WEP Warwick Evans Publishing

International Journal of Agriculture and Food Sciences Research
ISSN: 3006-7685 (Print), ISSN: 3006-3736 (Online) | Volume 3, Number 1, Year 2025
DOI: https://doi.org/10.62051/ijafsr.v3n1.02
Journal homepage: https://wepub.org/index.php/IJAFSR/index

A Comparative Study of the Important Aroma Components of Brandy and Rum

Xiaoyan Wo

Qilu University of Technology (Shandong Academy of Sciences), China
871404182@qq.com

ABSTRACT

The similarities and differences in the aroma composition of brandy and rum products and the effect of aging time on the aroma composition are one of the important issues of concern to international spirits production and consumption. In this study, gas chromatography-mass spectrometry (GC-MS) was used to qualitatively and quantitatively analyze the aroma compounds of rum and brandy from three different aging times, respectively. A total of 50 compounds with OAV > 1 were detected in brandy and rum, of which 20 were esters, 8 alcohols, 6 acids, 11 aldehydes and ketones, and 5 phenols. The results of the analysis showed that linalool, 3-methylpentanoic acid, guaiacol, ethyl caprylate, lauric acid and hexanol were significantly different between brandy and rum, while 18 compounds, including caprylic acid, ethyl caproate and ethyl caproate, were not significantly different between the two categories of distilled spirits. Ageing time had a significant effect on ethyl caproate and whisky lactone in brandy and ethyl palmitate in rum. Compounds such as ethyl caprylate, ethyl lactate, isoamyl acetate, and ethyl caprate in brandy and ethyl caprylate, ethyl caproate, genistein, and foliol in rum were less affected by different aging times.

KEYWORDS

Brandy; Rum; Aroma compounds; Gas chromatography-mass spectrometry (GC-MS); OAV method; OPLS-DA

1. INTRODUCTION

Brandy and rum are one of the six distilled spirits of the world, which are distilled spirits made from grapes and sugar cane molasses through fermentation, distillation and aging.

The aroma of brandy and rum is an important measure of their quality. Within the same category of brandy or rum, there are differences in aroma composition depending on the place of origin, the fermentation conditions and the ageing time. Research on the aroma of brandy has found that esters, especially ethyl esters, are important aroma substances for brandy (Zhao, Li, Xu, Fan, & Jiang, 2009). The lactone compounds of brandy may be related to the place of origin, with French brandy showing more γ-lactone and δ-lactone aroma characteristics, such as peach and apricot aromas, while Chinese brandy may show trans and cis-β-methyl-γ-octalactone aroma characteristics, such as cream aromas (Li, Li, Zhang, Shen, Xu, & Tang, 2021). In aging, phenolics in brandy have been shown to be associated with aging in several studies (Schwarz, Rodríguez, Guillén, & Barroso, 2011). There is currently some research on the aroma composition of rum. The OAV of vanillin, whisky lactone, 4-allyl-2-methoxyphenol and 3-methylbutyraldehyde were significantly different, and the researchers succeeded in modeling the aroma of different rums based on rum aroma analysis (Franitza, Granvogl, & Schieberle, 2016a). Previous studies utilizing Aromatic Extract Dilution Analysis (AEDA) to investigate key aroma compounds in rum found that the OAV of (E)-β-damascenone, ethyl (S)-2-methylbutyrate, and ethanol were the highest in rum (Franitza, Granvogl, & Schieberle, 2016a).

Brandy and rum aging studies have a large number of compounds that are repeatedly mentioned in both categories of distilled spirits at the same time. In studies of highly aged vintage rums, vanillin, ethyl caprylate, oak lactones, and phenylethanol are high, with additional notes of vanilla's dried fruitiness, caramel, oak, and coconut (Pino, Tolle, Gök, & Winterhalter, 2012). Ethyl esters such as ethyl caprylate also appear in brandy aging studies (Coldea, Socaciu, Mudura, Socaci, Ranga, Pop, et al., 2020). Oak lactones are also one of the most important compounds in the study of brandy aging (van Jaarsveld, Hattingh, & Minnaar, 2009). Vanillin is evident in rum, while vanillin is also found in brandy and is positively correlated with aging time (Han, Tian, Zheng, Jiang, & Bian, 2024). Comparison of brandy aged in oak chips with brandy aged in oak barrels showed that the overall quality of the brandy was not affected, but the color of the samples aged in oak chips was different (Caldeira, Belchior, & Canas, 2013). Although Brazilian law does not allow the use of oak chips for rum aging, there is still research on rum oak chips (Aguiar, Pereira, & Marques, 2021). And despite the inconsistencies in the wood used for aging, spirits, including brandy and rum, often have similarities in phenolic compounds during aging (Guerrero-Chanivet, Valcárcel-Muñoz, García-Moreno, & Guillén-Sánchez, 2020), and directly or indirectly affects the overall aroma of the spirit.

Brandy and rum are two categories of products with similar and different aroma styles. Except for the different raw materials, the distilled spirits of the two categories have similar production processes, common distillation methods and the same aging materials. Previous researchers have done a lot of analysis and research on the aroma components of brandy and rum, indicating that both categories of distilled spirits have the aroma characteristics of floral and fruity aroma, and at the same time, the characterization and analysis of volatiles in the six distilled spirits by using HS-SPME and GC-MS, which showed that the volatiles of brandy have the characteristics of a lower molecular weight (Zhao, Zheng, Song, Sun, & Tian, 2013).

There are fewer studies that carefully compare brandy and rum, and the effects of aging on compounds in both types of distilled spirits are yet to be compared, and potential marker compounds for both distilled spirits are yet to be discovered. In this paper, two brands representing two categories (brandy and rum) and products with different aging periods (three brandies: Cognac 10 years old, Cognac 15 years old and Martell; and three rums: Havana Club 3 years old, 7 years old and Havana Club Bottle Ronde) were selected. We prepared the samples using liquid-liquid extraction and analyzed them using GC-MS detection to show the similarities and differences in the types and contents of aroma components between the two categories and different aging times of the same category. The aim was to use these six wine samples for comparison to investigate the differences and similarities of aroma components in wine samples of the same category with different aging times, the differences and similarities of important compounds between categories, and to discuss the reasons for the above findings.

2. MATERIALS AND METHODS

2.1. Test Materials

2.1.1. Brandy and rum

Brandy:KOYA Brandy 10 and 15 years (CHANGYU) and Martell 12 years (Pernod Ricard). Rum: Havana Club 3 Years, 7 Years and Havana Club Bottle Fusion 25 Years (Pernod Ricard).

2.1.2. Reagents

Sodium chloride (analytically pure): Wuxi Yatai United Chemical Co., Ltd; anhydrous sodium sulfate (analytically pure): Tianjin Tianli Chemical Reagent Co.

2.2. Test Methods

2.2.1. Sample preparation

Take 25 ml of wine sample in a triangular flask, add 75 ml of distilled water to dilute to about 10 % alcohol (V/V), add 1 μg/L sec-octanol as internal standard. The extraction was repeated with 20 ml and 10 ml of dichloromethane for a total of three times. The organic phases of the three extractions were combined and 15 g of anhydrous sodium sulfate was added to remove water. The extracted organic phases were combined with 15 g of anhydrous sodium sulfate and dewatered, and then concentrated to 1 ml by rotary evaporator at 45 ℃ under atmospheric pressure, and then filtered and transferred to a 1.5 ml injection bottle for sampling.

2.2.2. Gas phase mass spectrometry methods

Gas chromatography and mass spectrometry conditions: HP-Innowax polarographic column (30 m×0.25 mm×0.25 μm); inlet and interface temperatures of 250 ℃; pressure of 53.5 kPa; carrier gas of helium (99.99%); flow rate of 1.0 mL/min; split ratio of 3:1; injection volume of 1 μL. The column heating program: 40 ℃ for 2 min, 4 ℃/min to 120 ℃ for 5 min, and then 5 ℃/min to 240 ℃ for 9 min. Mass spectrometry conditions: electron bombardment (EI) ion source; electron energy of 70 eV; detector voltage of 350 V; ion source temperature of 230 ℃; temperature of the quadruple rod of 150 ℃; temperature of the transfer line of 280 ℃; the use of full scan mode information acquisition; mass scan range of 35-550 amu; solvent delay of 4 min. The information was collected in full scan mode; the mass scan range was 35-550 amu; and the solvent delay was 4 min. Qualitative analysis: The total ionograms of the aroma components in the two brandies obtained by GC-MS were searched according to the NIST Spectral Library 14.L. Then the detected components were characterized according to the match of more than 80% with the retention time.

2.2.3. Identification of important aroma components

Quantitative and OAV analysis: According to the following formula, the content of each component was determined from the content of the internal standard, and the results were retained in two decimal places. Analysis of OAV values Compounds with OAV values >1 contributed to the aroma of the wine samples(Guth, 1997), Aroma Compound Thresholds from Compound Aroma Thresholds Compilation(Hemert, 2015). The OAV values are calculated as follows:

$$odor\ activity\ value = concentration\ (Wi)/threshold\ (Ci)$$

Comparison of aroma compositions of two categories of distilled spirits, with clustered heatmaps and box plots using the Lianchuan BioCloud platform, and Venn diagram using bioladder. Orthogonal Partial Least Squares Discriminant Analysis (OPLS-DA) was performed using simca 14.1 on the shared aroma compounds of the two categories of distilled spirits analyzed with OAV values >1 to compare the contribution of different compounds to the aroma of the samples. Use Graphpad Prism 8 to draw a bar graph.

2.3. Instrumentation and GC-MS

Agilent 789B-5977B, U.S.A. Dispensing funnel: Jiangsu Wenxuan Glass Instrument Factory (China).

3. RESULTS AND DISCUSSION

3.1. Qualitative and Quantitative Results of Samples

Two categories (brandy and rum) and six wine samples were analyzed by GC-MS, and a total of 110 aroma compounds were detected, with 50 compounds having OAV values greater than 1 (Annex 1). Among them, 20 esters, 8 alcohols, 6 acids, 11 aldehydes and ketones, and 5 phenols were detected.

Among brandies, Martell has 34 compounds, and Koa 10 years and 15 years both have 35 compounds. Among the rums, Havana 3-year, 7-year and Bottle Melt had 28, 24 and 31 compounds, respectively. Sixteen compounds were present in all three rums and 28 compounds were present in brandy.

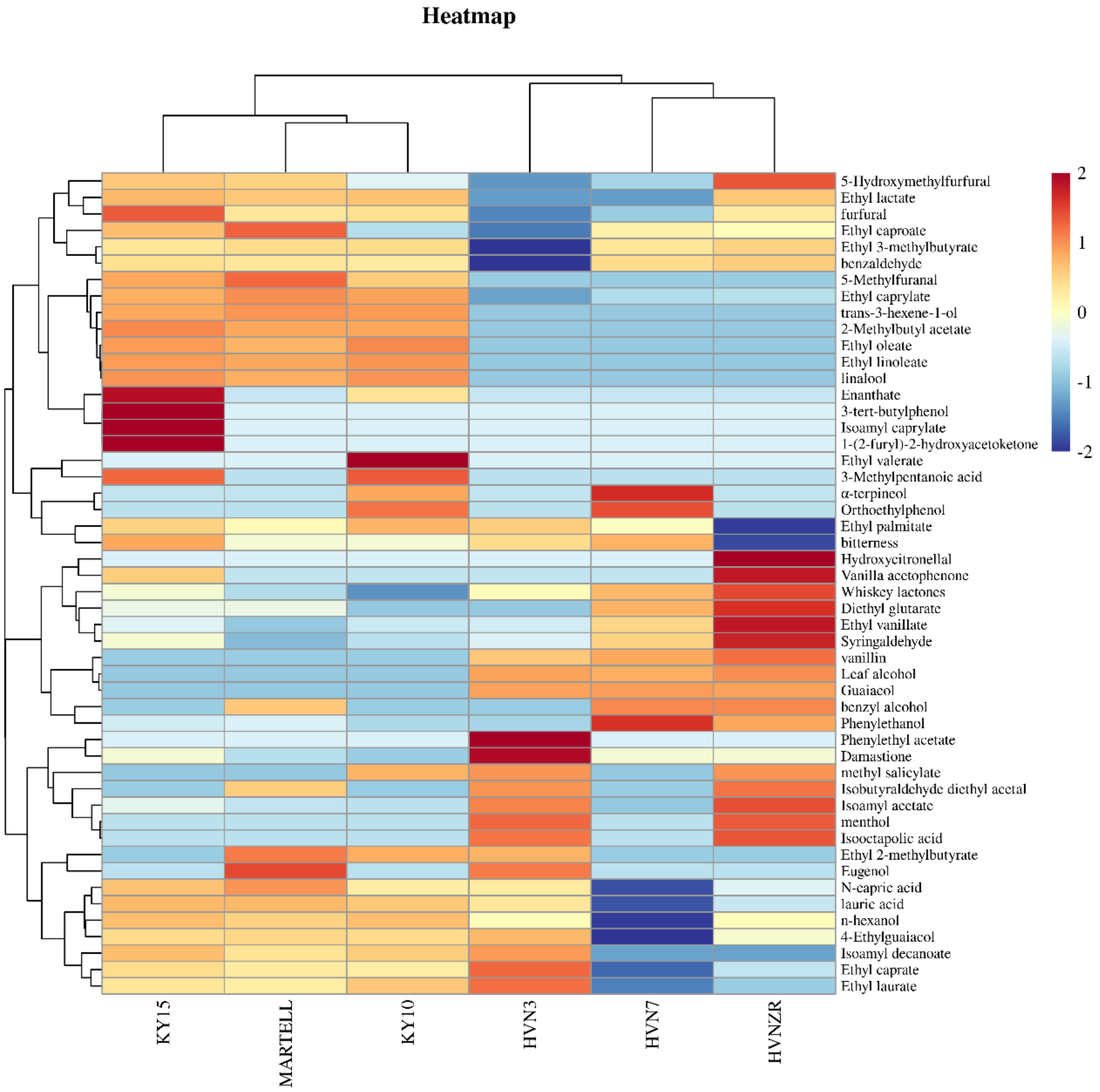
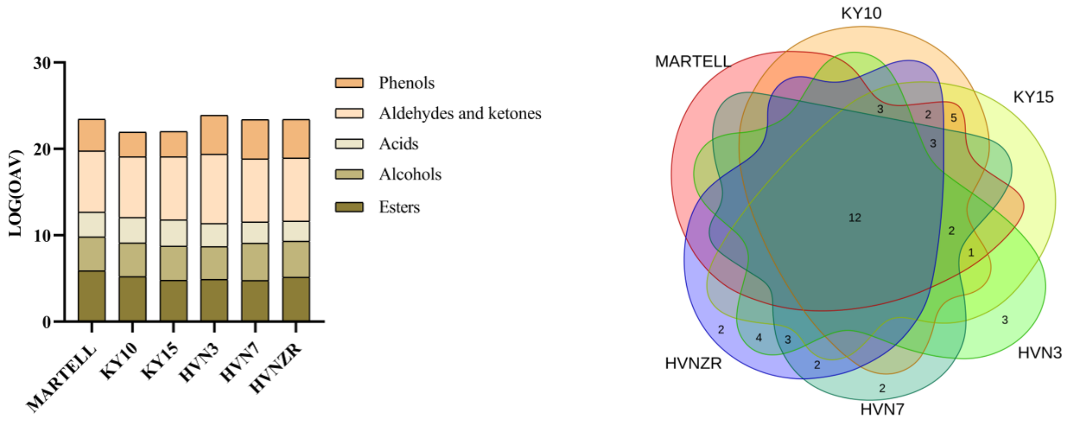


Figure 1. Heat map of OAV of compounds detected in brandy and rum with different aging times. Martell, KY10, KY15, HVN3, HVN7, HVNZR: Martell, Cognac 10 years, Cognac 15 years, Havana Club 3 years, Havana Club 7 years, Havana Club Bottle Rong

Cluster analysis showed a large difference in the OAV values of aroma compounds between brandy and rum. In the brandy group, the younger Coya 10 year old was more similar to Martell (12 year old), and the higher vintage Havana 7 year old in the rum group was more similar to the Havana Bottle Fusion (Figure 1). Aging has a significant effect on the content of aroma compounds in the body of the spirit, and some of these compounds are altered during rum aging. Prolonged aging exposes the body of both categories of distilled spirits equally to more aged wood, to the extent that the spirit develops significant amounts of volatiles produced by aging.

The total OAV of each type of compound in different wine samples also varied, as shown in Figure 2. The average OAV of ketoaldehydes, alcohols and phenolic compounds was greater than that of brandy in the three rums, while the rest of the type compounds were greater on average in brandy than in rum and the number of types of aroma compounds was greater in the brandy samples than in the rum samples. The total number of compounds with an OAV greater than 1 totaled 12 in the six wine samples (Fig. 2 b).



(a) (b)

Figure 2. Total OAV of different types of compounds(a), Venn diagram of OAV > 1 compounds in six wine samples (b). martell, ky10, ky15, hvn3, hvn7, hvnzr: martell, koa 10 year old brandy, koa 15 year old brandy, Havana Club 3 year old, Havana Club 7 year old, Havana Club Bottle Fusion

3.2. Differences and Similarities in Aroma Composition of Distilled Spirits of the Same Category with Different Aging Times

3.2.1. Similarities and differences within the brandy group

Twenty-eight compounds with OAV greater than 1 in all three brandy samples at the same time were common to brandy (Table 1). A total of 11 compounds, including ethyl lactate, isoamyl acetate, ethyl vanillate, ethyl caprylate, ethyl caprate, ethyl laurate, ethyl linoleate, trans-3-hexen-1-ol, n-decanoic acid, lauric acid, and 4-ethylguaiacol, did not show any significant differences among the three samples aged for different time periods, which can be regarded as the similarities among the brandies under the different aging vintages. The most abundant of the 11 compounds are esters, with 6. Among them, isoamyl acetate had the highest average OAV and was the largest source of common fruitiness in brandy. Ethyl caprate is the second largest source of cognac coconut and fruity aromas. The OAV values of isoamyl acetate, ethyl caprylate and ethyl caprate increased with the aging time, while the OAV values of ethyl linoleate increased.

Seventeen compounds were significantly different, with damascenone having the highest OAV. The OAV of some compounds were very similar in KOYA Brandy 10 and Martell, and for KOYA Brandy 10, even more similar than KOYA Brandy 15 years from the same manufacturer. The OAV for caprylic acid in the KOYA Brandy 15 year was much greater than the Martell and KOYA Brandy 10 year, and more than 15 times greater than the latter two. A notable variation exists in the OAV of linalool in the samples from two producers, with Martell exhibiting a considerably lower OAV compared to the two KOYA Brandy samples. In all three wine samples, there are variations observed between ethyl acetate and whiskey lactone. The concentration of whiskey lactone rises with the maturation years. Specifically, the whiskey lactone content in Macallan increased by 95.56% compared to Glenfarclas 10 years, and by 88.67% compared to 15 years. In comparison to Glenfarclas 10 years, it surged by 268.91%. Ethyl acetate levels in the two samples from Kaya exhibit higher concentrations in older vintage selections compared to younger vintages. In contrast, the ethyl acetate content in Martell surpasses that of the other two samples, potentially attributed to variations among brandy producers. In a comparative analysis between the 10-year and 15-year variations produced by the same distillery, Kaya, the ethyl acetate content in the latter is 125.1% higher than that in the former. The manufacturer's production process may also contribute to the variability in 5-methyl furfural levels. In addition, while benzaldehyde and 5-hydroxymethylfurfural levels are impacted by maturation, they do not exhibit a notable correlation with whisky lactone. Nonetheless, their concentrations rise with aging, and they are characterized by nutty and woody aromas.

Table 1. Common compounds in brandy samples aged at different ages

Compound	OAV		
	MARTELL	KY10	KY15
Ethyl lactate	4.16±1.52	4.35±1.31	5.41±0.54
2-Methylbutyl acetate	5.26±0.94b	5.16±0.62b	8.23±2.88a
Ethyl 3-methylbutyrate	79944.67±4677.67a	71702.75±8306.69a	34545±2238.21b
Isoamyl acetate	5455.8±284.69	5374.72±462.86	6119.4±483.14
Ethyl caproate	18133.89±1788.56a	13248.44±787.77c	16574.74±652.67b
Whiskey lactones	633.99±113.82b	324.2±18.45c	1184.4±137.47a
Ethyl vanillate	7.05±0.56	9.52±0.76	10.63±3.74
Ethyl caprylate	535.73±63.93	518.35±53.6	505.65±72.32
Ethyl caprate	1611.17±86.92	1564.97±137.29	1766.73±330.56
Ethyl laurate	267.05±11.04	339.38±26.26	281.15±50.4
Isoamyl decanoate	1.33±0.08b	1.79±0.08ab	2.3±0.33a
Ethyl palmitate	14.01±9.14b	30.73±1.16a	23.69±6.49ab
Ethyl linoleate	4.61±0.93	6.29±0.29	5.43±0.7
Ethyl oleate	1.74±0.08b	2.77±0.23a	2.26±0.77ab
Trans-3-hexene-1-ol	25.44±8.55	20.72±0.98	16.78±3.57
N-hexanol	168.19±59.95b	286.77±17.39a	267.9±79.13ab
Phenylethanol	7715.42±368.74a	6536.94±374.38b	7395.81±673.69ab
Linalool	555.21±100.22b	1047.95±66.42a	1038.95±244.13a
Octanoic acid	16.03±3.36b	15.64±0.9b	251.69±27.88a
N-capric acid	528.35±0	318.11±36.75	422.44±30.92
Lauric acid	183.43±251.55	133±7.52	179.63±32.6
Furfural	1352.44±27.83b	1437.65±117.62b	2625.42±387.78a
5-Methylfuranal	6.85±209.76a	1.61±0.16b	3.13±0.36b
5-Hydroxymethylfurfural	1.64±1.64a	0.34±0.03b	1.87±0.37a
Benzaldehyde	16.14±0.08b	14.09±0.68a	19.74±5.46b
Syringaldehyde	4.24±0.42b	5.79±0.36ab	8.49±2b
Damastione	12300000±168487.94b	10400000±49467.06b	19700000±401000.3a
4-Ethylguaiacol	812.7±303.02	679.28±41.64	690.9±104.01

3.2.2. Similarities and Differences within the Rum Group

Table 2 displays the common compounds found in the three rum samples. Notably, ethyl isovalerate, ethyl hexanoate, ethyl decanoate, ethyl octanoate, phenylethanol, diacetyl, and guaiacol exhibit relatively high Odor Activity Values (OAV). There are no significant differences in five compounds, such as namely ethyl hexanoate, ethyl octanoate, and linalool, among the rum samples with three distinct aging periods, suggesting a shared characteristic of rum. In particular, ethyl decanoate and decanoic acid exhibit the highest concentrations in the rum with shorter aging duration. In the study, it was observed that the concentration of isoamyl acetate is the lowest in HVN7 but the highest in HVNZR. Guaiacol was the most abundant in HVN7, with similar levels in the other two samples.

Most of the compounds in Table 2 are described as floral and fruity, but with subtle differences. For example, ethyl decanoate and isoamyl acetate are also described as having a fruity and floral aroma, but isoamyl acetate is described as having a banana aroma.

Table 2. Common compounds in rum samples aged at different ages

compound	OAV		
	HVN3	HVN7	HVNZR
Isoamyl acetate	10872.5±3529.01a	4765.91±1711.13b	12362.76±1994.71a
Ethyl caproate	11668.53±1392.1	15295.51±2876.98	14871.28±1597.37
Whiskey lactones	1437.32±368.23b	2853.6±650.98b	6231.24±904.73a
Ethyl vanillate	9.86±2.13b	20.44±5.14b	57.52±5.72a
Ethyl caprylate	294.73±51.21	339.27±137.24	340.51±84.29
Ethyl caprate	2852.16±1206.9a	521.52±53.3b	962.1±157.33b
Ethyl laurate	531.62±87.88a	76.02±17.52b	114.81±10.43b
Ethyl palmitate	24.83±8.55a	12.72±3.95b	1.33±0.21c
Leaf alcohol	98±24.35	76.17±18.93	154.53±31.74
Phenylethanol	6333.565±969.8	20848.79±1929.39	14174.61±590.89
N-capric acid	327.32±37.79a	74.78±18.68b	205.38±40.43ab
Furfural	421.4±118.63b	610.08±162.8b	1335.98±147.91a
Vanillin	171.5±39.35b	528.9±52.09b	3364.87±665.3a
Syringaldehyde	6.9±0.69b	13.51±3.85b	32.57±5.73a
Damastione	108000000±3137592.1a	19800000±581854.92b	19900000±207794.03b
Guaiacol	28823.29±3682.72	34729.41±8651.11	29322.29±6325.01

Comparing the OAV of compounds common to rums of different aging years, similar to brandy, the main aroma profile of rums of different aging years was floral and fruity, and the content of compounds with nutty and woody aromas increased with aging time. Six compounds, including ethyl caproate, guaiacol and ethyl caprylate, showed no significant difference in rum. Ethyl palmitate was the only compound exhibiting noteworthy variations among the three rum samples, displaying a decline in content with prolonged aging. Specifically, the concentration of ethyl palmitate reduced by 48.2% in HVN7 compared to HVN3, and by 94.6% in HVNZR compared to HVN3. In rum, the levels of whisky lactone and furfural rise with the duration of aging. And the concentration of whisky lactone in HVN7 and HVNZR is 198.5% and 433.5% higher than that in HVN3, respectively. The level of furfural in HVN7 and HVNZR is 144.9% and 317.1% of that in HVN3, respectively. This lack of significance across all three samples may be attributed to the lesser disparity in aging time between HVN3 and HVN7 in comparison to HVN7 and HVNZR.

3.3. Similarities and Differences in Key Aroma Components between Brandy and Rum

3.3.1. Points of Contrast in Key Aroma Compounds between Brandy and Rum

11 compounds were found only in three brandy samples. Among them, linalool, trans-3-hexen-1-ol, ethyl 2-methylbutanoate, linoleic acid ethyl ester, 5-hydroxymethylfurfural, and ethyl oleate were detected in all three brandy samples. Linalool has a high OAV, and 3-methylbutanoic acid was detected in two of the Cognac samples with a high OAV. 7 compounds were found only in rum. Vanillin, eugenol, and linalool were detected in all three rum samples, with eugenol having the highest content.

To comprehensively analyze the distinctions in aroma components between two types of distilled spirits, specifically brandy and rum, 32 aroma compounds with an average OAV exceeding 1 were chosen from the samples of each spirit category. A 0PLS-DA model was constructed for the OAV, depicted in Fig. 3(a), where the values R2X=0.671 and R2Y=0.903 indicate a strong fit, with both R2 and Q2 > 0.5. The samples of the two categories are not closely distributed in the graph, and the two categories of distilled spirits are strongly differentiated, and their VIP plots are shown in Fig. 3(b). To identify potential distinctive compounds, an analysis was performed to select compounds with VIP values exceeding 1, leading to the identification of 12 compounds for cluster analysis as presented in Fig. 3(c). In brandy samples, compounds like ethyl caproate, hexanol, and furfural are found in high concentrations, displaying notable distinctions from rum samples. Conversely, in rum samples, compounds including isoamyl acetate, methyl salicylate, and whiskey lactone are present at elevated levels, showcasing significant variations from brandy Among the shared alcohols, rum had a lower average content of higher alcohols than brandy. The OAV of damascenone was the highest and significantly different between brandy and rum.

As illustrated in Fig. 3(c), this study indicates significant disparities between rum and brandy in the levels of ethyl caprylate, lauric acid, and hexanol, with brandy showcasing higher concentrations of these compounds, as shown in Fig. 4. This study delves deeper into the notable variations in shared aroma compounds within two classifications of distilled spirits to differentiate between the two types of spirits. Importantly, the average OAV for acids and alcohols is higher in brandy compared to rum, which could potentially serve as a distinguishing factor between the two categories of distilled spirits. Furthermore, the diverse origins of brandy and rum result in a complex composition of aroma compounds in the spirits. Hence, there remains a need for further exploration into the distinctive compounds defining these two categories of distilled spirits.

Rum HVN3 with shorter aging years was found to be similar to the three brandy samples in the clustering in Fig. 3(c) and differed from the clustering in Fig. 1. This may be due to the fact that some of the compounds were screened out in Fig. 3 and that the low ageing years resulted in the retention of more compounds with smaller molecular weights and straight chains. Comparing HVN3 with a brandy sample and two other rum samples, respectively, it was found that ethyl 2-methylbutyrate and eugenol were the most important substances distinguishing HVN3 from the other two rum samples. 2-methylbutyrate has an apple aroma, and with its low molecular weight, it is significantly affected by aging. Eugenol has a clove odor and stimulating properties. Eugenol contains a carbon double bond and a phenolic hydroxyl group, which causes it to be easily oxidized, and this is the reason why it was detected more in HVN3 samples from low aging years.

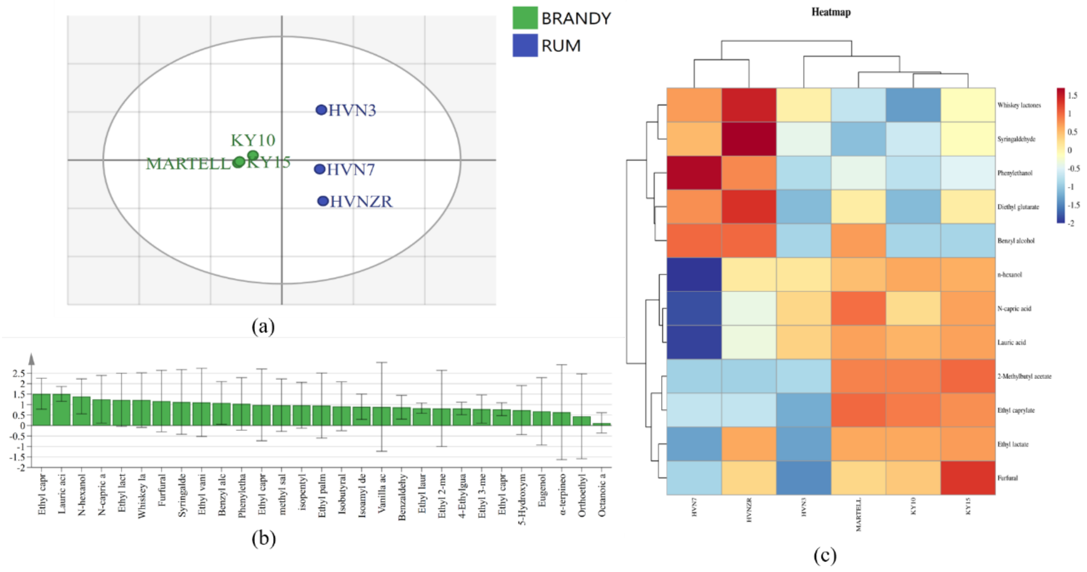


Figure 3. KY10 and KY15 represent Koa 10-year brandy and Koa 15-year brandy, respectively; HVN3, HVN7, and HVNZR represent Havana Club 3-year, 7-year, and Havana Club Bottle Rong, respectively. (a) OPLS-DA plots for 54 shared compounds; (b) VIP value plots; (c) heat maps for compounds with ViP values >1.

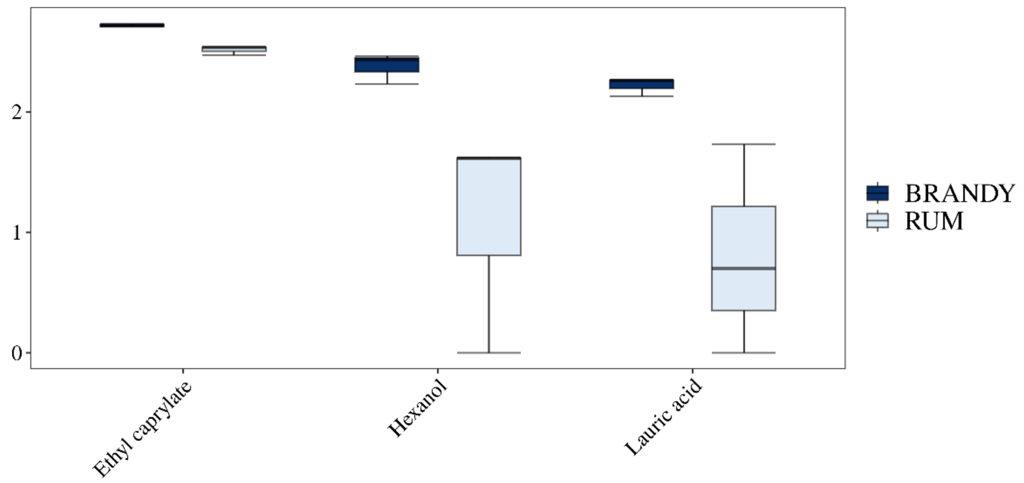


Figure 4. Box plots of ethyl caprylate, lauric acid and hexanol OAV in brandy and rum

3.3.2. Similarities in Key Aromatic Compounds between Brandy and Rum

In the OPLS-DA analysis of the 54 shared compounds of the two categories of samples described in 3.3.1, 18 had VIP values less than 1 and OAV values greater than 1. It can be assumed that these 18 compounds have a small difference between rum and brandy and contribute to the aroma of the spirit (Table 3). Caprylic acid was the compound with the smallest difference between brandy and rum, with a VIP value of only 0.17, followed by o-ethylphenol at 0.43.

Table 3. Common compounds with VIP<1

Compound	VIP
Ethyl caproate	0.96
Ethyl palmitate	0.95
methyl salicylate	0.94
Isoamyl acetate	0.94
Isobutyraldehyde diethyl acetal	0.91
Vanilla acetophenone	0.89
Isoamyl decanoate	0.87
benzaldehyde	0.86
Ethyl laurate	0.8
Ethyl 3-methylbutyrate	0.79
4-Ethylguaiacol	0.78
Ethyl 2-methylbutyrate	0.77
5-Hydroxymethylfurfural	0.76
Ethyl caprate	0.74
Eugenol	0.64
α-terpineol	0.62
Orthoethylphenol	0.43
Octanoic acid	0.17

The total OAV of esters was the largest of these 18 compounds, totaling 9, aldehydes and ketones totaling 4, and phenols totaling 3. Ethyl 2-methylbutyrate had the largest mean OAV and gave an apple aroma to the brandy and rum, followed by ethyl 3-methylbutyrate, and ethyl caproate in third place, and also had a fruity aroma. These three compounds are the greatest source of fruity flavors shared by brandy and rum. Vanillin was detected in both rum and brandy only in samples from high aging vintages, and both eugenol and isobutyraldehyde diethyl acetal were detected in samples from lower vintages (Martell and Havana 3 years old). The effect of aging on some of these compounds was similar in both rum and brandy, with eugenol being more prevalent in brandy than in rum, and the reverse was true for isobutyraldehyde diethyl acetal. Isoamyl decanoate was detected in all three brandies, but only in low aging vintage rums.

3.4. Discussion

3.4.1. Potential Reasons for the Differences within the Brandy Group

Many of the aroma compounds of brandy are affected by aging. Among them, compounds with nutty, woody and smoky aromas such as whisky lactones are significantly affected by aging. Furfural, like furfural, is affected by wood aging (Caldeira, Clímaco, de Sousa, & Belchior, 2006), but it has also been shown that furfural occurs during distillation and heating of the raw spirit (Madrera, Gomis, & Alonso, 2003), so that the final amount of furfural does not only depend on the barrel aging, which may be the reason why in the present study the final amount of furfural is not only dependent on the barrel aging. Therefore, the final content of furfural does not depend only on barrel aging, which may be the reason why furfural content was not strictly positively correlated with aging time in this study.

In addition to the infiltration effect of oak barrels, esterification reactions, oxidation reactions, and catabolic equilibrium during aging also affect the aromatic substances of brandy. Medium-chain fatty acid esters such as ethyl caproate and ethyl caprylate are generally believed to originate from yeast (González-Marco, Jiménez-Moreno, & Ancín-Azpilicueta, 2008), and in brandy and rum, which are acidic environments, esters are susceptible to hydrolysis in acidic environments, whereas with the presence of a large amount of ethanol and organic acids in the body of the wine and the presence of esterification reactions, the ester content in the liquor is subjected to both chemical reactions until a dynamic equilibrium is reached. Thus medium-chain fatty acid esters generally differed less among the three samples, with only ethyl caproate showing a significant difference. The increase in branched-chain fatty acid esters with ageing time and the decrease in small-molecule esters with ageing time within a certain range (Puertas, Cantos-Villar, Munoz-Redondo, Valcárcel-Muñoz, Solana, & Moreno-Rojas, 2022) could explain the increase in isoamyl acetate versus isoamyl caprate, and relevant studies in wine have also verified that some of the branched-chain fatty acid esters increase with ageing time, while some of the medium-chain fatty acid esters increase with ageing time. The increased content of amyl acetate and isopentyl decanoate, and related studies in wines have verified that the content of some branched-chain fatty acid esters increases with aging time (Cameleyre, Lytra, Tempere, & Barbe, 2017). In addition, the hydroxyl group in alcohols has a low oxidation state and is easily oxidized to aldehydes and ketones, which is the reason why 3-methyl-1-pentanol is the most abundant in KOYA Brandy10.

3.4.2. Potential reasons for the differences within the rum group

Rum was also significantly affected by aging. Isoamyl acetate and ethyl decanoate content increased with aging time, similar to previous studies in brandy. Ethyl hexanoate, ethyl caprylate and ethyl decanoate are derived from yeast metabolism, and again, because of the balance between hydrolysis and esterification of esters, ethyl caprylate and ethyl caproate did not differ significantly in rum, and the difference in ethyl decanoate was only seen in HVN3. Alcohols can be oxidized to aldehydes and ketones during the aging process, but at the same time, acids can be hydrogenated to produce alcohols, which could explain why the n-hexanol content in rum decreases and then increases(Tamura, Nakagawa, & Tomishige, 2020). In rum, the total content of alcohols and aldehydes and ketones increased with aging time, and the content of acids appeared to decrease and then increase(Fig. 2 a). During the aging process from HVN3 to HVN7, the decrease in esters and acids was greater than the increase in alcohols, and it is clear that not all of the decrease in these two groups originated from oxidation, which may be due to the large amount of volatilization of compounds at the early stage of aging, which is considered to be the main role of volatilization at the early stage of aging in this study. The increase in aldehydes and ketones cannot be attributed to the oxidation of the alcohols, but rather to the oak infiltration, which is even more pronounced with longer ageing. The increase in aldehydes and ketones is evident from HVN7 to HVNZR, and eight aldehydes and ketones, such as furfuryl hydroxymethyl ketone, are only detected in samples aged for a high number of years, and these compounds are most likely to have come from oak barrels and to have accumulated to a certain level in the barrels over the years before being detected.

3.4.3. The reasons for the differences between brandy and rum.

Compounds specific to both classes of distilled spirits are expressed. In brandy, there were more esters than in rum, and the reverse was true for alcohols. Linalool and 3-methylpentanoic acid were detected only in brandy and at higher levels. Guaiacol was higher in rum. Guaiacol is more derived from lignin degradation and linalool was found to be present only in some fruit brandies in previous experiments (Vyviurska, Zvrskovcová, & Spánik, 2017), Therefore, differences in raw materials may be responsible for this phenomenon. Through the OPLS-DA analysis of the compounds shared by the two categories of distilled spirits (Fig. 3), among the compounds shared by brandy and rum, ethyl caprylate, lauric acid, and hexanol differed significantly between rum and brandy, and these three compounds were found in higher amounts in brandy. In the study of brandy, hexanol was considered to be the aroma of the raw material, and ethyl caprylate was derived from fermentation, distillation and aging (Loncaric, Patljak, Blazevic, Jozinovic, Babic, Subaric, et al., 2022).

In addition, the threshold value of damascenone was extremely low, which made the aldehydes and ketones lower but higher total OAV in brandy versus rum and showed significant differences. And damascenone was higher in rum than brandy, which made the OAV of aldehydes and ketones in rum greater than that of brandy. Damascenone has been recognized in previous studies as the compound with the highest OAV in rum and is present in the raw molasses and is increased during the distillation process (Franitza, Granvogl, & Schieberle, 2016b). And the positive effect of soil nitrogen source elements on the content of damascene in plants (Yuan, Schreiner, & Qian, 2018), and in recent years, it has been found that the leguminous rhizobacterial flora is present in the root system of sugarcane in the grass family with strong nitrogen-fixing enzyme activity (Rouws, Leite, de Matos, Zilli, Coelho, Xavier, et al., 2014). This may also account for the higher damascenone content of the rum than the brandy. It is worth noting that KY15 has a lower damascenone content than the other two brandy samples of lower aging years, possibly due to the effect of aging, and that HVN3 has the highest damascenone content of all the rum samples instead, possibly due to the effect of aging.

4. CONCLUSION

In this work, we examined the aroma compounds of three brandies and three rums using GC-MS to compare the similarities and differences of the compounds in samples with different aging times. Analysis of the detected compounds with respect to aging revealed that the ester changes of the two types of distilled spirits were generally similar, with a curvilinear change of decreasing ester content in low aging years and increasing ester content in high aging years. The compounds ethyl lactate, isoamyl acetate and ethyl caprylate were not significantly different among the three brandy samples, while ethyl caproate and whisky lactone were significantly different among the three brandy samples. Five compounds, ethyl caproate, ethyl caprylate and leaf alcohol, were not significantly different in the three rums with different aging times, and ethyl palmitate was significantly different in all three rums. Among the compounds specific to brandy and rum, linalool and troncetol were the most abundant compounds in brandy and rum, respectively. Combining the OPLS-DA method to analyze the aroma compounds of brandy and rum, ethyl caprylate, lauric acid, and hexanol were higher in brandy than in rum, and were differentially present in both distillates.

Taken together, these results provide a new insight into the differences between the aroma compounds of brandy and rum, contributing to a more in-depth study of the development of the two categories of distilled spirits.

REFERENCES

[1] Aguiar, D., Pereira, A. C., & Marques, J. C. (2021). Agricultural Rum of Madeira matured on the seafloor: improved physicochemical changes induced by a pioneering seafloor ageing process. European Food Research and Technology, 247(12), 3023-3035.

[2] Caldeira, I., Belchior, A. P., & Canas, S. (2013). EFFECT OF ALTERNATIVE AGEING SYSTEMS ON THE WINE BRANDY SENSORY PROFILE. Ciencia E Tecnica Vitivinicola, 28(1), 9-18.

[3] Caldeira, I., Clímaco, M. C., de Sousa, R. B., & Belchior, A. P. (2006). Volatile composition of oak and chestnut woods used in brandy ageing: Modification induced by heat treatment. Journal of Food Engineering, 76(2), 202-211.

[4] Cameleyre, M., Lytra, G., Tempere, S., & Barbe, J. C. (2017). 2-Methylbutyl acetate in wines: Enantiomeric distribution and sensory impact on red wine fruity aroma. Food Chemistry, 237, 364-371.

[5] Coldea, T. E., Socaciu, C., Mudura, E., Socaci, S. A., Ranga, F., Pop, C. R., Vriesekoop, F., & Pasqualone, A. (2020). Volatile and phenolic profiles of traditional Romanian apple brandy after rapid ageing with different wood chips. Food Chemistry, 320, 10.

[6] Franitza, L., Granvogl, M., & Schieberle, P. (2016a). Characterization of the Key Aroma Compounds in Two Commercial Rums by Means of the Sensomics Approach. Journal of Agricultural and Food Chemistry, 64(3), 637-645.

[7] Franitza, L., Granvogl, M., & Schieberle, P. (2016b). Influence of the Production Process on the Key Aroma Compounds of Rum: From Molasses to the Spirit. Journal of Agricultural and Food Chemistry, 64(47), 9041-9053.

[8] González-Marco, A., Jiménez-Moreno, N., & Ancín-Azpilicueta, C. (2008). Concentration of volatile compounds in Chardonnay wine fermented in stainless steel tanks and oak barrels. Food Chemistry, 108(1), 213-219.

[9] Guerrero-Chanivet, M., Valcárcel-Muñoz, M. J., García-Moreno, M. V., & Guillén-Sánchez, D. A. (2020). Characterization of the Aromatic and Phenolic Profile of Five Different Wood Chips Used for Ageing Spirits and Wines. Foods, 9(11), 18.

[10] Guth, H. (1997). Quantitation and sensory studies of character impact odorants of different white wine varieties. Journal of Agricultural and Food Chemistry, 45(8), 3027-3032.

[11] Han, B. L., Tian, S. L., Zheng, S. H., Jiang, Y. Q., & Bian, M. H. (2024). Uncovering changes in mulberry brandy during artificial aging using flavoromics. European Food Research and Technology, 250(7), 1959-1967.

[12] Hemert, R. V. (2015). Compilation of compound flavor thresholds: Compilation of compound flavor thresholds.

[13] Li, Y. Y., Li, Q. Q., Zhang, B. C., Shen, C. H., Xu, Y., & Tang, K. (2021). Identification, quantitation and sensorial contribution of lactones in brandies between China and France. Food Chemistry, 357, 7.

[14] Loncaric, A., Patljak, M., Blazevic, A., Jozinovic, A., Babic, J., Subaric, D., Pichler, A., Flanjak, I., Kujundzic, T., & Milicevic, B. (2022). Changes in Volatile Compounds during Grape Brandy Production from '<i>Cabernet Sauvignon</i>' and '<i>Syrah</i>' Grape Varieties. Processes, 10(5), 13.

[15] Madrera, R. R., Gomis, D. B., & Alonso, J. J. M. (2003). Influence of distillation system, oak wood type, and aging time on composition of cider brandy in phenolic and furanic compounds. Journal of Agricultural and Food Chemistry, 51(27), 7969-7973.

[16] Pino, J. A., Tolle, S., Gök, R., & Winterhalter, P. (2012). Characterisation of odour-active compounds in aged rum. Food Chemistry, 132(3), 1436-1441.

[17] Puertas, B., Cantos-Villar, E., Munoz-Redondo, J. M., Valcárcel-Muñoz, M. J., Solana, R. R., & Moreno-Rojas, J. M. (2022). Development of a methodology based on headspace solid-phase microextraction coupled to gas chromatography-mass spectrometry for the analysis of esters in brandies. Journal of Food Composition and Analysis, 108, 10.

[18] Rouws, L. F. M., Leite, J., de Matos, G. F., Zilli, J. E., Coelho, M. R. R., Xavier, G. R., Fischer, D., Hartmann, A., Reis, V. M., & Baldani, J. I. (2014). Endophytic <i>Bradyrhizobium</i> spp. isolates from sugarcane obtained through different culture strategies. Environmental Microbiology Reports, 6(4), 354-363.

[19] Schwarz, M., Rodríguez, M. C., Guillén, D. A., & Barroso, C. G. (2011). Analytical characterisation of a Brandy de Jerez during its ageing. European Food Research and Technology, 232(5), 813-819.

[20] Tamura, M., Nakagawa, Y., & Tomishige, K. (2020). Recent Developments of Heterogeneous Catalysts for Hydrogenation of Carboxylic Acids to their Corresponding Alcohols. Asian Journal of Organic Chemistry, 9(2), 126-143.

[21] van Jaarsveld, F. P., Hattingh, S., & Minnaar, P. (2009). Rapid Induction of Ageing Character in Brandy Products - Part II. Influence of Type of Oak. South African Journal of Enology and Viticulture, 30(1), 16-23.

[22] Vyviurska, O., Zvrskovcová, H., & Spánik, I. (2017). Distribution of enantiomers of volatile organic compounds in selected fruit distillates. Chirality, 29(1), 14-18.

[23] Yuan, F., Schreiner, R. P., & Qian, M. C. (2018). Soil Nitrogen, Phosphorus, and Potassium Alter β-Damascenone and Other Volatiles in Pinot noir Berries. American Journal of Enology and Viticulture, 69(2), 157-166.

[24] Zhao, Y. P., Li, J. M., Xu, Y., Fan, W. L., & Jiang, W. G. (2009). Characterization of Aroma Compounds of Four Brandies by Aroma Extract Dilution Analysis. American Journal of Enology and Viticulture, 60(3), 269-276.

[25] Zhao, Y. P., Zheng, X. P., Song, P., Sun, Z. L., & Tian, T. T. (2013). Characterization of Volatiles in the Six Most Well-Known Distilled Spirits. Journal of the American Society of Brewing Chemists, 71(3), 161-169.