikan was perceived to be predominantly green, peely, and woody, which were contributed mainly by key odourants from the groups of alcohols, terpenes, and aldehydes. Ponkan had a higher sulphury rating, and Shiranui was the most albedo-like of the four Japanese mandarins. These findings contribute to advancing the understanding of the aroma profiles of the four Japanese mandarins and provide insightful information for further exploration of the key odourants in Japanese mandarins.

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Conflicts of Interest: Author Rui Min Vivian Goh, Yunle Huang, Kim-Huey Ee, Aileen Pua, Daphne Tan, Lionel Jublot and Bin Yu were employed by the company Mane SEA Pte Ltd. The remaining authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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