# Characterization of Volatile Components of Eight FengHuang Dancong Manufactured Teas and Fresh Leaves by HS-SPME Coupled with GC-MS

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**Abstract:** FengHuang Dancong tea is famous for its excellent aroma quality. In order to characterize the volatile components in different aroma types of FengHuang Dancong tea, both fresh leaves and manufactured teas of seven well-known aroma types and their ancestor variety, which were harvested from the same places and manufactured using the same procedure, were investigated using headspace solid-phase microextraction (HS-SPME) coupled with gas chromatography-mass spectrometry (GC-MS). Results indicated that the volatile composition and contents of manufactured teas and fresh leaves, including HuangZhi, XingRen, GuiHua, MiLan, JiangHua, YuLan YeLai and Fenghuang Shuixian, were obviously different. Linalool, *(E)*-2-hexenal, *cis*-3-hexenyl acetate, linalool oxide, methyl salicylate, geraniol, and nerolidol were the major volatile components in fresh leaves, and their total relative contents ranged from 78.44-90.07%. But in manufactured teas, hotrienol, linalool, *β*-myrcene, D-limonene, 1-ethyl-1*H*-pyrrole-2-carboxaldehyde, *β*-ocimene, linalool oxide, benzyl nitrile, indole, jasmone, and nerolidol were the major volatile components, ranged from 60.12-93.97%. Although there were some similarities in the aroma composition and content among the manufactured teas of different aroma types, each type had unique aroma characteristics. The obvious difference between FengHuang Shuixian and other aroma types of manufactured teas may be due to the higher content of alkene and pyrrole derivatives and lower content of alcohols, especial terpene alcohols. Furthermore, the correlations between manufactured teas and the fresh leaves indicated that the volatile compounds profile of fresh leaves may affect the aroma quality of the manufactured tea. This study provided a comprehensive comparison of the volatile profile in different aroma types of Fenghuang Dancong tea, which is a scientific foundation for further quality assessment of Fenghuang Dancong variety in the future.

**Keywords:** FengHuang Dancong, Volatile Components, HS-SPME, GC-MS

## 1. Introduction

Oolong tea is a semi-fermented Chinese traditional tea that dates back centuries and its unique characteristics are currently attracting more and more consumers worldwide [1]. Oolong tea combines the freshness of green tea with the fragrance of black tea. The numerous aromas of oolong tea are directly related to the type and extent of processing of the tea varieties [2]. Particular manufacturing processes give oolong tea unique flower and fruit flavors and variable aroma types [3].

In China, there are several famous oolong teas including Tie Guanyin tea, Wuyi rock tea, Dongding Oolong tea, and FengHuang Dancong [4]. FengHuang Dancong, one of the most famous oolong teas, is native to FengHuang town of Chao'an county in Guangdong Province [1]. FengHuang Dancong tea is famous for its compact appearance, high-quality aroma, and mellow taste. HuangZhi, XingRen,

ZhiLan, GuiHua, MiLan, JiangHua, YuLan, YeLai, RouGui, and MoLi are the ten famous aroma types of FengHuang Dancong tea [5].

The quality of oolong tea can be evaluated using aroma, flavor, color, and appearance. Aroma and flavor are the two most important quality indices [6]. Many extraction techniques have been developed to analyze volatile components including direct solvent extraction, simultaneous distillation-extraction (SDE) [7, 8], steam distillation-liquid/liquid extraction [9], vacuum hydrodistillation [10], thermal desorption [10], and headspace solid-phase microextraction (HS-SPME) [7, 11, 12] SPME, a sensitive method that is economical and does not require solvents, integrates extraction and concentration in a single step [13]. SPME exhibits advantages in collecting actual volatile components, preventing the breakdown of heat-instable volatile components, and maintaining analytic stability Tea volatile components can be affected by tea variety, environmental factors, cultivation conditions, and processing conditions [14]. In the present study, the same environmental factors, cultivation conditions, and processing conditions were used to obtain different aroma types of FengHuang Dancong tea in order to determine varietal factors. Fresh leaves of eight types of Dancong tea, including MiLan, XingRen, YeLai, YuLan, JiangHua, GuiHua, HuangZhi, and FengHuang Shuixian, were collected and processed into eight types of FengHuang Dancong manufactured tea. Volatile components were analyzed with HS-SPME-GC-MS to investigate differences in aroma determinants between different types of FengHuang Dancong fresh leaves and manufactured teas. The differences in aroma composition and content between fresh leaves and manufactured teas were also investigated.
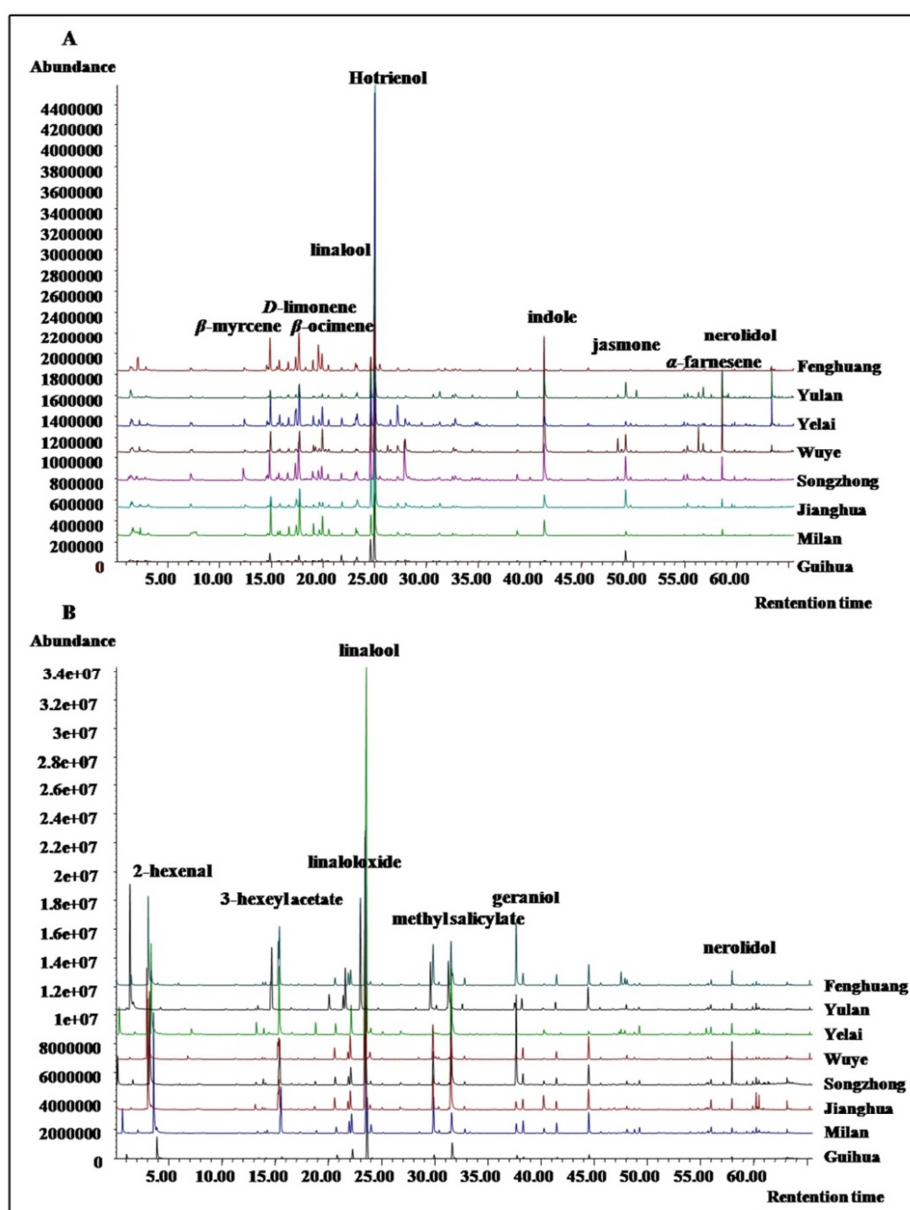


***Figure 1.*** *The total ion chromatograms of volatile components in FengHuang Dancong manufactured teas (A) and fresh leaves (B).*

# 2. Results

## 2.1. Sensory Evaluation of FengHuang Dancong Manufactured Teas with Different Aroma Types

Sensory evaluations were performed on extracted tea infusions from manufactured teas, including seven aroma types of FengHuang Dancong tea and the ancestral variety, FengHuang Shuixian. Results revealed that the major sensory characteristics for seven aroma types of FengHuang Dancong teas were flower-like aroma and honey-sweet taste, and FengHuang Shuixian had a sweet and pure aroma along with its fresh taste (Table 1). Compared with the seven aroma types of FengHuang Dancong tea, FengHuang Shuixian lacks the flower aroma and honey taste. All eight types of tea were long, thin and oily pieces, and the color of the brewed tea was light. All FengHuang Dancong manufactured teas in this study were evaluated as high quality teas (92.05-96.65 points) except FengHuang Shuixian (87.20 points).

## 2.2. Comparison of Volatile Compounds among FengHuang Dancong Teas with Different Aroma Types

The intensities of volatile compound peaks in the total ion chromatography (TIC) plot obtained from GC-MS analyses differed remarkably among the eight tea samples (Figure 1). A total of 82 peaks were identified based on the NIST mass spectral database, and the in-house database established using volatile authentic standards (Table 1 and Table A1).

Eighty–two volatile compounds in FengHuang Dancong oolong tea included aldehydes (6), alcohols (16), esters (8), ketones (5), alkenes (30), alkanes (5), and others (12) including indole and benzyl nitrile (Table 2). Of these compounds, the contents of alcohols (linalool or hotrienol) were significantly higher than the other ingredients both in fresh leaves and in manufactured teas except for FengHuang Shuixian. The major ingredients, however, were different in fresh leaves and manufactured teas (Figure 1).

Quantifications of volatile peaks were normalized based on signal intensity and used to perform multivariate statistical analyses. PCA with unsupervised pattern recognition was conducted to generate an overview of the metabolic pattern of eight groups of samples. As shown in Figure 2, there were significant differences in aromatic volatiles between the eight different types of Dancong teas both for fresh leaves and manufactured teas. Clear separation of samples was observed in MiLan, YeLai, YuLan, JiangHua, and HuangZhi fresh leaves, indicating that the volatile profiles were quite different among these five oolong varieties (Figure 2A). Consistent with the sensory evaluation results of Fenghuang Dancong manufactured teas, there were obvious differences in aromatic volatiles between FengHuang Shuixian and other tea types in the manufactured tea stage rather than in the fresh leaves stage (Figure 2B). The JiangHua type was clearly separated from the other aroma types (Figure 2B). Collectively, the results demonstrated that Fenghuang Dancong fresh leaves with different aroma types had different metabolic activity during oolong tea processing, although the same manufacturing process was used for all tea varieties.

*Table 1. Sensory evaluation of the aroma of manufactured tea samples.*

| | Shape (15%) | Soup color (10%) | Aroma (30%) |
|---|---|---|---|
| MiLan | Compact, long, thin strips yellow brown oily (95) | Bright oranger (95) | Honey, orchid aroma, long smell (94) |
| XingRen | Compact, long, thin strips, light brown oily (92) | Bright oranger (94) | Honeyand almond aroma, long and intense smell (94) |
| GuiHua | Compact, long, thin strips, yellow brown oily (95) | Clear, bright golden (96) | Osmanthus and honey aroma, long and intense smell (95.5) |
| HuangZhi | Compact, long, thin strips, yellow brown oily (96) | Clear, bright golden (96) | Gardenias and honey aroma, long and high smell (97) |
| YeLai | Compact, long, thin strips, light brown oily (92) | Bright golden (94) | Tuberose and honey aroma, long smell (90) |
| YuLan | Compact, long, thin strips, even, black brown oily (90) | Light yellow (92) | Magnolia randiflora and honey aroma, long and pleasant smell (98) |
| JiangHua | Tightly tired strip-type, yellow brown oily (95) | Bright golden (94) | Ginger and honey aroma, long smell (97) |
| FengHuang Shuixian | Tightly tired strip-type (88) | Soft light orange (92) | Sweet and pure aroma, long smell (87) |

*Table 1. Continued.*

| | Taste (35%) | Material (10%) | Total score |
|---|---|---|---|
| MiLan | Honey-sweet, full, fresh, infusion resistance (94) | Soft and bright, yellow red rimmed (95) | 94.35 |
| XingRen | Mellow, full, mi yun, infusion resistance (95) | Soft, red rimmed (92) | 93.85 |
| GuiHua | Honey-sweet, full, fresh, infusion resistance (96) | Soft, even, yellowish green, red rimmed (95) | 95.6 |
| HuangZhi | Honey-sweet, delicate, full, fresh, infusion resistance (97) | Soft, even, light yellow, red rimmed (96) | 96.65 |
| YeLai | Mellow, fresh, shanyun, infusion resistance (93) | Soft and bright, brown red rimmed (93) | 92.05 |
| YuLan | Mellow, fresh, shanyun, infusion resistance (93) | Soft and bright, yellow red rimmed (92) | 93 |
| JiangHua | Mellow, full, fresh and sweet, infusion resistance (95) | Soft and bright, yellow red rimmed (94) | 95.3 |
| FengHuang Shuixian | Taste great, fresh (86) | Soft and bright, red rimmed (86) | 87.2 |
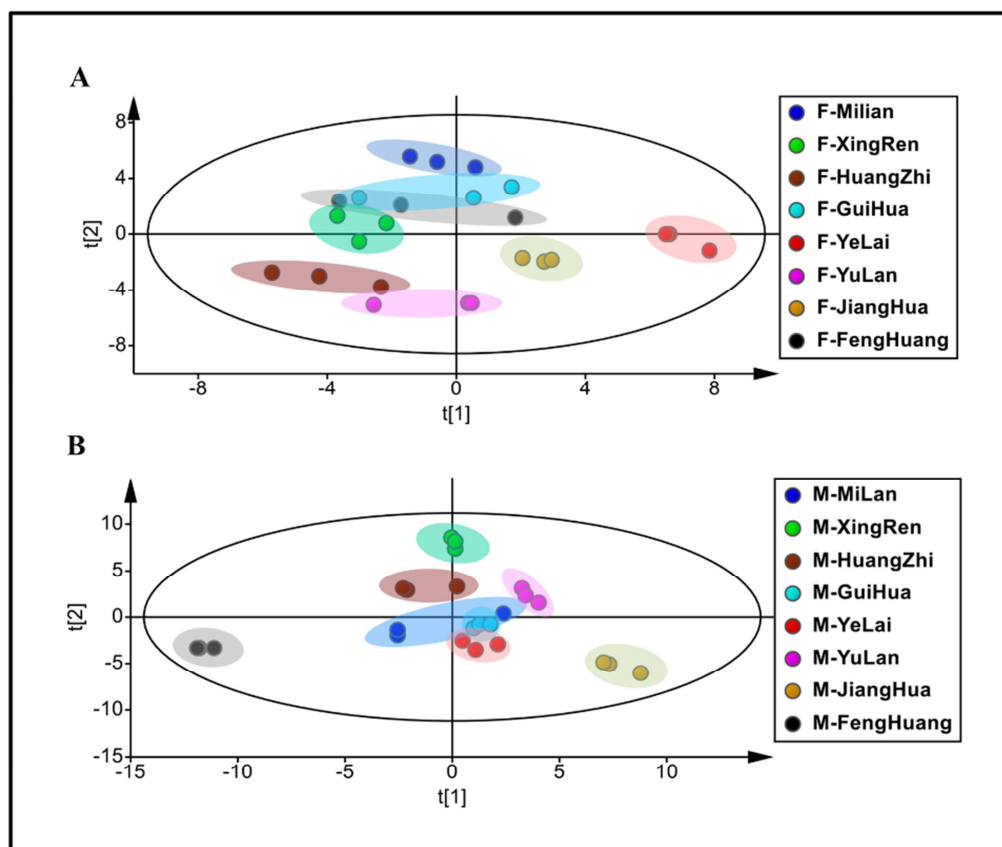
*Figure 2.* Volatile compound profiles of fresh leaves and manufactured teas of eight FengHuang Dancong varieties.

## 2.3. Comparison of Volatile Compounds Among Fresh Leaves and Manufactured Teas with Different Aroma Types

As shown in Figure 3, qualitative and quantitative differences were observed in volatile components between manufactured teas and fresh leaves. ANOVA was used to distinguish different tea samples by their aroma composition. Alcohols were the most important class of volatile components in both fresh leaves and manufactured teas except in FengHuang Shuixian manufactured tea. Aldehydes and esters were identified as the second most important flavoring components of fresh leaves while alkenes and other compounds such as indole, benzyl nitrile, and pyrrole derivatives were important for flavor of the manufactured teas.

Among aroma-active compounds, linalool, *(E)*-2-hexenal, *cis*-3-hexenyl acetate, linalool oxide, methyl salicylate, geraniol, and nerolidol were the major volatile components in fresh leaves, demonstrating relative percentages as high as 78.44-90.07% (Table 2). Hotrienol, linalool, $\beta$-myrcene, D-limonene, 1-ethyl-1*H*-pyrrole-2-carboxaldehyde, $\beta$-ocimene, linalool oxide, benzyl nitrile, indole, jasmone, and nerolidol were the major volatile components in manufactured teas and their total relative content ranged from 60.12-93.97% (Table 2). Although each volatile component changed independently after processing, three types of changing patterns were observed.

First, some components were only detectable, or increased, in the manufactured teas, such as hotrienol, 1-ethyl-1*H*-pyrrole and 1-ethyl-1*H*-pyrrole-2-carboxaldehyde. The content of hotrienol (28.30-41.20%) was highest in manufactured tea (Table 2). However, in fresh leaves, hotrienol was not detected and but linalool was at the highest concentration (34.20-42.00%) (Table 2). 1-ethyl-1*H*-pyrrole and 1-ethyl-1*H*-pyrrole-2-carboxaldehyde were not detected in fresh leaves but were detected in manufactured tea; content of 1-ethyl-1*H*-pyrrole was 0.55-5.82% and content of 1-ethyl-1*H*-pyrrole-2-carboxaldehyde was 0.53-9.20% (Table 2). Indole (0-19.54%) was another volatile compound found at relatively high concentration in manufactured teas but not detected in fresh leaves. Phenylpropanoid/benzenoid derivatives such as phenylethyl alcohol (0-0.93%), benzaldehyde (0.65-3.09%), benzene acetaldehyde (0-0.83%), and benzyl nitrile (0-9.64%) also increased after the processing procedure (Table 2); they are important contributors to the fruity and floral smells in manufactured teas [15].

Second, there were some components that decreased in the manufactured teas, such as methyl salicylate (0-1.78%), hexenal (0%), hexenol (0%), and *cis*-3-hexenyl acetate (0%), which were the major component in fresh leaves. Alcohols exhibited the third changing pattern (Table 2). The relative abundance of mainly linalool, nerolidol, and geraniol varied during processing. However, the total content of alcoholonly decreased largely in FengHuang Shuixian.

***Table 2.*** *Volatile compounds and their relative contents in eight aroma types FengHuang Dancong fresh leaves and manufactured teas.*

| | Retention time (min) | Volatile components | Relative percentage content [%] Fresh leaves Mi Lan | Xing Ren | Gui Hua | Huang Zhi | Ye Llai | Yu Lan | Jiang Hua | Feng Huang |
|---|---|---|---|---|---|---|---|---|---|---|
| **Alcohol** | | | | | | | | | | |
| 1 | 3.88 | 3-Hexen-1-ol | 0.43 | 1.11 | 0.86 | 1.5 | 1.02 | 2.85 | 0 | 3.55 |
| 2 | 7.39 | 2-Heptanol | 0 | 0 | 0 | 0 | 0.66 | 0 | 0.78 | 0 |
| 3 | 13.35 | 1-Octen-3-ol | 0.4 | 1.09 | 0.55 | 0.54 | 1.03 | 1.19 | 0 | 0.22 |
| 4 | 18.37 | 2-Ethyl-1-hexanol | 0 | 0 | 0 | 0.47 | 0 | 0.36 | 0 | 0 |
| 5 | 21.88 | Linaloloxide I | 1.13 | 2.41 | 2.19 | 1.6 | 0.79 | 0.9 | 3.06 | 1.62 |
| 6 | 23.3 | Linaloloxide II | 2.43 | 3.93 | 5.33 | 4.94 | 3.11 | 1.98 | 5.96 | 3.45 |
| 7 | 24.68 | Linalool | 41.92 | 35.92 | 42.02 | 34.16 | 53.71 | 41.56 | 50.95 | 36.38 |
| 8 | 25.04 | Hotrienol | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 9 | 25.51 | Phenylethyl alcohol | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 10 | 29.96 | Pyranoid linalool oxide | 0 | 0 | 0 | 0 | 0.36 | 0 | 0 | 0 |
| 11 | 32.6 | α-Terpineol | 0 | 0 | 0 | 0 | 0.12 | 0 | 0 | 0 |
| 12 | 38.81 | Geraniol | 12.56 | 1.87 | 2.73 | 3.57 | 0.17 | 1.42 | 1.48 | 10.95 |
| 13 | 58.62 | Nerolidol | 3.21 | 1.19 | 1.04 | 1.08 | 1.01 | 1.02 | 1.24 | 1.52 |
| 14 | 60.24 | α-cadinol | 0.56 | 1.68 | 0.5 | 0.86 | 0.4 | 0 | 0.27 | 0.42 |
| 15 | 60.5 | *tau*-Muurolol | 0.24 | 1.17 | 0 | 0.59 | 0.23 | 0 | 0.19 | 0 |
| 16 | 65.25 | Phytol | 0.04 | 0.13 | 0.13 | 0 | 0.11 | 0.15 | 0.29 | 0.21 |
| Total | | | 62.91 | 50.51 | 55.35 | 49.31 | 62.71 | 51.43 | 64.22 | 58.3 |
| **Alkene** | | | | | | | | | | |
| 1 | 14.46 | *cis*-2,6-Dimethyl-2,6-octadiene | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 2 | 14.99 | β-Myrcene | 0.57 | 0.35 | 0.36 | 0.64 | 0.51 | 0.33 | 0.56 | 0.54 |
| 3 | 15.62 | α-Phellandrene | 0 | 0 | 0 | 0 | 0.35 | 0 | 0 | 0 |
| 4 | 15.87 | 2,3,6-Trimethyl-1,5-heptadiene | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 5 | 16.73 | α-Terpinene | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 6 | 17.47 | *o*-Cymene | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 7 | 17.79 | D-Limonene | 0.2 | 0.14 | 0.15 | 0.22 | 0.23 | 0.18 | 0.28 | 0.29 |
| 8 | 19.13 | *trans*-β-Ocimene | 0.15 | 0 | 0.13 | 0 | 0.12 | 0 | 0.15 | 0.18 |
| 9 | 20.01 | β-Ocimene | 0.46 | 0.57 | 0.36 | 0.7 | 1.27 | 0.28 | 0.36 | 0.32 |
| 10 | 20.59 | γ-Terpinene | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 11 | 23.23 | Terpinolene | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 12 | 26.54 | 1,3,8-*p*-Menthatriene | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 13 | 27.29 | Cosmene | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 14 | 28.33 | *Neo-allo*-ocimene | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 15 | 39.65 | 1-Methyl-naphthalene, | 0 | 0 | 0 | 0 | 0.05 | 0.08 | 0 | 0 |
| 16 | 44.66 | α-Cubebene | 0.1 | 0.16 | 0 | 0.38 | 0.09 | 0 | 0 | 0.25 |
| 17 | 45.64 | Longicyclene | 0.22 | 0.3 | 0.2 | 0.5 | 0 | 0.41 | 0.42 | 0.32 |
| 18 | 45.66 | 1, 1, 5-Trimethyl-1, 2-dihydronaphthalene | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 19 | 45.95 | Ionene | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 20 | 47.44 | Copaene | 0 | 0.25 | 0.12 | 0.27 | 0 | 0 | 0 | 0 |
| 21 | 48.1 | Longifolene | 0.46 | 0.6 | 0.53 | 0.95 | 0 | 0.78 | 0.8 | 0.72 |
| 22 | 50.31 | Caryophyllene | 0.6 | 0.34 | 0 | 1.49 | 1.02 | 0 | 0 | 0.5 |
| 23 | 54.77 | α-Muurolene | 0.11 | 0.19 | 0.12 | 0.2 | 0.07 | 0 | 0.13 | 0.15 |
| 24 | 55.94 | *trans*-Calamenene | 0 | 0.15 | 0 | 0 | 0 | 0 | 0 | 0 |
| 25 | 56.32 | α-Farnesene | 0 | 0 | 0 | 0.45 | 1.14 | 0 | 0 | 0.4 |
| 26 | 56.01 | δ-Cadinene | 0.65 | 1.5 | 0.44 | 1.32 | 0.85 | 0.24 | 0.43 | 0.95 |
| 27 | 56.79 | α-Calacorene | 0.08 | 0.18 | 0 | 0 | 0.08 | 0 | 0 | 0.09 |
| 28 | 59.9 | Cubenene | 0.29 | 0 | 0 | 0.34 | 0.16 | 0 | 0.09 | 0 |
| 29 | 59.98 | Alloaromadendrene | 0.08 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 30 | 60.88 | Cadalene | 0.16 | 0.09 | 0.09 | 0.09 | 0.03 | 0.19 | 0.14 | 0.1 |
| Total | | | 4.14 | 4.83 | 2.49 | 7.54 | 5.97 | 2.49 | 3.36 | 4.82 |
| **Ketone** | | | | | | | | | | |
| 1 | 14.62 | 6-Methyl-5-hepten-2-one | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 2 | 26.26 | 2-Methyl-6-methylene-1,7-Octadie-3-one | 0 | 0.38 | 0 | 0 | 0.4 | 0.15 | 0 | 0 |
| 3 | 49.31 | Jasmone | 0.18 | 0 | 0 | 0 | 0.19 | 0 | 0 | 0 |
| 4 | 54.93 | *trans*-β-Ionone | 0.17 | 0.28 | 0.25 | 0.37 | 0.36 | 0.39 | 0.36 | 0.28 |
| 5 | 55.25 | Jasmine lactone | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Total | | | 0.34 | 0.66 | 0.25 | 0.37 | 0.95 | 0.54 | 0.36 | 0.28 |
| **Ester** | | | | | | | | | | |
| 1 | 15.47 | 3-Hexen-1-ol, acetate | 1.84 | 2.76 | 2.51 | 2.88 | 9.7 | 7.87 | 1.94 | 7.34 |
| 2 | 22.65 | Benzoic acid, methyl ester | 0 | 0 | 0 | 0 | 0 | 0.3 | 0 | 0 |
| 3 | 28.58 | Acetic acid, 2-ethylhexyl ester | 0.22 | 0.3 | 0.26 | 0.54 | 0 | 0.43 | 0.38 | 0.25 |
| 4 | 32.85 | Methyl salicylate | 14.87 | 14.62 | 20.14 | 6.43 | 7.18 | 4.65 | 6.25 | 8.47 |
| 5 | 48.5 | Hexanoic acid, 3-hexenyl ester, (Z)- | 0 | 0 | 0 | 0 | 0.59 | 0 | 0 | 2.24 |
| 6 | 48.89 | Hexanoic acid, hexyl ester | | | | | | | | |
| 7 | 63.35 | Phthalic acid, diisobutyl ester | 0 | 0 | 0 | 0 | 0.1 | 0 | 0.06 | 0.13 |
| 8 | 64.07 | Hexadecanoic acid, methyl ester | | | | | | | | |
| Total | | | 16.94 | 17.68 | 22.91 | 9.85 | 17.57 | 13.25 | 8.63 | 18.43 |
| **Alhyde** | | | | | | | | | | |
| 1 | 3.58 | 2-Hexenal | 11.42 | 18.72 | 14.1 | 23.77 | 9.26 | 24.34 | 17.33 | 12.9 |
| 2 | 12.49 | Benzaldehyde | 0.29 | 0.47 | 0.28 | 0.35 | 0.24 | 0.27 | 0.43 | 0.54 |
| 3 | 19.28 | Benzeneacetaldehyde | 0.16 | 0.25 | 0 | 0 | 0 | 0 | 0 | 0 |
| 4 | 24.04 | Nonanal | 0.54 | 0.92 | 1.16 | 1.91 | 0.92 | 1.26 | 1.66 | 0.74 |
| 5 | 34.43 | Decanal | 0 | 0 | 0.19 | 0.27 | 0.15 | 0.3 | 0.3 | 0 |
| 6 | 34.73 | 1-*p*-Menthen-9-al | 0 | 0 | 0 | 0 | 0.06 | 0 | 0 | 0 |
| Total | | | 12.41 | 20.36 | 15.74 | 26.31 | 10.63 | 26.17 | 19.71 | 14.18 |
| **Other** | | | | | | | | | | |

| | | | Relative percentage content [%] | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | **Fresh leaves** | | | | | | | |
| 1 | 2.32 | 1-ethyl-1*H*-Pyrrole | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 2 | 3.98 | *p*-Xylene | 0 | 0 | 0 | 0 | 0 | 0.29 | 0 | 0.41 |
| 3 | 19.68 | 1-ethyl-1*H*-Pyrrole-2-carboxaldehyde | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 4 | 23.31 | 1-Methyl-4-(1-methylethenyl)-benzene | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 5 | 25.53 | 4-Methoxy-N-methyl-benzenamine | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 6 | 28.06 | Benzyl nitrile | 0.38 | 0.73 | 0 | 0.15 | 0.82 | 0 | 0 | 0.27 |
| 7 | 29.55 | Nerol oxide | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 8 | 41.42 | Indole | 0.53 | 2.85 | 0.62 | 1.13 | 0.69 | 1.4 | 0.22 | 0.34 |
| 9 | 55.8 | Dibenzofuran | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 10 | 58.36 | Caryophyllene oxide | 0.26 | 0 | 0 | 0.36 | 0 | 0 | 0 | 0 |
| 11 | 60.64 | 2,2',5,5'-Tetramethyl-1,1'-biphenyl | 0.04 | 0 | 0 | 0 | 0 | 0.1 | 0 | 0 |
| 12 | 63.12 | Caffeine | 0.39 | 0.6 | 0.3 | 0.44 | 0.27 | 0.54 | 0.32 | 0.51 |
| total | | | 1.61 | 4.18 | 0.92 | 2.09 | 1.77 | 2.34 | 0.54 | 1.53 |
| Alkane | | | | | | | | | | |
| 1 | 32.87 | Dodecane | 0.38 | 0.49 | 0.45 | 1.04 | 0 | 0.74 | 0.72 | 0.68 |
| 2 | 41.49 | Tridecane | 0.77 | 1.07 | 1.1 | 1.98 | 0 | 1.44 | 1.57 | 1.37 |
| 3 | 49.76 | Tetradecane | 0.22 | 0.21 | 0.49 | 0.87 | 0.3 | 0.49 | 0.44 | 0.27 |
| 4 | 55.19 | Pentadecane | 0 | 0 | 0 | 0.28 | 0 | 0.34 | 0.17 | 0 |
| 5 | 59.36 | Hexadecane | 0.28 | 0 | 0.3 | 0.36 | 0.09 | 0.77 | 0.27 | 0.15 |
| Total | | | 1.65 | 1.77 | 2.34 | 4.53 | 0.39 | 3.78 | 3.18 | 2.47 |

***Table 2.** Continued.*

| | Retention time (min) | Volatile components | Relative percentage content [%] | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | **Manufactured tea** | | | | | | | |
| | | | Mi Lan | Xing Ren | Gui Hua | Huang Zhi | Ye Llai | Yu Lan | Jiang Hua | Feng Huang |
| Alcohol | | | | | | | | | | |
| 1 | 3.88 | 3-Hexen-1-ol | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 2 | 7.39 | 2-Heptanol | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 3 | 13.35 | 1-Octen-3-ol | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 4 | 18.37 | 2-Ethyl-1-hexanol | 0 | 0 | 0.69 | 0 | 0 | 0 | 0.16 | 0.94 |
| 5 | 21.88 | Linaloloxide I | 0.76 | 0.45 | 4.67 | 1.57 | 1.25 | 1.4 | 1.22 | 1.03 |
| 6 | 23.3 | Linaloloxide II | 0 | 0 | 4.51 | 0 | 0 | 1.95 | 2.04 | 1.63 |
| 7 | 24.68 | Linalool | 5.31 | 9.09 | 12.78 | 8.08 | 6.93 | 11.3 | 5.46 | 3.66 |
| 8 | 25.04 | Hotrienol | 40.72 | 25.26 | 38.91 | 28.33 | 48.35 | 41.18 | 72.56 | 15.66 |
| 9 | 25.51 | Phenylethyl alcohol | 0 | 0.34 | 0 | 0.93 | 0 | 0 | 0 | 0 |
| 10 | 29.96 | Pyranoid linalool oxide | 0.62 | 0 | 0 | 0 | 0.81 | 2.53 | 0 | 0 |
| 11 | 32.6 | *α*-Terpineol | 0.76 | 0 | 0 | 0.77 | 0.46 | 0.91 | 0.28 | 0.43 |
| 12 | 38.81 | Geraniol | 1.75 | 0.41 | 0.87 | 0.93 | 0.15 | 1.94 | 0 | 0.47 |
| 13 | 58.62 | Nerolidol | 1.2 | 6.73 | 0.37 | 1.94 | 0.13 | 3.49 | 0.73 | 0 |
| 14 | 60.24 | *α*-cadinol | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 15 | 60.5 | *tau*-Muurolol | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 16 | 65.25 | Phytol | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Total | | | 51.11 | 42.28 | 62.81 | 42.54 | 58.09 | 64.7 | 82.46 | 23.82 |
| Alkene | | | | | | | | | | |
| 1 | 14.46 | *cis*-2,6-Dimethyl-2,6-octadiene | 0 | 0.24 | 0.69 | 0.41 | 0.59 | 0 | 0 | 1.78 |
| 2 | 14.99 | *β*-Myrcene | 5.96 | 2.99 | 5.22 | 3.84 | 2.88 | 1.89 | 1.42 | 9.86 |
| 3 | 15.62 | *α*-Phellandrene | 0.61 | 0.25 | 0.42 | 0.3 | 1.48 | 0.27 | 0.2 | 1.41 |
| 4 | 15.87 | 2,3,6-Trimethyl-1,5-heptadiene | 0.96 | 0.66 | 1.12 | 0.94 | 1.16 | 0.05 | 0.48 | 3.27 |
| 5 | 16.73 | *α*-Terpinene | 1.4 | 0.71 | 0.73 | 1 | 1.07 | 0.93 | 0.35 | 2.71 |
| 6 | 17.47 | *o*-Cymene | 3.05 | 1.08 | 1.51 | 2.83 | 2.8 | 0.79 | 1.42 | 4.72 |
| 7 | 17.79 | D-Limonene | 8.21 | 3.71 | 5.2 | 6.31 | 6.67 | 3.8 | 3.07 | 13.93 |
| 8 | 19.13 | *trans*-*β*-Ocimene | 2.01 | 0.89 | 1.17 | 0.86 | 1.06 | 0.5 | 0.32 | 3 |
| 9 | 20.01 | *β*-Ocimene | 3.84 | 2.9 | 2.48 | 1.72 | 2.28 | 1.12 | 0.52 | 5.14 |
| 10 | 20.59 | *γ*-Terpinene | 1 | 0.49 | 0.83 | 0.59 | 0.81 | 0.74 | 0.33 | 1.93 |
| 11 | 23.23 | Terpinolene | 1.21 | 0.75 | 0 | 0.7 | 0.96 | 0.63 | 0 | 2.26 |
| 12 | 26.54 | 1,3,8-*p*-Menthatriene | 0 | 0.41 | 0 | 0 | 0.75 | 0 | 0 | 0 |
| 13 | 27.29 | Cosmene | 1.51 | 1.31 | 1.11 | 0.83 | 3.19 | 0 | 0.71 | 1.38 |
| 14 | 28.33 | *Neo-allo*-ocimene | 0 | 0.59 | 0.6 | 1.13 | 0.71 | 0 | 0 | 0 |
| 15 | 39.65 | 1-Methyl-naphthalene, | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 16 | 44.66 | *α*-Cubebene | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 17 | 45.64 | Longicyclene | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 18 | 45.66 | 1, 1, 5-Trimethyl-1, 2-dihydronaphthalene | 0 | 0.33 | 0 | 0.27 | 0.37 | 0 | 0 | 0.58 |
| 19 | 45.95 | Ionene | 0 | 0.18 | 0 | 0.1 | 0 | 0 | 0 | 0 |
| 20 | 47.44 | Copaene | 0 | 0.19 | 0 | 0 | 0 | 0.28 | 0 | 0 |
| 21 | 48.1 | Longifolene | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 22 | 50.31 | Caryophyllene | 0.21 | 0.16 | 0 | 0 | 0.22 | 1.8 | 0 | 0 |
| 23 | 54.77 | *α*-Muurolene | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 24 | 55.94 | *trans*-Calamenene | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 25 | 56.32 | *α*-Farnesene | 0 | 1.8 | 0.25 | 0 | 0.15 | 1.11 | 0.17 | 0 |
| 26 | 56.01 | *δ*-Cadinene | 0.35 | 1.32 | 0 | 0.48 | 0 | 2.37 | 0 | 0 |
| 27 | 56.79 | *α*-Calacorene | 0.25 | 0.23 | 0 | 0 | 0 | 0.5 | 0 | 0 |
| 28 | 59.9 | Cubenene | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 29 | 59.98 | Alloaromadendrene | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 30 | 60.88 | Cadalene | 0.1 | 0.08 | | 0.06 | 0.1 | 0 | 0 | 0 |
| Total | | | 30.66 | 21.29 | 21.32 | 22.38 | 27.25 | 16.78 | 8.99 | 51.97 |
| Ketone | | | | | | | | | | |
| 1 | 14.62 | 6-Methyl-5-hepten-2-one | 0 | 0.26 | 0.62 | 0.64 | 0.36 | 0.44 | 0 | 0.83 |
| 2 | 26.26 | 2-Methyl-6-methylene-1,7-Octadie-3-one | 0 | 1.01 | 0 | 0 | 0 | 0.37 | 0 | 0 |
| 3 | 49.31 | Jasmone | 1.72 | 3.1 | 6.63 | 3.83 | 0.79 | 3.88 | 2.43 | 0 |

| | | | Relative percentage content [%] | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | **Manufactured tea** | | | | | | | |
| 4 | 54.93 | *trans-β*-Ionone | 0 | 0.51 | 0.46 | 0.63 | 0.52 | 0.67 | 0.15 | 0.34 |
| 5 | 55.25 | Jasmine lactone | 0 | 1.08 | 0 | 0.9 | 0.43 | 0 | 0 | 0 |
| Total | | | 1.72 | 5.97 | 7.71 | 6 | 2.1 | 5.35 | 2.58 | 1.17 |
| Ester | | | | | | | | | | |
| 1 | 15.47 | 3-Hexen-1-ol, acetate | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 2 | 22.65 | Benzoic acid, methyl ester | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 3 | 28.58 | Acetic acid, 2-ethylhexyl ester | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 4 | 32.85 | Methyl salicylate | 0.65 | 0.63 | 0 | 1.15 | 1.53 | 1.78 | 0 | 0.82 |
| 5 | 48.5 | Hexanoic acid, 3-hexenyl ester, (Z)- | 0.29 | 1.91 | 0.24 | 0.4 | 0 | 0.74 | 0 | 0 |
| 6 | 48.89 | Hexanoic acid, hexyl ester | 0 | 0.55 | 0 | 0.13 | 0 | 0 | 0 | 0 |
| 7 | 63.35 | Phthalic acid, diisobutyl ester | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 8 | 64.07 | Hexadecanoic acid, methyl ester | 0 | 0.06 | 0 | 0 | 0.08 | 0.12 | 0 | 0 |
| Total | | | 0.94 | 3.16 | 0.24 | 1.68 | 1.61 | 2.64 | 0 | 0.82 |
| Alhyde | | | | | | | | | | |
| 1 | 3.58 | 2-Hexenal | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 2 | 12.49 | Benzaldehyde | 1.01 | 0.65 | 1.27 | 3.09 | 1.46 | 0.99 | 0.77 | 2.22 |
| 3 | 19.28 | Benzeneacetaldehyde | 0.59 | 0.83 | 0.74 | 0.7 | 0.27 | 0.4 | 0 | 0.37 |
| 4 | 24.04 | Nonanal | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 5 | 34.43 | Decanal | 0.32 | 0.49 | 0 | 0.39 | 0.44 | 0.59 | 0 | 0.21 |
| 6 | 34.73 | 1-*p*-Menthen-9-al | 0 | 0.12 | 0 | 0.33 | 0.6 | 0 | 0 | 0 |
| Total | | | 1.93 | 2.09 | 2.01 | 4.51 | 2.77 | 1.98 | 0.77 | 2.8 |
| Other | | | | | | | | | | |
| 1 | 2.32 | 1-ethyl-1*H*-Pyrrole | 1.29 | 0.55 | 1 | 0.72 | 0.56 | 0.33 | 0.56 | 5.82 |
| 2 | 3.98 | *p*-Xylene | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 3 | 19.68 | 1-ethyl-1*H*-Pyrrole-2-carboxaldehyde | 2.31 | 0.83 | 1.22 | 2.03 | 1.14 | 0.53 | 1.1 | 9.2 |
| 4 | 23.31 | 1-Methyl-4-(1-methylethenyl)-benzene | 0 | 0.79 | 0 | 2.28 | 2.49 | 0 | 0 | 1.91 |
| 5 | 25.53 | 4-Methoxy-N-methyl-benzenamine | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 2.1 |
| 6 | 28.06 | Benzyl nitrile | 1.24 | 2.88 | 2.41 | 9.64 | 1.31 | 0.95 | 1.22 | 0 |
| 7 | 29.55 | Nerol oxide | 0 | 0 | 0 | 0 | 0.55 | 0.55 | 0 | 0 |
| 8 | 41.42 | Indole | 7.34 | 19.54 | 1.08 | 7.58 | 1.86 | 6.59 | 2.19 | 0 |
| 9 | 55.8 | Dibenzofuran | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0.22 |
| 10 | 58.36 | Caryophyllene oxide | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 11 | 60.64 | 2,2',5,5'-Tetramethyl-1,1'-biphenyl | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 12 | 63.12 | Caffeine | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| total | | | 12.18 | 24.59 | 5.72 | 22.25 | 7.91 | 8.4 | 5.07 | 19.25 |
| Alkane | | | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 1 | 32.87 | Dodecane | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 2 | 41.49 | Tridecane | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 3 | 49.76 | Tetradecane | 0.37 | 0.33 | 0 | 0.43 | 0 | 0 | 0 | 0 |
| 4 | 55.19 | Pentadecane | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 5 | 59.36 | Hexadecane | 0.17 | 0.29 | 0.18 | 0.2 | 0.26 | 0.15 | 0.12 | 0.18 |
| Total | | | 0.54 | 0.62 | 0.18 | 0.63 | 0.26 | 0.15 | 0.12 | 0.18 |

## 2.4. Characteristic Volatile Compounds of the Fresh Leaves and Manufactured Teas with Different Aroma Types

In order to better visualize the structure and similarities among the samples, hierarchical cluster analysis (HCA) was performed with the full data set. It was clear that the volatile components of fresh leaves had significant differences in relative abundance that were related to aroma type (Figure 4A).

Volatiles of the fresh leaves included 14 alcohols, six aldehydes, five ketones, five alkanes, 19 alkenes, and six esters. The relative contents of aromatic components in eight types of fresh leaves were very different (Table 2). Linalool, linalool oxide, 2-hexenal, 3-hexeyl acetate, methyl salicylate, geraniol, and nerolidol were the major components, accounting for 81.60-92.00%. Linalool (34.20-42.00%) was the highest content of fresh leaves, followed by 2-hexenal (11.42-24.34%), and methyl salicylate (4.25-20.14%) (Table 2).

XingRen, HuangZhi, FengHuang Shuixian, and JiangHua were clearly separated in manufactured teas. In the manufactured teas, ten alcohols, four aldehydes, five ketones, five alkanes, 22 alkenes, and four esters were detected. Hotrienol, linalool, D-limonene, linalool oxide, *β*-myrcene, *β*-ocimene, benzyl nitrile, indole, jasmone, jasmine lactone, and nerolidol were the major components, accounting for 80.80-87.90%. Hotrienol constituted the highest amount (15.66-72.56%), followed by linalool (3.67-12.78%), and D-limonene (3.07-13.93%) (Table 2).

Contents of the major and characteristic components were very different in eight types of FengHuang Dancong manufactured tea. As shown in Figure 4B, geraniol was the characteristic compound in MiLan. Jasmine lactone, ionene, *α*-farnesene, 2-methyl-6-methylene-1,7-octadien-3-one, indole, nerolidol, hexanoic acid, and 3-hexenyl ester were characteristic components in XingRen. Jasmone, linalool, linalool oxide I, and linalool oxide II were characteristic in GuiHua. Phenylpropanoid/benzenoid derivatives, such as benzaldehyde, phenylethyl alcohol, and benzyl nitrile were the characteristic compounds in HuangZhi. 1-*p*-Menthen-9-al, cosmene, 1,3,8-*p*-menthatriene, and nerol oxide were the characteristic compounds in YeLai. *α*-Calacorene, copaene, cadinene, hexadecanoic acid, methyl ester, pyranoid linalool oxide, and caryophyllene were the characteristic compounds of YuLan. Hotrienol was the characteristic compound of JiangHua. Most terpenes and pyrrole derivatives were the characteristic compounds in FengHuang Shuixian. Most notably, the aroma profile of FengHuang Shuixian manufactured tea was quite different from the other types. Content of alkenes (51.97%) was the highest in FengHuang Shuixian oolong tea; content of alkenes ranged from 8.99-30.66% in other varieties. The content of alcohol in

FengHuang Shuixian was 23.82% but reached 42.28-82.46% in the other tea types. Notably, the content of 1-ethyl-1*H*-pyrrole and 1-ethyl-1*H*-pyrrole-2-carboxaldehyde reached 5.82% and 9.20%, respectively, in FengHuang Shuixian while the other tea varieties only had 0.33-1.29% and 0.53-2.31%, respectively, of these compounds (Table 2).
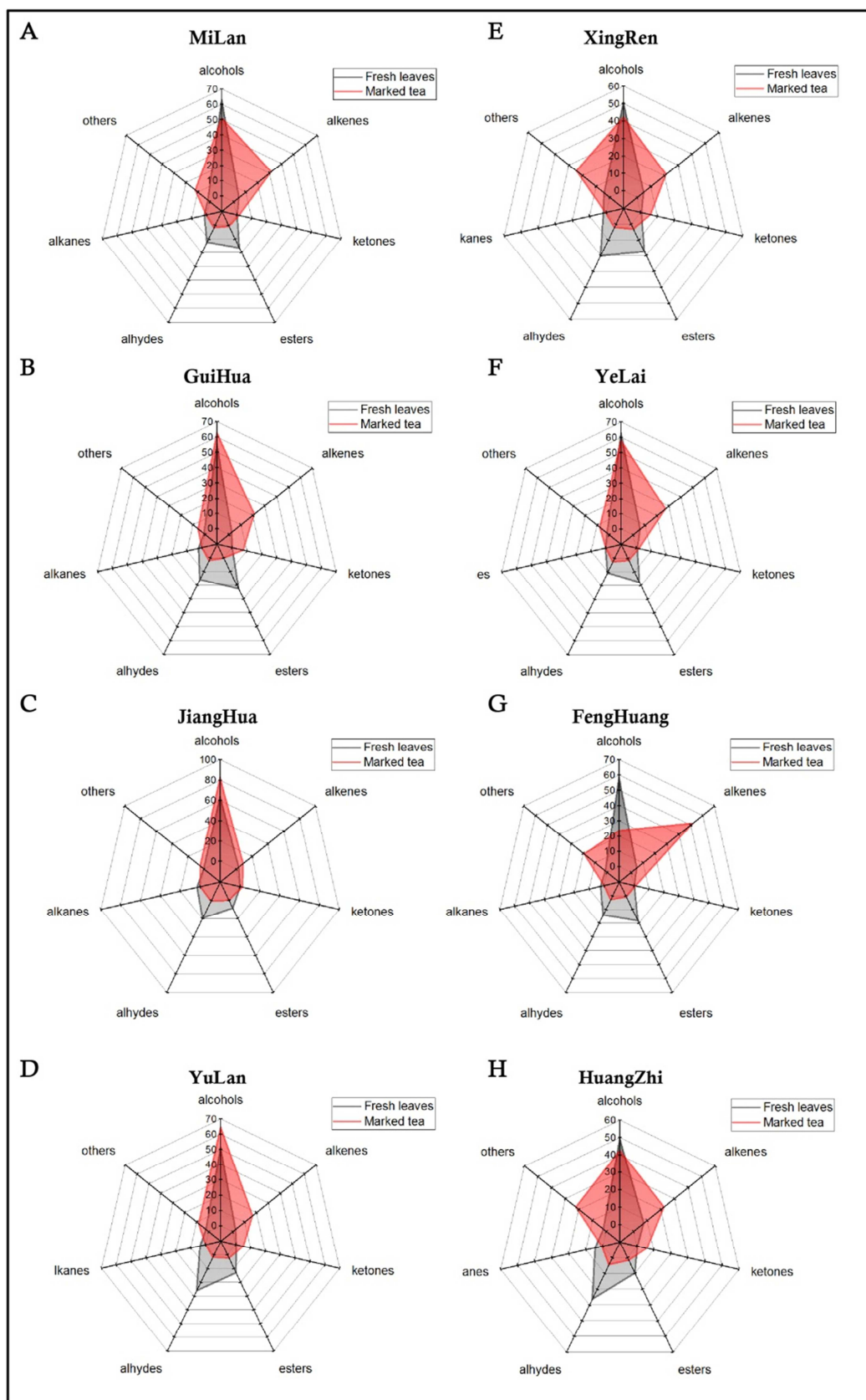


**Figure 3.** *PCA scores plot of fresh leaves (F-) and manufactured tea (M-) of eight types of FengHuang Dancong tea.*

In both the fresh leaves and manufactured teas, GuiHua, MiLan, and HuangZhi samples were not distinctly separated (Figure 2), indicating that their aromatic profiles are very similar. The characteristic compounds of manufactured teas were related to the fresh leaves (Figure 4A and 4B), such as geraniol in MiLan, indole and 2-methyl-6-methylene-1,7-octadien-3-one in XingRen, linalool and linalool oxide in GuiHua, and 1-*p*-menthen-9-al in YeLai. These components are important both in fresh leaves and manufactured teas. Interestingly, linalool and linalool oxide were the characteristic compounds in the fresh leaves of JiangHua but in the manufactured tea, hotrienol, the oxide of linalool, was the characteristic compound.

# 3. Discussion

Similarities and differences of volatile compounds between fresh leaves and manufactured oolong teas were identified in this study. Aroma type may play an important role in these differences. Alcohols were the most important components both in fresh leaves and manufactured teas of eight types of Dancong tea except FengHuang Shuixian manufactured tea (Figure 3). Alcohols are generally characterized by intense sensory descriptions and are associated with citrusy, fatty, and sweet odors [7]. Linalool, which plays an important role both in fresh leaves and manufactured tea, was recognized as one of the key odorants in several studies of black tea leaves and tea infusions, green tea, pu-erh raw tea, and contributes to citrus and floral aroma notes of teas [16]. Hotrienol, the most important compound in the eight types of Dancong manufactured teas but not detected in fresh leaves, may be produced by linalool oxidation during the fermentation procedure. Hotrienolis one of the major compounds in green oolong tea and can be relied on for distinguishing teas obtained from non-fermentation tea processing [17].

Jasmone has been identified as an important fatty acid derivative of the jasmine-like aroma of semifermented teas. Jasmone and jasmine lactone also increased in the manufactured teas, providing a floral aromatic odor [18]. Indole also has a flower-like aroma at a very low concentration [19, 20]. The content of indole was related to the degree of fermentation in a previous study. Indole increased quickly at the beginning of fermentation in oolong tea and then slowly decreased with continuing fermentation [21].

1-ethyl-1*H*-pyrrole and 1-ethyl-1*H*-pyrrole-2-carboxaldehyde provide burnt and sweet odors [22], which were characteristic components of manufactured teas. The two aromatic compounds were formed by a Maillard reaction with some soluble sugars and amino acids as substrates. The amount of pyrroles increased following increases in time and the temperature of thermal treatment. We found that the pyrroles were at a higher percentage in FengHuang Shuixian manufactured tea (15.02%) than in the other tea types (0.86-3.60%). FengHuang Shuixian manufactured tea had the worst aroma, lacking flower aroma and honey taste. This bad aroma maybe associated with the high content of pyrrole derivatives.

Saturated hydrocarbons usually make a minor contribution to the tea aroma, whereas unsaturated hydrocarbons are important contributors to the tea aroma [23].

D-limonene is considered an important volatile and is described as having a "lemon-like" aroma. Moreover, *β*-ocimene, another important volatile component, generates a strong "warm herbaceous" aroma [16]. Alkanes and polycyclic aromatic hydrocarbons, such as tridecane, tetradecane, and pentadecane have no effect on tea aroma while terpene compounds possibly play an important role [24]. These findings show that terpene compounds may be major contributors to the aroma of oolong tea [25].

Methyl salicylate appears only in teas that have at least a medium degree of fermentation but cannot be detected in unfermented or lightly fermented teas [21]. However, our results showed that methyl salicylate was present in fresh leaves at high concentrations but decreased after processing (Table 2). The results were similar with the research of Huang [26] who found that methyl salicylate was one of the major volatile components in the fresh leaves of different oolong teas using the SDE extraction method. Methyl salicylate was one of the major volatile components in fresh leaves using the HS-SPME method in eight FengHuang Dancong teas. C6 aldehydes, such as 2-hexenal, are considered to be detrimental volatile aroma compounds, and levels of these compounds are found to increase during the processing of oolong tea [27]. Interestingly, we found that C6 aldehydes were not detectable in any manufactured teas.

Production processes affect the aroma formation of oolong tea, which relate to chemical reactions [28]. In the present study, the floral aroma increased, and the grassy odors decreased during the tea manufacturing process. These results were consistent with those reported by Wang et al. [21, 29]. Tea leaf lipids are hydrolyzed, oxidized, and decomposed by a series of enzymatic reactions during the withering process. These reactions produce grassy odors in tea leaves. Linalool and geraniol are liberated from their glucosides by tea leaf glucosidase. Also, other aroma volatiles such as benzylalcohol, 2-phenylethanol, and methylsalicylate may be produced by hydrolysis of non-volatile compounds. These compounds are possibly principal contributors to the sweet floral aroma of oolong teas.

The major components we found were different from other studies on FengHuang Dancong teas [30, 31]. The number of alkenes was significantly higher than in other studies. The differences may be because different extraction and sample preparation methods (HS-SPME or SDE) were used.

Chemometric tools (like stepwise HCA and PCA) showed the separation of FengHuang Dancong teas. This study revealed that differences in aromatic profiles may be obvious for tea varieties with very similar origins. The volatile components of FengHuang Shuixian manufactured tea were obviously different from the other tea varieties, which is consistent with the results of sensory evaluation. We speculate that the higher content of alkene and pyrrole derivatives and lower content of alcohols may cause the bad sensory evaluation of this variety.
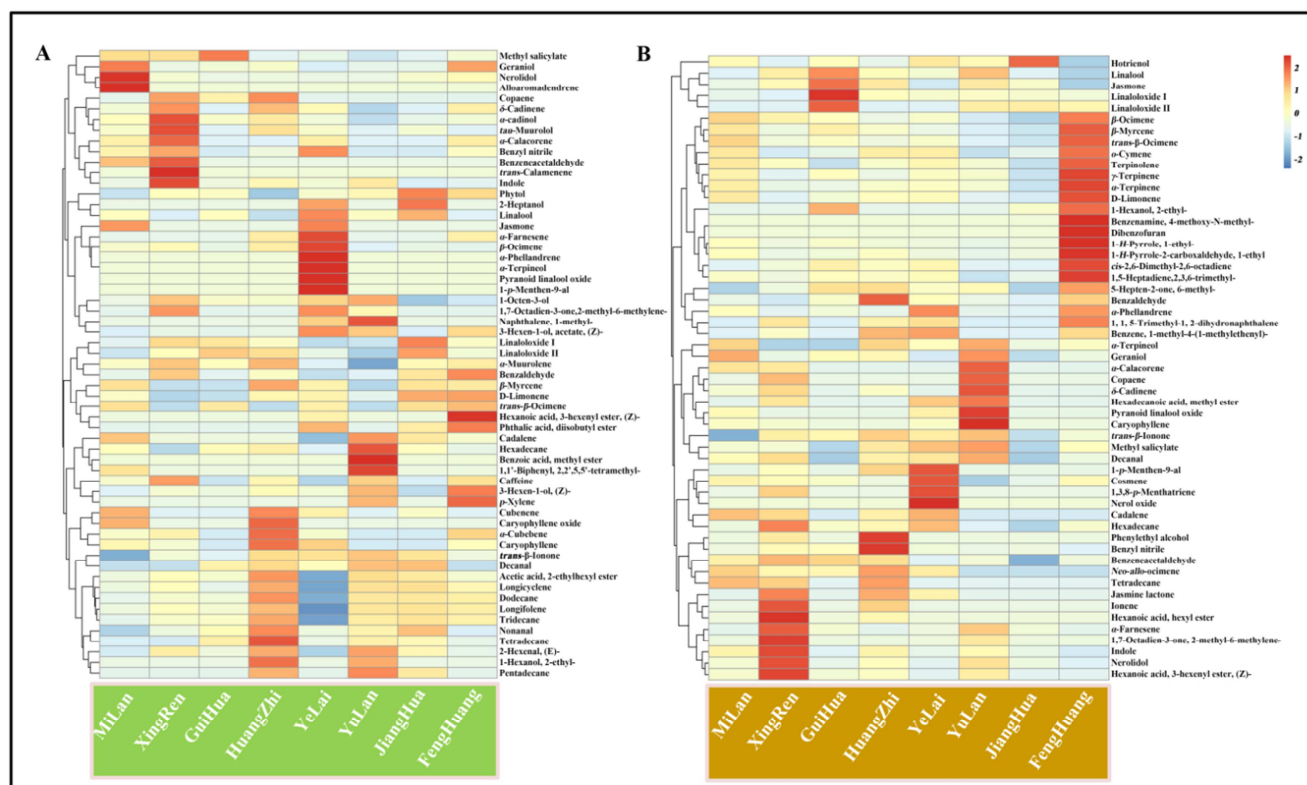
**Figure 4.** *Heatmap and clustering of volatile compounds in eight FengHuang Dancong fresh leaves (A) and manufactured teas (B).*

Each row represents a compound and each column represents a type of FengHuang Dancong. Values were centered and scaled in the row direction to form virtual colors as presented in the color key. Compounds with similar contributions were clustered together.

Our results also showed a correlation of the characteristic compounds between manufactured teas and fresh leaves (Figure 4). The correlations indicated that the volatile organic compounds profile of fresh leaves may affect the quality of the manufactured tea and thus require further study to determine if the volatile compounds of fresh leaves can be used as one standard to choose better varieties and processes to make higher quality teas.

## 4. Conclusion

In conclusion, we compared the volatile compound profiles of eight types of FengHuang Dancong tea. Among aroma-active compounds, linalool, *(E)*-2-hexenal, *cis*-3-hexenyl acetate, linalool oxide, methyl salicylate, geraniol, and nerolidol were the major volatile components in fresh leaves. But in manufactured teas, hotrienol, linalool, *β*-myrcene, D-limonene, 1-ethyl-1*H*-pyrrole-2-carboxaldehyde, *β*-ocimene, linalool oxide, benzyl nitrile, indole, jasmone, and nerolidol were the major volatile components. HCA analysis showed that relative contents of the major and characteristic components were remarkable different in eight types of FengHuang Dancong fresh leaves and manufactured teas. Most notably, the aroma profile of FengHuang Shuixian manufactured tea was quite different from other aroma varieties, and the difference may be associated with the higher contents of alkene and pyrrole derivatives; lower content of alcohols, especially terpene alcohols in FengHuang Shuixian. Each aroma type had unique aroma characteristics. We also found that the oolong tea processing not only increased the floral aroma but also decreased the grassy odor; in addition, the relative content of methyl salicylate decreased, and alkenes increased after processing. The characteristic compounds between manufactured teas and fresh leaves were closely correlated. But the clear metabolic changes of volatile components between fresh leaves and manufactured teas requires further investigation.

## 5. Materials and Methods

### 5.1. Chemicals

2-Hexenal (≥95%), *α*-terpinene (≥90%), D-limonene (≥99%), *γ*-terpinene (≥85%), benzyl nitrile (≥98%), *cis*-jasmone (≥92%) and caryophyllene (≥90%) were purchased from Shanghai Anpel Co., Ltd; *β*-ocimene (≥90%), benzaldehyde (≥99.5%), *β*-myrcene (≥95%), *α*-phellandrene (≥95%), methyl salicylate (≥99%), *σ*-cymene (≥95%), linaloloxide (≥97%), linalool (≥97%), nerolidol (≥98%), geraniol (≥98%) and phenylethyl alcohol (pharmaceutical secondary standard) were purchased from Sigma-Aldrich; *cis*-3-hexenyl acetate (100 mg/L dissolved in MeOH) was purchased from o2si smart solutions; indole (≥99.9%) was

purchased from Supelco; and jasmine lactone (≥97%)was purchased from Wako Pure Chemical Industries, Ltd. Ultra-pure water was obtained from a Milli-Q purification system (Millipore, Bedford, USA).

### 5.2. Plant Materials and Samplings

Fresh leaves of eight different types of Dancong tea were collected from reliable sources in FengHuang town of Chao'an county in Guangdong Province. The tea trees, which were between 30-50 years old, were all planted at an elevation of 8,000 feet. One strain of each aroma type was planted in a double line. Fifty trees of one strain were planted in one line. Three replicates of ten out of 100 trees were selected randomly. Fresh leaves from eight types of FengHuang Dancong tea were sampled and kept in liquid nitrogen.

The processing procedure to make oolong tea was as follows: tea leaves were plucked. After the tea leaves were exposed to sunlight for 30 min using a solar withering process, the leaves were turned over and collided with each other six times. Then the leaves were parched at 280 °C for 30 min to inactivate enzymatic activity. Leaves were then dried at 120 °C for 40 min and further dried at 105 °C for 1 h to produce oolong tea products. The manufactured teas were sampled from the local factory, and those teas were processed using the same manufactured techniques. The manufactured teas and fresh leaves were ground to powder using liquid nitrogen and then kept at -80 °C until use.

### 5.3. Sensory Evaluations

According to the NY/T 787-2004, the appearance of the tea was evaluated. Three grams of tea sample was extracted with 250 mL of 100 °C distilled water for five min. The extracted tea infusion was filtered and cooled to room temperature. Then, five evaluators identified the perceived quality scores of the extracted tea infusions based on the color, taste, and aroma of tea infusions (total score is 100 points). Higher scores mean better quality tea.

### 5.4. HS-SPME Analysis

The fiber coatings (30-50 μm divinyl benzene-carboxyl-polydimethyl siloxane (DVB-CAR-PDMS) were purchased from Supelco (57328U, Supelco). Prior to analyses, the fibers were equilibrated for 60 min at the manufacturer's recommended conditioning temperature.

Tea powder (200 mg) from each sample was extracted with 1.8 mL water in the headspace solid-phase microextraction (HS-SPME) device (57357U, Supelco), which included one manual SPME holder (57330U, Supelco), the SPME fiber, and one screw top vial (316018E-2170-10, ANPEL Laboratory Technologies Inc.) with PTFE/silicone septa (606050ULB-18-10, ANPEL Laboratory Technologies Inc.), and a Teflon cover (5310-18-10, ANPEL Laboratory Technologies Inc.). The SPME fiber was exposed to the tea sample headspace while the tea powder kept in the water was continuously heated on the heating block (IKA C-MAG HS 7) for 60 min at 85 °C and vigorously stirred. After extraction, the SPME fiber coating was immediately removed from the headspace vial and inserted into the GC injector for preconditioning for five min (250 °C). The experiment was carried out in triplicate for each tea sample.

### 5.5. GC-MS Analysis

Volatile compounds were analyzed using a 7890A gas chromatograph equipped with a 5975C mass spectrometer (GC-MS, Agilent Technologies, CA, USA). The compounds were separated using an HP-5 MS column (30 m × 0.25 mm i.d., film thickness 0.25 μm; stationary phase: diphenyl-95% dimethyl siloxane copolymer; Agilent) with helium (percentage purity > 99.999%) acting as the gas carrier; the flow rate was controlled at 1 mL/min. The injection temperature was maintained at 250 °C; the detector temperature was 280 °C; the ion source temperature was 230 °C; and the quadrupole temperature was 150 °C. The following temperature increase program was used for the column: 35 °C for 2 min; then increased to 40 °C at a rate of 3 °C/min and then held at 40 °C for 3 min; then increased by 3 °C/min to 60 °C and held at 60 °C for 3 min; then to 90 °C at 1.5 °C/min and held at 90 °C for 3 min; then to 125 °C at 2 °C/min; then to 150 °C at 5 °C/min; and finally to 250 °C at 15 °C/min. Splitless mode was used. The MS parameters of ionization energy 70 eV with 3.5 scans/s and mass range m/z 40 - 450 were used.

### 5.6. Data Analysis

The constituents of the volatile compounds were identified by matching the mass spectral data with those stored in the NIST11 spectral library and partly confirmed using standard samples of each volatile compound (1-ethyl-1*H*-pyrrole, benzyl nitrile, 2-hexenal, benzaldehyde, *β*-myrcene, *α*-phellandrene, 3-hexenyl acetate, *α*-terpinene, *σ*-cymene, D-limonene, *β*-ocimene, *γ*-terpinene, phenylethyl alcohol, benzyl nitrile, methyl salicylate, indole, *cis*-jasmone, caryophyllene, jasmine lactone, linalool, linaloloxide, linaloloxid II, nerolidol, and geraniol).

The data set was processed using different pattern recognition methods, including principal component analysis (PCA) and hierarchical cluster analysis (HCA). Statistical analysis was performed using SIMCA software (V14, Umetrics AB, Umea, Sweden), and figures were constructed using Origin software (version 8.0, Origin Lab Inc., USA).

## Acknowledgements

# Appendix

**Table A1.** *The characteristic fragment ions of volatile compounds.*

| Compound | Ion fragment ions of volatile authentic standards | Ion fragment ions of volatile compounds in tea samples |
|---|---|---|
| 1-ethyl-1*H*-pyrrole | 41.1, 53.1, 67.0, 80.1, 95.1 | 41.0, 53.0, 67.0, 80.1, 95.1 |
| Benzyl nitrile | 51.1, 63.1, 77.1, 90.1, 117.1 | 51.0, 63.0, 77.0, 90.0, 117.1 |
| 2-Hexenal | 41.1, 55.1, 69.1, 83.0, 98.0, 147.0 | 41.1, 55.1, 69.1, 83.1, 98.1 |
| Benzaldehyde | 51.1, 77.1, 105.1 | 51.0, 77.0, 105.1 |
| *β*-Myrcene | 41.1, 69.1, 77.0, 93.1, 119.1, 136.1 | 41.1, 69.1, 77.0, 93.1, 119.1, 138.1 |
| *α*-Phellandrene | 41.0, 51.0, 65.0, 77.0, 93.1, 105.1, 119.1, 134.2 | 41.0, 51.1, 65.0, 77.0, 93.1, 105.1, 119.1, 134.2 |
| 3-Hexen-1-ol, acetate | 43.1, 54.0, 67.1, 82.1 | 43.1, 54.1, 67.1, 82.1 |
| *α*-Terpinene | 41.1, 65.0, 93.1, 121.1, 136.1 | 41.0, 65.0, 93.1, 121.1, 136.1 |
| *σ*-Cymene | 41.0, 51.0, 65.0, 77.0, 91.1, 103.1, 119.1, 134.1 | 41.0, 51.0, 65.0, 77.0, 91.1, 103.1, 119.1,134.1 |
| D-Limonene | 41.1, 53.1, 68.1, 79.1, 93.1, 107.1, 119.1,136.1 | 41.1, 53.1, 68.1, 79.1, 93.1, 107.1, 119.1,136.1 |
| *β*-Ocimene | 41.1, 65.1, 79.1, 93.1, 105.1, 121.1, 136.1 | 41.1, 65.0, 79.0, 93.1, 105。1, 121.1, 136.1 |
| *γ*-Terpinene | 41.1, 65.0, 77.0, 93.1, 105.1, 121.1, 136.1 | 41.0, 65.0, 77.0, 93.0, 105.1, 119.1, 136.2 |
| Phenylethyl alcohol | 51.1, 65.1, 78.1, 91.1, 104.1, 122.1 | 51.0, 65.0, 78.1, 91.1, 104.0, 122.1 |
| Benzyl nitrile | 51.1, 63.1, 77.1, 90.1, 117.1 | 51.0, 62.9, 77.0, 90.0, 117.1 |
| Methyl salicylate | 65.1, 92.1, 120.1, 152.1 | 65.0, 92.0, 120.0, 152.1 |
| Indole | 50.1, 63.1, 90.1, 117.1 | 51.0, 63.0, 90.0, 117.1 |
| *cis*-Jasmone | 41.1, 55.1, 67.1, 79.1, 91.1, 110.1, 122.1, 135.1, 149.1, 164.1 | 41.0, 55.0, 67.0, 79.0, 91.1, 110.1, 122.1, 135.1, 149.1, 164.1 |
| Caryophyllene | 41.1, 55.1, 79.1, 91.1, 105.1, 119.1, 133.1, 147.2, 161.1, 175.2, 189.2, 204.2 | 41.1, 55.1, 79.1, 91.1, 105.1, 120.1, 133.1, 147.2, 161.1, 175.1, 189.2, 204.1 |
| Jasmine lactone | 43.0, 55.0, 71.1, 81.1, 99.0, 117.0,150.2,168.1 | 43.0, 55.0, 71.0, 81.1, 99.0, 117.0,150.1,168.1 |
| Linalool | 41.1, 55.1, 71.1, 93.1, 107.1, 121.1, 136.1 | 41.1, 55.1, 71.1, 93.1, 107.1, 121.1, 136.1 |
| Linaloloxide | 43.0, 59.1, 81.1, 94.1, 111.1, 137.1, 155.1 | 43.0, 59.0, 81.0, 94.0, 111.1, 137.0, 155.1 |
| Nerolidol | 41.1, 55.1, 69.1, 93.1, 107.1, 121.1, 136.1, 161.1, 175.2, 189.2,204.2 | 41.1, 55.0, 69.1, 93.1, 107.1, 121.1, 136.1, 161.2, |
| Geraniol | 41.1, 55.1, 69.1, 93.1, 107.1, 123.1, 136.1, 206.9 | 41.0, 55.0, 69.0, 93.1, 107.1, 123.1, 136.0, 206.9 |

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