Identification of volatile components form fresh, sun-dried and shade-dried *Musa nana* Lour. flowers and bracts by Headspace Solid-Phase Microextraction and Gas Chromatography–Mass Spectrometry

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Keywords: *Musa nana* Lour. flower and bract; volatile compounds; identified; different drying conditions; gas chromatography-mass spectrometry (GC-MS).

Abstract. The flower of *Musa nana* Lour., also named '*XiangJiaohua'* in Chinese, is a commonly used herbal drug in traditional Chinese medicine (TCM). *Musa nana* Lour. flower and bract were usually discarded after banana fruit ripening, which leaded to resource waste and environmental pollution. It can not only protect the environment but also reduce the waste of resources to improve the utilization of the banana *(Musa nana* Lour.) flower and bract, so we analyzed volatile compounds of fresh, sun-dried and shade-dried *Musa nana* Lour. flowers and bracts by gas chromatography-mass spectrometry (GC-MS) technique with head-space solid micro-extraction (HS-SPME). The number of volatile ingredients from three kinds of *Musa nana* Lour. flowers were identified 29, 39 and 43, respectively. Thirteen common constituents were found in all of the three flowers. While three kinds of *Musa nana* Lour. bracts were identified 30, 36 and 37 volatile ingredients, respectively. In addition, twenties common constituents were found in all of the three bracts. It can be seen the compounds between flowers and bracts in different drying conditions were different apparently. This is the first ever report revealing the differences of volatile components between *Musa nana* Lour. flowers and bracts in different drying conditions.

Introduction

Musa nana Lour. is originating in Southeast Asia, including southern China. In China, it is mainly distributed in subtropical regions, such as Guangdong, Guangxi, Fujian, Taiwan, Yunan and Hainan. Its flower is referring the flower or flower bud of *Musa nana* Lour. And it is also known as banana flower. Banana (*Musa nana* Lour.) flowers are wastes after picking the ripe banana. Currently, most of them are directly discarded in producing area. Many Asian countries such as Sri Lanka, Malaysia, Indonesia, the Philippines, Laos, Myanmar and other countries make the banana flowers as vegetables, usually by the way of cooking and frying[1]. In India, banana flowers were used as medicine to increase female's breast milk, mitigate dysmenorrhea, and treat diabetes for thousands of years[2]. There are some studies showing that the water, chloroform, ethanol extraction of banana flowers all have significant hypoglycemic and antioxidant activity[3-5]. In China, a research that hypoglycemic effect in diabetic mice with alkaloids from banana stamen was carried out, the result showed that the banana stamen can reduce blood glucose level of alloxan-induced diabetic mice significantly[6]. Someone used supercritical CO_2 extraction technology to extract the essential oil of fresh and dried banana bud, and the essential oil was analyzed by GC-MS. There were 13 and 14 compounds identified respectively from fresh and dried banana bud, of which 9 common components[7]. There wasn't any report about the kinds and content of volatile components of banana flowers and bracts whether or not they affected by both the drying methods previous. In order to further improve the utilization of banana flowers and expand the medicinal resources, we analyze the chemical composition of volatile substances of fresh, sun-dried and shade-dried *Musa nana* Lour. flowers and bracts by utilizing GC-MS. We could find out the difference of kinds and content of volatile components of *Musa nana* Lour. flowers and bracts with variant processing methods, so as to provide the reference for the drying methods of drying for *Musa nana* Lour. flowers and bracts.

Experimental

Plant Materials. The flowers and bracts of *Musa nana* Lour. were collected from Zhangzhou City, Fujian Province in May, 2015 and further identified by Dr. X.P. Wang, Department of Pharmacognosy, Guiyang University of Chinese Medicine, P. R. China. All voucher specimens were deposited in the Department of Pharmacognosy, Guiyang University of Chinese Medicine, P.R. China. The bracts and flowers were cut into small pieces, and they were divided into three parts, respectively. One part of them were put in storage bags, and the bags were kept in the refrigerator at -20°C, respectively. And another two parts were dealt with drying in the sun(stored at 30-40°C in sunshine to dry) and drying in the shade(were stored at 20-30°C in darkness to air dry), respectively.

Solid-phase micro extraction procedure. The flowers and bracts of *Musa nana* Lour. were accurately weighed (6.0g) and placed into 25-mL sample vials from Supelco (Bellefonte, USA), respectively. Then, a 2cm-50/30um DVB-CAR-PDMS Stable Flex fiber (Bellefonte, USA) was used to the headspace above the samples for extracting 40 min under about 100 °C. then the extraction head was removed from sample vials and immediately inserted onto the GC injection port. The SPME fiber head was hung over the vial for 3 min and then directly desorbed and analyzed.

Gas Chromatography–Mass Spectrometry

The analyses of gas chromatography was performed on a Hewlett-Packard 6890GC-5973C MSD (Agilent, Palo Alto, CA, U.S.A.) using a ZB-5MSi (5% phenyl-95% dimethylpolysiloxane) fused silica capillary column (30m×0.25mm×0.25 mm). The oven temperature was programmed as follows: held at 40°C for 2 min, adjusted to 270°C at a rate of 5°C/min, run 48 min. The injector temperature was 250°C. High-purity helium (99.999%) was used as the carrier gas at a flow rate of 1.0 ml/min with splitless injection.

The mass spectrometer was fitted with an electron ionization source operated at 70eV. The source temperature was 230°C, and the interface temperature was 280°Cwith a solvent delay of 1.5min. The emission current was 34.6μA, and the multiplier voltage was 1294V. Mass spectra were recorded from m/z 29–450 amu in the full scan mode. Volatile compounds were identified by comparison of mass spectra of the analytes with those of authentic standards from the NIST2005 and Wiley275 libraries. The instrument Chemstation data processing system was used to determine the relative concentrations of the analytes by the peak area normalization method.

Results and Discussion

The volatile components were isolated and identified by experimental methods and experimental conditions. The relative percentage of compounds were measured by retention index and peak area normalization method. The total ion chromatogram of *Musa nana* Lour. flower of different drying methods are shown in Fig.1, Fig.2, Fig.3, Fig.4, Fig.5 and Fig.6, and the corresponding volatile compounds are listed in Table 1 and Table 2. A total of 60 volatile components were identified from fresh, sun-dried and shade-dried *Musa nana* Lour. flowers by GC-MS technology. 43, 29 and 39 components were identified in all of them, respectively. There are 13 collaborative components were found all of three flowers, accounting for 51.178%, 79.088%and 75.325%, separately. A total of 55 volatile components were identified from fresh, sun-dried and shade-dried *Musa nana* Lour. bracts by GC-MS technology. And 30, 36 and 37 components were identified in all bracts, respectively. There are 20 collaborative components were found all of three bracts, accounting for 63.387%, 89.329%and 84.361%, separately.

As shown in Table 1, the main components of the volatile oil in all flowers are aldehydes and alcohols, while aldehydes, alcohols, ethers and ketones in all bracts. We found that fresh flowers had a high content of alkanes than other two kinds of flowers, but the content of aldehydes were higher in sun-dried flower than others and ketones had a higher content in shade-dried flower. In Table 2, we have obtained that fresh bracts had a high content of olefins than other two kinds of bracts, but the content of alcohols and ketones were higher in sun-dried bracts than others and aldehydes and ketones had a higher content in shade-dried bracts. All the flowers and bracts in this research were from the same plant, however, there was a big difference between their volatile components. The volatile compositions of flowers and bracts with different drying methods are also variant, so we can choose different drying methods for our objective. Banana flowers are rich in fiber, and the vitamin and anthocyanin of fiber can eliminate free radicals in the body to delay senility and prevent and reduce the incidence of cardiovascular disease and cancer after being absorbed. In addition, banana flower also contains plenty of protein, fat, sugar, amino acids, trace elements, etc.

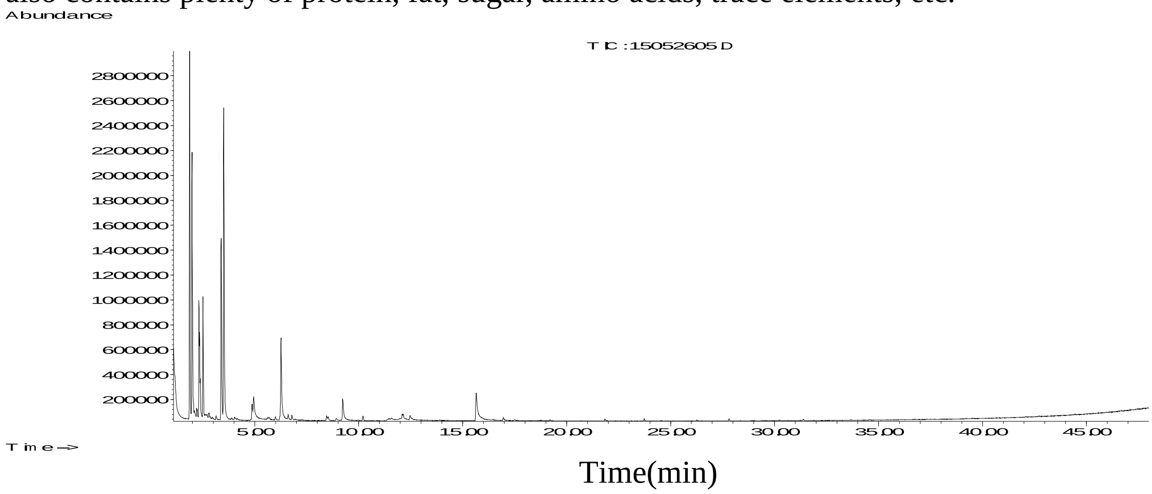


Fig1. TIC of volatile components extracted from *Musa nana* Lour. flower drying in the sun.

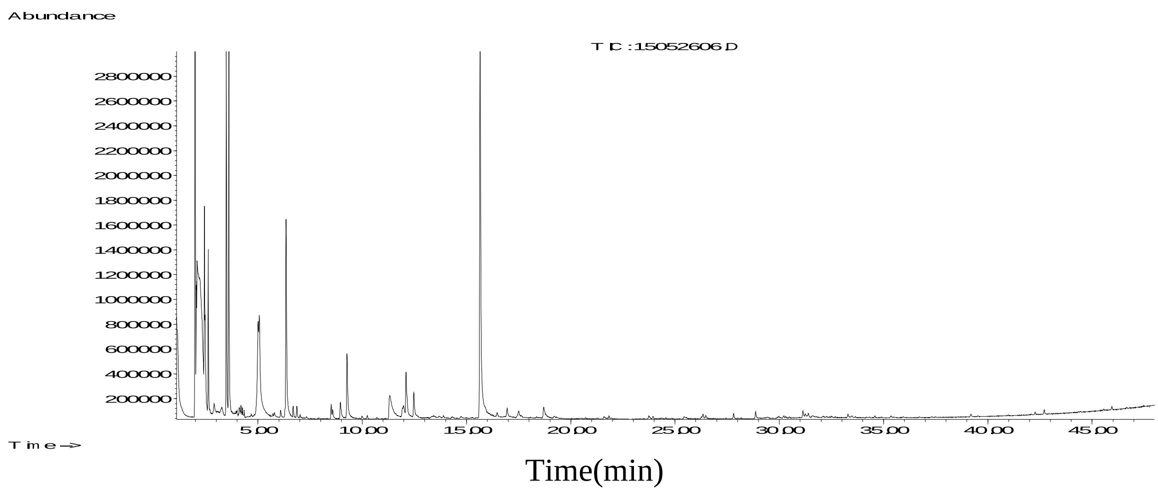


Fig2. TIC of volatile components extracted from *Musa nana* Lour. flower drying in the shade.

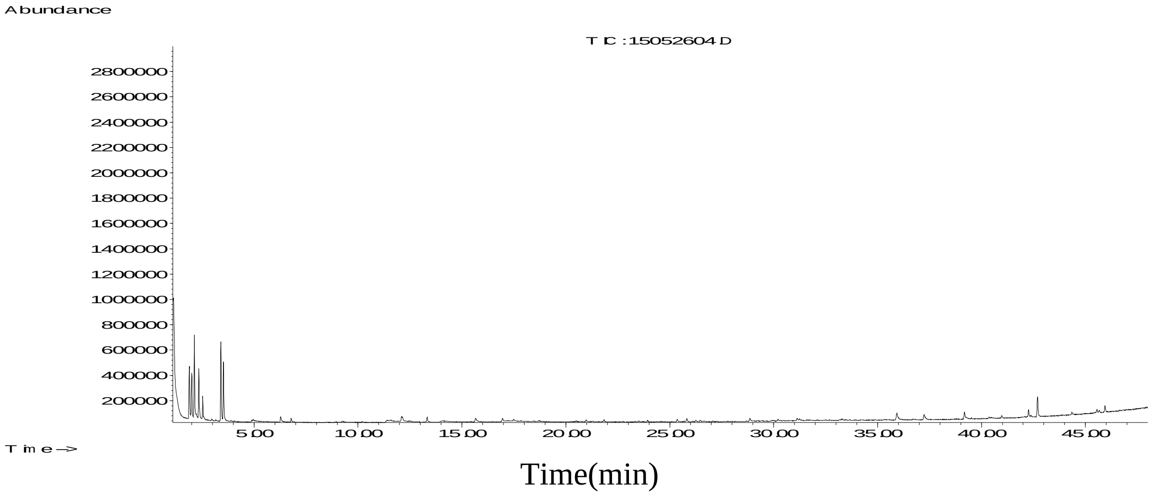


Fig3. TIC of volatile components extracted from fresh *Musa nana* Lour. flower.

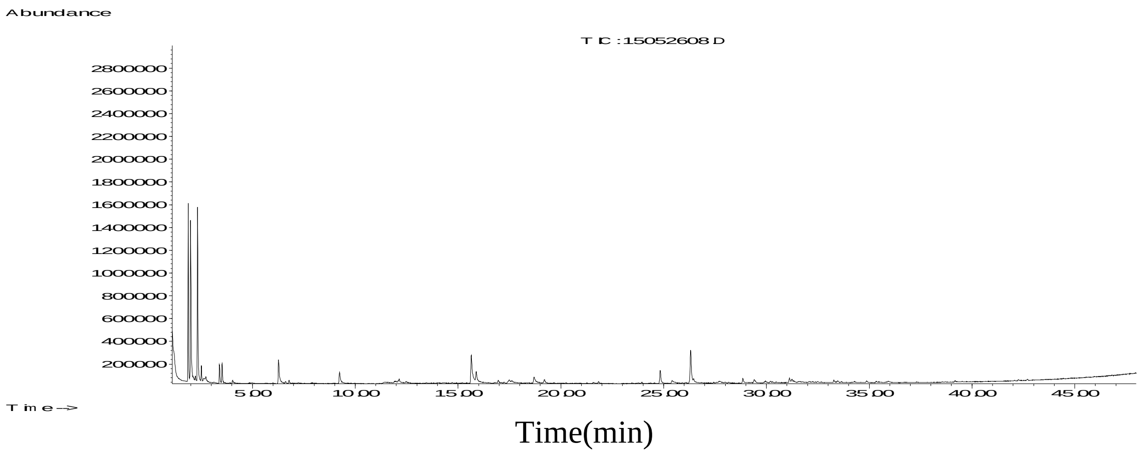


Fig4. TIC of volatile components extracted from *Musa nana* Lour. bract drying in the sun.

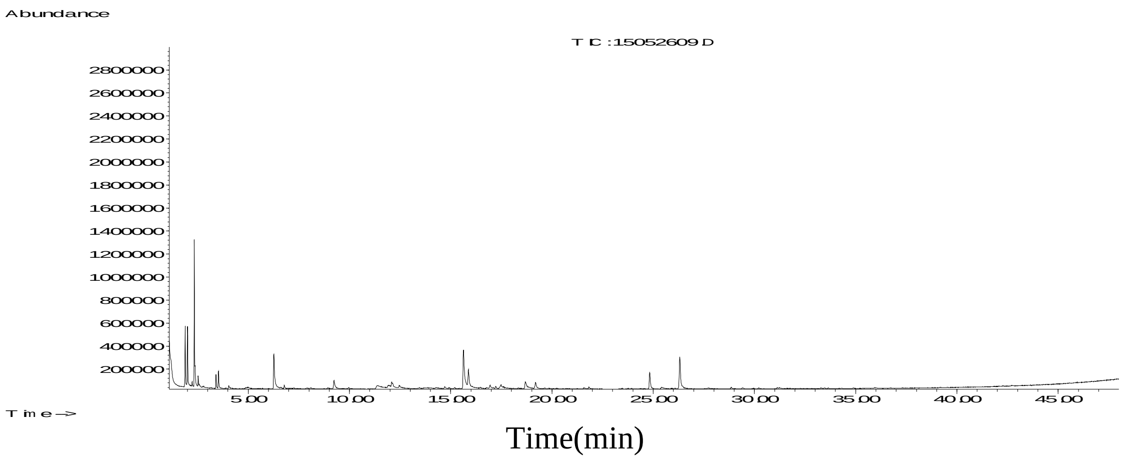
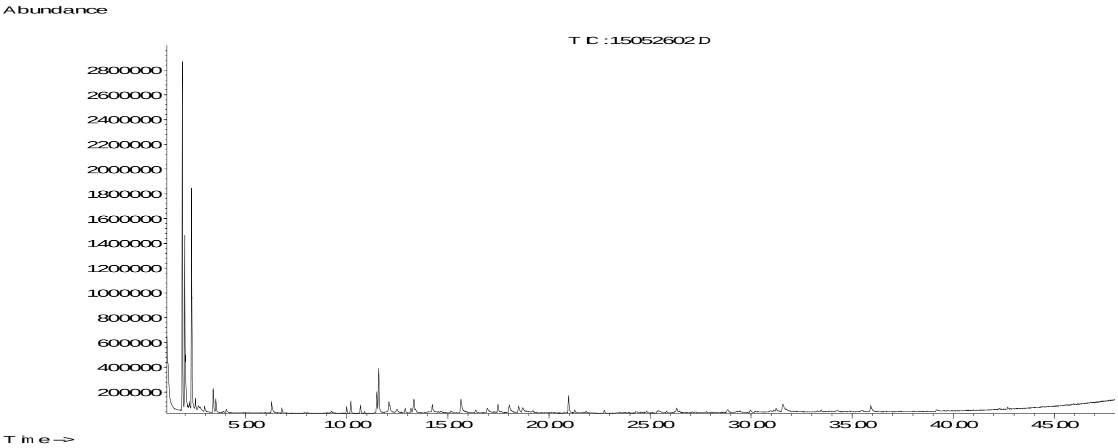


Fig5. TIC of volatile components extracted from *Musa nana* Lour. bract drying in the shade.



Time(min)

Fig6. TIC of volatile components extracted from fresh *Musa nana* Lour. bract.

Table1.Percentages of volatile components extracted from *Musa nana* Lour. flowers

No.	Retention time(min)	Compound	Flowers' Percentage(%)		
			Fresh	sun	shade
1	2	methanol	9.424	17.771	23.301
2	2.13	ethyl alcohol	14.187	—	—
3	2.21	acetone	—	0.603	3.441
4	2.34	dimethyl sulfide	7.079	8.679	3.518
5	2.38	methyl acetate	1.276	1.397	2.362
6	2.53	2-methyl-propanal	2.932	5.611	2.936
7	2.9	2-butanone	—	0.358	0.406
8	2.97	ethyl acetate	0.356	—	—
9	3.16	2-methyl-propanol	0.246	0.224	0.369
10	3.4	3-methylbutanal	13.878	13.437	7.585
11	3.53	2-methylbutanal	11.079	24.065	9.073
12	3.89	2-pentanone	0.164	—	—
13	4.11	pentanal	—	0.199	0.158
14	4.89	3-methyl-1-butanol	0.332	1.373	4.056
15	4.95	(E)- 2-methyl-2-butenal	—	3.668	—
16	4.96	2-methyl-1-butanol	1.89	—	—
17	5.72	isobutyl acetate	—	—	0.046
18	6	1-octene	—	0.243	—
19	6.3	octane	—	0.116	0.11
20	6.35	hexanal	2.034	8.86	6.178
21	6.69	2-octene	—	0.341	0.25
22	7.02	3-cyclohepten-1-one	—	0.06	0.067
23	8.46	3-methylbutyl acetate	—	0.419	0.43
24	8.53	2-methylbutyl acetate	—	0.381	0.259
25	8.92	2-heptanone	0.234	0.254	0.695
26	9.25	heptanal	0.399	1.373	2.614
27	9.99	methyl caproate	—	—	0.092
28	10.2	.alpha.-pinene	0.221	1.373	0.105

29	11.44	benzaldehyde	1.802	1.373	2.486
30	11.59	.beta.-pinene	0.205	0.11	—
31	11.99	6-methyl-5-hepten-2-on e	—	0.111	0.766
32	12.1	2-amylfuran	1.081	0.413	1.386
33	12.47	octanal	—	0.548	1.047
34	13.33	1,8-cineole	1.409	—	—
35	14.1	phenylethanal	1.854	—	—
36	15.66	nonanal	2.102	5.086	16.57
37	17.49	pinocarvone	0.408	0.072	0.35
38	18.7	decanal	0.391	—	0.788
39	20.98	.alpha.-fenchyl acetate	0.601	—	—
40	23.51	.alpha.-copaene	0.266	—	—
41	23.94	tetradecane	0.5	—	0.074
42	25.36	Seychellene	0.73	—	—
43	25.44	geranyl acetone	—	—	0.116
44	25.82	aromadendrene	0.864	—	—
45	26.47	pentadecane	0.495	—	0.085
46	27.25	.delta.-cadinene	0.15	—	—
47	28.86	hexadecane	0.798	—	0.226
48	31.13	heptadecane	0.558	—	0.237
49	31.25	pristane	0.299	—	—
50	33.29	octadecane	—	—	0.105
51	35.35	nonadecane	—	—	0.045
52	35.93	methyl palmitate	2.865	—	—
53	37.23	ethyl palmitate	2.304	—	—
54	39.18	heneicosane	2.666	—	—
55	40.98	docosane	0.573	—	—
56	42.26	(Z)-9-tricosene	1.691	—	0.058
57	42.7	tricosane	5.337	—	0.13
58	44.35	tetracosane	0.472	—	—
59	45.55	Z-12-pentacosene	0.667	—	—
60	45.95	Pentacosane	1.438	—	0.103

Table2. Percentages of volatile components extracted from *Musa nana* Lour. bracts

No.	Retention time(min)	Compound	Bracts' Percentage(%)		
			Fresh	sun	shade
1	2	methanol	20.288	23.232	7.473
2	2.21	acetone	—	0.521	0.547
3	2.34	dimethyl sulfide	22.457	22.425	16.002
4	2.38	methyl acetate	—	—	2.575
5	2.53	2-methyl-propanal	0.968	1.772	1.04

6	2.76	2,3-butanedione	—	—	0.137
7	2.81	2-butanone	—	—	0.067
8	2.96	2-methyl-3-buten-2-ol	0.623	—	—
9	3.15	2-methyl-propanol	—	—	0.058
10	3.4	3-methylbutanal	3.124	2.457	2.183
11	3.53	2-methylbutanal	1.878	2.713	2.82
12	3.89	2-pentanone	0.231	—	—
13	4.04	pentanal	—	0.369	0.58
14	6.27	hexanal	2.267	5.363	10.79
15	6.61	(Z)-4-octene	—	0.232	0.14
16	8.95	2-heptanone	0.106	—	—
17	9.24	heptanal	0.351	3.137	2.583
18	9.95	methyl caproate	—	—	0.356
19	9.99	.alpha.-phellandrene	0.925	—	—
20	10.2	.alpha.-pinene	1.68	—	—
21	10.68	camphene	1.134	—	—
22	11.41	benzaldehyde	0.128	0.771	2.916
23	11.49	sabinene	3.146	—	—
24	11.58	.beta.-pinene	6.95	—	—
25	11.99	3-octanone	—	0.593	1
26	12.09	2-amylfuran	—	0.244	0.998
26	12.48	octanal	0.798	0.329	0.598
28	12.89	.alpha.-terpipene	0.677	—	—
29	13.17	para tymene	0.704	—	—
30	13.32	1,8-tineole	2.667	—	—
31	14.23	.gamma.-terpinene	1.204	—	—
32	14.7	cis-linaloloxide	—	—	0.448
33	15.16	terpinolene	0.434	—	—
34	15.65	nonanal	4.085	8.446	14.899
35	17.48	pinocarvone	1.278	—	—
36	18.04	terpineol-4	2.049	—	—
37	18.5	myrtenal	1.357	—	—
38	18.69	decanal	1.321	2.337	2.655
39	19.2	.beta.-cyclocitral	0.269	0.856	1.884
40	20.97	.alpha.-Fenchyl acetate	2.893	—	—
41	21.28	dihydroedulan I	0.4	—	—
42	24.84	.alpha.-ionone	0.262	3.08	5.197
43	25.41	geranyl acetone	1.183	1.286	0.968
44	25.82	Patchoulene	0.211	—	—
45	26.32	.beta.-ionone	1.009	8.289	11.009
46	26.46	pentadecane	0.285	0.654	0.454
47	28.85	hexadecane	0.64	0.829	0.37
48	29.42	.alpha.-Cedrol	—	0.988	0.333

49	31.12	heptadecane	—	0.817	0.203
50	31.24	pristane	0.468	0.634	0.155
51	33.29	octadecane	—	0.4	0.11
52	33.47	phytan	0.283	0.298	0.131
53	34.89	isobutyl phthalate	—	0.427	0.145
54	35.35	nonadecane	—	0.216	0.053
55	35.96	methyl palmitate	1.323	0.421	0.234

Conclusions

Banana flowers were usually discarded after banana fruit ripening, including banana bracts, which leaded to resource waste and environmental pollution. In this paper, 43, 29 and 39 components were identified in fresh, sun-dried and shade-dried *Musa nana* Lour. flowers, respectively. The identified volatile components in this project are more than those in banana bud[7], which may be due to they used the different extraction methods. The essential oil composition and content of *Musa nana* Lour. flowers and bracts had changed after drying. This situation also appeared in the analysis of essential oils in the fresh and dry banana bud[7]. The first reason may be the original chemical composition in fresh flower and bract derived from other volatile compounds by oxidation and other reactions during the drying process, and the second probability is that volatile components are volatilized or converted to other compounds during the drying process. The compositions and contents of *Musa nana* Lour. flowers and bracts volatiles changed significantly during the drying process. Improving the utilization of the banana(*Musa nana* Lour.)flower and bract can not only protect the environment but also reduce the waste of resources. The results of this article provides fundamental information for the further development and utilization of *Musa nana* Lour. flowers and bracts.

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