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GC/MS analysis of traditional barrel aged whisky and whisky treated with accelerated aging techniques

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Accelerated aging techniques are an ongoing frontier in the production of whisky because they do not require traditional barrel aging methods to mature. Whisky samples from the Jack Daniels family as well as whisky from Elkins Distilling Co. that used accelerated aging techniques were tested by direct injection Gas Chromatography Mass Spectrometry. Chromatograms of samples were analyzed against NIST mass spectra to develop and compare sensory profiles of whisky. Results obtained from known commercial brands were used to build a baseline of sensory profiles, providing a framework for whiskies produced by the company using accelerated aging techniques and used to show comparable compounds between the barrel-aged whiskies and whiskies aged by accelerated aging techniques. This study provides qualitative data on sensory compounds present in whisky that underwent accelerated aging techniques, including treatment by ultrasonic waves, injection of atmospheric oxygen, and maceration on pieces of used whisky barrels from well-known brands that were also analyzed in this study. The data showed that injection of atmospheric oxygen had no result on the compounds detected, that ultrasonic waves have some effectiveness on the compounds present, and that maceration of wood chips showed the greatest effect on the compounds present.

Key words: Whisky, whiskey, barrel aged, accelerated aging, distilling.

INTRODUCTION

Craft spirit distilleries are looking for ways to decrease the time to market for whiskies produced in order to be competitive with long-established distilleries in Kentucky and Tennessee, who produce most of the whisky made in the United States (USA, 2021). As seen by Lennon and Shohfi (2021), bourbon prices have been increasing 9.1% or more per year.

Using accelerated aging techniques on distilled spirits is attractive for several reasons. Not all distilleries are financially able to have space conducive to barrel storage (Weber, 1974). If aging spirits can be achieved in less

time by accelerated methods, the use of a barrel would be unnecessary (Chang, 2005). Also, faster aging methods would satisfy the increasing demand for whisky products worldwide (Rarick, 2015). As accelerated aging techniques can age whisky more quickly than a barrel, the demand for whisky products can be met more easily. During an interview with Bryan Davis of Lost Spirits Distillery regarding accelerated aging, Matt Pietrek of Cocktail Wonk (2015) quotes, "It can provide an invaluable tool to distillers to more confidently tailor the recipes and techniques they use to craft a target flavor

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profile,” implying that accelerated aged whiskies could be a custom-made product, perhaps different and more targeted than some traditional barrel aged whiskies.

Many of the methods used to accelerate aging of newly distilled whisky were pioneered on other alcoholic beverages such as sake, rum, and brandy (Chang, 2005; Pugliese, 2017). In particular, ultrasonic treatment of alcoholic beverages has been very popular recently and its effects have been reported here and in popular media (Pugliese, 2017). It has also been the subject of successful patents (Terressentia, 2016; Knapp, 2013). Ultrasonic wave treatments have the potential to produce whisky products comparable to barrel aged products given the success of ultrasonic wave treatments on improving the flavor of other alcoholic beverages (Matsuura, 1994; Chang and Chen, 2002; Shyr and Yang, 2016). A study by Chang (2005) found that the ultrasonic wave process creates an environment in which elevated temperature and pressure generated from the waves causes chemical polymers to break into sub-particles and then recombine within the whisky. Chang accomplished this by comparing compounds of an alcoholic rice beverage aged one year in a barrel, and a comparable alcoholic rice beverage aged by ultrasonic wave treatments (an accelerated aging process). Samples were comparable as they were produced using as close to similar beverage-making techniques as possible. It was found that an alcoholic rice beverage aged by 16 treatments of 20 kHz ultrasonic waves was comparable in sensory profile to an alcoholic rice beverage aged 1 year in a barrel (Chang, 2005). Additional research has shown that ultrasonic wave treatments have been effective in changing the chemical and sensory profiles of coffee-liquors, sake, and rice and corn wine (Chang and Chen, 2002; Chang, 2005; Shyr and Yang, 2016). Terressentia Corporation is exploring accelerated aging with TerrePURE, a process involving the use of ultrasonic energy, oxygen, and heat to remove impurities from spirits that negatively affect the taste (Terressentia, 2016). However, distilleries using accelerated aging techniques publicize little to nothing about their methods as it is proprietary technology.

Analyzing compounds in alcoholic beverage is problematic because ethanol is volatile and can overwhelm the instrumentation used depending on the type of analysis being conducted. Several methods exist for analyzing compounds present in whiskey that either involve the use of a solvent to extract the desired compounds or non-solvent methodologies. Analytical methods involving the use of solvents include: Comparative Aroma Extract Dilution Analysis (AEDA), Stable Isotope Dilution Assays (SIDA), and Odor Activity Values (OAVs). These methods are problematic because the compounds extracted are solvent-dependent such that solvent choice also relies on the specific compounds being studied. Of these methods, SIDA is likely the best because it reduces bias in compounds analyzed resulting from extraction, but it is limited to the compounds that are

extracted by the solvents. SIDA also reduces bias in compounds detected after extraction, but the method cannot be used to analyze compounds not extracted or compounds lost during extraction (Caldeira et al., 2007; Lahne, 2010; Kerley and Mufano, 2020).

Methodologies that do not include the use of solvents include: Phase Microextraction (SPME), Sample Dilution Analysis (SDA) and Gas Chromatography Mass Spectrometry (GC/MS) (MacNamara and Hoffmann, 1998; Plutowska and Wardencki, 2008; Lahne, 2010; Kerley and Mufano, 2020). Solid-Phase Microextraction (SPME) involves an adsorbent, coated, fiber which is submerged into the sample. The reproducibility of SPME along with being able to analyze a large number of samples are its main advantages. Its main disadvantage is that compounds of interest have varying absorption affinity depending on the coating used on the adsorption fiber. This can result in a failure to collect a representative sample of the compounds of interest. SPME is also costly thus being prohibitive for studies analyzing a wide range of compounds (Camara et al., 2007). Lahne (2010) showed Sample Dilution Analysis (SDA) to be a non-extractive, direct method of analyzing distilled spirits that provide equivalent results to AEDA while reducing analysis time and avoiding extraction bias.

This study uses GC/MS analysis of chemical compounds present in whisky to focus on a subset of compounds common in barrel-aged whisky (Table 1) and emphasizes comparison between the compounds present in traditional, barrel aged whiskies and whiskies that have been treated using accelerated aging techniques, including ultrasonic treatment. The compounds present in whiskey samples can be determined using Gas Chromatography Mass Spectrometry. Gas Chromatography Mass Spectrometry (GC/MS) separates and identifies components of complex chemical mixtures (Gates and Bull, 2008). Compound profiles are dependent on the type of whisky being tested (Piggott, 2016). Compound analysis for whiskey samples can be provided by GC/MS analysis and shows similarities among different whiskies for the major volatile congeners they contain as seen by Owens (2016), whose studies direct injection liquid chromatography along with Aylott (2010) who showed the utility of direct injection to analyze whisky. Russell and Stewart (2014) also found that of the spectrometric analysis methods available, chromatography offers advantages in speed, selectivity, and sensitivity. This research was conducted using GC/MS analysis of whisky samples aged by ultrasonic waves and wood chips at Elkins Distilling Co., a variety of Jack Daniel's Tennessee Whiskey products, and several whiskies from Elkins Distilling Co. that have not come into contact with wood.

While GC-MS analysis provides a framework for analyzing compounds present in whisky, little research has been published on products aged by accelerated aging techniques, especially whisky. For this research, we compared the compounds present between colorless,

Table 1. Main compounds of interest present in whisky samples from the study.^a

Approximate retention time (min)	Common Name, Molecular Formula, Mass (g/mol)
5.5	Furfural, C ₅ H ₄ O ₂ , 96.08
5.7	Isoamyl acetate, C ₇ H ₁₄ O ₂ , 130.19
7.4	Ethyl hexanoate, C ₈ H ₁₆ O ₂ , 144.21
10.5	Phenylethyl alcohol, C ₈ H ₁₀ O, 122.16
11.1	Ethyl caprylate, C ₁₀ H ₂₀ O ₂ , 172.27
11.3	Diethyl succinate, C ₈ H ₁₄ O ₄ , 174.19
11.9	Octanoic acid, C ₈ H ₁₆ O ₂ , 144.2
13.0	2-Phenylethyl acetate, C ₁₀ H ₁₂ O ₂ , 164.02
15.1	cis-Whiskeylactone, C ₉ H 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 ₈ H ₈ O 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 ₉ H 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

Source: Author

unaged whisky, whisky that has been treated with accelerated aging techniques, and whisky that has been traditionally aged by barrel method. It is suspected that whiskies having undergone barrel aged methods will yield a more chemically complex profile, which Mosedale and Puech (1998) found to be true as, "The extraction of compounds from the oak cask during barrel aging is a leading determinate of flavors representative of specific sensory-related compounds present."

METHODOLOGY

Collection of raw materials

Jack Daniel's Tennessee Whiskey has several products that have been treated differently: the original 'Old No. 7' which is their flagship, Gentleman Jack which has undergone 'charcoal aging' twice before bottling, and Single Barrel which is limited to less than four hundred 750 ml bottles per barreling. These products from Jack Daniel were also tested for their chemical compounds in this research. Jack Daniel is of particular interest because Elkins Distilling Co. uses chips of Jack Daniel's barrels as part of their accelerated aging treatments as of this writing.

Production of whiskey by traditional and accelerated aging techniques

Each stage of the whisky production process plays a role in the final product's character (Piggott, 2015). Understanding the whisky production process can help to explain which compounds are

available for reactions when undergoing mellowing. In whisky production, the first step is the processing of grains to release starch, which is then converted into fermentable sugar with the addition of enzyme-rich malted barley (Russell and Stewart, 2014). Fermentation then begins and alcohol is created from the addition of yeast. After fermentation is complete, distillation of the alcohol produced occurs. By vaporizing the alcohols off the fermented mash, the alcohols undergo a phase change from liquid to vapor. The vapors rise, travelling into a column surrounded by cool water called a condenser, which forces the vapors to condense back into a liquid. Separation of distilled liquid components is based on differences in volatility, or vaporization ability (Russell and Stewart, 2014). The resulting distillate is colorless. The colorless whisky is most often put into oak barrels for storage and maturation to mellow until it is ready for bottling. When whisky is mellowed in a barrel chemical polymers originate from the barrel itself. The extraction of compounds from the oak cask during barrel-mellowing is a leading determinate of flavors representative of compounds present (Mosedale and Puech, 1998).

Each part of the production process can be seen as a variable, and variables such as yeast strain, fermentation specifications, distillation equipment and processes, blending techniques, and the type and duration of time the whisky spends in a barrel ultimately lead to sensory compounds that determine the whisky's character (Russell and Stewart, 2014). It is therefore significant to study the chemical reactions and compounds produced in whisky mellowed by barrels in order to determine the desired compounds that need to be created through accelerated mellowing techniques to produce a comparable product.

Elkins Distilling Co. does not use traditional barrel methods to age some of the whisky they produce. Their whisky is aged using three accelerated aging treatments: injection of atmosphere, maceration on wood chips, and ultrasonic wave treatment (Figure 1). The injection of atmosphere is done using a VicTsing Ultra



Figure 1. Ultrasonic setup at Elkins Distilling Co. Shows wave generator, immersion bath with ultrasonic transducer, and stainless-steel reaction vessel containing whisky, wood chips, and air pump.
Source: Author

Table 2. Names of whisky samples analyzed during this study via GC/MS analysis.

Jack Daniel
 Jack Daniel's Single Barrel Select
 Gentleman Jack
 Elkins Colorado Whisky
 Elkins Unsonocated Colorado Whisky
 Elkins "Hearts" tank
 Elkins injected with Atmosphere

Source: Author

Silent High Out Energy Efficient Aquarium Air pump with 2 Air stone/2M Silicone Tube. Maceration on wood was done using 29.4 L of Jack Daniel's Tennessee Whiskey Barrel Smoking Chips, 2 L of toasted French oak 1 cm x 1 cm cubes, 2 L of 1 cm x 1 cm toasted American oak cubes, and 75.7 L of unaged white corn whisky at 75% ABV. The ultrasonic wave treatments were completed using a wave generator producing ultrasonic waves at 46 kHz at 1.8 Amps to an ultrasonic transducer. The process takes 10 days from mashing, fermentation, distillation, accelerated aging, to bottling. A sample of each step in their accelerated aging

processes was collected and analyzed to determine what effect each step (variable) has on the chemical compounds present in the resulting whisky.

GC/MS analysis

Unopened, commercially-available, barrel aged whiskies by Jack Daniel's brand were purchased from retail settings in liquor stores in Colorado and can be found in Tables 2 and 3. Elkins Distilling Co.

Table 3. Compound presence in Jack Daniel's sample set. The values represent retention times and dashed lines mean the compound was not found.

Compound	Jack Daniel	Jack Daniel's Single Barrel	Gentleman Jack
Furfural	-	-	-
Isoamyl acetate	5.7	5.6	5.7
Ethyl hexanoate	7.4	7.4	7.4
Phenylethyl alcohol	-	10.5	10.2
Ethyl caprylate	11.1	11.1	11.1
Diethyl succinate	-	11.3	-
Octanoic acid	-	-	-
2-Phenylethyl acetate	13.0	13.0	13.0
cis-Whiskeylactone	15.1	-	15.1
Ethyl caprate	15.6	15.6	15.6
Decanoic acid	-	-	-
Vanillin Lactoside	17.7	17.6	17.7
Vanillin	-	17.7	-
Ethyl laurate	-	20.1	-
Isoamyl decanoate	-	-	-
Syringaldehyde	23.8	23.8	23.8
Ethyl myristate	-	24.4	-
Ethyl palmitate	-	28.3	-
Ethyl linoleate	-	-	-
Ethyl oleate	-	-	-

Source: Author

provided samples (at least 50 mL of each) of their corn whisky from various stages in the accelerated aging process and results for these can be found in Tables 3 and 4. During this research, 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 to 50 ml vials, labeled. Upon analysis, a subset of each sample was transferred into a 3 mL capped glass vial and labeled. For each sample, 1 μ L was collected in a Hamilton gastight 25 μ L syringe with a cemented needle and sampled through the injection port of the gas chromatograph. The samples were then individually analyzed and separated through an Agilent 7890 GC column with a 5975a MSD using helium as a carrier gas (Buckeye Welding) at 0.5 mL/min, which can be seen in other spirit analysis done using GC-MS (Lynman and Zou, 2016). The Agilent column had wax specifications listed 30 m length, 0.25 mm internal diameters, and 0.25 μ m film thickness. Tank pressure was 60 psi. The mass detector in the analyses used an electron impact ionization (EI) with a single hyperbolic quadrupole mass filter. 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

Although there are a vast number of compounds to be tested for, as seen by Gonzalez-Robles (2018), only a small portion of compounds were tested for here due to program and equipment limitations. The following compounds were chosen as a sample list and found among the whiskies listed in Table 1: furfural, 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 (Figures 2 to 8). All the compound names are listed in Table 1.

The Jack Daniel's sample set has a seven compound difference between phenylethyl alcohol, diethyl succinate, cis-whiskeylactone, vanillin, ethyl laurate, ethyl myristate, and ethyl palmitate (Table 3). The Jack Daniel's Single Barrel Tennessee whiskey has the greatest number of compounds present with a total of 13 compounds. The Jack Daniel's Tennessee Whiskey has the fewest number of compounds present with a total of eight compounds. The compounds exhibited by Jack Daniel's Single Barrel Tennessee whiskey but not by Jack Daniel's Tennessee whiskey are phenylethyl alcohol, diethyl

Table 4. Compound presence in Elkins Distilling Co. Whisky sample set.

Compound	Elkins Colorado Whisky ^a	Elkins Unsonicated Colorado Whisky ^b	Elkins Sonicated "Hearts" ^c	Elkins Atmosphere ^d	Elkins "Hearts" tank ^e
Furfural	5.6	-	-	-	-
Isoamyl acetate	-	-	-	-	-
Ethyl hexanoate	7.4	-	-	-	-
Phenylethyl alcohol	-	10.5	10.5	10.5	10.5
Ethyl caprylate	11.1	11.1	11.1	11.1	11.1
Diethyl succinate	-	-	-	-	-
Octanoic acid	-	-	-	-	-
2-Phenylethyl acetate	-	-	-	-	-
cis-Whiskeylactone	15.9	15.8	-	-	-
Ethyl caprate	15.6	15.6	15.6	15.6	15.6
Decanoic acid	-	-	-	-	-
Vanillin Lactoside	17.7	17.7	-	-	-
Vanillin	-	-	-	-	-
Ethyl laurate	20.1	20.1	20.1	20.1	20.1
Isoamyl decanoate	21.2	-	21.2	21.2	21.2
Syringaldehyde	23.8	23.8	-	-	-
Ethyl myristate	24.4	24.4	24.4	24.4	24.4
Ethyl palmitate	28.3	28.3	28.3	28.3	28.3
Ethyl linoleate	31.5	31.5	31.5	31.5	31.5
Ethyl oleate	-	-	-	-	-

The values represent retention times and dashed lines mean the compound was not found. ^aElkins Colorado Whisky was steeped with Jack Daniel's barrel chip pieces while undergoing ultrasonic wave treatments for three days along with atmosphere. ^bThe Elkins Unsonicated Colorado Whisky steeped with Jack Daniel's Tennessee whiskey barrel chips, but no ultrasonic treatment or atmosphere. ^cThe Elkins Sonicated "Hearts" is undiluted whisky from the "hearts" tank mellowed with ultrasonic wave treatments for three days. ^dThe Elkins Atmosphere whisky is "hearts" whisky that has been injected with atmosphere and steeped with barrel chips. ^eThe Elkins "Hearts" tank is whisky produced from the final spirits run and is undiluted with no treatment of barrel chip.

Source: Author

succinate, vanillin, ethyl laurate, ethyl myristate, and ethyl palmitate.

The Elkins Distilling Co. sample set has an eight compound difference. The differing compounds include furfural, isoamyl acetate, ethyl hexanoate, phenylethyl alcohol, cis-whiskeylactone, vanillin lactoside, isoamyl decanoate, and syringaldehyde (Table 4). The Elkins Colorado Whisky has the greatest number of compounds present with a total of 12 compounds. The Elkins "Hearts" tank has the fewest number of compounds present totaling eight compounds. The compounds found in Elkins Colorado Whisky but not in Elkins "Hearts" tank are furfural, ethyl hexanoate, cis-whiskeylactone, vanillin lactoside, and syringaldehyde.

DISCUSSION

Barrel aging of whisky seems to be primarily an additive process through the spirit entering the wall of a cask and passing back to the bulk liquid while also carrying smaller compounds (Le Floch et al., 2015; Heinz and Elkins,

2019). Accelerated aging processes also appear additive but result in differing or additional compounds than those present in barrel aged whiskies, with some similarities. In general, barrel aged whiskies contain compounds with high retention times, which refers to the amount of time it takes from injection to detection of solute components, dependent upon parameters set within the GC-MS program. High retention times are typically an indication of longer chain compounds (Lynman and Zou, 2016). The unaged colorless whiskies mimic characteristics found in a barrel aged whisky, but are likely missing some longer chain compounds (Liebman and Scherl, 1949).

The complexity of whisky subjected either to accelerated aging or traditional barrel aging methods both have similarity as shown here. Accelerated aged whisky seems to be comparable to the complexity of barrel aged whiskies when looking at their compound breakdowns, and this could contribute to the fact that at times during the production process, accelerated aged whisky samples (as seen here) were treated with retired Jack Daniels whiskey barrels. In other words, the compounds present in Elkins accelerated aged whiskies

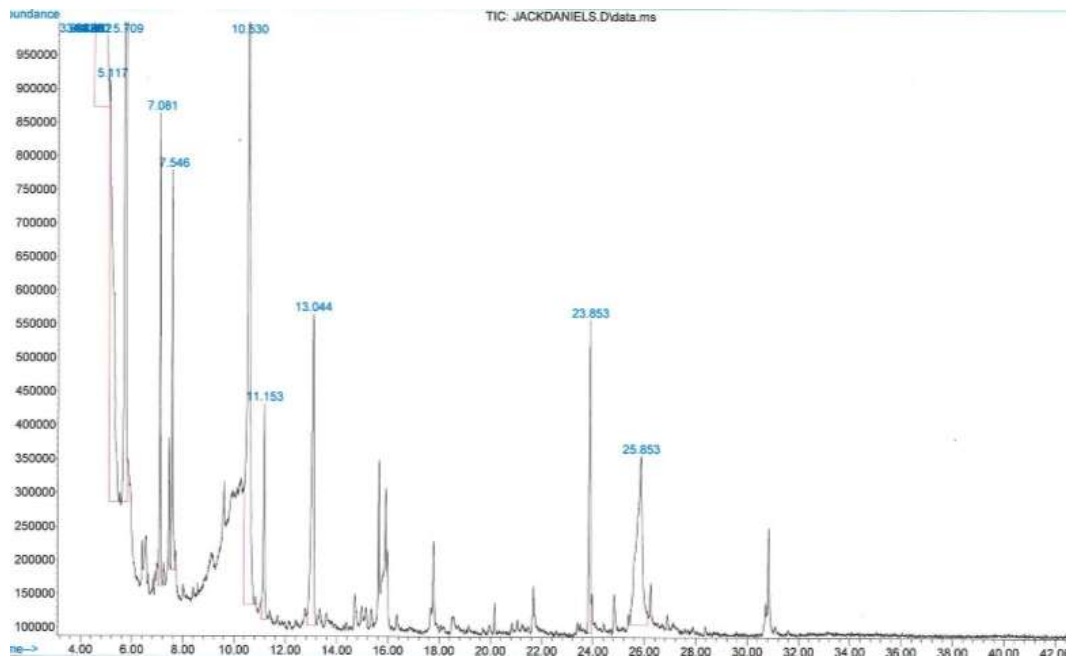


Figure 2. Total Ion Chromatogram (TIC) showing compounds present in Jack Daniels. Numbers in blue represent retention times.
Source: Author

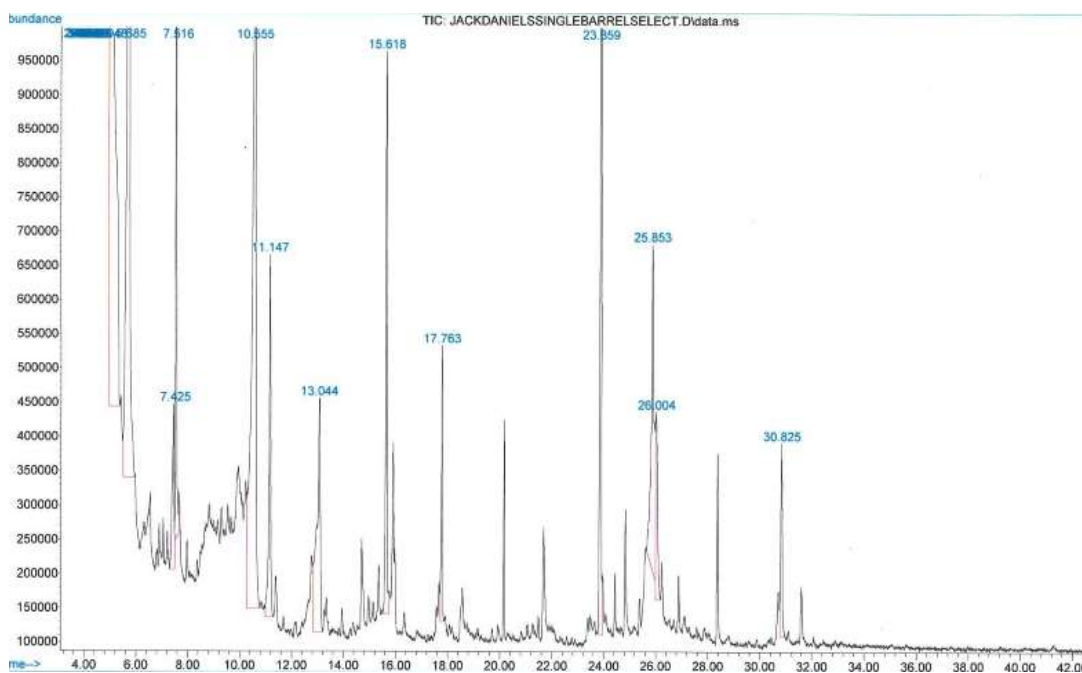


Figure 3. Total Ion Chromatogram (TIC) showing compounds present in Jack Daniels Single Barrel Select. Numbers in blue represent retention times.
Source: Author

are found mainly due to barrels (in the use of chips or cubes) used in their maturation process. These same compounds were found in the barrel-aged whisky whose

barrel would eventually become part of the accelerated aging process. Specifically, Elkins Colorado Whisky uses Jack Daniel's Tennessee Whiskey barrel chips as part of

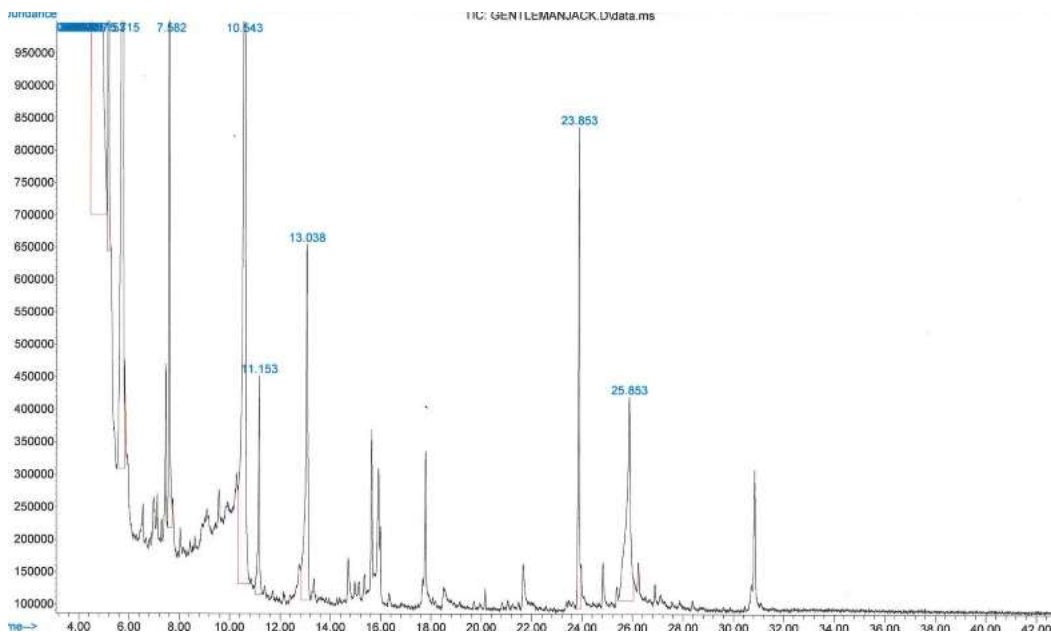


Figure 4. Total Ion Chromatogram (TIC) showing compounds present in Gentleman Jack. Numbers in blue represent retention times.

Source: Author

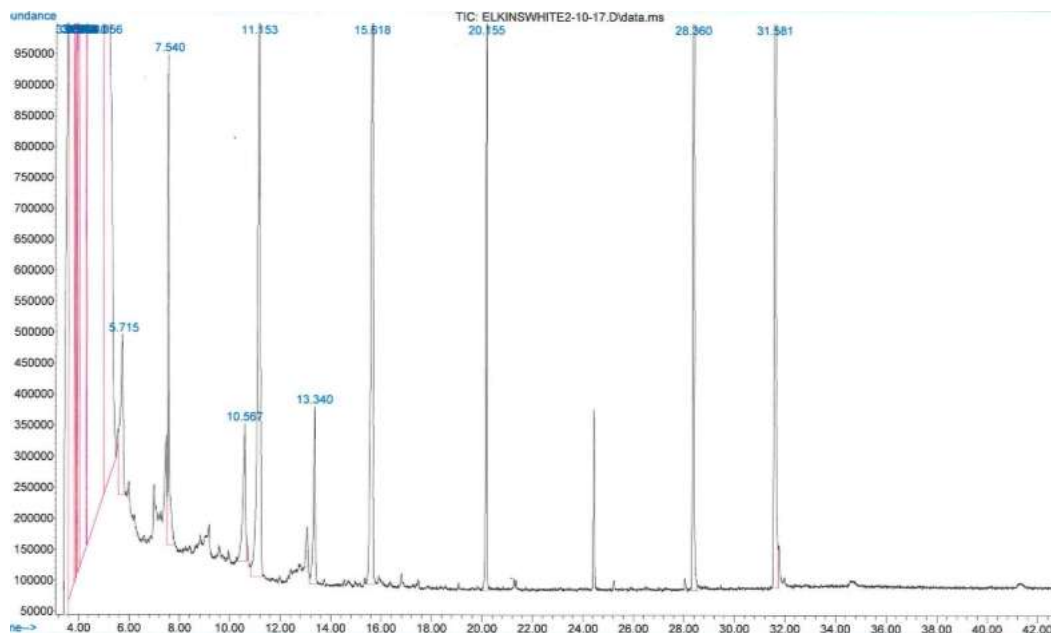


Figure 5. Total Ion Chromatogram (TIC) showing compounds present in Elkins White Corn Whisky. Numbers in blue represent retention times.

Source: Author

their accelerated aging process and the compound similarities between Elkins Colorado Whisky and Jack Daniel's Tennessee Whiskey are generally consistent. It was found that Jack Daniel's whiskey samples yield a

more complex profile, which agrees with Reazin (1981) suggesting a marker for aging exists when increased compound concentration are found within an aging spirit inside a barrel.

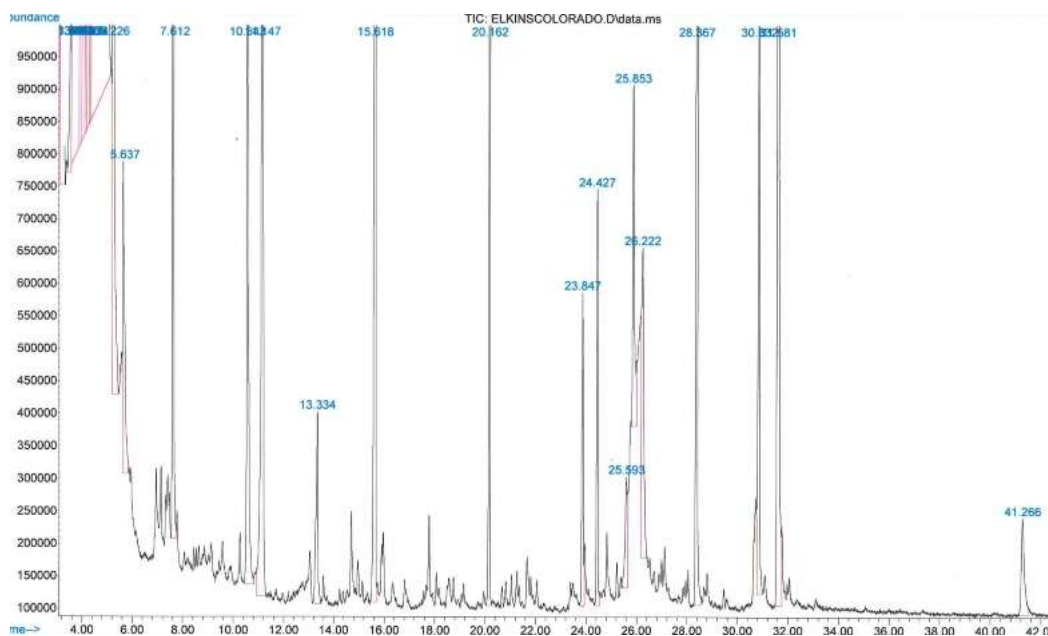


Figure 6. Total Ion Chromatogram (TIC) showing compounds present in Elkins Colorado Whisky. Numbers in blue represent retention times.
Source: Author

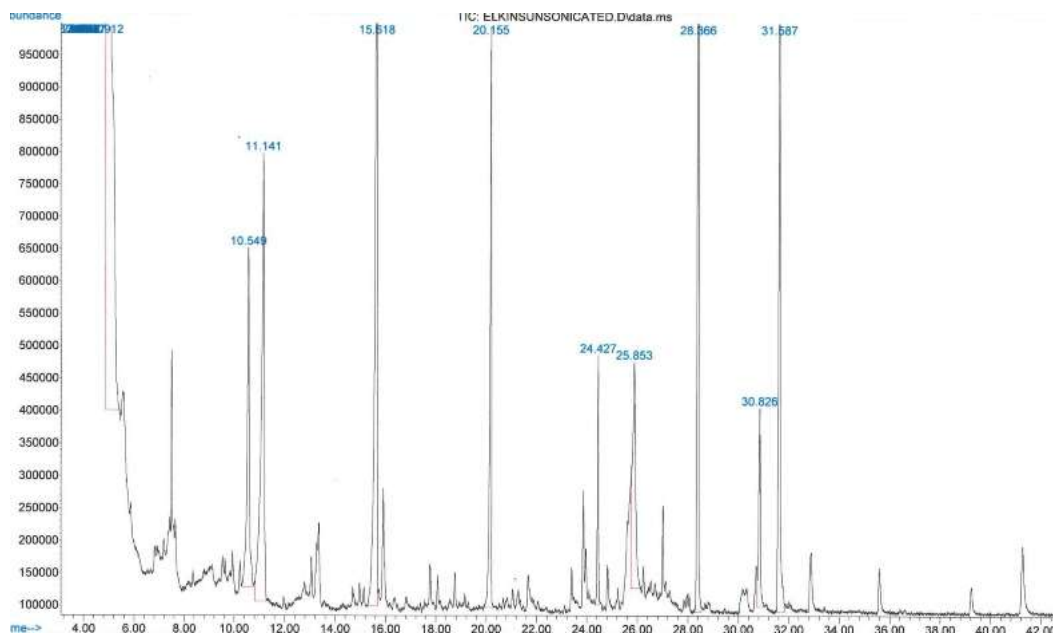


Figure 7. Total Ion Chromatogram (TIC) showing compounds present in Elkins Whisky Unsonicated. Numbers in blue represent retention times.
Source: Author

A trend among whisky samples with a barrel aged and unaged version is the increase in compounds within the barrel aged version. The presence of syringaldehyde and vanillin, for example, among the barrel aged versions and

not their unaged versions was noticed across Elkins whisky samples (Table 4). Ethyl hexanoate was also only present in whiskies (studied here) that had an interaction with toasted or charred wood, and not present in any

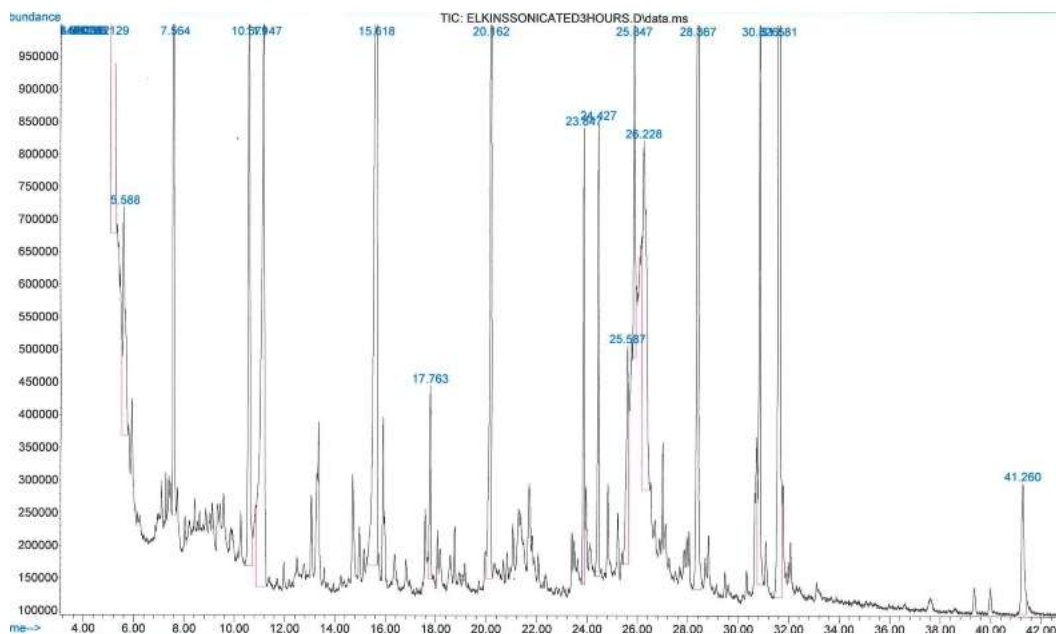


Figure 8. Total Ion Chromatogram (TIC) showing compounds present in Elkins Whisky Sonicated 3 Hours. Numbers in blue represent retention times. Source: Author

unaged samples. Aldehydes and esters contribute to the flavor of barrel aged products and can be used as aging markers (Liebmann and Scherl, 1949). Thus, it is likely that the presence of these compounds and their sensory contributions is due to barrel aging or the interaction with retired barrels.

The following compounds were found among all whisky samples tested shown in Table 4: phenylethyl alcohol, ethyl caprylate, ethyl caprate, ethyl laurate, and ethyl palmitate. These compounds are likely to have been produced during the fermentation process and seem to have remained stable throughout distillation. There are several esters and fusel alcohols that will form during fermentation and remain throughout the maturation process (Sun, 2013).

cis-Whiskeylactone, vanillin lactoside, and syringaldehyde are types of ellagitannin compounds and are easily extracted from wood by water-alcohol mixtures (Viriot, 1993). cis-Whiskeylactone is found in all the barrel aged whiskies except for Jack Daniel's Single Barrel Tennessee Whiskey, which is either due to a literal compound difference or sensitivity issues regarding the method of GC/MS usage. Regardless, cis-Whiskeylactone is not found in any of the unaged whiskies implying it is a product of barrel aging.

Not all compounds have a predictable or intuitive presence among all the whisky samples. Isoamyl decanoate appears in unaged colorless Elkins corn whisky and Elkins Colorado Whisky. However, an important note is the milder temperature at which wood is toasted versus the temperature at which it is charred. A

larger array of compounds are available within toasted products (Russell, 2014; Rogerson, 2016). It is likely that isoamyl decanoate is a product of the toasted cubes used during Elkins's accelerated aging process. Furfural gave inconclusive results as it was only found in the Elkins Colorado Whisky sample and none of the Jack Daniel's samples tested, which could be due to method error or sensitivity issues within the GC/MS. As stated by Spedding (2018), there is still much to understand about control within these systems.

Analysis of Elkins Colorado Whisky (accelerated aged) shows similarities to the compounds present within barrel aged whiskies. The following compounds are present in Elkins Colorado Whisky shown Table 4: ethyl hexanoate, cis-whiskeylactone, vanillin lactoside, and syringaldehyde. Steeping with Jack Daniel's Tennessee Whiskey barrel chips, but not ultrasonic wave treatment, yielded the same list of compounds just mentioned. Given that the Elkins whisky process involves toasted wood cubes and the Jack Daniels whiskey process does not, it is likely that the differences in compound extraction can be attributed to the depth and type of heat treatment used on the wood types. Rogerson (2016) states, "Toasted staves extracted more oak compounds than charred staves for specific oak compounds. However, for overall color, total soluble phenolics, and pH level, charred and toasted staves equally extracted more after 3 months than at time 0." As the whisky comes into contact with the wood, merely soaking without the use of sonication, reactions begin and compounds are exchanged, suggesting the use of ultrasonic waves alone have less of an impact

than physical connection (and time) between whisky spirit and wood.

Generally, there is an increase in the number of compounds within Elkins' whiskies at each step of the accelerated aging process (Table 4). However, there are no compound differences between the Elkins "Hearts" tank and Elkins Atmosphere, suggesting that oxidation without wood present is either not occurring or undetectable using this GC/MS method. Oxygen and oxidation reactions play a valuable role in barrel aging as they allow for the production of acetaldehyde from ethanol, which then cascades into further reactions impacting flavor, aroma, and phenolic composition (Spedding 2017a, Spedding, 2017b, Spedding, 2018). Without the formation of acetaldehyde, it's likely the sensory profile of the finished whisky would be lacking in complexity or flavor.

The fact that no compound differences occur between the "Hearts" tank, the sample treated only with atmosphere, or the sample treated only with ultrasonic wave treatments indicate that those steps of the accelerated aging process are either ineffective at causing changes in the unaged whiskies, that they require wood as an organic material from which to exchange compounds and form esters, or that the GC/MS methodology used in this study is not sensitive enough to detect the compound differences that occur. As shown in Tables 3 and 4, the chemical complexity of samples grows as their production process involves the interaction of wood.

As previously mentioned, there are compounds present in Elkins Colorado Whisky that are also present in barrel aged whiskies. Chang (2005) shows that compounds resulting from traditional aging techniques (barrel aging) can also be replicated using ultrasonic wave treatments. Thus, it is possible that the compounds present in Elkins Colorado Whisky are the result of ultrasonic wave treatments. However, all the compounds present in Elkins Colorado Whisky are present in all Jack Daniel's products. Elkins Colorado Whisky is steeped on Jack Daniel's barrel chips. It is therefore reasonable to deduce that compounds found in Jack Daniel's that are found in Elkins Colorado Whisky are most likely the result of steeping Elkins Colorado Whisky on Jack Daniel's Barrel chips.

A consideration to be made related to the compounds present among whiskies sampled here are limitations of the GC/MS methodology and the methodology's ability to detect all compounds present.

Conclusion

Generally, compounds present in the unaged colorless whiskies are also present in the barrel aged and accelerated aged whisky samples. Those compounds are a product of mashing and fermentation and have the structural stability to withstand the distillation process.

Compounds appearing in the barrel aged whiskies not present in the unaged colorless counterparts are most likely the product of barrel aging and suggest that the interaction with charred, toasted, or treated wood, plus the addition of time and a controlled environment, is the primary source. Therefore, barrel aging is an additive process and the most significant part of the whisky production process in terms of sensory compounds being formed.

From the results here, steeping unaged whisky with Jack Daniel's wood chips or toasted cubes seemed to have the most significant effect on increasing the compounds present of the finished product. Pumping atmosphere into the whisky, along with ultrasonic wave treatment, do not appear to influence the compounds present in the samples as detected by this GC/MS methodology. However, Elkins Colorado Whisky contains furfural, which is not present in any of the other whiskies sampled. This suggests that the presence of furfural is the result of the cumulative effects of the accelerated aging process or a sensitivity issue with the GC/MS instrument or methodology.

Isoamyl decanoate provided inconclusive results regarding the effects of aging as its presence was widely inconsistent across the sample sets suggesting the possibility of issues with GC/MS sensitivity or methods used.

Additional compounds of significant finding are cis-whiskeylactone, syringaldehyde, and vanillin in both the Elkins Colorado sample and Jack Daniel's traditional barrel aged samples. The presence of these suggests barrel aging, or the interaction with such retired barrels, as the primary additive process in the formation of potent and desirable compounds.

It is the opinion of these researchers, based on the data here, that ultrasonic wave treatments are effective in producing compound differences from unaged, colorless whisky to whisky aged by accelerated methods with the addition of wood. However, it is also the opinion of these researchers that accelerated aging techniques have more ground to cover in terms of their ability to produce a comparable whisky to traditional barrel aged products of similar mash bill. Whereas the data presented here suggests ultrasonic wave treatments have some effect on the compounds present in an accelerated aged whisky, the data still shows barrel aged whiskies to be of higher complexity in terms of their compounds available to experience.

CONFLICT OF INTERESTS

The authors have not declared any conflict of interests.

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