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Characterization of Aroma Volatiles in Xilin Fire Ginger Oils by HS-SPME-GC-MS

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ABSTRACT

Ginger is widely used as either a food product or a herbal medicine around the globe. In the current study, we used headspace solid-phase microextraction and gas chromatography-mass spectrometry technology (HS-SPME-GC-MS) with *n*-butyl acetate as an internal standard to characterize three kinds of ginger oil in Xilin fire ginger, which included ginger essential oil (GEO), ginger oleoresin extracted with petroleum ether (PEGO) and ginger oleoresin extracted with absolute ethanol (AEGO). Cluster analysis of heatmap was used to reveal the differences in concentration in these oils. Odor activity value, in combination with principal component analysis, was further used to analyze the contribution to the aroma. This study demonstrated that despite the similarities in the aroma compounds and content of three kinds of ginger oil, GEO exhibited a better aroma quality, followed by AEGO and PEGO.

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KEYWORDS

Xilin fire ginger oils; Aroma compounds; HS-SPME-GC-MS; Principal component analysis (PCA); Heatmap cluster analysis

INTRODUCTION

Ginger oils are an essential kind of extract of ginger, with vital phytochemical characteristics that reflect the sensory characteristics and biological activity of ginger. Based on the extraction method, it can be classified into two categories, ginger essential oil (GEO) and ginger oleoresins (GOs).^[1,2] Ginger essential oil is mainly prepared by hydrodistillation, while ginger oleoresins are prepared by various methods, such as pressing method, liquid CO₂ extraction method, supercritical CO₂ extraction method and solvent extraction method that can also be combined with ultrasonic method and microwave.^[3,4] Due to different extraction methods, the compounds and aroma of ginger oils are quite different. Volatiles, including sesquiterpene and monoterpenoid hydrocarbons in GEO, are the main constituents to provide distinct aromas and tastes. GOs, which also contain nonvolatile phenolics known as gingerols, embody pungent characteristics.^[5–8]

The aroma is one of the vital categories for the sensory evaluation of ginger oils, and plays a substantial role in defining the product's quality, and greatly influences consumers' attraction and purchasing.^[9] The headspace compounds are more similar to that of inhaled or sniffed aroma.^[10] HS-SPME is also one of the main measurement methods of aroma compounds, with a simple device, easy operation, fast sampling, good reproducibility and avoiding chromatographic column contamination, etc.^[11] It in combination with GC-MS has been widely used in many oils for quantifications, such as grape seed oil,^[12] camellia seed oil,^[13] garlic oil,^[14] tuna oil^[15] and ginger oleoresins.^[16] Previously,

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different multivariate statistical techniques, such as principal component analysis (PCA), generalized procrustes analysis (GPA), and cluster analysis, were tried to find patterns in volatiles that correspond with specific sensory aroma profiles.^[10]

Xilin fire ginger has pungent aroma, spicy flavor and good taste. It has been listed as China's national geographical medicinal product due to its various therapeutic uses, including cough expectorant, removing puff from eyes, helping in digestion and spleen disorders.^[17] To the best of our knowledge, there are no studies documented on Xilin fire ginger oil. Therefore, the present study aims to characterize three kinds of Xilin fire ginger oil by the HS-SPME-GC-MS with n-butyl acetate as the internal standard. The content of aroma compounds were compared by heatmap, their aroma contributions were characterized by odor activity values (OAVs), and the differences in aroma of ginger oils were further explored by PCA.

Materials and Methods

Reagents and materials

Dried ginger slices of Xilin fire ginger were obtained from Xilin county Guangxi Province fuyuan plant development co., LTD. The parameters set for processing through hot air drying are: temperature 60 °C–80 °C and time 8 h. Petroleum ether (analytical grade), absolute ethanol (analytical grade), and methanol (chromatographic grade) were provided by Sinopharm Group Chemical Reagent Co., LTD (Shanghai, China). C8-C40 normal alkane standard was purchased from Beijing Balinway Technology Co., LTD (Beijing, China). A SPME holder and a fiber with a 100 µm layer of polydimethylsiloxane (PDMS, 100 µm) were purchased from Shanghai ANPEL Laboratory Technologies Co., LTD (Shanghai, China).

Ginger oils samples

The dried ginger slices were pulverized into a 40 mesh molecular sieve and were used for extraction. The essential oil was extracted by hydrodistillation process using a Clevenger's type apparatus with material ratio of 1:16 (g: mL), and the volume of oil kept constant indicating extraction end. The clear and transparent yellow oil was collected from the upper layer and dried with a minimum amount of anhydrous sodium sulfate to remove any remaining moisture traces.

Two oleoresins were extracted from the Soxhlet apparatus using petroleum ether and absolute ethanol at a temperature of 85 °C and 95 °C, respectively, and the material ratio of 1:8 (g: mL). The extraction process was continued until the reflux liquid became colorless and transparent and concentrated at 50 °C. The essential oil and oleoresins were stored at low temperature (4 ± 2 °C) in the dark for further use.

HS-SPME

The best HS-SPME conditions as follows were optimized in our previous studies. 0.1500 g ginger essential oil (GEO), 0.4000 g ginger oleoresin extracted with petroleum ether (PEGO) and 0.4000 g ginger oleoresin extracted with absolute ethanol (AEGO) were, respectively, added to 0.5500 g, 2.0000 g, and 1.000 g of n-butyl acetate methanol internal standard solution (0.0010 g/g), respectively. Then, each solution was placed into a 15 mL headspace vials and thoroughly mixed. After adsorption, the SPME fiber was inserted through the septum and exposed to the headspace for desorption and further analyses. GEO was adsorbed for 3.5 min and desorbed for 3 min, each oleoresin was adsorbed for 7.5 min and desorbed for 2 min.

GC-MS analysis

A gas chromatograph (Hewlett Packard 7890) coupled with HP 5973 C MS detector (Agilent Technologies, USA) with a BR-5 ms capillary column (selectivity similar to 5% diphenyl/95% dimethyl polysiloxane, 60 m × 0.25 mm, 0.25 µm film thickness) was used to analyze volatile aroma compounds. Helium (99.999%) was used as a carrier gas at a constant flow of 1.20 mL/min. The split injection was applied, and the split ratio was set at 10:1. The oven temperature parameter was set as: 50 °C for

1 min; 3 °C/min ramp to 150 °C and holding for 2 min; 20 °C/min ramp to 250 °C and holding for 2 min. The mass detector was conducted with electronic impact (EI) mode at 70 eV, and the ion-trap manifold temperature of 230 °C and source temperature of 250 °C, the scanning rate of 1 scan s⁻¹ and mass acquisition range was set between 35 and 550 amu.

The volatile compounds were identified by NIST 11 Database, which required positive and negative matching degrees greater than 800 and comparing their retention indices (RI) with those previously reported in the literatures. The RI of volatile compounds was calculated by sample injection with a homologous series of straight-chain *n*-alkanes (C8-C40) under the same conditions. Each volatile concentration in ginger oils was calculated by comparing it with the concentration of the internal standard.

Statistical analysis

To quantify the volatiles, each sample was analyzed in triplicate, and the results are expressed as the mean ± standard deviation of three measurements. Heatmap analysis was performed by an online platform using Metabo Analyst 3.5 at <https://www.metaboanalyst.ca>. Data were compared using a one-way analysis of variance followed by Duncan's post-hoc tests (among groups) using SPSS 25.0. Principal component analysis (PCA) was conducted using SIMCA14.1, and the data were preprocessed by log₂-transformed and UV scaling prior to analysis.

RESULTS AND DISCUSSION

Aroma compounds analysis of ginger oils

Lowercase letters a, b, and c in the same row represented significant differences ($P < .05$).

Odor descriptions were obtained from <https://webbook.nist.gov/chemistry/name-ser/>, and related literature h,^[18] i,^[19] j.^[20]

Odor thresholds in water (mg/kg) were obtained from «Compilations of odor Threshold Values in Air, Water, and Other Media (second enlarged and revised edition)», and related literature d,^[21] e,^[22] f,^[23] g.^[24]

The OAVs were calculated by dividing the concentration of the odorants by their threshold.

Figure 1 shows typical GC-MS total ion chromatogram (TIC) levels of ginger oils aroma compounds. The base line of the total ion flow diagram was stable, with a good degree of separation of individual substance peak and no supersaturation state. GEO, PEGO, and AEGO contained 45, 42, and 45 aroma compounds, respectively, and their concentrations are shown in Table 1. GEO was detected in 28 monoterpenes with a content of 144.31 g/kg, mainly β-phellandrene (40.00 g/kg), camphene (36.33 g/kg), α-pinene (17.85 g/kg), α-citral (9.04 g/kg), β-citral (8.11 g/kg), β-myrcene (7.84 g/kg), eucalyptol (4.63 g/kg), and 8 sesquiterpenes, with a content of 12.52 g/kg, mainly (-)-zingiberene (7.61 g/kg), β-sesquiphellandrene (2.03 g/kg), α-curcumene (1.79 g/kg), β-bisabolene (1.20 g/kg). PEGO was detected in 22 monoterpenes with a content of 24.39 g/kg, mainly β-phellandrene (6.92 g/kg), camphene (5.81 g/kg), eucalyptol (4.43 g/kg) and 13 sesquiterpenes, with a content of 12.52 g/kg, mainly (-)-zingiberene (6.89 g/kg), β-sesquiphellandrene (1.64 g/kg), α-curcumene (1.11 g/kg) and β-bisabolene (0.98 g/kg). AEGO was detected in 21 monoterpenes with a content of 9.18 g/kg, mainly eucalyptol (3.54 g/kg), β-phellandrene (2.49 g/kg), and 19 sesquiterpenes, with a content of 14.9 g/kg, mainly (-)-zingiberene (7.95 g/kg), β-sesquiphellandrene (1.96 g/kg), α-curcumene (1.35 g/kg) and β-bisabolene (1.17 g/kg). The aroma compositions of ginger oils were similar, mainly terpene hydrocarbons, alcohols, aldehydes, ketones and esters, and terpene hydrocarbons were the most abundant aroma compounds, accounting for more than 70% in all (Figure 2).

(GEO (a), PEGO (b), AEGO (c))

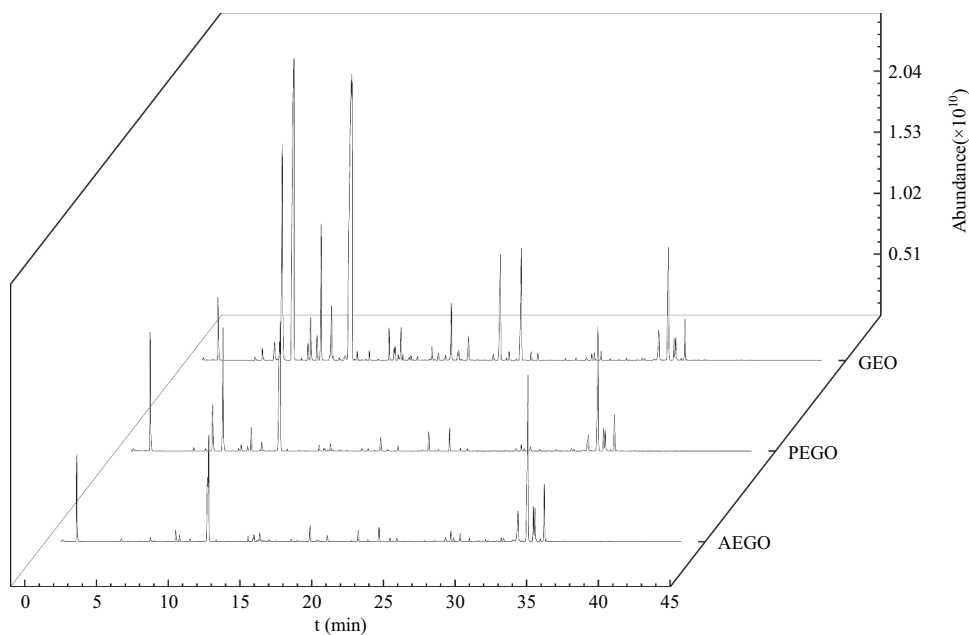


Figure 1. Total ion current chromatogram of ginger oils aroma compounds by HS-SPME-GC-MS.

Heatmap clustering analysis

Heatmap can simply and intuitively display the similarity and difference of multiple samples at various classification levels through the color gradient and degree of similarity, it is often used to study the similarity in data between samples.^[25] The heatmap of 55 aroma compounds' concentrations in Table 1 expecting δ -Eiemenene, α -selinene and (Z,E)- α -farnesene who were automatically filtered out because only little was detected in AEGO of the three kinds of ginger oil are shown in Figure 3.

(GEO (A1, A2, A3), PEGO (B1, B2, B3), AEGO (C1, C2, C3), and each number corresponding to substance is consistent with that in Table 1)

As shown in Figure 3 the color orange (blue) represents a larger (smaller) value. The differences in the concentration of 52 aroma compounds were clearly shown. And the closer the color is, the closer the clustering relationship is. As a result, the three kinds of ginger oil also successfully carried out hierarchical clustering through these compounds. First, the heatmap accurately clustered three kinds of ginger oil represented by each parallel sample (A, B, and C) and then clustered the ginger oleoresins (B and C) together, and finally clustered with ginger essential oil.

The content of all monoterpenes and most sesquiterpenes aroma compounds in ginger essential oil were much higher compared with the ginger oleoresins. This may be due to the hydrodistillation method, which is the main extraction method to extract volatile compounds, and ginger essential oil has good fluidity that is more conducive to aroma compounds volatilization. In addition, the presence of citronellol acetate, α -bergamotene, γ -elemene, (E)- β -farnesene, aromandendrene, (-)- α -muurolene and (+)- δ -cadinene in ginger oleoresins were not detected in ginger essential oil. Therefore, the clustering relationship was far.

In ginger oleoresins, the species of monoterpenes were rare and their content was lower, while the sesquiterpenes were abundant and the content was higher in AEGO, such as the content of (+)-cyclosativene, copaene, trans- α -bergamotene, (-)-zingiberene, (E,E)- α -farnesene, β -bisabolene and β -sesquiphellandrene in AEGO were significantly higher than PEGO. And citronellol acetate, trans- α -bergamotene and (-)- α -muurolene were not detected in PEGO. However, the content of camphene and eucalyptol in PEGO was significantly higher than AEGO, and tricyclene, α -pinene, (-)-verbenone

Table 1. The concentration, odor descriptions, odor thresholds (OT) and odor activity values (OAVs) of aroma compounds in ginger oils.

No.	Compound	Odor description	odor threshold (g/kg)	GEO		PEGO		AEGO		RI	Identification
				con. (g/kg)	OAV	con. (g/kg)	OAV	con. (g/kg)	OAV		
1	2-Heptanone	fruity, sweet, herbal, woody	0.14	1400.33	nd	nd	nd	nd	891	MS	
2	2-Heptanol	grass, fruity, earthy	0.065235	9998.03	0.14 ± 0.01 ^b	2135.72	0.09 ± 0.00 ^b	1356.91	901	RJ,MS	
3	Tricyclene	nr	Na	nc	0.10 ± 0.01	nc	nd	nd	920	RJ,MS	
4	α-Pinene	camphor, pine, earthy	0.014	175033.69	2.00 ± 0.10	142550.78	nd	nd	934	RJ,MS	
5	Camphene	woody, fir needle, cooling, minty	1.86	36.33 ± 0.27 ^a	5.81 ± 0.22 ^b	3122.33	0.14 ± 0.01 ^c	77.47	952	RJ,MS	
6	Sabinene	woody, camphor, pine	0.98	0.85 ± 0.07 ^a	0.10 ± 0.00 ^b	97.18	0.03 ± 0.00 ^b	33.73	969	MS	
7	β-Pinene	woody, pine, minty, camphor	0.14	2.30 ± 0.16 ^a	0.26 ± 0.01 ^b	1824.88	0.34 ± 0.01 ^b	2456.76	976	RJ,MS	
8	5-Hepten-2-one, 6-methyl-	citrus, lemon, apple	0.068	1.27 ± 0.05	0.18 ± 0.00	2654.20	nd	nd	985	RJ,MS	
9	β-Myrcene	peppery, spicy	0.0012	7.84 ± 0.46 ^a	0.89 ± 0.03 ^b	740698.93	0.18 ± 0.01 ^c	150409.56	992	RJ,MS	
10	Octanal	citrus	0.000587	0.17 ± 0.00	286855.77	nd	nd	nd	1004	MS	
11	α-Phellandrene	citrus, woody, peppery	0.04	3.42 ± 0.28 ^a	0.31 ± 0.01 ^b	7871.68	0.07 ± 0.00 ^b	1705.11	1006	RJ,MS	
12	α-Terpinene	woody, lemon, citrus	0.082	0.18 ± 0.01	2185.38	nd	nd	nd	1017	RJ,MS	
13	p-Cymene	fresh citrus, woody	0.00501	0.41 ± 0.03	81328.55	nd	nd	nd	1024	RJ,MS	
14	β-Phellandrene	mint, terpentine	0.036	40.00 ± 0.82 ^a	6.92 ± 0.13 ^b	192132.89	2.49 ± 0.10 ^c	69116.32	1029	RJ,MS	
15	Eucalyptol	eucalyptus, camphor	0.0011	4.63 ± 0.55 ^a	4.43 ± 0.15 ^a	4027482.13	3.54 ± 0.10 ^b	3217182.71	1035	RJ,MS	
16	2-Heptanol, acetate	fenugreek, fruity	0.89	0.36 ± 0.03 ^a	0.06 ± 0.00 ^b	72.41	0.05 ± 0.00 ^b	59.47	1039	MS	
17	γ-Terpinene	pine, lemon	1	0.41 ± 0.03	413.04	nd	nd	nd	1057	RJ,MS	
18	Terpinolene	pine, citrus	0.2	1.50 ± 0.15 ^a	7478.97	0.22 ± 0.01 ^b	0.15 ± 0.01 ^b	737.70	1083	MS	
19	2-Nonanone	weedy, earthy, herbal	0.061	0.55 ± 0.05 ^a	8972.21	0.09 ± 0.00 ^b	0.09 ± 0.01 ^b	1473.93	1090	MS	
20	(-)-Verbenone	spicy, mint, camphor	Na	0.64 ± 0.05	nc	nc	nd	nd	1092	MS	
21	β-Linalool	citrus, floral, sweet	0.00022	1.61 ± 0.16 ^a	7339020.95	0.29 ± 0.00 ^b	0.29 ± 0.02 ^b	1311731.76	1098	RJ,MS	
22	2-Nonanol	waxy, soapy, green, fruity	0.07	0.25 ± 0.02 ^a	3591.29	0.04 ± 0.00 ^b	0.04 ± 0.00 ^b	571.84	1102	MS	
23	dis-β-Terpineol	lila ^c	Na	0.21 ± 0.02	nc	nd	nd	nd	1103	MS	
24	(-)-Camphor	camphor	0.52	0.56 ± 0.05 ^a	1074.05	0.10 ± 0.00 ^b	0.07 ± 0.01 ^b	143.64	1142	MS	
25	Citronellal	sweet, floral, citrus	0.006	0.46 ± 0.01 ^a	77364.94	0.10 ± 0.00 ^b	0.06 ± 0.01 ^c	9859.96	1151	RJ,MS	
26	endo-Borneol	pine, camphor	0.18	3.09 ± 0.25 ^a	17157.04	0.57 ± 0.00 ^b	0.52 ± 0.04 ^b	2882.47	1168	MS	
27	Terpinen-4-ol	pepper, musty woody, earthy	1.2	0.34 ± 0.03 ^a	282.19	0.06 ± 0.01 ^b	0.04 ± 0.00 ^b	33.95	1178	RJ,MS	
28	Verbenol	fresh pine	Na	0.35 ± 0.02	nc	nd	nd	nd	1180	MS	
29	α-Terpineol	pine, lilac, citrus	1.2	1.36 ± 0.09 ^a	1131.73	0.22 ± 0.01 ^b	0.20 ± 0.02 ^c	164.12	1193	MS	
30	Citronellol	Rose, citrus	1.069	0.35 ± 0.01	330.90	nd	0.03 ± 0.00	30.29	1229	RJ,MS	
31	β-Citral	Sweet, lemon	0.053	8.11 ± 0.31 ^a	152930.84	0.76 ± 0.01 ^b	0.32 ± 0.03 ^b	6013.55	1236	MS	
32	Geraniol	floral, fruity, rose, citrus	0.0011	0.49 ± 0.01 ^a	441242.61	0.90 ± 0.00 ^b	0.06 ± 0.00 ^b	51053.12	1251	RJ,MS	
33	α-Citral	citrus, lemon	0.032	9.04 ± 0.18 ^a	282370.81	0.97 ± 0.01 ^b	0.39 ± 0.04 ^c	12149.95	1266	MS	
34	Bornyl acetate	woody, pine, camphor	0.075	0.41 ± 0.02 ^a	5509.35	0.11 ± 0.00 ^b	0.11 ± 0.01 ^b	1427.71	1283	RJ,MS	
35	2-Undecanone	fatty, orris floral	0.0055	0.34 ± 0.02 ^a	61219.15	0.08 ± 0.00 ^b	0.09 ± 0.01 ^b	17236.09	1292	RJ,MS	
36	δ-Elementene	spicy, fennel ^d	Na	nd	nd	nd	0.03 ± 0.00	nc	1333	RJ,MS	
37	Citronellol acetate	rose, citrus, woody	1	nd	nd	nd	0.04 ± 0.00	39.33	1349	RJ,MS	
38	(+)-Cyclosativene	nr	Na	0.19 ± 0.01 ^a	nc	0.15 ± 0.00 ^b	0.17 ± 0.02 ^a	nc	1365	RJ,MS	
39	Copaene	woody, spicy, honey	0.006 ^d	0.32 ± 0.02 ^a	53292.59	0.26 ± 0.01 ^b	0.32 ± 0.03 ^a	52601.44	1373	RJ,MS	

(Continued)

Table 1. (Continued).

No.	Compound	Odor description	odor threshold (g/kg)	GEO		PEGO		AEGO		RI	Identification
				con. (g/kg)	OAV	con. (g/kg)	OAV	con. (g/kg)	OAV		
40	geranyl acetate	lemon, rose, lavender	0.15	0.37 ± 0.02 ^a	2447.18	0.09 ± 0.00 ^b	608.28	0.11 ± 0.01 ^b	726.09	1377	MS
41	(-)-β-Elementene	spicy, fennel ⁱ	0.004 ^e	0.41 ± 0.01 ^a	102774.81	0.18 ± 0.01 ^c	44607.72	0.25 ± 0.02 ^b	61555.84	1387	RI,MS
42	α-Bergamotene	lemon ^j	Na	nd	nd	0.07 ± 0.00	nc	0.10 ± 0.01	nc	1401	MS
43	γ-Elementene	spicy, fennel	Na	nd	nd	0.06 ± 0.00	nc	0.07 ± 0.01	nc	1427	RI,MS
44	trans-α-Bergamotene	woody, warm, tea	Na	nd	nd	nd	nd	0.04 ± 0.01	nc	1432	RI,MS
45	(E)-β-Farnesene	woody, citrus, herbal	0.16 ^f	nd	nd	0.12 ± 0.00	734.38	0.13 ± 0.01	806.48	1453	MS
46	Aromandendrene	woody	Na	nd	nd	0.08 ± 0.00	nc	0.09 ± 0.01	nd	1457	RI,MS
47	(-)-α-murolene	black pepper ^j	Na	nd	nd	nd	nd	0.05 ± 0.01	nc	1473	MS
48	α-Curcumene	herbal	Na	1.79 ± 0.06 ^a	nc	1.11 ± 0.03 ^c	nd	1.35 ± 0.10 ^b	nc	1480	RI,MS
49	α-Selinene	amber	0.001	nd	nd	nd	nd	0.01 ± 0.00	14661.06	1486	MS
50	(-)-Zingiberene	spicy	Na	7.61 ± 0.29 ^a	nc	6.89 ± 0.14 ^b	nc	7.95 ± 0.27 ^a	nc	1496	RI,MS
51	(E)α-Farnesene	citrus, bergamot	0.16 ^g	0.98 ± 0.08 ^a	6119.25	0.92 ± 0.02 ^b	5750.25	1.09 ± 0.07 ^a	6813.63	1505	MS
52	β-Bisabolene	balsamic, woody	Na	1.20 ± 0.08 ^a	nc	0.98 ± 0.03 ^b	nc	1.17 ± 0.09 ^a	nc	1507	MS
53	(+)-δ-Cadinene	thyme, herbal, woody	Na	nd	nc	0.06 ± 0.00	nc	0.09 ± 0.01	nc	1516	MS
54	β-Sesquiphellandrene	herbal, woody	Na	2.03 ± 0.05 ^a	nc	1.64 ± 0.03 ^b	nc	1.96 ± 0.11 ^a	nc	1523	MS
55	(Z)E)-α-Farnesene	fruity, floral	0.02 ^f	nd	nd	nd	nd	0.03 ± 0.01	1661.93	1525	MS

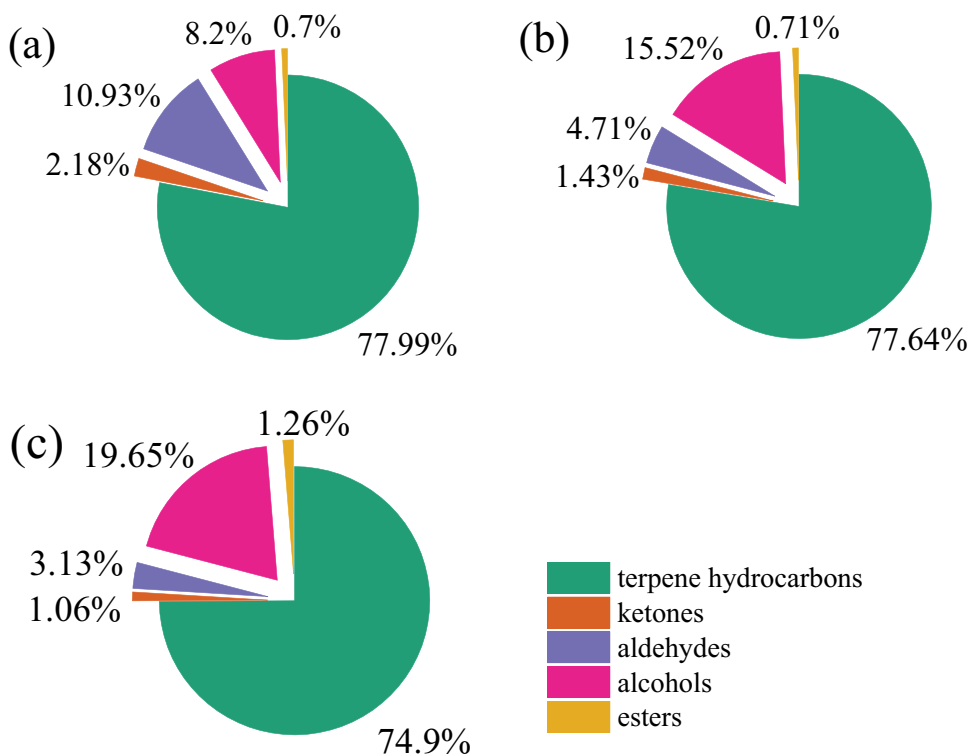


Figure 2. Aroma compositions of ginger oils.

were not detected in AEGO. This may be due to sesquiterpenes and total terpenoids, which increase with the increasing polarity of the extraction solvent. While monoterpenes decreased with the increasing polarity of the extraction solvent. However, the total terpenoid content of AEGO was lower than that of PEGO, which may be due to high viscosity of AEGO than PEGO, which affects the volatilization of aroma compounds. The contents of other aroma compounds were slightly different, so they showed an excellent clustering relationship.

Characteristic aroma compounds

Concentration is one of the major factors affecting aroma, not directly proportional to aroma due to the odor threshold. OAV is used to estimate the contribution of a certain aroma compound in the total. Previous studies reported that compounds with $OAV \geq 1$ contribute to aroma presentation, and the greater the OAV, greater will be the contribution.^[26]

Thirty-nine aroma compounds in Table 1 were found to have corresponding thresholds, and OAVs were calculated as shown. All OAVs ranged from dozens to hundreds of thousands because ginger oils were undiluted. Ten major aroma compounds of essential oil and each of the oleoresins were as given under: GEO: β -linalool, β -myrcene, eucalyptol, α -pinene, β -phellandrene, geraniol, octanal, α -citral, β -citral, (-)- β -elemene; PEGO: eucalyptol, β -linalool, β -myrcene, β -phellandrene, α -pinene, geraniol, α -farnesene, (-)- β -elemene, copaene, α -citral; AEGO: eucalyptol, β -linalool, β -myrcene, β -phellandrene, (-)- β -elemene, α -farnesene, copaene, geraniol, 2-undecanone and α -selinene.

Our result showed that β -myrcene, β -phellandrene, eucalyptol, β -linalool, (-)- β -elemene and geraniol had significant aroma contributions in the three kinds of ginger oil, suggesting that these were important characteristic aroma compounds of fire ginger oils. Based on the odor descriptions of

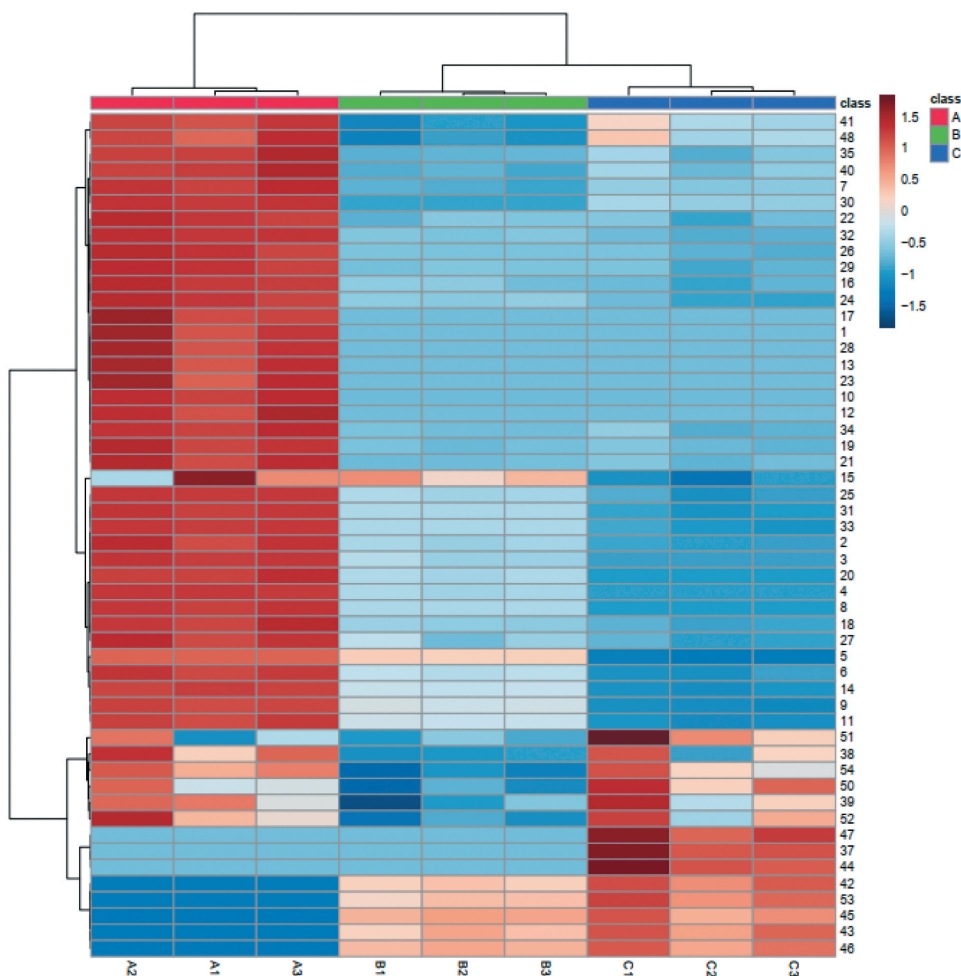


Figure 3. Clustering heat maps of aroma compounds of ginger oils.

aroma compounds in [Table 1](#), these compounds contributed a similar aroma profile to that of fresh, fruity, spicy, woody and sweet balsamic smells. These findings were consistent with the conclusions of Yinggam et al.^[27] and Manuhara et al..^[28]

Principal component analysis

(GEO (A1, A2, A3), PEGO (B1, B2, B3), AEGO (C1, C2, C3) and each number corresponding to substance is consistent with that in [Table 1](#))

Although the overall aroma contour of the three kinds of ginger oil was very similar, but the aroma of GEO was significantly more refreshing, fruity, and woody. PEGO was bland and mild, while AEGO was stimulating, spicy, and herbal. PCA can reduce complex data to low dimensions on the principle of ensuring full utilization of data, and reveals hidden simple and useful important information, which is objective, fair, and scientific.^[29] Therefore, PCA of OAVs was performed using the SIMCA14.1 software to explore the fragrance differences of various ginger oils. Our results show that the initial 39 variables were reduced to 2 principal components, variance with 82.6% and 15% were explained by the first principal component (PC1) and second principal component (PC2), respectively ([Figure 4](#)). The contribution rate of the principal component's cumulative variance was 97.6%, replicating most of the

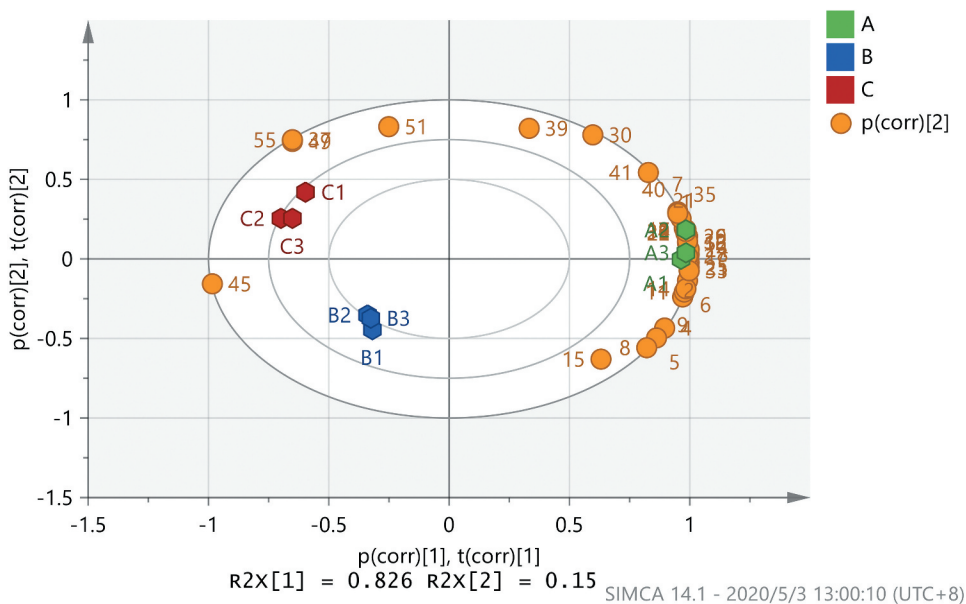


Figure 4. Biplot of principal component analysis of aroma compounds of ginger oils.

information and successfully achieving dimension reduction. In [Figure 4](#), PEGO and AEGO were closely clustered together, GEO and GOs (PEGO and AEGO) were located in obviously different regions, which suggests that the extraction method caused a big difference in aroma, while the extraction solvent caused a small difference. The main loading summary of ginger oils are shown in [Table 2](#). And the main aroma compounds of different ginger oils were analyzed by combining [Table 2](#) and [Figure 4](#).

Except eucalyptol, the geraniol, copaene, (E,E)- α -farnesene, α -selinene and citronellol acetate, the other 32 aroma compounds had high absolute load values in PC1, which played an important role in the expression of aroma. The loading values of 31 aroma compounds, such as terpinolene, citronellal, 2-heptanol, β -citral, α -citral, (-)-camphor, endo-borneol and bornyl acetate were positively correlated with ginger essential oil, indicating that aroma contribution of them in ginger essential oil was higher than that in ginger oleoresins. Among them, α -pinene, camphene, sabinene, β -pinene, β -phellandrene, endo-borneol and bornyl acetate have typical fresh and cool odor of camphor and pine alike. Octanal, α -terpinene, *p*-cymene, α -citral, β -citral and 6-methyl-5-hepten-2-one have strong citrus and lemon aroma. β -linalool, citronellal, geraniol, 2-undecanone and geranyl acetate rich in flowers, besides the aroma of fruit; β -Myrcene and (-)- β -elemene are responsible for the spicy flavor. As a result, all these exhibit a fresh, fruity, and floral aroma of ginger essential oil compared with the ginger oleoresins. However, the load value of (E)- β -farnesene was only positively correlated with ginger oleoresins, indicating that its aroma contribution in ginger oleoresins was higher than that of ginger essential oil. (E)- β -farnesene mainly shows woody, citrus, and herbal flavor, so it plays a more significant role in this kind of aroma expression of ginger oleoresins.

PC2 was mainly affected by 14 aroma compounds including (E,E)- α -farnesene, copaene, citronellol, (Z,E)- α -farnesene, citronellol acetate, α -selinene, (-)- β -elemene, β -pinene, geranyl acetate, 2-undecanone, α -pinene, camphene, 6-methyl-5-hepten-2-one and eucalyptol. Among them, the load values of α -pinene, camphene, and 6-methyl-5-hepten-2-one and eucalyptol were positively correlated with PEGO, indicating a higher contribution to the aroma of PEGO. Except for 6-methyl-5-hepten-2-one which has an intense fruity aroma, the camphoraceous aroma could be attributed to others; hence, this aroma in PEGO is more intense. The loading values of (E,E)- α -farnesene, copaene, citronellol, (Z,E)- α -farnesene, citronellol acetate, and 2-undecanone were positively correlated with AEGO, indicating

Table 2. Loading matrix of principal components of ginger oils.

No.	Compound	PC1	PC2
1	2-Heptanone	0.173	0.074
2	2-Heptanol	0.176	-0.011
4	α -Pinene	0.158	-0.180
5	Camphene	0.152	-0.205
6	Sabinene	0.174	-0.058
7	β -Pinene	0.167	0.123
8	6-methyl-5-Hepten-2-one	0.145	-0.231
9	β -Myrcene	0.171	-0.099
10	Octanal	0.173	0.073
11	α -Phellandrene	0.172	-0.085
12	α -Terpinene	0.173	0.073
13	p-Cymene	0.173	0.074
14	β -Phellandrene	0.173	-0.077
15	Eucalyptol	0.111	-0.259
16	2-Heptanol, acetate	0.175	0.040
17	γ -Terpinene	0.173	0.074
18	Terpinolene	0.176	0.012
19	2-Nonanone	0.173	0.075
21	β -Linalool	0.173	0.081
22	2-Nonanol	0.173	0.069
24	(-)-Camphor	0.176	0.025
25	Citronellal	0.176	-0.022
26	endo-Borneol	0.174	0.057
27	Terpinen-4-ol	0.175	0.007
29	α -Terpineol	0.174	0.057
30	Citronellol	0.105	0.323
31	β -Citral	0.176	-0.030
32	Geraniol	0.175	0.046
33	α -Citral	0.176	-0.030
34	Bornyl acetate	0.173	0.073
35	2-Undecanone	0.170	0.104
37	Citronella acetate	-0.115	0.308
39	Copaene	0.058	0.337
40	Geranyl acetate	0.168	0.120
41	(-)- β -Elemene	0.146	0.226
45	(E)- β -Farnesene	-0.173	-0.066
49	α -Selinene	-0.115	0.307
51	(E,E)- α -Farnesene	-0.044	0.343
55	(Z,E)- α -Farnesene	-0.115	0.308

that the aroma contribution to AEGO was higher. Among them, geraniol, citronellol acetate, (E,E)- α -farnesene, (Z,E)- α -farnesene, and 2-undecanone create a fruity and flowery aroma. α -selinene is resinous, (-)- β -elemene, eopaene, and β -pinene are spicy and fennel. Taken together, these results show that AEGO is more fruity and pungent than PEGO.

α -Pinene, camphene, β -pinene, 6-methyl-5-hepten-2-one, 2-undecanone, geranyl acetate, and (-)- β -elemene had significant absolute load values in both PC1 and PC2, therefore they were the main compounds responsible for the difference in aroma among three kinds of ginger oil. There are 16 aroma compounds, which could not use OAV for aroma evaluation due to the lack of odor threshold. Previous studies have found that (-)-zingiberene, β -bisabolene, β -sesquiphellandrene, and α -curcumenone are highly significant for aroma characteristics of ginger.^[30,31] In addition, they also had high content in this study, so the effect of aroma was analyzed based on the results of one-way analysis of variance of their concentrations. The concentration of α -curcumenone shows a significant difference among GEO, PEGO and AEGO, while (-)-zingiberene, β -bisabolene and β -sesquiphellandrene did not show significant differences between GEO and AEGO, which were significantly different when comparing GEO with PEGO. These aroma compounds are mainly responsible for the expression of stimulating, spicy, and herbal smells in all compounds (Table 1). So, they were the main reasons why the aroma of GEO and AEGO were more stimulating, spicy, and herbal compared with the PEGO.

CONCLUSION

In this study, HS-SPME-GC-MS combined with multivariate statistical techniques made aroma compounds of Xilin fire ginger oils qualitative and quantitative, and made a detailed material analysis on aroma presentation and difference. GEO, PEGO, and AEGO, respectively, were determined 44, 41, and 44 aroma compounds and were clearly reflected in their differences and divided into ginger essential oil and ginger oleoresins by heatmap based on the concentration. The OAVs of 39 aroma compounds were used to analyze the aroma contribution. β -Myrcene, β -phellandrene, eucalyptol, β -linalool, β -elemene and geraniol were important characteristic aroma compounds of ginger oils. PCA was used to further explore the aroma differences of ginger oils, 32 aroma compounds, such as terpinolene, citronellal, 2-heptanol, β -citral, α -citral, (-)-camphor, geraniol, 2-heptanol, acetate, terpinen-4-ol, and α -terpineol sufficiently explained the large difference in aroma of ginger essential oil and ginger oleoresins due to different extraction methods. And, 14 aroma compounds, consisting of (E,E)- α -farnesene, copaene, geraniol, (Z,E)- α -farnesene, citronellol acetate, α -selinene, (-)- β -elemene, β -pinene, geranyl acetate, 2-undecanone, α -pinene, camphene, 6-methyl-5-hepten-2-one, and eucalyptol showed that different extraction solvent of two kinds of ginger oleoresin had small difference in aroma. The results of single-factor analysis of variance of (-)-zingiberene, β -bisabolene, β -sesquiphellandrene, and α -curcumene whose OAVs cannot be calculated, showed that they had an important effect on the aroma of GEO and AEGO. The findings of the current study can provide significant applications in food, spices, perfumes, and other products. Nevertheless, using OAV to analyze aroma contribution is only limited to known aroma threshold volatiles, so further studies will be required to measure and supplement the threshold value of these substances or combined with other methods.

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Disclosure statement

No potential conflict of interest was reported by the author(s).

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