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Characterization of key aroma compounds in Gujinggong Chinese Baijiu by gas chromatography–olfactometry, quantitative measurements, and sensory evaluation

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ABSTRACT

One of famous Chinese Baijiu, Gujinggong (GJG) that is produced in Anhui province, belongs to the famous Luzhou-aroma type of Baijiu in regards of its unique flavor characteristics. However, its key aroma-impact volatiles have not been clearly characterized. In this study, a total of 60 aroma compounds of GJG were identified by GC-O and GC–MS, and 35 of them were further recognized as important aroma compounds owing to their OAVs ≥ 1 and sensory evaluation. As a result, its aroma profile was successfully simulated by reconstitution of those 35 and other 11 aroma compounds based on their measured concentrations in the GJG. Moreover, omission test was applied to investigate the effects of the important aroma compounds on the whole aroma profile of GJG. In this context, 9 aroma compounds were confirmed as the key aroma compounds of GJG.

1. Introduction

Chinese Baijiu (CB) is a traditional indigenous distilled spirit prepared from grain fermentation, of which the technique can be dated back for 5000 years. As the most popular alcoholic beverage in China, its annual output has exceeded 13 million kiloliters (kL) in 2016, with a year-on-year growth of 3.23% (based on data from the China Industry Information Network). Among them, Luzhou-aroma (or officially called the strong-aroma) type of Chinese Baijiu (LACB) is among the leading desirable CB because of its unique taste and smell associated with “softness and fullness of aromas”.

Without doubt, aromas of CB determine the consumers' acceptance and preference, which has prompted the study of characterization of volatile compounds, particularly the key aroma-impact volatiles in various CB. Previous studies have found thousands of chemically diverse volatile compounds in alcoholic beverages, representing a variety of different chemical classes, with a wide range of boiling points, different aroma potencies and presence in concentrations in a range from mg/L to ng/L (Ebeler, 2001). Up to now, 1737 volatiles in various CB have been reported based on our records, including alcohols, aldehydes, ketones, acids, esters, nitrogen-containing, and sulfur-containing compounds, etc. (Sun, Wu, Huang, Sun, & Zheng, 2015).

In recent years, many studies have focused on the characterization of aroma compounds of LACB due to its unique flavor. Wang reported that 13 aroma compounds were determined as the key aroma-impact volatiles in the Daohuaxiang liquor due to their higher odor activity values (OAVs) (Wang, Li, Qi, Li, & Pan, 2015). Among them, esters accounted for the dominant majority group, especially ethyl hexanoate (OAV ≥ 15,200), which has been well recognized as the main aroma compound in LACB (Fan & Qian, 2005, 2006a, 2006b; Xiao, Yu, Niu, Ma, & Zhu, 2016; Zheng, Liang, Wu, Zhou, & Liao, 2014). However, different brands of LACB have their own aromatic characteristics owing to their different composition of aroma compounds besides the ethyl hexanoate, as well as their delicate differences in the smell and taste. At present, the aroma compounds in several famous brands of LACB, such as Wuliangye (Fan & Qian, 2006b), Jiannanchun (Fan & Qian, 2006b), Yanghe Daqu (Fan & Qian, 2005; Fan & Qian, 2006a), and Luzhou Laojiao (Ding, Wu, Huang, & Zhou, 2015; Xiao et al., 2014), have been reported. Unfortunately, no study has reported the key aroma-impact volatiles in another LACB, Gujinggong (GJG), although a few research works have been merely devoted to identify and quantify the volatile compounds in the liquor (Wu et al., 2015; Zhou et al., 2016; Li, Xu,

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et al., 2016; Li, Liu, et al., 2016; Huang et al., 2006; Guo & Lu, 2001).

GJG is one of the famous LACB, which is produced in Anhui province, People's Republic of China. It is traditionally considered as one of the eight noble CB, and its annual cash revenue is over 7 billion Renminbi (RMB, Chinese Yuan), approximately 1.1 billion dollars in 2016. Previous studies have shown the volatile composition of GJG is quite complex. For example, Li et al., identified 188 volatile compounds in GJG by liquid–liquid extraction (LLE) coupled with gas chromatography–mass spectrometry (GC–MS), including 74 esters, 26 alcohols, 25 aromatic compounds, 20 acids, 14 alkanes, 8 aldehydes and ketones, 8 sulfur-containing compounds, 7 acetals, 4 heterocyclic compounds, and 2 lactone compounds (Li, Liu, et al., 2016). Although several studies have inferred that the unique flavor characteristics of GJG is due to its subtle difference in composition of volatile compounds from those in other LACBs (Guo & Lu, 2001; Huang et al., 2006), there remains a lack of direct evidence in regards of the aroma-impact volatiles in the previous literatures. Therefore, it is worth to distinguish the critical aroma-active compounds from the bulk of "non-active" volatile compounds in the GJG in an effort to maintain and improve its quality.

Gas chromatography–olfactometry (GC-O) coupled with other detectors has given the possibility for researchers to confirm the aroma-active compounds (Herrero et al., 2016; Malfondet, Gourrat, Brunerie, & Quéré, 2016; Zhu et al., 2016). For instance, aroma extract dilution analysis (AEDA) and OAV have been widely used to evaluate the aroma compounds in alcoholic beverages and other foods (Matheis & Granvogl, 2016; Pino & Queris, 2011; Poisson & Schieberle, 2008; Wang, Gambetta, & Jeffery, 2016; Xie, Hu, Song, Xi, & Zhang, 2016).

In addition, aroma reconstitution and omission test combined with sensory evaluation have been extensively applied to confirm the key aroma compounds of alcoholic beverages, such as wine (Mayr, Geue, Holt, Pearson, & Francis, 2014), brandy (Willner, Granvogl, & Schieberle, 2013), beer (Langos, Granvogl, & Schieberle, 2013), and Chinese Baijiu (Fan, Fan, & Xu, 2015; Gao, Fan, & Xu, 2014). For example, Zheng et al., initially identified a total of 56 volatile flavors in a sesame (or called Zhima in China) aroma-type Chinese Baijiu by AEDA and GC–MS (Zheng et al., 2016). Furthermore, 26 of the above aroma compounds were confirmed as the important odorants due to their higher OAVs. Particularly, methional and ethyl hexanoate were corroborated as the critical key aroma-impact flavors making significant contributions to the unique sesame-aroma of the CB by the omission test. Afterwards, another volatile chemical, 2-furfurylthiol, was identified to be a key odorant in the liquor associated with a roasted sesame-like flavor by the omission test (Sha, Chen, Qian, Wang, & Xu, 2017).

To our knowledge, no study has reported the characteristic aromas of the Chinese Baijiu, Gujinggong (GJG). Therefore, the main objectives of this study were to (1) identify and quantify the aroma compounds of GJG by LLE and direct injection (DI) combined with GC-O, gas chromatography–flame ionization detector (GC-FID), and GC–MS; (2) confirm the important and key aroma-active compounds in GJG by flavor dilution (FD) value, OAV, aroma reconstitution and omission tests; and (3) investigate the effects of the important aroma-active aroma compounds on the whole aroma profile of GJG.

2. Materials and methods

2.1. Chinese Baijiu samples

Five commercial GJG samples (labelled as GJG-1, GJG-2, GJG-3, GJG-4, and GJG-5, pH = 3.5), which were classified into the same aroma profile by the manufacturer and used for the GC-O and GC–MS analyses, were obtained from Anhui Gujing Distillery Co., Ltd. (Anhui province, P. R. China). All samples (each in a volume of 425 mL and 45% vol. of alcohol in each bottle) were made from sorghum combined with wheat, corn, rice and sticky rice, and were stored at 4 °C until analysis. Herein, mentioning of a brand name is only for research, rather than for advertising purposes.

2.2. Chemicals

All chemicals were of analytical reagent grade, with at least 97% purity except for nonanal and methyl lactate (at least 95%). Ethyl acetate, 2-methyl-1-propanol, 1-butanol, 3-methyl-1-butanol, 2-methyl-1-butanol, ethyl hexanoate, propyl hexanoate, 2-heptanol, ethyl heptanoate, trimethyl pyrazine, acetic acid, ethyl octanoate, isopentyl hexanoate, tetramethyl pyrazine, 1-(2-furanyl)-ethanone, 1-octanol, phenylacetaldehyde, 3-methylbutanoic acid, diethyl butanedioate, γ-hexalactone, (2,2-diethoxyethyl)-benzene, pentanoic acid, ethyl phenylacetate, 4-methylpentanoic acid, ethyl dodecanoate, 2-phenylethanol, heptanoic acid, 4-methylguaiacol, phenol, 4-ethylguaiacol, ethyl tetradecanoate, 4-methylphenol, vanillin, 2,4-bis(1,1-dimethylethyl)-phenol, ethyl oleate, and benzenepropanoic acid were purchased from J&K Scientific Co., Ltd. (Beijing, China). Ethyl pentanoate, isobutyl hexanoate, nonanal, ethyl 2-hydroxybutanoate, hexyl hexanoate, butanoic acid, 3-methyl-2(5H)-furanone, γ-heptalactone, hexanoic acid, ethyl 3-phenylpropanoate, γ-nonalactone, octanoic acid, nonanoic acid, ethyl propanoate, ethyl butanoate, ethyl lactate, 2-phenylethyl acetate, 4-ethylphenol, and ethyl hexadecanoate were purchased from Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan). 1,1-Diethoxy-3-methylbutane was purchased from Matrix Scientific (Shanghai, China). Propanoic acid was purchased from Accustandard (Beijing, China). 1-Hexanol and 2-methylpropanoic acid were purchased from Macklin (Shanghai, China). 1,1,3-Triethoxypropane was purchased from Alfa Aesar (Tianjin, China). A C_8–C_{40} *n*-alkane mixture (Sigma–Aldrich, Shanghai, China) was used for determination of linear retention indices (RIs). Methyl lactate (internal standard (IS), IS1) and 4-octanol (IS2) were purchased from Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan). 2-Methylhexanoic acid (IS3) was purchased from Sigma–Aldrich (Shanghai, China).

Dichloromethane, absolute ethanol, sodium chloride (NaCl), anhydrous sodium sulfate (Na_2SO_4), sodium carbonate (Na_2CO_3), and hydrochloric acid (HCl) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Beijing, China) to prepare chemical standards and/or extract volatiles from the samples, or help improving the chemical extraction.

2.3. Isolation of aroma compounds

According to the method of Zheng with slight modifications (Zheng et al., 2016), the GJG sample (GJG-1, 50 mL) was diluted to 15% of ethanol by boiled Milli-Q water (Millipore, Bedford, MA), saturated with NaCl, and extracted 3 times by freshly distilled dichloromethane (50 mL each time). The combined extract was further separated into neutral/basic and acidic fractions (NBF and AF) by the following methods. The combined extract (about 150 mL) was extracted 3 times by the Na_2CO_3 solution (50 mL each time; 0.50 mol/L; pH 10.0) and then washed by 50 mL of the saturated NaCl solution. The organic phase, containing the neutral/basic aroma compounds, was named as the neutral/basic fraction (NBF). The combined aqueous phase (about 200 mL) was acidified to pH 2.0 with HCl (4.0 mol/L), and extracted 3 times by the freshly distilled dichloromethane (70 mL each time). The combined extract (about 210 mL), containing the remaining acidic aroma compounds, was named as the acidic fraction (AF). After being dried over anhydrous Na_2SO_4, both fractions were concentrated to 500 μL by a rotary evaporator and stored at − 20 °C prior to the AEDA-GC-O, and GC–MS analyses.

2.4. Identification of aroma compounds

Identification of aroma compounds was performed on an Agilent 7890B gas chromatograph, equipped with an Agilent 5977A mass-selective detector (Agilent Technologies, USA) and an olfactometer (ODP C200, Gerstel, Germany).

Each concentrated fraction (1 μL), either the NBF or the AF, was