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Comparison of unaged and barrel aged whiskies from the same Mash Bill using gas chromatography/ mass spectrometry

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This study provides qualitative data on sensory compounds present in barrel aged U.S. corn-based whiskies (primarily bourbon) and their unaged counterparts. Whisky samples of commercial brands by Heaven Hill, Buffalo Trace, Maker's Mark, and Nelson's Greenbrier Distillery were tested by direct injection gas chromatography/mass spectrometry. Chromatograms of samples were analyzed against NIST mass spectra to develop and compare sensory compounds present in the whiskies analyzed. Results obtained from commercial whisky brands were used to build a baseline of sensory compounds present, providing a framework to show comparable compounds between the barrel aged whiskies and colorless, unaged whisky. Results show that barrel aging is an additive process in terms of total sensory compounds present and that sensory compounds resulting from barrel aging having longer retention times than those found in unaged whisky.

Key words: Whiskey, barrel aging, GC/MS, bourbon.

INTRODUCTION

Aging whisky in oak barrels is the preferred method for mellowing whisky and results in the most significant changes in the sensory compounds found between whisky that has been aged in barrels and colorless, unaged whisky (Mosedale and Puech, 1998; Spedding, 2018). In the United States, whisky has become increasingly popular. This popularity has led to a resurgence of small craft distilleries, most of which are producing whisky, in particular corn-based whisky such as bourbon and corn whisky (Adams, 2014; Rarick and Mich, 2015). Because there is little published research on the sensory compound changes that barrel aging corn-based whisky brings, most new distillers are unaware of what sensory compounds are formed as a result of barrel aging and its influence on the sensory profile of the final product. Most literature concerning the effects of aging alcoholic beverages in barrels have on the sensory profile of those beverages deals with wine and Scotch whisky (Spedding, 2017a). It is therefore significant to study the sensory compound profiles produced by barrel aging U.S., corn-based whisky and to compare those compounds with those found in unaged counter parts. To do that, colorless, unaged corn-based whisky as well as barrel aged whisky produced by the same manufacturer

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using the same mash bill to produce both products were obtained for analysis.

Unaged bourbon whisky is rarely offered for purchase in retail settings, but the following brands sell both barrel aged and unaged versions of their whiskies: Buffalo Trace and Maker's Mark. In addition to comparing the sensory profiles of barrel aged and unaged whiskies, the authors of this study were curious about the effects that increasing time whisky was stored in barrels had on the sensory compounds present in whiskies. Heaven Hill Distillery of Bardstown Kentucky makes 80 different brands of whisky using the 'same mash bill', the only stated difference between their brands being the length of time the whisky spends in a barrel and the percent alcohol by volume to which is its diluted. Thus, Heaven Hill samples in this research show the effects of time spent in a barrel on sensory compounds present in the whisky.

Use of gas chromatography/mass spectrometry (GC/MS) to analyze distilled spirits is a common method for determining the sensory compounds present in spirits. Spirits analyzed by GC/MS vary in sensory compound complexity from somewhat neutral and sensory compound simple vodkas, which are mostly ethanol, to barrel aged whiskies and cognacs containing hundreds of sensory compounds (Mosedale and Puech, 1998; SavchukV et al., 2001; Pietrek, 2015, Piggott, 2016; Spedding, 2018). GC/MS separates and identifies components of complex sensory compound mixtures (Gates and Bull, 2008). Sensory compound profiles are dependent on the type of whisky being tested (such as bourbon, Scotch, and Canadian) (Piggott, 2016) and show similarities among different whiskies for the major volatile congeners they contain (Owens et al., 2016). Russell and Stewart (2014) also found that of the spectrometric analysis methods available, chromatography offers advantages in speed, selectivity and sensitivity. Aylott and MacKenzie (2010) showed the utility of direct injection liquid chromatography method to analyze whisky.

It is a goal in this research to provide distillers and scientists that study the production of distilled spirits with data that show how aging corn-based whisky in barrels changes sensory compounds in that whisky due to the dearth of studies on the subject involving bourbon specifically (Spedding, 2018). A comparison of the sensory compounds present in colorless, unaged whisky to barrel aged whisky from the same mash bill and manufacturer was conducted. A comparison of sensory compounds present among the effects that time in a barrel has on the sensory compounds present in whisky produced from a single manufacturer who uses a single recipe and process for a variety of brand names whose main variable is time.

METHODS

Unopened, commercially-available, barrel aged and unaged whiskies produced by Maker's Mark, Nelson's Greenbrier, Buffalo Trace, and Heaven Hill were purchased from retail settings at liquor stores in Colorado (Table 1). 50 ml of each product where poured into 50 ml amber sample vials and sealed with no headspace. Both barrel aged and unaged whiskies were analyzed within three months of the products being transferred from their original bottles as bottled by the manufacturer. All whisky samples were tested at the %ABV of the purchased product as bottled by the manufacturer.

Immediately prior to analysis, a subset of each whisky product was transferred from its 50 ml amber vial to a 3 mL capped glass vial and was labeled. For each sample, 1 µL was collected in a Hamilton gastight 25 µL syringe with a cemented needle and sampled through the injection port of the gas chromatograph. The samples were then analyzed by an Agilent 7890 GC with an Agilent 5975a triple axis MS detector using helium (Buckeye Welding) as a carrier gas at 0.5 mL/min (Lynman, 2016). Tank pressure was 60 psi.

The mass detector in the analyses used electron impact ionization (EI) with a single hyperbolic quadrupole mass filter. The analysis for whisky ethanol GC was performed on a DB-1301 (wax, 30 m, 0.25 mm internal diameter and 0.25 µm film thickness; Agilent Technologies, Waldbron, Germany). The initial oven temperature was set at 60°C with a solvent delay of 3 min. After the solvent delay, the oven was ramped up to 100°C at a rate of 20°C/min. Once at 100°C, the oven was ramped to 240°C at 5°C/min and held for 10 min followed by cool down. Compounds eluting from the column were collected as a Total Ion Current Chromatogram (TIC). Peaks of interest were evaluated against the NIST library of compounds and recorded for comparisons. In between each sample, the Hamilton gastight syringe was rinsed thoroughly with deionized water. Effort was made to ensure the absence of air bubbles during sampling.

The TIC produced for each whisky sample and the included peaks of interest were labeled according to NIST library comparisons and percent probability. All TICs were saved to the computer in the University of Northern Colorado Analytical Chemistry Lab.

RESULTS

The following compounds were found among the whiskies sampled: Isoamyl acetate, ethyl hexanoate, phenylethyl alcohol, ethyl caprylate, diethyl succinate, octanoic acid, 2-phenylethyl acetate, cis-whiskeylactone, ethyl caprate, decanoic acid, vanillin lactoside, vanillin, ethyl laurate, isoamyl decanoate, syringaldehyde, ethyl myristate, ethyl palmitate, ethyl linoleate, and ethyl oleate (Table 2).

Whisky samples having both a barrel aged and unaged counterpart varied in their differences with respect to the sensory compounds present (Tables 3 and 4). The Buffalo Trace whiskies have an eight compound difference between the barrel aged and unaged products including ethyl hexanoate, 2-phenylethyl acetate, cis-whiskeylactone, decanoic acid, vanillin lactoside, vanillin, isoamyl decanoate, and syringaldehyde (Table 3). The Nelson's Greenbriar whiskies have a four compound difference between the barrel aged and unaged products including cis-whiskeylactone, vanillin lactoside, syringaldehyde, and ethyl linoleate (Table 3). The Makers Mark whiskies have a three compound difference between their barrel aged and unaged products including 2-phenylethyl acetate, vanillin lactoside, and

Table 1. Brand names of whisky samples analyzed during this study via GC/MS analysis.

Whisky brand name
Whisky brands sampled having a an unaged and barrel aged whisky from the same mash bill:
Buffalo Trace Bourbon
Buffalo Trace White Dog Mash
Nelson's Greenbriar Corn Whiskey
Nelson's Greenbriar White Whiskey
Makers Mark Bourbon
Makers White
Whisky brands produced by a distillery (Heaven Hill) from the same mash bill where age is the variable:
Cabin Still Bourbon
Bourbontown Club Bourbon
Fighting Cock Bourbon
Larceny Bourbon
Evan Williams Bourbon
Evan Williams Single Barrel Vintage Bourbon
Evan Williams 1783 Bourbon
Elijah Craig Bourbon
Henry McKenna Single Barrel 10 Year Bourbon

Table 2. Main sensory compounds of interest present in whisky samples from the study.

Approximate retention time (min)	Common name, molecular formula, mass (g/mol)
5.7	Isoamyl acetate, $C_7H_{14}O_2$, 130.19
7.4	Ethyl hexanoate, $C_8H_{16}O_2$, 144.21
10.5	Phenylethyl alcohol, $C_8H_{10}O$, 122.16
11.1	Ethyl caprylate, $C_{10}H_{20}O_2$, 172.27
11.3	Diethyl succinate, $C_8H_{14}O_4$, 174.19
11.9	Octanoic acid, $C_8H_{16}O_2$, 144.2
13.0	2-Phenylethyl acetate, $C_{10}H_{12}O_2$, 164.02
15.1	cis-Whiskeylactone, $C_9H_{16}O_2$, 156.22
15.6	Ethyl caprate, $C_{12}H_{24}O_2$, 200.32
16.3	Decanoic acid, $C_{10}H_{20}O_2$, 172.27
17.6	Vanillin Lactoside, $C_{20}H_{28}O_{13}$, 476
17.7	Vanillin, $C_8H_8O_3$, 152.15
20.1	Ethyl laurate, $C_{14}H_{28}O_2$, 228.37
21.3	Isoamyl decanoate, $C_{15}H_{30}O_2$, 242.40
23.8	Syringaldehyde, $C_9H_{10}O_4$, 182.17
24.4	Ethyl myristate, $C_{16}H_{32}O_2$, 256.42
28.3	Ethyl palmitate, $C_{18}H_{36}O_2$, 284.48
31.5	Ethyl linoleate, $C_{20}H_{36}O_2$, 308.50
31.6	Ethyl oleate, $C_{20}H_{38}O_2$, 310.51

syringaldehyde (Table 3).

A 14 compound difference occurs among the Heaven Hill whiskies which are made from the same mash bill. The number of sensory compounds present increased corresponding to increase time the whisky spent in barrels (Table 4). The differing compounds are isoamyl acetate, phenylethyl alcohol, diethyl succinate, octanoic acid, 2-phenylethyl acetate, cis-whiskeylactone, decanoic acid, vanillin lactoside, vanillin, isoamyl decanoate, ethyl myristate, ethyl palmitate, ethyl linoleate, and ethyl oleate. In general, whiskies that were aged for long in barrels had a higher total number of sensory compounds

Table 3. Compound presence in whisky sample set that have an un-mellowed, colorless and barrel mellowed component.

Compound	Buffalo Trace	Buffalo Trace White Dog	Nelson's Greenbriar Corn	Nelson's Greenbriar White	Makers Mark	Makers White
Furfural	-	-	-	-	-	-
Isoamyl acetate	-	-	5.6	5.6	5.7	5.7
Ethyl hexanoate	-	7.4	7.4	7.4	7.4	7.4
Phenylethyl alcohol	10.5	10.5	10.5	10.5	10.5	10.5
Ethyl caprylate	11.1	11.1	11.1	11.1	11.1	11.1
Diethyl succinate	11.4	11.3	-	-	-	-
Octanoic acid	-	-	-	-	-	-
2-Phenylethyl acetate	-	13.0	13.0	13.0	-	13.0
cis-Whiskeylactone	15.1	-	15.8	-	-	-
Ethyl caprate	15.6	15.6	15.6	15.6	15.6	15.6
Decanoic acid	16.3	-	-	-	-	-
Vanillin Lactoside	17.6	-	17.7	-	17.7	-
Vanillin	17.7	-	-	-	-	-
Ethyl laurate	20.1	20.1	20.1	20.1	20.1	20.1
Isoamyl decanoate	-	21.3	-	-	-	-
Syringaldehyde	23.8	-	23.8	-	23.8	-
Ethyl myristate	24.4	24.4	24.4	24.4	-	-
Ethyl palmitate	28.3	28.3	28.3	28.3	28.3	28.3
Ethyl linoleate	31.5	31.5	31.5	-	-	-
Ethyl oleate	-	-	-	-	-	-

The values represent retention times and dashed lines mean the compound was not found.

present than whiskies aged for shorter periods of time.

DISCUSSION

The effect of barrel aging whisky seems to be primarily an additive process in terms of sensory compounds present. In general, barrel aged whiskies contain sensory compounds with higher retention times compared to the sensory compounds found in their colorless, unaged counterparts (Tables 3 and 4). The sensory compound differences between them are mostly likely present due to contact with oak and the chemical reactions taking place in the barrel during residence time (Mosedale and Puech, 1998; Spedding, 2018). The results of this study are similar to the findings of Owens et al. (2016) (Table 5) and MacNamara et al. (2001) which showed compounds derived from wood were found in samples they analyzed. The colorless, unaged whiskies also lack complexity with regard their sensory profiles (Tables 3 to 5).

The Heaven Hill whiskies generally show an increase in the number or sensory compounds present as the residence time of the whisky in barrels increased. As the Heaven Hill whiskies all originate from the same grain bill, their sensory compound differences indicate residence time in a barrel is the variable responsible for the differences between younger whiskies and older whiskies.

A common trend when comparing whisky brands with a barrel aged and unaged counterpart is the increase in the number of sensory compounds within the barrel aged versions. A noticeable trend is the presence of syringaldehyde and vanillin lactoside among the barrel aged whiskies and are not present in their unaged counterparts. Thus, it is likely that the presence of these sensory compounds and their sensory contributions is due to barrel aging.

The following compounds were found among both barrel aged whiskies and their unaged counterparts: phenylethyl alcohol, ethyl caprylate, ethyl caprate, ethyl laurate, and ethyl palmitate. These compounds are likely to have been produced during the fermentation process, remain stable throughout distillation, and survive the barrel aging process. Ethyl caprylate and ethyl caprate were the only two compounds found consistently within all the whiskies analyzed in the study; barrel aged and unaged whiskies alike.

Cis-whiskeylactone is found in all the barrel aged whiskies except Maker's Mark, Elijah Craig, and Henry McKenna. It is possible this particular sensory compound is discriminated against by manufacturers in premium whiskies, such as those listed here, due to its sensory profile being "spicy" (Table 5). However, cis-whiskeylactone is not found in any of the unaged whiskies implying that it is a product of barrel aging.

Not all sensory compounds have a predictable or

Table 4. Compound presence in Heaven Hill whisky sample set that have increasing residence time in barrels.

Compound	Bourbontown Club	Cabin Still	Evan Williams	Evan Williams 1783	Evan Williams Single Barrel Vintage	Elijah Craig	Fighting Cock	Henry McKenna 10 Year	Larceny
Furfural	-	-	-	-	-	-	-	-	-
Isoamyl acetate	5.6	-	5.7	5.7	-	5.7	5.7	5.7	5.7
Ethyl hexanoate	7.4	7.4	7.4	7.4	7.4	7.4	7.4	7.4	7.4
Phenylethyl alcohol	10.5	10.5	-	10.5	-	-	10.1	-	-
Ethyl caprylate	11.1	11.1	11.1	11.1	11.1	11.1	11.1	11.1	11.1
Diethyl succinate	11.4	-	-	-	-	11.4	-	-	-
Octanoic acid	11.9	-	-	-	-	-	11.9	-	-
2-Phenylethyl acetate	-	13.0	-	-	-	-	13.0	-	-
cis-Whiskeylactone	15.8	15.8	15.8	15.8	15.8	-	15.8	-	15.8
Ethyl caprate	15.6	15.6	15.6	15.6	15.6	15.6	15.6	15.6	15.6
Decanoic acid	16.3	-	-	-	-	16.3	16.3	16.3	-
Vanillin Lactoside	17.7	17.7	-	17.7	-	-	-	-	-
Vanillin	-	-	17.7	-	17.7	17.7	17.7	17.7	17.7
Ethyl laurate	20.1	20.1	20.1	20.1	20.1	20.1	20.1	20.1	20.1
Isoamyl decanoate	-	-	21.2	-	-	-	21.2	21.2	-
Syringaldehyde	23.8	23.8	23.8	23.8	23.8	23.8	23.8	23.8	23.8
Ethyl myristate	-	-	24.4	-	24.4	24.4	24.4	24.4	24.4
Ethyl palmitate	28.3	-	28.3	-	28.3	28.3	28.3	28.3	28.3
Ethyl linoleate	-	-	-	-	-	-	31.5	-	-
Ethyl oleate	-	-	31.6	-	-	31.6	-	31.6	-

The values represent retention times and dashed lines mean the compound was not found.

intuitive presence among all the whiskies samples. Isoamyl decanoate appears in Buffalo Trace White Dog, but is not seen in its barrel aged counterpart, Buffalo Trace Bourbon (Table 3). It also appears in a few barrel aged whiskies from Heaven Hill, but not all of them (Table 4). Isoamyl decanoate also appears in unaged whisky and in 10-year-old whiskies (Henry McKenna 10 year-the oldest in our study), making it difficult to determine its origin in whisky production. Further refinement of the GC/MS methodology holds great possibility for the detection of compounds not present in this study.

Conclusion

GC/MS analysis of whisky samples from a variety of Heaven Hill bourbon brands, a variety of Maker's Mark products, a variety of Buffalo Trace products, and barrel aged and un-aged corn whiskies from Nelson's Greenbrier Distillery (Table 1) show sensory compound differences between barrel aged and unaged whiskies (Tables 3 and 4). Generally, sensory compounds present in the colorless, unaged whiskies are also present in their barrel aged counterparts. Those sensory compounds are a product of mashing and fermentation and have the stability to withstand the distillation process. Compounds appearing in the barrel aged whiskies, which were not present in the unaged counterparts, are the product of barrel aging. Also, the total number of sensory compounds present in barrel aged whiskies generally increases with residence time spent in barrels.

Specifically, cis-Whiskeylactone and syringaldehyde were found in most barrel aged versions, but not their unaged counterparts. Therefore, barrel aging is an additive process. Isoamyl decanoate provided inconclusive

Table 5. Sensory compounds of interest found in the whisky samples in this study.

Common name	Sensory descriptor
Isoamyl acetate	Sweet, fruity, banana, solvent
Ethyl hexanoate	Sweet, fruity, pineapple, waxy, green, banana
Phenylethyl alcohol	floral, rose, dried rose flower, rose water
Ethyl caprylate	-
Diethyl succinate	Mild, fruity, cooked apple, ylang
Octanoic acid	Fatty, waxy, rancid, oily, vegetable, cheesy
2-Phenylethyl acetate	Sweet, honey, floral, rosy with a slight green nectar fruity body and mouth feel
cis-Whiskeylactone	Spicy
Ethyl caprate	-
Decanoic acid	Unpleasant, rancid, sour, fatty, citrus
Vanillin Lactoside	-
Vanillin	Vanilla, vanillin, sweet, chocolate, creamy, spicy, phenolic, and milky
Ethyl laurate	-
Isoamyl decanoate	Fruity, wine, waxy, sweet, apricot, banana, brandy, pear, pineapple, mushroom, cognac
Syringaldehyde	Mild, plastic, woody, tonka, sweet
Ethyl myristate	-
Ethyl palmitate	-
Ethyl linoleate	Mild, fatty, fruit
Ethyl oleate	Fatty, oil, dairy, milky, waxy, tallow

The sensory descriptors are taken from other works synthesized by Owens et al. (2016).

results regarding the effects of barrel aging as its presence was widely inconsistent across the sample sets.

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CONFLICT OF INTERESTS

The authors have not declared any conflict of interests.

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