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RESEARCH ARTICLE

Characterization of key aroma compounds in Laobaigan Chinese Baijiu by GC×GC-TOF/MS and means of molecular sensory science

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Abstract

Laobaigan (LBG) Baijiu is recognized as one of the famous Chinese liquors due to its unique flavor characteristics. However, its key aroma-active volatiles are still unknown. In this study, 414 volatile chemicals in the LBG Baijiu were initially detected by comprehensive two-dimensional gas chromatography-time-of-flight mass spectrometry (GC×GC-TOF/MS). Then, 52 of them were determined by sample dilution analysis (SDA) for screen of aroma-active compounds. Based on their odor–activity values (OAVs) that were determined by the external standard method performed on the GC×GC-TOF/MS, 32 volatile compounds were further recognized as important odorants, which were reconstituted to simulate and validate the aroma profile of the LBG Baijiu. Moreover, omission experiments were conducted to corroborate the importance of key odorants. As a result, nine aroma compounds were finally confirmed as the key aroma-active compounds of the LBG Baijiu.

KEYWORDS
aroma recombination, GC×GC-TOF/MS, Laobaigan Chinese Baijiu, OAVs, omission experiments, SDA

1 | INTRODUCTION

Chinese Baijiu, known as the national liquor of China, is a special distilled liquor all over the world because of its production involving the use of special ingredients and unique processing techniques, and more importantly, of its desirable aromas. For example, it adopts *Jiuqu* as a fermentation starter and grains as the major raw materials for the production of alcohol. In regards to the processing, it involves cooking, saccharification, fermentation, distillation, aging, and blending in order to produce a large amount of ethanol enriched with a trace amount of desirable aroma compounds.[1] In general, 98% of the Chinese Baijiu is the ethanol and water, with only 2% of the liquor composed of other trace amounts of flavoring ingredients, which results in various aroma profiles of the Chinese Baijiu. Traditionally, Chinese Baijiu is classified into 12 different types based on their distinctive aroma profiles, in which Laobaigan (LBG) Baijiu is recognized for its unique aroma with soft mellow characteristics and a rich mouthful taste.[2]

Production of the LBG Baijiu is similar to that of the light-aroma-type Baijiu, except a processing step for the former that adopts a "Three or Five Batches of Distillation"[3-5] while the latter uses a "Two Batches of Distillation." LBG Baijiu is made from sorghum as the raw material with aid of fermentation by *Daqu* that is one of the most widely used *Jiuqu* to yield alcohol. There are eight major steps for the production of LBG, including ingredient formulation, grinding, soaking and cooking, cooling; mixing with *Daqu*, being loaded into the earthen jars, alcoholic fermentation, distillation, and aging.[2]

Numerous studies have been conducted in order to identify complex volatile compounds in various Chinese Baijiu. Up to now,

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1874 flavor compounds have been identified and/or reported in Chinese Baijiu, which include acetals, acids, alcohols, aldehydes, esters, ketones, lactones, nitrogen-containing compounds, sulfur-containing compounds, and so on.[1] In recent years, the LBG Baijiu has been investigated too. For instance, Ding et al.[5] adopted liquid-liquid extraction (LLE) coupled with GC-O and GC-MS to analyze the volatiles in the LBG. As a result, 90 volatile compounds were detected. Among them, 4-ethyl guaiacol, 2-phenylethyl acetate, butanoic acid, 3-methylbutanol, 2-phenylethanol, 2-acetyl-5-methylfuran, ethyl 3-phenylpropanoate, γ-nonalactone, 3-methylbutanoic acid, vanillin, and ethyl acetate were suggested to make significant contributions to the general aroma profile of LBG.

GC×GC, a comprehensive two-dimensional separation technology, has been applied with time-of-flight mass spectrometer (TOF-MS) more frequently in recent years because it can effectively solve the problems in terms of the low sensitivity and resolution, the insufficient peak capacity, and the coelution of GC-MS for the analyses of complex volatiles in trace amounts in samples.[6,7] For example, this technique has been used to analyze the volatile components in different Chinese Baijiu, including the sauce-aroma-type,[8,9] light-aroma-type,[9] and strong-aroma-type[9-11] Baijiu. However, there is no report of the application of GC×GC-TOF/MS on the analysis of the LBG flavors.

The gas chromatography–olfactometry (GC-O) with sample dilution analysis (SDA) has been widely used to determine the aroma-active compounds.[12-15] The key odorants can be further identified by the aroma recombination and omission experiments, which have been applied for the determination of important flavors in some Chinese Baijiu, such as light-aroma-type,[16] *Chixiang*-aroma-type,[17] sesame-aroma-type,[18,19] and strong-aroma-type[20] Baijiu.

However, to our knowledge, few studies have been conducted to determine the volatile compounds of the LBG Baijiu, and none of them has clearly characterized the relevant key aroma-active compounds. For example, Huo et al.[21] quantitated 36 volatile components of LBG by an internal standard method. Wang et al.[22] and Du et al.[23] compared the efficiency of different fibers of HS-SPME on the extraction of volatiles of LBG and reported that 50/30 μm divinylbenzene/carboxen/polydimethylsiloxane (DVB/CAR/PDMS) fiber was the most suitable for acquiring volatiles in LBG.

Therefore, the objectives of this study were to identify the important aroma compounds in the Laobaigan Baijiu by GC×GC-TOF/MS, GC-O analysis and confirm the key aroma-active compounds through the determination of their sample dilution (SD) values, OAVs, aroma recombination, and omission experiments. By this study, we hope to identify the key odorants and clarify their contribution to the whole aroma profile of the LBG Baijiu.

2 | MATERIALS AND METHODS

2.1 | Chinese Baijiu samples

The base distillate of the Chinese Baijiu Laobaigan (LBG) that was processed using a unique technique called "Three Batches of Fermentation" was supplied by Hebei Hengshui Laobaigan Liquor Co., Ltd., on April 26, 2017. The sample was judged as the first-class grade of the LBG Baijiu, possessing the typical flavor characteristics of Laobaigan-aroma-type Baijiu, based on the sensory evaluation of a panel which consisted of three national Baijiu panelists and four provincial Baijiu panelists (one male, six females) in the technical center of the aforementioned company. The sample (450 mL and 70% alcohol by volume) was stored in a lab refrigerator at 4 °C until its analyses by GC×GC-TOF/MS and GC-O. Besides, it is worthy of mention that the brand name, Laobaigan, is only for research rather than for advertising purposes.

2.2 | Chemicals

The following standards were obtained from commercial sources. Ethyl acetate, 2-methylpropyl acetate, 1-propanol, hexanal, 2-methyl-1-propanol, 3-methylbutyl acetate, 1-butanol, 2-heptanone, 3-methyl-1-butanol, 2-pentylfuran, 3-hydroxy-2-butanone, propyl hexanoate, ethyl heptanoate, ethyl octanoate, acetic acid, tetramethylpyrazine, benzaldehyde, ethyl nonanoate, 1-octanol, nonyl acetate, 2-undecanone, 1-nonanol, diethyl succinate, 1-decanol, (*E*,*E*)-2,4-decadienal, ethyl phenylacetate, ethyl dodecanoate, geranyl acetone, 2-phenylethanol, 4-methylguaiacol, ethyl undecanoate, (*E*)-ethyl cinnamate, and decanoic acid were purchased from J&K Scientific Co., Ltd. (Beijing, China). Diethyl acetal, 3-methylbutanal, ethyl 2-methylbutanoate, ethyl 3-methylbutanoate, ethyl hexanoate, dimethyl trisulfide, furfural, ethyl decanoate, ethyl benzoate, 2-phenylethyl acetate, 4-ethylguaiacol and octyl propanoate (internal standard (IS)) were purchased from Sigma Aldrich Trading Co., Ltd. (Shanghai, China). Ethyl butanoate, ethyl pentanoate, ethyl lactate, nonanal, hexanoic acid, ethyl 3-phenylpropanoate, and ethyl hexadecanoate were purchased from Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan). 1-Hexanol was purchased from Shanghai Macklin Biochemical Co., Ltd. (Shanghai, China). All of the standards mentioned above were of analytical reagent grade, with at least 97% purity.

A C_6-C_{30} *n*-alkane mixture (Sigma Aldrich Trading Co., Ltd.) was used for determination of linear retention indices (RIs). Absolute ethanol and sodium chloride were purchased from Sinopharm Chemical Reagent Co., Ltd. to prepare stock solutions of the chemical standards or to help improve the chemical extraction.

2.3 | Aroma extraction methods

Extraction of volatile compounds in the LBG Baijiu was based on the method of Zheng et al.[18] with slight modifications. Briefly, the LBG sample was diluted with Milli-Q water (Millipore, Bedford, MA) to 10% alcohol by volume. Eight milliliters of the diluted solution with 10 μL of octyl propanoate (114.50 mg/L in ethanol) was put into a 20 mL screw-capped vial and then saturated with 4.5 g of sodium chloride. After the static balance of volatiles in headspace at 45 °C for 20 minutes, the SPME fiber (50/30 μm DVB/CAR/PDMS, 1 cm) was inserted into the headspace for the absorption of volatiles for 40 minutes. After the extraction, the loaded SPME fiber was

immediately removed from the sample vial and inserted into the injection port of GC×GC-TOF/MS or GC-O for 5 minutes for further chemical analysis.

2.4 | Identification of volatile compounds

The GC×GC-TOF/MS instrument was composed of an Agilent 7890B gas chromatograph (Agilent Technologies), equipped with a cold-jet modulator and a Pegasus 4D time-of-flight mass spectrometer (LECO Corp., St. Joseph, MI, USA). The GC oven contained two capillary columns connected in tandem via the cold-jet modulator.

The first analytical column was a DB-WAX column (30 m × 0.25 mm i.d., 0.25 μm film thickness, Agilent Technologies, Palo Alto, CA, USA), and the second column was a DB-5 column (1.64 m × 0.10 mm i.d., 0.10 μm film thicknesses, Agilent Technologies). Helium was used as the carrier gas at a constant flow rate of 1 mL/min. The front inlet was programmed in a splitless mode with the injector temperature at 250 °C. The oven temperature for the first (main) column was held at 45 °C at first, then raised to 150 °C at 3 °C/min and held for 1 minute, and finally increased at 5 °C/min to 230 °C, and held for 10 minute. The oven temperature for the second column was higher than that for the first column by 5 °C, and the modulator temperature was higher than that for the first column by 15 °C. The modulation period is 7 seconds, and the cold blow time is 700 ms. The modulator was cooled down by liquid nitrogen gas to modulate the cold pulses.

The MS was operated in an electron ionization (EI) mode at 70 eV. The temperatures of the interface and the ion source were, respectively, set at 250 and 230 °C. The identification of aroma compounds was conducted in a full-scan mode with the mass range within 35–400 amu.

The total ion chromatographic (TIC) graph of GC×GC-TOF/MS was profiled by the LECO Chroma TOF version 4D software to process data with an aid of the NIST14 spectrum library to search chemicals. After removing the suspected compounds without aroma contribution, repetitive substances, and column loss substances from the chemical list, the chemical identification was achieved by comparison of mass spectrum and the experimental retention index of the detected chemicals with those of the authentic chemicals or those reported in literature.[24]

The GC-O analysis was performed on an Agilent 7890B gas chromatograph (Agilent Technologies), equipped with an olfactometer (ODP C200, Gerstel, Germany). Its analytical column was a DB-WAX column (60 m × 0.25 mm i.d., 0.25 μm film thickness, J&W Scientific, USA). Helium was used as the carrier gas at a constant flow rate of 1 mL/min. The injection was in a splitless mode, and the injector temperature was set at 250 °C. The oven temperature was initially held at 45 °C, then raised to 150 °C at 3 °C/min and held for 1 minunte and finally increased at 5 °C/min to 230 °C and held for 10 minutes. The temperature of the olfactory port was kept at 250 °C. All analyses were repeated in triplicate.

Identification of aroma compounds were carried out by comparison with their aroma, retention indices (RIs), NIST14 spectrum library, and the aforementioned pure standards. RI was calculated using the C_6-C_{30} *n*-alkane mixture under the same condition described above.

2.5 | Sample dilution analysis (SDA)

Sample dilution analysis was performed by GC-O on a DB-WAX column (60 m × 0.25 mm i.d., 0.25 μm film thickness, J&W Scientific, USA). The sample was diluted stepwise with 70% volume of aqueous ethanol solution in a series of 1:2, 1:4, 1:8,..., 1:131 072 dilutions. Each dilution was subjected to the GC-O analysis until no aroma compound could be perceived.

The sample dilution (SD) value of each odorant, which represents its maximum dilution when the compound could be perceived, was determined by the aforementioned SDA method by three experienced assessors. All analyses were repeated in triplicate by each panelist. Before the GC-O analysis, each panelist was trained by sniffing at 50 standard compounds at concentrations five times above their odor thresholds in air for at least five times.[25]

2.6 | Quantitative analysis of aroma compounds

Each standard stock solution was prepared by dissolving the pure standard compound in the model solution, which was prepared in 70% volume of aqueous ethanol solution in Milli-Q purified water, of which the pH was adjusted to 3.8 by hydrochloric acid (1.0 mol/L). Each standard solution was later diluted to eight different concentrations so as to construct its standard calibration curve, which was determined by the method as same as that for the GC×GC-TOF/MS analysis described above. These standard solutions were added with the same amount of internal standard (IS) as the diluted solutions of Baijiu sample mentioned above. The monitored ion of octyl propanoate (IS) was *m/z* 75. The concentrations of the target aroma compounds were calculated based on their respective standard curves, which were constructed by plotting the response ratio of target compounds and internal standard against the ratio of their concentrations. The analytical limits of quantitation (LOQ) were obtained from the lowest concentrations of the respective standard solutions based on a signal-to-noise ratio of 10. To determine the recovery rate, known amounts of the standards (amounts close to their contents in the sample) were spiked into the samples of Baijiu. Then the concentrations of the compounds were determined before and after the chemical spiking to calculate the recovery rate. All analyses were repeated in triplicate.

2.7 | Sensory panel and descriptive profile tests

The sensory panelists for the sensory evaluation of aromas included five males and five females, with ages between 23 and 27 years old, who belong to the School of Food and Chemical Engineering, Beijing Technology and Business University. All of

them were previously trained by describing and recognizing the characters of 52 standard odorants as shown in the section entitled "Chemicals."

Sensory analyses were performed in a sensory evaluation room maintained at (21 ± 1) °C in three different sessions. The assessors were subjected to a rating test with a series of eight characteristic aroma attributes,[18] including ethyl hexanoate (275.00 μg/L, fruity), acetic acid (800.00 mg/L, acidic), γ-nonalactone (455.00 μg/L, sweet), ethanol (70% alcohol by volume, alcoholic), 2-phenylethanol (144.50 mg/L, floral), 3-methylbutanal (85.00 μg/L, malty), 4-methylguaiacol (1.58 mg/L, smoky), and steamed sorghum (grain aroma) that was prepared by steaming 20 g sorghum in boiling water for 30 minutes.

The overall aroma profile of LBG Baijiu sample was evaluated by 10 panelists. They were asked to evaluate the odor intensities of the eight attributes as 0 (not perceivable), 1 (weak), 2 (significant), and 3 (strong) using a 7-point scale of 0, 0.5, 1.0, 1.5,..., 3.0.[26] The obtained results were averaged based on the scores of the 10 panelists for each attribute and plotted in a spider web diagram.

2.8 | Aroma recombination of the sample

In order to validate the aroma profile of LBG, an aroma recombination was performed based on measured concentrations of the aroma compounds in the LBG sample. This approach, named "molecular sensory science," can elucidate aroma-active compounds in a complex aroma profile.[27,28] The aroma recombination model solution, which consisted of 32 aroma compounds with their OAVs ≥ 1 and high SD values, was dissolved in a model solution (70% alcohol by volume, pH = 3.8). The aroma profile of the reconstituted model solution was determined in the same way as that for the LBG Baijiu sample described above. The similarity of the aroma profiles between the LBG sample and the model solution was estimated by a 7-point scale from 0 to 3.

2.9 | Omission experiments

Simulated models were prepared by omitting one or a group of selected components from the aforementioned 32 odorants in the complete reconstituted model; then they were evaluated against two complete reconstituted models by the sensory panelists in a triangle test. Each test was repeated in triplicate. The sensory panelists and procedures for the omission experiments were the same as those for the descriptive profile tests mentioned above.

Data of sensory evaluation were analyzed by one-way analysis of variance (ANOVA) at a significant level of $\alpha \leq 0.05$ by use of SPSS 20.0 software package (SPSS Inc., Chicago, IL, USA).

3 | RESULTS AND DISCUSSION

3.1 | Identification and SD values of aroma compounds in Laobaigan Baijiu

Aroma compounds in the Laobaigan (LBG) Baijiu were extracted by the SPME and analyzed by the SDA-GC-O and GC×GC-TOF/MS. A total of 414 volatile compounds (Table S1) were identified by the GC×GC-TOF/MS analysis, including 131 esters, 43 aldehydes, 14 acids, 67 alcohols, 4 lactone, 3 anhydrides, 7 phenols, 14 ethers, 17 furans, 19 acetals, 46 ketones, 12 nitrogenous, 13 sulfur-containing chemicals, 12 terpenes, and 12 other miscellaneous volatile compounds. Among those 414 volatile chemicals, 272 compounds (Table S1) were tentatively identified by comparing their RIs with those previously reported. Among them, 52 flavors were identified after the comparison of their RIs and mass spectra with the pure standards and confirmed by the SDA-GC-O (shown in Table 1). Besides, the perceived overall aroma profile of the LBG extract was described by the three trained assessors to be in grain, malty, sweet, acidic, fruity, floral, smoky, and alcoholic aroma notes. As presented in Table 1, the SD values of those 52 volatile compounds are shown in a range from 2 to 131 072 based on the SDA-GC-O analysis. Among them, 20 volatile compounds with their SD ≥ 512 (Figure 1; Table 1) were preliminarily considered as the important aroma-active compounds of the LBG Baijiu.

In detail, both (*E*)-ethyl cinnamate ((*E*)-ethyl 3-phenylpropenoate) and ethyl 3-phenylpropanoate were determined with the highest SD values in 131 072. The former presented an aroma note of honey, while the latter showed an aroma note with both floral and jujube flavors, which was considered as a characteristic aroma of LBG.[29] Besides, both ethyl hexanoate and ethyl octanoate showed the second highest SD values (65 536; fruity), followed by ethyl acetate+diethyl acetal (fruity) and ethyl nonanoate (honey) that showed the middle SD values of 32 768. The important aroma-active compounds of the acidic volatiles included hexanoic acid (sweaty), acetic acid (sour), and decanoic acid (sweaty). In addition, 4-ethylguaiacol (smoky) and 3-methylbutanal (malty) also had relatively high SD values at 4096. Other aroma-active compounds with their SD factors higher than 1 included ethyl pentanoate (1024; apple), ethyl butanoate (1024; apple), dimethyl trisulfide (1024; sulfury), and ethyl lactate (512; fruity). Most of these compounds have been identified earlier as aroma compounds in other aroma types of Chinese Baijiu.[30,31] In contrast, alcohols seem to be not so important for aroma contribution because of their lower SD values except 1-nonanol (1024; green). This result seems to be consistent to Zhao's study of the Gujinggong Baijiu.[20]

3.2 | Separation and identification of ethyl acetate and diethyl acetal

Laobaigan-aroma-type Baijiu is characterized by its complex aromas, particularly well known by the existence of ethyl acetate, which endows the LBG with a top note of a light and elegant fruit aroma. Moreover, it was suggested that an existence of a trace amount of diethyl acetal could improve the aroma profile of LBG with a mellow and full-bodied flavor note.[21]

However, both volatiles mentioned above have similar molecular weights and polarity that prevented them from separation on a DB-WAX column in GC-MS. Fortunately, they were successfully

TABLE 1 Aroma compounds identified using gas chromatography-olfactometry and comprehensive two-dimensional gas chromatography with time-of-flight mass spectrometry in Laobaigan Baijiu

No.	Aroma compound	Odor	Base of ID[a]	RI[b]	SD[c]
1 + 2	Ethyl acetate+diethyl acetal	Fruity	MS, RI, S	893	32 768
3	3-methylbutanal	Malty	MS, aroma, RI, S	922	4096
4	2-methylpropyl acetate	Fruity	MS, aroma, RI, S	1012	4
5	Ethyl butanoate	Apple	MS, aroma, RI, S	1039	1024
6	1-propanol	Alcoholic	MS, aroma, RI, S	1045	4
7	Ethyl 2-methylbutanoate	Fruity	MS, aroma, RI, S	1055	4096
8	Ethyl 3-methylbutanoate	Fruity	MS, aroma, RI, S	1069	16 384
9	Hexanal	Orange	MS, aroma, RI, S	1088	8
10	2-methyl-1-propanol	Fruity	MS, aroma, RI, S	1118	4
11	3-methylbutyl acetate	Banana	MS, aroma, RI, S	1121	32
12	Ethyl pentanoate	Apple	MS, aroma, RI, S	1133	1024
13	1-butanol	Alcoholic	MS, aroma, RI, S	1144	8
14	2-heptanone	Fruity	MS, aroma, RI, S	1170	128
15	3-methyl-1-butanol	Fruity	MS, aroma, RI, S	1215	32
16	2-pentylfuran	Green	MS, aroma, RI, S	1228	16
17	Ethyl hexanoate	Fruity	MS, aroma, RI, S	1234	65 536
18	3-hydroxy-2-butanone	Cream	MS, aroma, RI, S	1307	16
19	Propyl hexanoate	Fruity	MS, aroma, RI, S	1327	8
20	Ethyl lactate	Fruity	MS, aroma, RI, S	1342	512
21	Ethyl heptanoate	Fruity	MS, aroma, RI, S	1344	2
22	1-hexanol	Green	MS, aroma, RI, S	1351	16
23	Dimethyl trisulfide	Sulfury	MS, aroma, RI, S	1369	1024
24	Nonanal	Soapy	MS, aroma, RI, S	1396	128
25	Ethyl octanoate	Fruity	MS, aroma, RI, S	1431	65 536
26	Acetic acid	Sour	MS, aroma, RI, S	1440	16
27	Furfural	Sweet	MS, aroma, RI, S	1449	512
28	Tetramethylpyrazine	Nutty	MS, aroma, RI, S	1485	2
29	Benzaldehyde	Almond	MS, aroma, RI, S	1526	2
30	Ethyl nonanoate	Honey	MS, aroma, RI, S	1541	32 768
31	1-octanol	Green	MS, aroma, RI, S	1558	128
32	Nonyl acetate	Sweet	MS, aroma, RI, S	1575	8
33	2-undecanone	Green	MS, aroma, RI, S	1592	128
34	Ethyl decanoate	Fruity	MS, aroma, RI, S	1643	16
35	1-nonanol	Green	MS, aroma, RI, S	1659	1024
36	Ethyl benzoate	Floral	MS, aroma, RI, S	1666	16 384
37	Diethyl succinate	Fruity	MS, aroma, RI, S	1673	2
38	Ethyl undecanoate	Coconut	MS, aroma, RI, S	1742	2
39	1-decanol	Fat	MS, aroma, RI, S	1760	16
40	Ethyl phenylacetate	Sweet	MS, aroma, RI, S	1781	8
41	(*E*,*E*)-2,4-decadienal	Fat	MS, aroma, RI, S	1807	8
42	2-phenylethyl acetate	Floral	MS, aroma, RI, S	1812	4096

(Continues)

TABLE 1 (Continued)

No.	Aroma compound	Odor	Base of ID[a]	RI[b]	SD[c]
43	Hexanoic acid	Sweaty	MS, aroma, RI, S	1850	32
44	Geranyl acetone	Green	MS, aroma, RI, S	1854	1024
45	Ethyl dodecanoate	Fruity	MS, aroma, RI, S	1858	32
46	Ethyl 3-phenylpropanoate	Floral	MS, aroma, RI, S	1894	131 072
47	2-phenylethanol	Rosy	MS, aroma, RI, S	1916	128
48	4-methylguaiacol	Smoky	MS, aroma, RI, S	1961	4
49	4-ethylguaiacol	Smoky	MS, aroma, RI, S	2036	4096
50	(*E*)-ethyl cinnamate	Honey	MS, aroma, RI, S	2124	131 072
51	Ethyl hexadecanoate	Waxy	MS, aroma, RI, S	2210	16
52	Decanoic acid	Sweaty	MS, aroma, RI, S	2264	4

[a]MS, aroma compounds were identified by MS spectra; aroma, aroma compounds were identified by comparison to reference standards by GC-O; RI, aroma compounds were identified on DB-WAX by comparison to the retention indices of reference standards. S, aroma compounds were identified by pure standards.
[b]RI, linear retention index.
[c]SD, sample dilution.

separated and quantified by GC×GC-TOF/MS (Figure 2), as well as determined for their contributions to the LBG aroma. As a result, the odor activity values (OAVs) were determined (Table 2) to be 12 for ethyl acetate and 26 for diethyl acetal, respectively. Therefore, the ethyl acetate and diethyl acetal were both suggested to be important contributors to the aroma profile of LBG.

3.3 | Quantification of aroma compounds in Laobaigan Baijiu

The aforementioned 52 odorants detected by the SDA-GC-O were further quantitated by GC×GC-TOF/MS (shown in Table 3). Although ethyl lactate did not present the highest SD value, it had the highest concentration (410 mg/L), followed by ethyl acetate (383 mg/L) and 3-methyl-1-butanol (272 mg/L). Besides, the following odorants had shown relatively higher concentrations, including 1-propanol (188 mg/L), ethyl dodecanoate (119 mg/L), 2-methyl-1-propanol (98 mg/L), and acetic acid (79 mg/L). Although the concentrations of dimethyl trisulfide (14.00 μg/L), 4-ethylguaiacol (321.00 μg/L), and ethyl 3-methylbutanoate (454.00 μg/L) were all lower than most of the other compounds, they had high SD values (SD = 1024, 4096, and 16 384, respectively), due to their lower odor-threshold values. In comparison, ethyl hexanoate, hexanoic acid, and hexyl hexanoate are normally the top three volatiles with the highest concentrations in the strong-aroma-type Baijiu. The light-aroma-type Baijiu has the following top three volatiles in the largest amounts, including ethyl acetate, 2-methylpropyl acetate, and 3-methylbutyl acetate, and the sauce-aroma-type Baijiu has the highest concentrations for ethyl 2-methylpropanoate, ethyl 3-methylbutanoate, and furfural.[32] Such differences in the contents of volatile compounds lead to the unique smell and taste of different aroma types of Chinese Baijiu, including the LBG Baijiu. Moreover, the obtained calibration curves were found to have good linearity with correlation coefficient ($R^2 \geq 0.99$); RSDs in triplicate of the samples were ≤ 10%, which indicated their acceptable precision of the quantitative analyses in this study.

3.4 | Odor activity values (OAVs) of aroma compounds in Laobaigan Baijiu

The contribution of flavor compounds in Chinese Baijiu was determined not only by their contents, but also by their SD values, as well as by their interactions. Therefore, in order to get a deep insight into the contribution of each flavor compound, their odor activity values (OAVs) were also need to be determined.[33,34] As shown in Table 2, a total of 32 aroma compounds were confirmed with their OAVs ≥ 1, suggesting they are the important aromas of LBG. Among them, the highest OAV was bestowed to the ethyl octanoate (fruity, OAV = 2908), followed by the second highest OAV for the 3-methylbutanal (malty, OAV = 701), then by ethyl dodecanoate (fruity, OAV = 238) and ethyl pentanoate (apple, OAV = 223). There were 17 esters with high OAVs (≥ 1), which provided the fruity or floral notes of LBG. In addition, geranyl acetone and 4-ethylguaiacol, which were respectively responsible for the green-aroma note and smoky-aroma note, were observed with their OAVs ≥ 1. Most of those 32 volatile compounds that had high OAVs also showed high SD values. However, there are some exemptions. Ethyl dodecanoate showed a high OAV (238), but it had a relatively low SD value (32). In contrast, ethyl 3-phenylpropanoate had a high SD value (131 072) but a relatively low OAV (10). These abnormal phenomena indicated that either there was an influence of the food matrix on the volatility of aroma compounds[35] or the previously reported thresholds of those volatiles were not appropriate for this case, which needs to be redetermined and/or adjusted in the current medium, such as the alcoholic solution.[36] Nevertheless, the OAV has been considered as an important factor and commonly used for screen of aroma-active compounds in flavor research.

3.5 | Aroma recombination to simulate the aroma profile of Laobaigan Baijiu

According to the above-mentioned quantitative results, an aroma recombination was carried out with the aforementioned 32 aroma compounds with their OAVs ≥ 1 (Table 2). All compounds were dissolved in a 70% ethanol solution (by volume), while its pH was adjusted to 3.8 by hydrochloric acid (1.0 mol/L). The aroma attributes of the LBG sample and the reconstituted solution were evaluated by the sensory panelists, and their aroma profiles are shown in Figure 3. As a result, the aroma profile of the reconstituted solution showed a good aroma similarity as that of the original LBG sample in regards to the smoky, floral, sweet, and fruity aroma notes. However, scores of the malty- and grain-aroma notes of the reconstituted sample were slightly lower than those of LBG, and the alcoholic- and acidic-aroma notes were slightly stronger in the reconstituted model. In general, the overall similarity of the aroma profiles between the LBG Baijiu sample and the recombination model was judged to be 2.7 out of 3.0 points. Therefore, it seemed that the reconstituted model has successfully simulated the aroma profile of the original LBG sample.

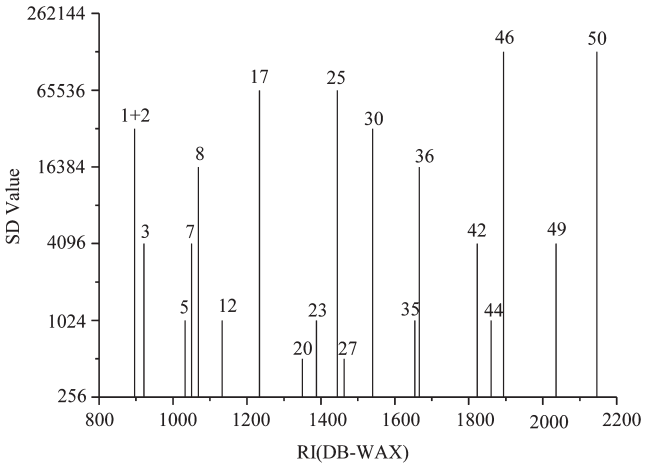

FIGURE 1 Sample dilution (SD) value chromatogram of aroma compounds (SD value ≥ 512) in Laobaigan Baijiu. Number is used to label the aroma compounds as listed in Table 1

3.6 | Omission Experiments

In order to confirm the contributions of those aforementioned volatile compounds in the reconstituted model to the overall aroma profile, a total of 21 aroma-omission models, in which a single compound or a group of components were subtracted, were evaluated and compared with the complete reconstituted model by the same sensory panelists through a triangle test. The results of 21 omission experiments are listed in Table 4.

The results (Table 4) show that all assessors were able to distinguish the omission of the group of all esters (model 1) with a high significance ($\alpha \leq 0.001$), which means the esters with the fruity or floral aromas have played an important role for the overall aroma profile of the LBG Baijiu. Furthermore, ethyl octanoate (model 1-1) was correctly detected for its omission by all the assessors in the triangle tests, which indicated its critical role in the flavoring profile due to its highest OAV (Table 2). Therefore, this compound was considered the most important contributor to LBG due to its fruity aroma. In addition, when ethyl butanoate was subtracted (model 1–5) from the complete model, a high significance ($\alpha \leq 0.001$) of their difference was observed too. Besides, the

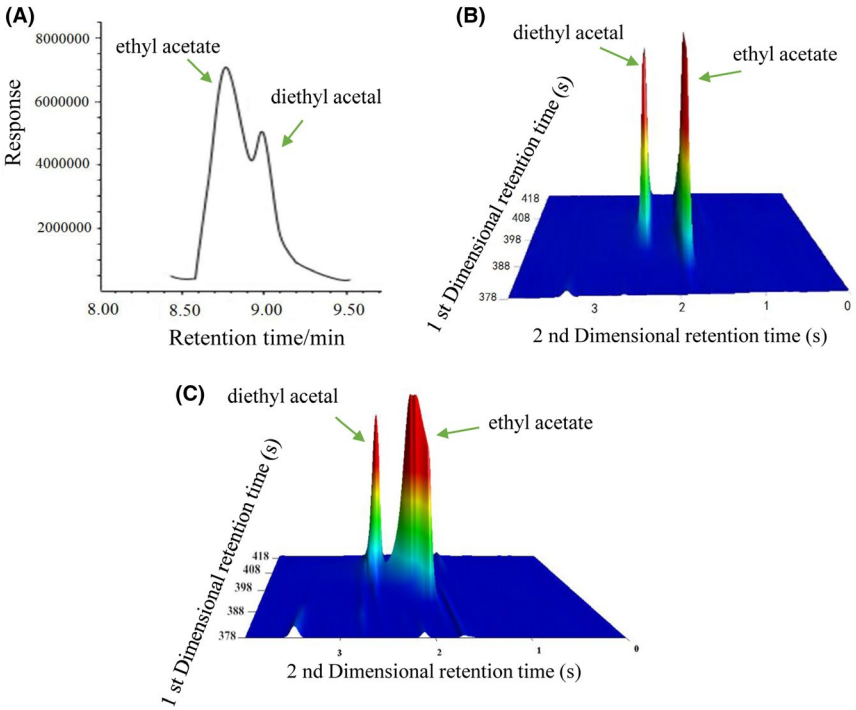

FIGURE 2 (A) GC-MS chromatogram of ethyl acetate and diethyl acetal in Laobaigan Baijiu; (B) GC×GC-TOF/MS chromatography 3D plot of ethyl acetate and diethyl acetal in Laobaigan Baijiu; (C) GC×GC-TOF/MS chromatography 3D plot of ethyl acetate and diethyl acetal in standard solution. [Colour figure can be viewed at wileyonlinelibrary.com]

TABLE 2 Odor activity values (OAVs) of 52 aroma compounds in Laobaigan Baijiu

No.[a]	Aroma compound	Odor threshold(μg/L)	OAV[g]
25	Ethyl octanoate	13[b]	2908
3	3-methylbutanal	17[d]	701
45	Ethyl dodecanoate	500[e]	238
12	Ethyl pentanoate	27[b]	223
17	Ethyl hexanoate	55[b]	148
5	Ethyl butanoate	82[b]	128
11	3-methylbutyl acetate	94[b]	81
8	Ethyl 3-methylbutanoate	7[b]	65
44	Geranyl acetone	60[b]	63
18	3-hydroxy-2-butanone	259[c]	55
50	(*E*)-ethyl cinnamate	0.7[e]	40
9	Hexanal	26[b]	36
23	Dimethyl trisulfide	0.4[d]	36
2	Diethyl acetal	719[b]	26
7	Ethyl 2-methylbutanoate	18[c]	21
1	Ethyl acetate	32 600[b]	12
46	Ethyl 3-phenylpropanoate	125[b]	10
34	Ethyl decanoate	1120[b]	10
36	Ethyl benzoate	1430[b]	8
30	Ethyl nonanoate	3150[b]	5
43	Hexanoic acid	2520[b]	5
49	4-ethylguaiacol	123[b]	3
6	1-propanol	54 000[d]	3
13	1-butanol	2730[b]	3
20	Ethyl lactate	128 000[b]	3
42	2-phenylethyl acetate	909[b]	3
10	2-methyl-1-propanol	28 300[b]	3
27	Furfural	44 000[b]	2
52	Decanoic acid	13 700[d]	2
15	3-methyl-1-butanol	179 000[b]	2
4	2-methylpropyl acetate	922[b]	1
35	1-nonanol	806[d]	1
22	1-hexanol	5370[b]	<1
33	2-undecanone	6[b]	<1
41	(*E*,*E*)-2,4-decadienal	8[c]	<1
31	1-octanol	1100[d]	<1
14	2-heptanone	140[b]	<1
26	Acetic acid	160 000[b]	<1
47	2-phenylethanol	28 900[b]	<1
24	Nonanal	122[b]	<1
48	4-methylguaiacol	315[b]	<1
39	1-decanol	400[b]	<1
40	Ethyl phenylacetate	407[b]	<1
38	Ethyl undecanoate	1000[b]	<1
29	Benzaldehyde	4200[b]	<1
21	Ethyl heptanoate	13 200[b]	<1
37	Diethyl succinate	353 000[b]	<1
28	Tetramethylpyrazine	80 100[d]	<1
19	Propyl hexanoate	12 800[d]	<1
51	Ethyl hexadecanoate	-[f]	
16	2-pentylfuran	-[f]	
32	Nonyl acetate	-[f]	

[a]Numbers were the same as numbers listed in Table 1.
[b]Odor thresholds were determined in 46% alcohol by volume from reference 16.
[c]Odor thresholds were determined in 46% alcohol by volume from reference 17.
[d]Odor thresholds were determined in 46% alcohol by volume from reference 21.
[e]Odor thresholds were determined in 60% alcohol by volume from reference 26.
[f]Odor thresholds was unavailable.
[g]OAVs were calculated by concentration by the odor threshold.

results showed that the absences of ethyl pentanoate (model 1-2), ethyl hexanoate (model 1-3), ethyl lactate (model 1-6), and ethyl acetate (model 1-9) were recognized by eight out of 10 assessors ($\alpha \leq 0.01$). These results indicated that those esters have provided the typical fruity and floral notes to the LBG aroma profile and were important aroma-active compounds.

As shown in Table 4, the omission of the group of all acids was rated (model 2) with a significant difference ($\alpha \leq 0.01$). This indicated the important role of the acidic aromas to the overall aroma profile. When only hexanoic acid was removed (model 2-1), the assessors could detect a significant difference ($\alpha \leq 0.01$) as well, which was confirmed by eight out of 10 assessors. However, removal of the alcoholic compounds from the complete recombination model did not cause a significant difference, and only seven out of 10 assessors could recognize the omission of all alcohols (model 3). Therefore, alcohols, except ethanol as the base solvent, were not considered as the key aromas according to the results of omission experiments.

The omission of the group of all aldehydes and ketones was observed (model 4) with a high significant difference ($\alpha \leq 0.001$). Additionally, when 3-methylbutanal that is responsible for the malty aroma note was removed (model 4-1), the assessors could detect a significant difference ($\alpha \leq 0.01$), which meant the compound was important for the aroma profile of the LBG. Besides, when 4-ethylguaiacol was omitted (model 5), the "smoky" intensity significantly decreased, which demonstrated that it had made an important contribution to LBG. In summary, the aforementioned omission

TABLE 3 Aroma compounds in Laobaigan Baijiu were quantitated by GC×GC-TOF/MS

No.[a]	Aroma compound	Quantitate ion	Standard curve[b]	R^2	LOQ (μg/L)	Recovery (%)	AV[c](μg/L)	RSD[d](%)
20	Ethyl lactate	45	$y = 1.036x + 7.340$	0.991	5.212	94	409 692	5.0
1	Ethyl acetate	43	$y = 0.078x + 3.799$	0.993	1.671	99	382 586	9.0
15	3-methyl-1-butanol	31	$y = 0.038x + 0.209$	0.992	0.432	89	271 996	6.0
6	1-propanol	31	$y = 0.005x + 0.109$	0.998	0.112	96	188 382	8.8
45	Ethyl dodecanoate	88	$y = 0.071x + 6.780$	0.992	0.993	97	118 863	7.5
10	2-methyl-1-propanol	41	$y = 0.020x - 0.029$	0.993	0.244	97	98 052	8.1
26	Acetic acid	45	$y = 0.022x + 0.006$	0.992	3.846	84	79 352	9.2
27	Furfural	39	$y = 0.128x + 0.427$	0.994	1.544	96	73 056	3.3
25	Ethyl octanoate	88	$y = 0.324x + 0.001$	0.993	2.749	96	37 800	5.9
52	Decanoic acid	60	$y = 0.010x + 0.124$	0.990	1.693	93	22 740	9.3
2	Diethyl acetal	45	$y = 0.321x + 2.360$	0.990	1.591	97	18 392	8.6
30	Ethyl nonanoate	88	$y = 0.432x + 5.200$	0.994	0.115	91	15 161	4.3
47	2-phenylethanol	91	$y = 0.116x + 0.063$	0.995	0.247	97	14 139	3.2
18	3-hydroxy-2-butanone	45	$y = 0.007x - 0.001$	0.990	0.271	92	14 137	9.1
3	3-methylbutanal	58	$y = 0.142x + 0.217$	0.990	4.968	97	11 912	6.7
43	Hexanoic acid	60	$y = 0.069x - 0.078$	0.990	4.145	109	11 348	5.9
36	Ethyl benzoate	105	$y = 0.255x + 6.030$	0.992	1.085	119	11 327	9.6
34	Ethyl decanoate	88	$y = 0.625x + 8.601$	0.991	0.004	108	10 904	8.8
5	Ethyl butanoate	71	$y = 0.253x + 1.667$	0.998	0.965	96	10 469	6.5
17	Ethyl hexanoate	88	$y = 0.818x + 3.052$	0.996	0.027	89	8114	8.7
51	Ethyl hexadecanoate	88	$y = 0.434x + 0.584$	0.991	1.716	97	7978	7.8
13	1-butanol	56	$y = 0.054x + 0.007$	0.992	0.517	91	7883	5.2
11	3-methylbutyl acetate	70	$y = 1.175x + 6.750$	0.996	0.083	98	7644	8.2
37	Diethyl succinate	101	$y = 0.431x + 0.500$	0.999	0.171	95	6254	9.8
12	Ethyl pentanoate	88	$y = 0.265x + 1.008$	0.994	0.056	91	6010	9.2
22	1-hexanol	56	$y = 0.240x + 0.184$	0.996	0.068	109	4929	4.0
16	2-pentylfuran	81	$y = 0.923x + 0.573$	0.993	0.235	91	3846	5.2
44	geranyl acetone	43	$y = 0.570x - 0.058$	0.993	3.175	89	3808	2.5
42	2-phenylethyl acetate	43	$y = 1.524x + 3.292$	0.998	0.052	102	2421	6.7
4	2-methylpropyl acetate	43	$y = 0.598x + 4.220$	0.996	0.148	107	1359	5.6
28	Tetramethylpyrazine	54	$y = 0.382x + 0.105$	0.998	0.117	85	1317	2.5
46	Ethyl 3-phenylpropanoate	91	$y = 0.445x + 0.671$	0.998	5.366	105	1229	9.6

(Continues)

TABLE 3 (Continued)

No.[a]	Aroma compound	Quantitate ion	Standard curve[b]	R^2	LOQ (μg/L)	Recovery (%)	AV[c](μg/L)	RSD[d](%)
9	Hexanal	44	$y = 0.161x + 0.040$	0.996	0.005	108	948	9.5
35	1-nonanol	56	$y = 1.053x + 0.737$	0.996	0.545	117	867	2.8
31	1-octanol	41	$y = 0.791x + 0.227$	0.993	0.093	86	803	4.6
21	Ethyl heptanoate	88	$y = 0.029x + 0.101$	0.991	1.573	108	502	3.0
8	ethyl 3-methylbutanoate	88	$y = 0.697x + 0.400$	0.994	0.017	109	454	7.2
7	Ethyl 2-methylbutanoate	102	$y = 0.922x + 0.244$	0.998	0.258	90	379	3.0
49	4-ethylguaiacol	137	$y = 0.757x - 0.016$	0.997	0.216	94	321	4.3
29	Benzaldehyde	77	$y = 1.496x + 0.483$	0.996	0.105	105	218	9.7
48	4-methylguaiacol	123	$y = 0.118x + 0.006$	0.997	0.061	105	99	7.6
38	Ethyl undecanoate	88	$y = 5.584x + 1.227$	0.991	0.966	15	88	8.9
14	2-heptanone	58	$y = 3.173x + 0.455$	0.992	2.896	102	80	9.4
39	1-decanol	41	$y = 2.148x + 0.314$	0.997	1.527	104	71	8.9
40	ethyl phenylacetate	164	$y = 3.863x + 1.193$	0.991	2.869	106	61	10.0
24	Nonanal	57	$y = 1.934x + 2.330$	0.999	0.047	101	49	9.1
50	(*E*)-ethyl cinnamate	131	$y = 3.377x - 0.008$	0.997	0.976	113	28	4.6
23	Dimethyl trisulfide	126	$y = 2.646x + 0.538$	0.991	0.044	105	14	4.5
41	(*E*,*E*)-2,4-decadienal	81	$y = 7.346x + 0.593$	0.997	1.538	106	6	7.7
33	2-undecanone	58	$y = 16.97x + 6.527$	0.991	0.059	99	5	5.8
19	Propyl hexanoate	61	$y = 3.644x + 0.450$	0.995	0.514	117	3	3.9
32	Nonyl acetate	43	$y = 36.29x + 2.688$	0.991	0.049	106	2	6.5

[a]Numbers were the same as numbers listed in Table 1.
[b]x is the concentration ratio of the target compound and internal standard. y is the response ratio of the target compound and internal standard.
[c]AV, average concentration of triplicates.
[d]RSD, relative standard deviation of the average concentration.

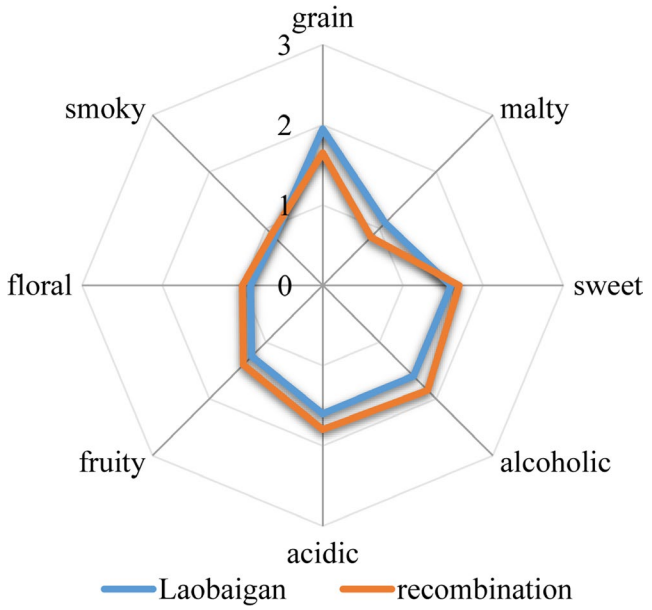

FIGURE 3 Aroma profile of Laobaigan Baijiu and the aroma recombination in 70% volume of aqueous ethanol solution. [Colour figure can be viewed at wileyonlinelibrary.com]

TABLE 4 Omission experiments from complete recombination of 32 aromas

Number	Odorants omitted from the complete recombinate	N[a]	Significance[b]
1	All esters	10	***
1-1	Ethyl octanoate	10	***
1-2	Ethyl pentanoate	8	**
1-3	Ethyl hexanoate	8	**
1-4	Ethyl dodecanoate	6	
1-5	Ethyl butanoate	9	***
1-6	Ethyl lactate	8	**
1-7	(*E*)-ethyl cinnamate	4	
1-8	Ethyl 3-phenylpropanoate	5	
1-9	Ethyl acetate	8	**
2	All acids	8	**
2-1	Hexanoic acid	8	**
3	All alcohols	7	
3-1	1-nonanol	6	
3-2	2-methyl-1-propanol	5	
4	All aldehydes and ketones	10	***
4-1	3-methylbutanal	8	**
4-2	Diethyl acetal	7	
4-3	Geranyl acetone	4	
5	4-ethylguaiacol	8	**
6	Dimethyl trisulfide	7	

[a]Number of correct judgments from 10 assessors evaluating the aroma difference by the triangle test.
[b]Significance: *$\alpha \le 0.05$; **$\alpha \le 0.01$; ***$\alpha \le 0.001$.

experiments have proven that esters, acids, aldehydes, and ketones played key roles in making contributions to the aroma profile of LBG.

4 | CONCLUSION

In summary, this study has initially detected a total of 414 aroma compounds from the LBG sample, and 52 volatile compounds were further quantitated using GC×GC-TOF/MS. Based on the SDA-GC-O analysis, 32 out of the aforementioned 52 odorants were further suggested as the important odorants due to their higher OAVs. As a result, those 32 aroma compounds (OAVs ≥ 1) were used to reconstitute an aroma recombination solution to simulate the aroma profile of the Laobaigan Baijiu based on their measured concentrations in this study. The reconstituted model has successfully simulated the aroma profile of the LBG sample, which was judged by the sensory panelists in 2.7 out of 3.0 points.

Furthermore, the omission experiments evaluated the contributions of the aroma compounds to the overall aroma profile of the LBG Baijiu. The ethyl octanoate, ethyl pentanoate, ethyl hexanoate, ethyl butanoate, ethyl lactate, ethyl acetate, hexanoic acid, 3-methylbutanal, and 4-ethylguaiacol were confirmed as the key aroma-active compounds of the Laobaigan Baijiu.

CONFLICT OF INTEREST

The authors declare no competing financial interest.

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SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of the article.

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