UNDERSTANDING THE COMPLEX AROMA CHEMISTRY OF PREMIUM AGED RUMS

BY

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DISSERTATION

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Abstract

Rum is produced by the fermentation of sugar cane juice, syrup or molasses, followed by distillation and then aging in oak barrels. Rum is a highly diverse distilled spirit because it has a somewhat simple standard of identity, with the only requirement being that it must be produced from sugar cane or its byproducts. The lack of regulation allows for manufacturers to pick and choose from a variety of manufacturing practices when they are creating their rum. Rum cannot only be made from different types of starting materials but variation exists in type of yeast and bacteria used for fermentation, length of fermentation, distillation apparatus used, barrel type and length of maturation. In today's drink and bar culture, rum is experiencing a resurgence. High quality rums, typically those aged at least five years and regarded as best of their class, are being compared with fine spirits, such as Bourbon, Brandy, Cognac and Scotch. Therefore, the goal of the study was to better understand the complex flavor chemistry of rum, including its aroma composition and the effect of ethanol on flavor perception, with a main focus on premium aged rums. Nine rums were evaluated consisting of two mixing rums (Bacardi Superior [BW], Bacardi Gold [BG]) and seven premium rums (Appleton Estate V/X [AE], Appleton Estate Extra [AE12], Ron Abuelo: Añejo 7 years [RA7], Diplomatica Reserva Exclusiva [DR12], El Dorado 12 year old [ED12], Ron Zacapa (Centenario) XO: Solera Gran Reserva Especial [RZ], Dictador XO Insolent [DX]).

Identification of the odor-active compounds in the nine rums by gas chromatography-olfactometry (GCO) and GC-mass spectrometry (GC-MS) analysis yielded 59 odor-active regions containing 64 odor-active compounds. Aroma extract dilution analysis (AEDA) provided a ranking of the potency of odorants. The most potent rum ordorants, although not necessasarily present in every rum, were found to be acetal (melon), 2-/3-methyl-1-butanol (chocolate), β-damascenone (applesauce), 2-phenethyl alcohol (roses), *cis*-whiskey lactone/4-methylguaiacol (sweet, coconut-like), eugenol (spicy, clove), sotolon (curry, maple-like), syringol (smoky, spicy), (*E*)-isoeugenol (floral, clove), vanillin (vanilla, sweet-like), ethyl vanillate (vanilla, sweet-like), and syringaldehyde (vanilla). Thirty-four of the compounds identified by GCO and AEDA were quantitated by stable isotope dilution analysis. Differences among the samples included the absence of 4-ethylguaiacol and eugenol in BW and the presence of ethyl vanillin in only DR12 and DX. The mixing rums and DX were found to have the lowest concentrations of all compounds quantitated in the rums. The quantitation results were

converted to odor activity values (OAVs) to gain a better understanding of the importance of the compounds to the overall aroma of the rum. Twenty-six compounds were found to have OAVs >1 in at least one rum. Fifteen compounds had OAVs >1 in all nine samples including 2-methylpropanal, acetal, 3-methylbutanal, 2-methylbutanal, ethyl 2-methylpropanoate, ethyl butanoate, ethyl 2-methylbutanoate, ethyl 3-methylbutanoate, 3-methyl-1-butanol, 2-methyl-1-butanol, ethyl hexanoate, β-damascenone, guaiacol, *cis*-whiskey lactone and vanillin.

In order to characterize the sensory differences among rum products a rum flavor lexicon was created through the use of web-based material. This is the first lexicon to be created for rum as well as the first to use web-based materials for the lexicon development. The final lexicon consisted of 147 terms sorted into 22 categories. Descriptive sensory analysis was then conducted to verify the rum flavor lexicon and to quantitate the sensory differences among nine rums previously evaluated by analytical measures. Thirty-three of the 38 terms used to evaluate the rums were found on the flavor wheel, validating that the lexicon contained terms relevant to the sensory evaluation of rums. Twenty-three sensory attributes were found to be significantly different among rums. Two rums, DX and DR12, were characterized by having higher intensity ratings for brown sugar, caramel, vanilla and chocolate aroma, caramel, maple and vanilla aroma-by-mouth, and caramel aftertaste compared to the other seven rums. Sensory profiles of the other seven rums were similar to one another.

Descriptive analysis was also conducted to gain insight into the effect of ethanol on flavor perception. Two rums, RA7 and DR12, were evaluated at three different dilution levels: straight rum, 1:2 dilution with water, and a 1:2 dilution with 40%ABV. Dilutions of rum with water, while hypothesized to alter the flavor profile of rum, yielded similar profiles to straight rum, except with slightly lower attribute intensity ratings. However, dilution with 40% ethanol did significantly change the profile of rum and also had the lowest intensity rating in the dilution series for most attributes.

Finally, chemometric analysis was conducted to correlate the sensory and analytical data using principal component analysis consisting of quantitation, OAV and flavor dilution factor data. Correlations between sensory evaluations with either quantitation or OAV data explained the most variation among rums, accounting for 68.6% or 65.5%, respectively. Results indicate the changes in vanilla, caramel, maple and chocolate aromas are driven by vanillin and ethyl vanillin. Additionally, roasted aroma is defined by an absence of compounds rather than increases in concertation of any

specific aroma compounds. Overall, the main differences between mixing and premium rums is the concentrations of compounds, with mixing rums having lower concentrations of all compounds. Differences in concentration and ratios of compounds relative to each other seem to be the driving forces behind the difference in flavor perception among rums. These findings help to better characterize rum as a category and articulate the differences that exist among rum categories. Sensory evaluation of rum provides insight into how rums are perceived by the human senses and the developed flavor lexicon will aid in communication between all levels of rum production and consumers.

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Chapter 1: Introduction

For over 350 years, rum has been produced by the fermentation of sugar cane juice, syrup or molasses, followed by distillation and then aging in oak barrels. Historically, rum production has been associated with the Caribbean, which is still a major sugar cane and rum producing region. Because it has a somewhat simple standard of identity, rum is a highly varied product, with the only requirement being that it must be produced from sugar cane or its byproducts. The limited definition allows for a breadth of product variety that is not typical of other spirit classes. Classifications of rum include white, gold, aged, over-proof, light, heavy, industrial and Agricole. Additionally, wide variation exists within these categories as well. The lack of a rigid standard of identity and limited regulation allows for manufacturers to pick and choose from a variety of manufacturing practices when they are creating their rum. Not only can rum be made from different types of starting materials but variation also exists in types of yeast and bacteria used for fermentation, length of fermentation, distillation apparatus and method used, barrel type and length of maturation. As a result, currently over 1,500 individual rums are on the market, not including the hundreds of flavored and spiced rums also being produced. In today's drink and bar culture, rum is experiencing a resurgence. High-quality rums, typically those aged at least five years and regarded as best of their class, are being compared with fine spirits, such as Bourbon, Brandy, Cognac, and Scotch. The average consumer is starting to regard rum as more than just a spirit to add to mixed drinks such as daiquiris or mojitos.

Even with the recent cultural interest in rum, scientific research evaluating rum flavor as it pertains to the category as a whole is lacking. Other distilled spirits, particularly Scotch and Irish whiskeys, have research centers dedicated to the study of the complex chemistry of these beverages. Numerous studies have been performed identifying the volatile compounds present in rum (Batiz & Rosado, 1978; Bober & Haddaway, 1963; Leppänen, Denslow, & Ronkainen, 1979; Liebich, Koeing, & Bayer, 1970; Maarse & tem Noever de Brauw, 1966; Ng, 1999; Pino et al., 2002; Pino, 2007; ter Heide, Schaap, Wobben, de Valosis, & Timmer, 1981; Timmer, ter Heide, Wobben, & de Valois, 1971; Wobben, Timmer, ter Heide, & de Valois, 1971). These studies primarily focused on identifying all of the instrumentally detectable volatile compounds and provided no indication of the odor-activity or importance of the compounds identified to overall rum flavor. Only in the last

decade have studies begun to identify the odor-active compounds present in rum through the use of gas chromatography-olfactometry (GC-O) (Burnside, 2012; de Souza, Vásquez, del Mastro, Acree, & Lavin, 2006; Franitza, Granvogl, & Schieberle, 2016a, 2016b; Monsalve, Lopez, & Zapata, 2016; Pino, Tolle, Gök, & Winterhalter, 2012). The limiting factor of these studies is that only one or two rum samples were evaluated, with the exception of Monsalve's evaluation of six Colombian rums, and minimal if any product information was given for the rums, making it almost impossible to repeat the studies. As a result, it is difficult to comment on the overall distinguishing attributes of rum as a beverage class. This is especially important in the case of rum since production is highly variable due to the simplicity of its standard of identity and diversity within the product class. Therefore, flavor analysis of several different types of rums needs to be conducted.

Limited sensory analysis has been conducted on rums as well. Aroma profile analysis has been used in a few studies to gain a basic understanding of the sensory attributes perceived in the samples and was later used for comparison of the created models (Franitza et al., 2016a, 2016b). Sensory analysis has also been used to compare rum and cachaça samples through descriptive analysis panels (de Souza et al., 2006; Magnani, 2009). The most comprehensive study on rums was done by Gomez (2002), who developed a preliminary lexicon for rum aroma followed by a descriptive analysis panel evaluating nine rums. Rum is typically characterized as caramel, spicy (clove-like), fruity, and vanilla. Sensory studies focusing on understanding rum as a class and the differences which exist between and within the different categories still need to be performed. Additionally, being able to articulate and describe the aroma perceptions experienced when drinking rum is important. This is essential not only for the manufacturer to market their product but also for the consumer to be able to verbalize what they are experiencing as they drink rum. Currently, no flavor wheel or lexicon has been published for rum. Flavor wheels have been created for a variety of other distilled spirits including brandy, cognac, and whiskey. While these wheels may contain many terms useful for describing rums, they are missing certain attributes that are more nuanced and specific to rum. Development of a flavor lexicon that encompasses many different types of rum would help to articulate the flavor differences of rums within a single category as well as among different styles of rum.

While rum flavor is largely driven by the odor-active constituents, the overall sensory perception can also be affected by the alcohol concentration, as well as non-volatile compounds. Consumers drink rum in a variety of ways including straight, "on the rocks" (with ice), or diluted with water. Similarly,

it is normal practice in the whiskey industry to dilute samples to ~23% alcohol by volume (ABV) before accessing the aroma for blending purposes. The given explanation for this practice is to reduce the pungency of ethanol experienced at high alcohol concentrations. In addition to reducing pungency, studies have also shown that changing the water/ethanol ratio also can significantly impact the solubility and partition coefficients of the flavor compounds (Aznar, Tsachaki, Linforth, Ferreira, & Taylor, 2004; Boothroyd, Linforth, & Cook, 2012; Taylor et al., 2010; Tsachaki et al., 2008; Tsachaki, Aznar, Linforth, & Taylor, 2006; Tsachaki, Linforth, & Taylor, 2005). These changes are dependent on if the beverage is evaluated in a static or dynamic system. This work has primarily been done in model wine matrixes (12% ABV), and no studies have examined the effect of higher ethanol concentrations on alcoholic systems under dynamic conditions. Nevertheless, none of this work has been linked with sensory data to understand if consumers perceive changes in the overall aroma as a result of changes in ethanol concentration. Establishing if there are perceivable sensory changes caused by differences in ethanol concentration should be established before further physiochemical interactions are investigated.

The central hypothesis of this study is that premium aged rums, while produced using a variety of methods, still have a defining set of aroma characteristics caused by a unique combination of flavor compounds that set these rums apart from those of lower quality, or so-called mixing rums, and that ethanol concentration plays an important role in the perception of overall rum flavor. Therefore, the goal of the study was to better understand the complex flavor chemistry of rum, including its aroma composition and the effect of ethanol on flavor perception; with a main focus on premium aged rums.

This objectives of this study were to 1) analyze a variety of premium aged rums, those consistently rated by experts as being the best of the class, and several lower quality or mixing rums, to identify the key aroma compounds, 2) quantitate the key aroma compounds in each of the nine rums and compare the odorant compositions of the premium rums with those of lower quality or mixing rums, 3) develop a rum flavor lexicon for sensory evaluation of premium aged rums, 4) evaluate the sensory attributes of the nine rum samples to validate the rum lexicon as well as to correlate the sensory attributes of the rums with the analytical findings from aims one and two, and 5) evaluate the importance of ethanol concentration on the perception of flavor in premium aged rums through sensory studies.

Rum is an important distilled spirit in the global alcoholic beverage market with an ever increasing market share. The goal of this study was to better understand the flavor chemistry of rum products as a whole, primarily premium rum, in terms or analytical and sensory evaluation. Increasing the understanding of the flavor chemistry of rum products will help to better define rum as a category and articulate the differences that exist between rum categories. Sensory evaluation of rum will begin to establish how rums are perceived by consumers and a developed flavor lexicon will aid in communication between all levels of rum production and consumers.

This research is novel in variety of ways as it is the first to 1) identify and quantify the odor-active compounds for more than two rum samples in the same study, 2) focus on the difference between mixing and premium rums, 3) create a flavor lexicon for rum, 4) develop a flavor lexicon using web-based material rather than a traditional descriptive analysis panel, 5) evaluate the changes in sensory perception as a results of changes in ethanol concentration, and 6) use chemometrics to correlate sensory attributes with analytical analyses of rum.

1.1 References

Aznar, M., Tsachaki, M., Linforth, R. S. T., Ferreira, V., & Taylor, A. J. (2004). Headspace analysis of volatile organic compounds from ethanolic systems by direct APCI-MS. *International Journal of Mass Spectrometry*, *239*, 17–25. http://doi.org/10.1016/j.ijms.2004.09.001

Batiz, H., & Rosado, E. (1978). A Single Column Gas Chromatographic Method for the Direct Trace Analysis of High Boiling Components in Rums. *The Journal of Agriculture of University of Puerto Rico*, *62*(4), 330–343.

Bober, A., & Haddaway, L. W. (1963). Gas Chromatographic Identificaon of Alcoholic Beverages. *Journal of Gas Chromatography*, *1*(12), 8–13.

Boothroyd, E. L., Linforth, R. S. T., & Cook, D. J. (2012). Effects of Ethanol and Long-Chain Ethyl Ester Concentrations on Volatile Partitioning in a Whisky Model System. *Journal of Agricultural and Food Chemistry*, *60*, 9959–9966. http://doi.org/10.1021/jf3022892

Burnside, E. E. (2012). *Characterization of Volatiles in Commercial and Self-Prepared Rum Ethers and Comparison with Key Aroma Compounds of Rum*. University of Illinois at Urbana-Champaign. Retrieved from https://www.ideals.illinois.edu/handle/2142/34368

de Souza, M. D. C. A., Vásquez, P., del Mastro, N. L., Acree, T. E., & Lavin, E. H. (2006). Characterization of Cachaça and Rum Aroma. *Journal of Agricultural and Food Chemistry*, *54*, 485–488. http://doi.org/10.1021/jf0511190

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*, 637–645. http://doi.org/10.1021/acs.jafc.5b05426

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*, 9041–9053. http://doi.org/10.1021/acs.jafc.6b04046

Gómez, S. M. (2002). *Rum Aroma Descriptive Analysis*. Louisiana State University. Retrieved from http://etd.lsu.edu/docs/available/etd-1114102-110301/

Leppänen, O., Denslow, J., & Ronkainen, P. (1979). A Gas Chromatographic Method for the Accurate Determination of Low Concentration of Volatile Sulfur Compounds in Alcoholic Beverages. *Journal of the Institute of Brewing*, *85*, 350–353.

Liebich, H. M., Koeing, W. A., & Bayer, E. (1970). Analysis of the Flavor of Rum by Gas-Liquid Chromatography and Mass Spectrometry. *Journal of Chromatographic Science*, *8*, 527–533. Retrieved from http://chromsci.oxfordjournals.org/content/8/9/527.short

Maarse, H., & tem Noever de Brauw, M. C. (1966). The Analysis of Volatile Components of Jamaica Rum. *Journal of Food Science*, *31*(6), 951–955. Retrieved from http://onlinelibrary.wiley.com/doi/10.1111/j.1365-2621.1966.tb03275.x/full

Magnani, B. D. (2009). *Estudo Comparativo das Características Sensoriais do Rum e da Cachaça Estudo Comparativo das Características Sensoriais do Rum e da Cachaça*. Universidade Estadual Paulista.

Monsalve, J. O., Lopez, C., & Zapata, J. (2016). Characterization of aroma compounds in Colombian rums by HS-SPME-GC-MS-O. *Revista Colombiana de Química*, *45*(2), 48–54. http://doi.org/http://dx.doi.org/10.15446/rev.colomb.quim.v45n2.60406.

Ng, L.-K. (1999). Analysis of Vodkas and White Rums by SPME-GC-MS. In J. Pawliszyn (Ed.), *Applications of Solid Phase Microextraction* (pp. 393–406). Cambridge, UK: The Royal Society of Chemistry. http://doi.org/10.1039/9781847550149-00393

Pino, J. A. (2007). Characterization of rum using solid-phase microextraction with gas chromatography–mass spectrometry. *Food Chemistry*, *104*, 421–428. http://doi.org/10.1016/j.foodchem.2006.09.031

Pino, J. A., Tolle, S., Gök, R., & Winterhalter, P. (2012). Characterisation of odour-active compounds in aged rum. *Food Chemistry*, *132*, 1436–1441. http://doi.org/10.1016/j.foodchem.2011.11.133

Pino, J., Martí, M. P., Mestres, M., Pérez, J., Busto, O., & Guasch, J. (2002). Headspace solid-phase microextraction of higher fatty acid ethyl esters in white rum aroma. *Journal of Chromatography A*, *954*, 51–57.

Taylor, A. J., Tsachaki, M., Lopez, R., Morris, C., Ferreira, V., & Wolf, B. (2010). Odorant Release

from Alcoholic Beverages. *ACS Symposium Series*, *1036*, 161–175. http://doi.org/10.1021/bk-2010-1036.ch012

ter Heide, R., Schaap, H., Wobben, H. J., de Valosis, P. J., & Timmer, R. (1981). Flavor Constituents in Rum. In *The Quality of Foods and Beverages* (pp. 183–200).

Timmer, R., ter Heide, R., Wobben, H. J., & de Valois, P. J. (1971). Phenolic Compounds in Rum. *Journal of Food Science*, *36*, 462–463.

Tsachaki, M., Aznar, M., Linforth, R. S. T., & Taylor, A. J. (2006). Dynamics of flavour release from ethanolic solutions. *Developments in Food Science*, *43*, 441–444. http://doi.org/10.1016/S0167-4501(06)80104-4

Tsachaki, M., Gady, A.-L., Kalopesas, M., Linforth, R. S. T., Athès, V., Marin, M., & Taylor, A. J. (2008). Effect of Ethanol, Temperature, and Gas Flow Rate on Volatile Release from Aqueous Solutions under Dynamic Headspace Dilution Conditions. *Journal of Agricultural and Food Chemistry*, *56*, 5308–5315. http://doi.org/10.1021/jf800225y

Tsachaki, M., Linforth, R. S. T., & Taylor, A. J. (2005). Dynamic Headspace Analysis of the Release of Volatile Organic Compounds from Ethanolic Systems by Direct APCI-MS. *Journal of Agricultural and Food Chemistry*, *53*, 8328–8333. http://doi.org/10.1021/jf051202n

Wobben, H. J., Timmer, R., ter Heide, R., & de Valois, P. J. (1971). Nitrogen Compounds in Rum and Whiskey. *Journal of Food Science*, *36*, 464–465.

Chapter 2: Literature Review

2.1 Introduction

Rum and sugar cane have been major products and exports of the Caribbean since the region was discovered by the Western world. Over the course of centuries, rum has evolved from the initial harsh, unpleasant spirit to a sophisticated beverage that can be served neat similar to aged whiskeys and Scotch. Even though rum has been studied since the early 20th century, literature about the aroma of rum is limited.

2.2 History and Production of Rum

Rum is a distilled spirit made from sugar cane and commonly associated with the Caribbean. The federal standard of identity for rum states:

"Rum" is an alcoholic distillate from the fermented juice of sugar cane, sugar cane syrup, sugar cane molasses, or other sugar cane by-products, produced at less than 190° proof in such manner that the distillate possesses the taste, aroma, and characteristics generally attributed to rum, and bottled at not less than 80° proof; and also includes mixtures solely of such distillates. (Labeling and advertising of distilled spirits, 27 C.F.R. § 5.22, 1969).

As can be seen from the definition above, there are no manufacturing regulations imposed on rum other than it must come from sugar cane. This is different from other distilled spirits, which are highly regulated. Bourbon for instance must be at least 51% corn, distilled to not more than 160° proof, placed into the barrel for aging at no more than 125° proof and then aged for at least 2 years in charred new oak barrels (Labeling and advertising of distilled spirits, 27 C.F.R. § 5.22, 1969). Rum has none of these limitations. The spirit can be distilled by a variety of methods, aged in any type of barrel, and the age label is not standardized but rather set by each country of production. As a result, rum is a highly variable spirit.

Rums can be sorted into a number of categories including white, gold, aged, black, over-proof, flavored, and spiced (Ayala, 2001; Fahrasmane, 2014). White rums are usually unaged or aged for only a short amount of time in oak barrels or stainless steel vats and then filtered through charcoal to remove any trace of color that may have developed during aging. Gold rums are typically aged for 1 to 3 years and have a light amber color. Aged rums are matured in wood barrels anywhere from 3 to 20 plus years and acquire a darker brown color due to the extended time in the barrel. Rums within this category are those typically regarded as higher quality or premium rums. Black rums are those that have excess caramel added to give them a darker color and therefore color is an indicator that the rum has been aged for an extended period of time. Overproof rums are bottled at higher alcohol contents, typically anywhere from 125° to 160° proof (62 - 80%ABV). Finally, flavored and spiced rums have flavored extracts or fruits added to them after distillation and before bottling, or have spices added prior to aging, respectively. Since fruits, flavors, and spices are added to change the overall flavor of these rums, these products should not be compared with rums aged in the traditional manner.

Rum can additionally be categorized based on the sugar cane product used for fermentation. When sugar cane juice is the starting material, the final rum is labeled as *rhum agricole* (Ayala, 2001; Fahrasmane, 2014). This is a production style that is usually found in the French Caribbean, specifically the island of Martinique. If the rum is produced instead from molasses, it is categorized as *rhum industriel*. This French term is typically not used for marketing purposes outside of the French Isles (Fahrasmane, 2014).

Rums can also be categorized as light, heavy and traditional rums. Light rums are both light in color and light in flavor and are produced using continuous distillation (Fahrasmane, 2014). Light rums are traditionally produced on the islands of Cuba, the Dominican Republic, Haiti, Puerto Rico, and the Virgin Islands (Jeffers, 1997). Heavy rums are those distilled using pot stills and fermented for a longer period of time with both yeast and bacteria to produce a more complex and aromatic rum. Jamaican rums are typically produced in this style (Fahrasmane, 2014). Traditional rums are those in between, which have a medium flavor intensity (Fahrasmane, 2014).

Rum is an interesting and complex spirit, encompassing a variety of different flavor profiles and production styles. Likewise, the history of the spirit may be as complex and vague as the spirit itself.

History of Sugar

It word be inadequate to discuss the history of rum without first making a brief mention of the history of sugarcane, the main ingredient and standard of identity for rum. The origin of sugar cane (*Saccharum officinarum*) goes back at least 10,000 years where it is thought to be first cultivated in New Guinea (Foss, 2012; Macinnis, 2002). From there cultivation expanded to the other islands of East Asia where it is still produced today. Sugar cane then traveled to India and is known to be cultivated there by 500 B.C. as it is referenced in several texts (Macinnis, 2002). Sugar cane eventually made its way to the Middle East although how and when this occurred is not documented. As sugar cane became established in the Middle East, cultivation and production began to prosper (Williams, 2005). Sugar cane requires a lot of water, a warm and sunny environment to grow, and a large labor force to process the cane into sugar. The Arabs were the first to introduce irrigation to sugar cane production, which allowed for more continuous and even water to be delivered to the crop. Arabs were also the first people to use slaves as the labor force for sugar cane production, and slave labor would continue to be tied to sugar cane production until the late 1800's.

During this time, the Muslims in the Middle East began trading sugar with Europeans. The first written record of sugar trade with the West dates back to 95 AD (Foss, 2012). This was the begging of a long history of Europeans trading with the Middle and Far East for sugar. It would not be until the 1400's that Europeans would decide to cultivate sugarcane on their own, constructing sugar plantations in the colonies they were acquiring, instead of paying the high prices for purchasing sugar from the East.

The first to do this were the Spanish, who first planted sugar cane on the Azore islands off the western coast of Africa. This was a good place for sugar cane cultivation although the winds blowing out to sea from the Sahara made it difficult to travel down the coast to transport the sugar cane. From there as the European mother countries began to settle the islands as colonies in the Caribbean sugar cane plantations began to spring up on those. Sugar cane was brought to the Caribbean by Christopher Columbus on his second voyage to the West Indies in 1493 (Blue, 2004; Macinnis, 2002). Sugar cane plantations began soon after, with records of plantations in the Caribbean dating back to the early 1500's (Foss, 2012). By the middle of the 1600's sugarcane plantations were prospering in the West Indies.

History of Rum

Although sugar cane was first cultivated in the Pacific Islands, it was not transformed into the distilled beverage that we know today until some several thousand years later and half way around the globe. One of the earliest mentions of a fermented beverage being produced from sugar cane is recorded in the Indian Vedic texts around 2000 B.C. (Nicol, 2003). The two main alcoholic beverages referred to were called 'sidhu' and 'gaudi', made from cane juice and molasses respectively. While these are the first recorded beverages produced from sugar cane, they were much different than the refined distilled spirit that we know today as rum. Distillation would not be discovered until sugar reached the Middle East and the beverage would not make its final transformation into rum until sugar began being cultivated in the Caribbean.

Early sugar cane plantations focused solely on sugar production and refinement. The major by-product of the process, molasses, as essentially a waste product (Blue, 2004). It had no inherent value to the plantation owners and was typically fed to animals in their feed or used as fertilizer. It wasn't until the discovery that molasses could be fermented and distilled into a potable beverage that molasses was seen as a valuable material.

No one is quite sure when or where molasses was first converted into rum. The most likely story is that a slave dipped a spoon or cup into a bucket of molasses that had been sitting out for several weeks. While siting the molasses had fermented and mixed with water, becoming the first crude form of rum (Blue, 2004). Rum was most likely a drink for the slaves when it was first produced, and it is unlikely that the Plantation owners would have made mention of the crude spirit their slaves were drinking before it has begun to be refined. The birthplace of rum is typically associated with Barbados, even though this was probably not the first or only island in the Caribbean producing rum at this time (Foss, 2012). This most likely because the earliest written mention of rum is in a 1651 letter written by a visitor to the island of Barbados. In his letter he mentions, "The chief fuddling they make in the island is Rumbullion, alias Kill-Divil, and this is made of sugar canes distilled, a hot, hellish, and terrible liquor" (Blue, 2004). This 'terrible' liquor would over time be refined into a spirit desired by both the colonies and Motherlands. Early references to rum also include *eau de vie de cannes* (Smith, 2005), guildive and taffia (Fahrasmane, 2014).

There is quite a bit of lore and uncertainty that also surrounds how rum got its name. Some claim rum is derived from 'brum', a cane based drink that has been made by the Malays for thousands of years (Blue, 2004). Some think that rum comes from the Dutch whose seaman had drinking glasses called 'rummers'. Another common thought is that rum is an abbreviation of the Latin word for sugar, Saccharum (Blue, 2004; Mariani, 1983; Nicol, 2003). There is also some thought that the work rum comes from the Spanish word for the spirit 'ron', as the Spanish were distilling a sugar cane beverage in the Caribbean before the British set foot there (Blue, 2004; Nicol, 2003). However, it is more likely that the Spanish and French adopted the English term rum and subsequently translated it to 'ron' and 'rhum' (initially rome), respectively (Barty-King & Massel, 1983; Smith, 2005). The most likely theory is that rum is a shortening of the Devon word 'Rumbullion', which means a great tumult (Barty-King & Massel, 1983; Blue, 2004; Mariani, 1983; F. H. Smith, 2005). This has more merit as the first mention of rum, quoted above, used this term to describe the beverage. By the 18th century the spirits produced from sugar cane and molasses were commonly called rum (Nicol, 2003).

As rum was being produced and refined in the Caribbean, the main ingredient, molasses, was also being exported to New England where rum production quickly became established (Foss, 2012). Rum production in New England began in the mid 1600's and there are records of several distilleries having been built in Long Island and Boston by the 1660s. Because molasses was so cheap to import, a gallon of molasses could be turned into a gallon of rum and sold for over five times the initial price. As a result, rum became a staple beverage for the New England colonies. Comparing New England rum to those produced in the West Indies, New England rum was by far the inferior product. Due to the colder climate of New England the aging process took longer and so the rum that was imported from the Caribbean was always of higher quality and higher value. Rum became such a mainstay of the economy in the American colonies that it was even used in place of currency. There are many records of carpenters and workers being paid rum as part of their salary as well as records of rum being treated and bartered between colonists.

As a means to try and control the where colonies were buying their goods from, Great Britain implemented several taxes under the Acts of Trade and Navigation. These Acts included the Molasses Act of 1733, the Gin Act of 1736, and the Sugar Act of 1764 which placed taxes on products such as sugar, molasses and rum production. This was done to ensure that the colonists bought their supplies from British merchants or stopped producing rum, which lead to smuggling of

molasses from Spanish and French merchants (Nicol, 2003). It is thought that the taxation of molasses and sugar for rum production is one of the indirect causes of the American Revolution.

The New England colonists were also instrumental in the formation of the Triangle Trade. Sugar production is a labor intensive process and requires a large work force to plant, maintain and harvest the sugar cane. In the early days, English slaves were the predominant workforce on the plantations but by the late 1600's African slaves were the majority of plantation workers (Gately, 2008). These slaves were brought to the Caribbean through an economic trade system known as the Triangle Trade. Molasses and sugar produced in the Caribbean islands was traded to New England and in New England the molasses was made into rum. The rum was then shipped to West Africa to trade for African slaves who were then shipped to the Caribbean to work on the sugar cane plantations (Foss, 2012). Britain was also a key player in the Triangle Trade, with goods from the Caribbean being shipped to Liverpool and Bristol rather than New England. The triangle trade continued in the Caribbean until the 1800's when slavery started to be abolished.

Moving into the 19th century, rum production and popularity declined due to many factors. Contributing to this was the Civil War, the creation of bourbon, the abolishment of rum rations in the Navies (U.S. and Britain) and prohibition. Rum, however, has been recently experiencing a renaissance. The introduction of Bacardi and Captain Morgan are responsible for helping to increase the popularity of rum (Delavante, 2004). Today some premium rums are seen as being on par with traditional top-shelf spirits such as Scotch and whiskey (Miles, 2015; Padgett, 2017). The recent interest in rum is evident by the publications of several new books on the topic including Rum – The Manual (Broom, 2016), Rum Curious: The Indispensable Tasting Guide to the World's Spirit (Minnick, 2017), and The Curious Bartender's Rum Revolution (Stephenson, 2017).

Current Rum Market

A rum renaissance has been claimed for the past several years (Eberle, 2014; Freedman, 2016; Irani, 2013; Padgett, 2014, 2017; Ward, 2015). Premium rums are commonly compared with other high-end distilled beverages such as Scotch and cognac (Fahrasmane, 2014; Freedman, 2016; Miles, 2015; Padgett, 2017). While growth has occurred in the rum market, it has not seen the explosive growth that was expected (Ward, 2015). However, experts in the field still predict growth in the rum market in the coming years (Shoup, 2017).

From 2000 to 2010 the rum category increased 40% (by volume sales) (Hopkins, 2015). However since 2012 rum has seen a slight decline (Shoup, 2017). From 2014 to 2015 rum sales declined 0.8%. Additionally, only 39% of rum sales were premium products, meaning most consumers are purchasing lower quality mixing rums ("Global Rum Insights - Market Forecasts, Product Innovation and Consumer Trends," 2016). In the United States total rum consumption declined 1.5% (by sales volume) during the same time period, while premium rums rose 2.8% (in volume) (Swartz, 2016).

As of 2015, rum comprised 5.6% of the global spirit's market (by value) (*Global Spirits*, 2016). In the United States, rum makes up 13.7% of the market value, trailing vodka (30.5%) and whiskey (23.6%) (*Spirits in the United States*, 2016).

Rum is still predicted to grow over the next several years particularly in the premium rum category (Business Monitor International Research, 2016). One of the factors expected to drive this trend is that global rum manufacturers are expected to increase their portfolio to include premium rums. Nevertheless, other analysists predict that the global rum market will decline in the next five years. The Rum Global Insights group predicts that rum consumption will drop 0.5% per year ("Global Rum Market Set to Decline Over the Next Five Years," 2017). However declines are mostly expected for mixing rums, and premium rum sales are still expected to increase ("Global Rum Market Set to Decline Over the Next Five Years," 2017).

Currently, the top 5 rum brands worldwide are Mc.Dowell's No.1 Celebration, Bacardi, Tanduay, Captain Morgan and Havana Club ("Global Rum Market: Leading Brands Based on Sales Volume 2015," 2017). Additionally, the top rum market in the world is India (404.2 million liters), followed by the United States (241.9 million liters), the Philippines (169.7 million liters), the Dominican Republic (54.7 million liters) and France (36 million liters) according to 2012 data (Hopkins, 2014).

Overall, it is difficult to predict what consumers will like and when their preference in their distilled spirit of choice will change. Rum is noted as an underexploited category (Hopkins, 2015; Ward, 2015), while rum's versatility is commonly referred to a strength of the category, suggesting lots of room for growth ("Global Rum Insights - Market Forecasts, Product Innovation and Consumer Trends," 2016; Ward, 2015). The increase interest and trend for brown spirits, particularly whiskey also bodes well for rum, exposing people to the realm craft spirits that are available (Ward, 2015).

Additionally, as the price of premium whisk(e)y continues to rise, consumers may turn to rum as a cheaper alternative of similar quality (Eberle, 2014; Freedman, 2016; Shoup, 2017).

2.3 Rum Production

There are many factors which affect the final flavor of the rum. These include things such as sugar cane variety, maturity of the sugar cane when harvested, the proof of the molasses used in the fermentation as well as the type of yeast, the type of distillation performed, the type of barrel that the final spirit is aged in and how the final product is blended.

The first step in the production of rum is the collection of the raw materials. Rum is typically produced from molasses, a by-product of sugar production. Other forms of sugar cane can be used to produce rum such as cane syrup or sugar cane juice.

Sugar Production

When the sugar cane is ready to be harvested, the cane fields are set on fire to sterilize the soil and help limit moisture loss once the grass has been cut. The sugar cane can be harvested mechanically, but it is usually done by hand, an extremely labor intensive process, as it is thought to produce a superior final product. The sugar cane is then transported to the mill by truck or canal. Most sugar cane is processed within 24 hours after harvesting to minimize moisture loss and conversion of the sucrose to glucose and fructose by invertase or into a polysaccharide, dextran, by the soil contaminant *Leuconostoc mesenteroides* (Nicol, 2003). When the cane reaches the factory, the leafy tops are removed and the stalks are then cut and milled to release the can juice. Every hundred tons of sugar cane harvested will yield ten tons of cane juice with a 10% sucrose w/w concentration. This cane juice is the first by-product of sugar cane that can be used for rum production.

The cane juice will then move through a series of evaporators producing cane syrup which can also be used in rum production (Nicol, 2003). The syrup is then left to crystallize and is finally centrifuged to separate the sugar crystals from the remaining syrup. The crystals will be further refined and sold as sugar, and the syrup left over once all the sucrose has crystallized out is known as blackstrap molasses. This is the starting material for most rums. Many factors contribute to molasses

quality, including unfermentables, gums, nitrogen, and sulfur, with sugar content being the most important.

Fermentation

Traditional rum production relied on wild fermentation, using yeasts and bacteria present in the air and naturally occurring in the molasses. Today most fermentations are done using pure cultures of yeast. The most common yeast used in rum fermentation is *Saccharomyces cerevisiae*, although *Saccharomyces bayanus* and *Schizosacharomyces pombe* are also used (Nicol, 2003). Dunder can also be employed to increase the production of volatiles during fermentation, as it consists of wild yeasts and anaerobic bacteria. The dunder is the residue from wash distillations which are left to ferment in a dunder pit before being added to the fermentation vat or the wash before distillation (Rogers, 2014). The bacteria that is present in the dunder produce volatile compounds that would not be formed during a yeast only fermentation. The use of dunder in combination with *Schizosacharomyces* yeast is typically used for the production of heavy rums (Fahrasmane, 2014).

The molasses is added to a fermentation tank and diluted to 16 - 20 degrees Brix for fermentation (Nicol, 2003). The molasses needs to be diluted to reach the optimal sugar concentration for yeast to ferment effectively without being stressed or having too much sugar available. During the filling of the tank, the yeast inoculum is also added. The temperature of the vat is closely monitored and maintained at 30 – 33°C. Fermentations left on their own would approach temperatures over 40 °C, which would kill the yeast and hinder the alcohol production. The fermentations tanks are typically cooled by circulating water through heat exchangers (Nicol, 2003). During the fermentation process, the yeast convert glucose into ethanol and carbon dioxide.

During the initial fermentation (first 24 hours) a wash of 5-7% alcohol is produced. While fermentation can be completed in as few as 24 hours, darker rums can be fermented for up to three weeks (Blue, 2004). The shorter fermentation results in a lighter rum and longer fermentations produce heavier rums that have higher concentrations of esters and other congeners.

Distillation

The wash is then distilled, increasing the alcohol concentration from 7% to 80 -94% ABV. There are two main types of distillation apparatus used in rum production. These include pot and continuous distillation.

The using of pot stills is the traditional method of rum distillation. This can be a single pot system (Figure 2.1) or a double pot distillation system where two pot stills are connected in tandem. In this technique the rum is added to a large wooden vat or copper pot, above which sits a copper shoulders and swan neck which empties into a retort (Nicol, 2003). One of the reasons copper has been used for stills is that it helps to remove off flavors by binding sulfur compounds (Fahrasmane, 2014). On top of the retort is a rectifier, which is connected through another tube to the condenser (Nicol, 2003). Some simpler designs do not include the retort and rectifier portion.

At the beginning of the distillation, the pot is filled with ~6,000 L of wash and the retort is filled with low wines remaining from the previous distillation at ~51-52% ABV (Nicol, 2003). The still is heated by either steam or bagasse, the unusable portion of the sugarcane stalk. As the ethanol and volatiles evaporate from the pot, they then travel through the swan neck into the retort where the vapors collect and are known as low wines. The ethanol will then evaporate from the retort and pass through the rectifier, essentially a condenser consisting of a container of water held at 45-50°C which copper tubes pass through carrying the rum vapors. When the ethanol and volatiles leave the rectifier they enter the condenser, from which the rum is collected at ~85% ABV. Rum is collected from the condenser until the distillate reaches 43%ABV, at which point it is directed back to the low wines. The low wines collected from the distillation are then used during the next distillation. Pot distillation is slow process and the extended time the rum spends being heated for distillation also allows for the reactions and formation of aroma compounds (Fahrasmane, 2014).

The other and more common technique is continuous distillation. These can be both single or multiple column systems, with single column distillations used for the production of traditional rums and multiple column distillations used for lighter body rums (Fahrasmane, 2014). Continuous distillation is capable of producing ten times more rum than a traditional pot still and is therefore favored by larger companies that receive molasses from several sugar manufacturers (Nicol, 2003).

Depending on the type of still used for distillation, different final products can be achieved. The pot still is known for producing heavier rum with a higher amount of congeners. Column stills, on the other hand, have the ability to alter which fractions are collected for the final product and can therefore alter the level of various volatiles present in the final beverage.

Maturation

The aging of rums is one of the most important aspects of production. The length of time spent in the cask dictates the type of rum that is being produce, with white rums only being aged for a couple of years or less, gold rum for 2-5 years and aged rums for 5–20+ years. The type of barrel used will greatly influence the final flavor profile. Rum, unlike other aged spirits such as Bourbon which has strict laws regulating the types of barrels that can be used, can be aged in any type of barrel that the manufacture chooses (Foss, 2012). This can include new oak barrels, used barrels that have been previously used for beverages such as sherry, wine, whiskey, bourbon, cognac, etc. Additionally, barrels that have been used several times may be better suited for light rums while newer casks should be used for aged rums (Nicol, 2003).

The barrels are typically filled with rum at 83-85%ABV. Once filled, the barrels will be stored in a warehouse until the desired organoleptic qualities have been achieved. Some rums will be transferred to several casks during maturation, each imparting a different flavor profile to the final beverage. Other rums may be blended after several months, and then the blend will continue aging until ready to be bottled.

The solera aging system is another way to blend and age the rum (Figure 2.2). This style of maturation is typically associated with the aging of sherry and thought to produce consistent quality and character (Gonzáles Gordon, 1990; Reader & Dominguez, 2003). Casks on the bottom or solera level, are those that hold the oldest rums. These casks are partially emptied, and the rum removed is sent to bottling. Rum from the previous level or criaderas is removed to fill the solera level. The rum removed from the barrels is first transferred to a tank where the rum from all the casks is blended before being added to the next level. This continues for each criaderas, and then the youngest criaderas is then filled with new rum. The amount of rum removed from each level, the frequency of transfer between levels, and the number of criaderas is dependent on the producer. The levels do not need to be stacked on top of each other and may even be stored in different warehouses.

In terms of maturation, it is also important to consider the climate that rums are aged in. Unlike many of the distilled spirits made and aged in America or Europe which is a considerably cooler climate, rum is aged in the hot tropical environment of the Caribbean. The hot and humid climate (27-32°C and 75-90% humidity consistently) increases the speed of maturation (Foss, 2012; Nicol, 2003). Therefore if the same spirit was aged it in Scotland and the Caribbean, the aging process would progress much quicker in the Caribbean making it easier to achieve a well-aged rum in a shorter amount of time. The downside of this is that because of the hotter climate and increased humidity there is a larger loss of rum to evaporation over time.

During the maturation process, the rum interacts with both itself and the barrel it is being aged in (Fahrasmane, 2014). First, wood constituents are extracted from the barrel into the rum. Additionally, the lignin extracted from the barrel as well as alcohols present in the rum can undergo oxidation. And finally, new volatile compounds can form from the interactions of various compounds in rum.

Blending and Bottling

When maturation is completed, the rum will be dumped from the cask and transferred to the bottling facility. Along the way, the rum will be diluted to its final strength of 40-43% ABV. White rum will be sent through charcoal filtration systems before bottling to remove any color that may have developed during aging. This process can also remove some of the volatiles from the spirit as well.

Almost all rums that are produced and sold are blends. It is very uncommon to see a rum which is from a single cask. Most rums are a blended from numerous casks which consists of rums which have aged for different amounts of time (Blue, 2004). The blending of rum allows for a consistent product that is reproducible, something that is not achievable in a single barrel. Most distilleries have a master blender who is in charge of creating and maintaining the specific blend for a brand or line of rums.

2.4 Flavor Research on Rum

While rum has been produced since the 1600's, it was not until the early twentieth century that rum flavor started to be analyzed scientifically. Although rum has been studied academically for the past 70+ years, there is still a relatively small body of literature regarding the flavor characteristics of rum. Rum is first mentioned in the 1939 paper entitled "The Aroma of Rum" (Arroyo, 1939), in which the author discusses the general composition of rum. Even though rum had been produced for hundreds of years by this time, the author makes it a point to note that they understand the difficulty in producing rum and that creating a consistent product even within the same factory was very difficult. However, they were beginning to gain a better understanding of the impact of processing on the final aroma. Arroyo notes that the two most important factors contributing to the final rum aroma are the compounds formed during fermentation, which remain after distillation, and those formed during the maturation process. A limiting factor in their ability to understand the aroma of rum was the primitive analytical techniques available at the time. At this point in time, only classes of compounds could be distinguished, such as esters, alcohols, and phenolics and not individual components.

As rum research moved into the 1960's and 1970's, gas-chromatography became more prevalent and allowed researchers to identify for the first time the individual components of rum. There was extensive research during this time into understanding the volatile composition of rum, but there are many limitations on this research and how it can be applied today.

Initial research was performed by the U.S. Customs laboratory, trying to determine how to distinguish authentic spirits from those that had been doctored or counterfeited (Bober & Haddaway, 1963). Gas chromatography paired with a flame ionization detector (FID) was used to compare chromatograms of different products. This technique also allowed them to quantify a small number of compounds including n-propyl alcohol, isobutyl alcohol, d-amyl alcohol, isoamyl alcohol, n-butyl alcohol, furfural, ethyl hexanoate, and ethyl octanoate. However, many of the peaks on the chromatogram could not be identified at that time.

It was not until 1966 and introduction of gas chromatography paired with mass spectrometry that many of the unknown compounds in rum were first identified (Maarse & tem Noever de Brauw, 1966). Maarse & tem Noever de Brauw examined the composition of Jamaica Rum and were able to

identify over 50 unique compounds. In order to identify the volatiles present in these samples, the rum was extracted with pentane-ether, concentrated, and then fractionated by running the extract through silica gel. Each fraction was then analyzed for the individual compounds using techniques such as mass spectrometry, nuclear magnetic resonance, infrared spectroscopy, and comparison to known standards (Liebich, Koeing, & Bayer, 1970; Maarse & tem Noever de Brauw, 1966).

During this time, a number of studies focused on identifying a key group of compounds present in rum. These studies included identifications of ethyl esters of fatty acids (Stevens & Martin, 1965), phenolic compounds (Timmer, ter Heide, Wobben, & de Valois, 1971), nitrogen compounds (Wobben, Timmer, ter Heide, & de Valois, 1971), high boiling constituents (Batiz & Rosado, 1978), and sulfur compounds (Leppänen, Denslow, & Ronkainen, 1979). Additionally, ter Heide and colleagues attempted to identify all of the volatile compounds present in rum (ter Heide, Schaap, Wobben, de Valosis, & Timmer, 1981). This lead to the identification of over 400 compounds, 214 of which were identified for the first time in rum. While this study shows the complexity of rum flavor, the main problem with this research is that the volatile components were identified regardless of the whether they were odor active or not. Additionally, compounds with low odor thresholds that would have an impact on the aroma but would not be present in high enough concentration to be detected were missed by this method of identification.

There are a number of other disadvantages to these studies that make the data collected difficult to use in a meaningful way. First, technology has significantly advanced in the last 40 year, both in terms of more sensitive and robust instrumentation, as well as overall knowledge of extraction techniques and understanding of flavor in general. Additionally, many of the early methods created artifacts, compounds that are not present in the actual samples but are formed during the extraction or analysis. A huge disadvantage to studying the aroma chemistry of rum is that there was no way to identify which of the volatile components where odor-active. None of the studies report odors for individual compounds. A common practice of the time was to smell the fractions for aroma. This only informed the scientist that a compound in that fraction was odor-active but they were not able to determine which specific compounds were responsible for the odors. Furthermore, there is no way to rank how individual compounds contribute to the overall aroma of rum.

As flavor research moved into the 1990's, rum analysis saw the introduction of solid phase microextraction (SPME) (Ng, 1999). Direct analysis of liquid samples as well as headspace sampling

can be performed with SPME. The use of SPME for sample analysis provided a number of advantages. First, pre-concentration of the samples can be performed without the need of solvent. This helped to reduce the number of artifacts formed, although new artifacts from the fiber were present. Additionally, minimal sample preparation was required saving time previously spent for sample extraction and concentration. However, SPME also has several limitations. Several different fibers are available for SPME, and each one has a different affinity for different compounds. This requires advanced knowledge of your target compounds to be able to choose the best fiber. Also, SPME can over represent certain compounds, particularly smaller and more volatile ones, that have a greater affinity for the fiber than heavier less volatile larger molecules. Furthermore, the extraction time is very important to get an accurate representation of the volatiles present. Longer extraction times allow more time for exchange or displacement among compounds absorbed in the fiber.

Additional research on rums using SPME was done by Jorge Pino. His first paper used SPME for the extraction and quantification of ethyl esters in seven white rums (Pino et al., 2002). Extensive method development was performed to accurately quantify the esters in alcoholic matrices, determining that diluting the samples to 12% ABV along with the addition of salt to the sample provided the best results. Ethyl hexanoate, ethyl octanoate, ethyl decanoate and ethyl dodecanoate were quantified, and the results showed that ethyl decanoate was present in highest concentration in every rum followed by ethyl octanoate, and ethyl dodecanoate. Ethyl hexanoate had the lowest concentration of the esters analyzed in every rum sample. Recently, Pino has validated this method for analysis of ethyl esters as well as the whiskey lactones in white rums (Pino & Roncal, 2016). Pino then went on to use SPME to characterize the volatiles present in six samples of three and seven year old rums (Pino, 2007). Pino was able to identify 184 different volatile compounds, but no quantification was performed other than comparing peak areas.

It was not until the past decade that gas-chromatography olfactometry (GCO) was first utilized in rum flavor research to identify the odor-active volatile compounds present in the beverage despite the fact that the technique was introduced in the 1960's (Acree & Barnard, 1994). The first GCO study compared the aroma of cachaça, a Brazillian distilled spirit also produced from sugar cane, and an unidentified Bacardi rum (de Souza, Vásquez, del Mastro, Acree, & Lavin, 2006). Researchers used GCO on extracts of each spirit and compared the results to those obtained by descriptive sensory analysis for the same samples. The top twenty odor-active compounds were quantified and ranked according to their odor intensities. While this was the first study to identify the odor-active

compounds in rum, no quantitation of the compounds was performed. Rum was only compared to cachaça by sensory evaluation and comparison of odor spectrum values (OSV), which is similar to flavor dilution (FD) factors. β-Damascenone, diethyl acetal, ethyl 2-methylbutyrate, ethyl isobutyrate and an unknown compound (RI 866 on DB5 column), were found to be the five most potent aroma compounds in rum.

A second GCO study was conducted by Pino (Pino, Tolle, Gök, & Winterhalter, 2012). He identified and quantified potent odorants that had a FD factor of 32 or higher. Compounds noted as being important to the aroma of rum include diethyl acetal, ethyl 2-methylpropanoate, ethyl butyrate, ethyl 2-methylbutanoate, 3-methylbutyl acetate, ethyl hexanoate, ethyl octanoate, ethyl decanoate, 2-phenethyl acetate, β-damascenone, 2-phenylethanol, 2-methoxyphenol, 4-ethylguaiacol, 4-propyl-guaiacol, *trans*-whiskey lactone, *cis*-whiskey lactone, γ-nonalactone, eugenol and vanillin. This was the first study to quantify the odor-active volatiles present in rum. Quantification was done by internal standard methodology but using methyl octanoate. Additionally, this paper identified all of the volatile compounds found in the rum sample. No unknowns were listed suggesting a lack of verification with authentic standards.

Recent work done by the Cadwallader lab evaluated the similarity between rum and rum ethers (Burnside, 2012). The study identified the most odor-active compounds present in Bacardi white and gold rums, as well as in nine commercial and self-prepared rum ethers. Several compounds were found to be essential to both rum and rum ether but both contained their own individually important compounds. Forty-four compounds were identified in the two rum samples. AEDA was used to determine the most potent odorants in the rums: ethyl propanoate, ethyl isobutyrate, isoamyl alcohol, acetic acid, β-damascenone, phenethyl alcohol, *cis*-whiskey lactone, and vanillin. No quantification was performed on the samples.

Another recent study evaluated nine Columbian rums by headspace SPME coupled with GC-MS-O (Monsalve, López, & Zapata, 2016). Forty-six compounds were identified between the nine samples. The results indicated that some compounds were able to be detected in all rums while others were only present in some of the samples. No quantification of the identified compounds was conducted.

The two most thorough studies on rum were recently done by Franitza (Franitza, Granvogl, & Schieberle, 2016a, 2016b). The first study evaluated two rum products, a solera aged rum produced

from molasses (rum A) and a lower quality rum readily purchased from a local store (Rum B) (Franitza et al., 2016a). Samples were analyzed by GCO and AEDA leading to the identification of 40 odor-active compounds in rum A and 26 in rum B with FD factors between 8 and 2048. Overall, a total of forty-five odorants were identified and quantified by stable isotope dilution analysis (SIDA) in both rums. Odor activity values we also calculated for all compounds to gain a better understanding of their overall impact on rum flavor. Ethyl 2-methylbutyrate, β-damascenone, 3-methylbutanal, 2,3-butanedione, ethyl butyrate, 1,1-diethoxyethane, ethyl 3-methylbutanoate, ethyl pentanoate, and ethyl hexanoate were all found to have OAV's greater than 1 (indicating they are present in concentrations above their odor threshold in the sample) in both rums. Several compounds had OAV's above 1 in just one of the samples including vanillin, *cis*-whiskey lactone, eugenol, and guaiacol for rum A and 2-methylbutanal and 4-propylguaiacol for rum B.

Their second study evaluated how the flavor constituents of rum change throughout the production process (Franitza et al., 2016b). The study specifically focused on the flavor of the molasses, fermentation mash, distillation and final product. Forty-five compounds were identified in at least one of the four production stages. The concentration of all volatile compounds increased during the fermentation of the molasses except butanoic acid, phenylacetic acid, vanillin and (R)-2-methyl-1-butanol which was only detected in the molasses [(S)-2-methyl-1-butanol was found in all samples]. During the distillation step, the concentration of most volatiles again increased except acetic acid, butanoic acid, phenylacetic acid, vanillin, 3-methylbutanoic acid, (R)- & (S)-2-methyl butanoic acid, 3-(methylthio)propanol, decanoic acid, 3-hydroxy-4,5-dimethylfuran-2(*5H*)-one, 2-phenylethanol, 4-ethylphenol, and 4-methylphenol. During the aging of the rum, many of the volatile compounds decreased or stayed at the same concentration. Compounds that increased during aging were acetic acid, phenylacetic acid, vanillin, 3-(methylthio)propanal, decanoic acid, 3-hydroxy-4,5-dimethylfuran-2-(*5H*)-one, 2-methoxyphenol, 4-ethylphenol, 4-methylphenol, 4-ethylguaiacol, 4-propylguaiacol, and ethyl 3-methtylbutanoate, suggesting these compounds were either extracted from the wood barrels or formed from reactions that occurred between compounds in the rum over time. *Cis*- and *trans*-whiskey lactones were the only two compounds detected in the final aged product only, verifying that they are extracted from the wooden barrels during aging.

Even though rum has been studied for almost 100 years, there is still much to learn in terms of the flavor chemistry of rum. Studies that have identified the aroma-active compounds only look at one or two rum samples. Since rum is such as highly variable spirit due to the different and numerous

manufacturing practices employed, the current body of literature is not able to completely describe what defines rum as a class. Studies that survey a variety of rum types and manufacturing practices are needed for a more thorough understanding of the aroma of rum.

2.5 Sensory Studies on Rum

A minimal amount of work has been performed to define the sensory characteristics of rum. A master's thesis by Gómez (2002), was the first sensory study to analyze the aroma profile of rums. Gomez used a descriptive analysis panel to develop a flavor lexicon consisting of 33 aroma attributes, developed from the evaluation of 15 rums. The second part or the research used a descriptive analysis panel to describe the aroma differences for nine rums that varied in production methods. Even though a lexicon had been constructed in the initial work, it was not adequate to describe all of the differences perceived by the panel in the second study. Of the 22 terms evaluated, seven were not found in the initial lexicon. This suggests that the rums chosen for the creation of the lexicon did not adequately cover all product variations. The rum samples were able to be differentiated with the main aroma differences in woody, buttery, caramel, honey, vanilla, cinnamon, artificial fruit, cardboard, and ocean-like attributes.

A descriptive analysis panels have also been conducted to identify the sensory differences between rum and cachaça (de Souza et al., 2006; Magnani, 2009). The first study by de Souza (2006) compared a Joao Mendes cachaça to a Bacardi rum (only brands were specified, not specific products). Ten aroma attributes were evaluated, and rum was found to be higher in caramel and vanilla notes, while caramel was higher in grassy, sulfury, vinegar, spicy, citrus, alcohol, and melon notes. Another descriptive analysis panel was performed by Magnani (2009) who evaluated two rums and two cachaça samples for aroma and in-mouth sensory perceptions for seventeen attributes. The results showed the cachaça and rum differed in terms of golden color, body appearance, turbidity, wood aroma, wood flavor, sweet taste, and viscosity.

Several studies have characterized the aroma of rum through the aroma profile method (Franitza et al., 2016a, 2016b). Both studies characterized rum as ethanolic, malty, butter-like, fruity, clove-like and vanilla-like. The second study added the terms baked apple-like and caramel like (Franitza et al., 2016b).

Overall, rum has been consistently described as caramel, spicy (clove-like), fruity and vanilla. While several studies have evaluated the sensory profiles of rum, the significant variation in rum products necessitates additional sensory studies on rum flavor.

2.6 Flavor Wheels

Lexicons and flavor wheels are created and used to provide a standardized vocabulary for enhanced communication and discussion between sensory scientists, product developers, business clients and consumers. Lexicons have been developed for a variety of different food products including whiskey, wine, beer, brandy, cognac spices, cheese, bread, olive oil, almonds, tea and orange juice (Capone, Tufariello, & Siciliano, 2013; Civille, Lapsley, Huang, Yada, & Seltsam, 2010; Drake, McInvale, Gerard, Cadwallader, & Civille, 2001; Jolly & Hattingh, 2001; Kleinert, Bongartz, Raemy, & Wadenswil, 2009; Koch, Muller, Joubert, van der Rijst, & Næs, 2012; Lawless, Hottenstein, & Ellingsworth, 2012; Lee, Paterson, Piggott, & Richardson, 2001; Lurton, Ferrari, & Snakkers, 2012; Mojet & de Jong, 1994; Pérez-Cacho, Galán-Soldevilla, Mahattanatawee, Elston, & Rouseff, 2008; Schmelzle, 2009). The wine flavor wheel is the most well-known, recognized by coinsurers and consumers alike. Having a set of standard terms, definitions, and references for the product descriptors allows users to ensure that they are describing the same aspect of the product.

Lexicons are typically developed by a team of trained sensory panelists. Panelists usually have hundreds of hours of training evaluating different food products performing descriptive analysis. To develop a complete lexicon, a variety of different products that encompasses all of the different aspects of a product category need to be evaluated. Taking the cheddar cheese lexicon as an example, samples were chosen to comprise cheese from different geographical regions, producers, and a range cheese maturity to develop the most comprehensive lexicon as possible (Drake et al., 2001). Once the products to be evaluated have been selected panelists will generate terms to describe their perception, determine appropriate chemical or food stuff references, developing specific definitions for each attribute. After the initial term generation, any terms that are redundant are removed from the list. Panelists will then practice scaling the attributes according to the selected reference. Each sample will then be evaluated by the panelists with each individual attribute being

rated in comparison to the reference. The compiled data allows researchers to identify how the products within the category differ from each other.

Once a lexicon has been developed, it can be converted into a flavor wheel, which provides a visual representation of the generated terms. Terms are typically grouped by category, with the grouping identified in the inner circle and the specific term listed along the outside. The completed wheel can then be used to train new panelists as an aid to help with term selection and be able to communicate with other scientists or consumers.

Rum is an extremely complex product due to its limited standard of identity. Since rum can come from a variety of sugar cane by-products, be distilled in multiple ways and aged in any type of barrel the manufacturer desires, there is a significant amount of variation between the products classified as rum. There is currently no rum flavor wheel or lexicon available. Developing a lexicon would aid both manufacturers and consumers in being able to better understand and describe the products.

2.7 Effects of Ethanol on Flavor Perception of Alcoholic Beverages

Ethanol is the major component of alcoholic beverages, other than water, but relatively little is known about its effects on flavor perception. The alcoholic beverages industry is a $189 billion industry, comprising 56% of the total beverage industry as of 2011 (Park Street, 2011). Alcoholic beverages fall into three main categories, beer (4-10% ABV), wine (9-14% ABV) and distilled spirits (20-95% ABV).

Gaining a better understanding of ethanol's effect on flavor could aid in production of better alcohol-free wine and beers, correcting flavor imbalances that occur as we try to continuously increase the alcohol content of beer and wine, and to gain a better understanding of why many people prefer distilled spirits in a diluted rather than neat form. In the whiskey industry, master blenders have been diluting the whiskey to 23% to evaluate the different blends. The most often noted reason for this is to decrease the pungency of the alcohol, but others also mention that it does a better job of releasing the flavor profile of the spirit (Smith & Roskrow, 2012). Even though this been common knowledge in the industry for years, there is no research looking into how those flavor effects translate to what is happening analytically with the beverage.

Additionally, everyone has their favorite way of drinking whiskey. Some people swear that the only way to drink whiskey is neat, straight out of the bottle at room temperature. Others state that it needs a splash of water to open up the aroma. Still, others prefer their whiskey on the rock, which both dilutes and cools the drink. Finally, still others would say that it needs to be diluted closer to 23% ABV to get the best perception of the aroma profile. The proper way to drink whiskey is obviously personal preference, but there must be obvious flavor differences between these different drinking styles for people to have a preference and little is known regarding what is driving the flavor differences.

While it is known that ethanol is an important component to alcoholic beverages, studying these various drinks pose several problems during analysis. First, the abundance of ethanol makes it difficult to analyze the other less abundant volatile compounds. The increased concentration of ethanol can interfere with GC-MS analysis, and it also causes problems for SPME analysis since the excess ethanol will absorb to the fiber more readily than the other aroma compounds of interest, making it hard to detect those compounds. Most of the research that has been done utilized static equilibrium systems, but this is not capable of mimicking what is actually occurring in a beverage glass during consumption, with the various air currents in the room and the evaporation of ethanol from the glass. One possible solution is to control the airflow by constructing a shield around the beverage glass, but this has been shown to create an artificial buildup of odorants over time (Taylor et al., 2010). Real life dynamic systems are very difficult to monitor but there has been some improvement in the past decade with the use of real-time mass spectroscopy using, such as atmospheric pressure chemical ionization (ACPI)-MS that has been modified to use ethanol as the charge transfer medium (Aznar, Tsachaki, Linforth, Ferreira, & Taylor, 2004).

First, an understanding of the basic physiochemical interactions between water and ethanol is helpful. The water-ethanol matrix changes significantly as is it changes from being a 100% aqueous solution to a 100% ethanoic solution. Starting with the aqueous solution, all of the water molecules are participating in a highly-structured hydrogen-bonded network. This unique property of water is what gives it such a high surface tension compared to what would be predicted for a molecule of its size. As ethanol is added to the solution, the ethanol is monodispersed throughout the water until 15%ABV (Conner, Birkmyre, Paterson, & Piggott, 1998; Conner, Paterson, & Piggott, 1999; D'Angelo, Onori, & Santucci, 1994). At this concentration the ethanol-water matrix changes, whereby the ethanol molecules in the solution aggregate to form micelles, basically forming a micro

emulsion of ethanol in water. This takes place at alcohol concentrations of 17-57% ABV. Once the ethanol concentration of a solution is above 57%, the remaining water molecules lose their hydrogen-bonded structure and the solution primarily become ethanoic with the water monodispersed throughout.

The primary method for monitoring the headspace concentration above alcoholic beverages has been static headspace analysis. Static headspace analysis is where the beverage is placed in a sealed vial and then allowed to come to an equilibrium where the volatiles partition into the headspace. Several studies have looked into the effect of ethanol on the headspace concentration of alcoholic beverages, and what concentration of ethanol begins to effect the partitioning. Several studies showed that the critical ethanol concentration is 17%, above which the headspace concentration of compounds in the ethanol matrix is significantly decreased compared to the 100% water matrix (Conner et al., 1998; Escalona-Buendia, Piggott, Conner, & Paterson, 1998). Other studies have shown this effect can be seen at ethanol concentrations as low as 12% (Aznar et al., 2004; Tsachaki, Aznar, Linforth, & Taylor, 2006). In both situations, the addition of ethanol tends to increase the solubility of compounds in the matrix thereby decreasing their concentration in the headspace. This effect is compound specific, with some compounds affected more strongly than others and some not affected at all by the change in alcohol concentration. The trend seems to follow that the increase in ethanol makes non-polar compounds more soluble, but this does not hold true for all compounds.

A newer technique for the analysis of alcoholic beverages has been ACPI-MS which allows for the evaluation of dynamic systems. When performing the same type of experiment as above except with continual airflow through the system, the results obtained are reversed. The headspace concentration above the ethanol solution (12% ABV) is higher than the concentration above the water solution (Taylor et al., 2010; Tsachaki et al., 2008, 2006; Tsachaki, Linforth, & Taylor, 2005). This phenomenon can be explained though both the Marangoni effect and the Rayleigh-Bernard convection, both of which explain the same phenomena on surface tension effects and temperature density, respectively. The Marangoni effect occurs due to the fact that ethanol lowers the surface tension of the solution. As a result, it is easier for the ethanol to evaporate, which as it does so creates areas of higher surface tension due to the ethanol leaving. Since the solution will want to come to equilibrium, the other ethanol molecules will rearrange, moving to the surface to reduce the surface tension. In doing this flavor molecules will also move will the ethanol molecules, becoming

more available for evaporation. This movement creates a current that essentially stirs the solution, continually bringing more aroma compounds to the surface for evaporation.

The first study to look at the effects of ethanol on the flavor perception of alcoholic beverages was done in 1972. In the study entitled "Flavor effects of ethanol on alcoholic beverages," five beverages, (cider, wine, sparkling wine, sherry, and whiskey) were evaluated for how their flavor profile changed when ethanol was removed from the beverages (Williams, 1972). What they found upon sensory analysis was that when the ethanol was removed, the resulting solution had a stronger fruity aroma for the cider, wine, and sparkling wine. Likewise, the wine also had increased oxidized aromas and sour taste compared to the original with ethanol. The sherry was also perceived with increased sweetness and amyl and hexyl notes with the removal of ethanol. The de-ethanolized whiskey was perceived as being the most similar to the original compared with the other four products, but that the removal of ethanol decreased the bite and made the de-ethanolized beverage drier. Williams and Rosser (1981) then went on to study the effect of ethanol on fruitiness perception, specifically in cider. In their study, a prepared cider extract was diluted it to volume with either straight water or various ethanol solutions. Using a sensory panel to compare the aqueous vs. ethanolic solutions, they found that between 0.1-0.75% ethanol that alcohol increased the fruitiness perception. Outside of that range, the aqueous solution was always perceived as fruitier.

There has been a significant amount of work looking into the effect of ethanol on whisky, done primarily by the Scotch Whisky Research Institute. One of their initial studies examined the effect of ethanol concentration on the solubility of ethyl esters (Conner, Paterson, & Piggott, 1994). Their results showed that when whiskey is diluted from 40% ABV to 23% ABV that the solubility of the ethyl esters decreases, creating a super-saturated solutions with esters. As a result, the esters come together to form agglomerates or micelles, which prevent aroma compounds from partitioning into the headspace. At the same time, other aldehydes or alcohols may become part of the micelles, or trapped within it, also affecting their release from the solution. A follow-up study to this examined the effect of alcohol concentration on the headspace concentration of various ethyl esters (Conner et al., 1998). Headspace concentrations were calculated for each ethyl ester at alcohol concentrations of 5%, 10%, 17%, 23% and 40%. At the three lower ethanol levels, the headspace concentrations were relatively similar, once the 23% solution was reached there was a decrease in concentration by almost half, and there was another significant decrease at 40%. These headspace concentrations were converted to activity coefficients (concentration of the compound above the solution over the

concentration of the compound above pure compound) and found that for all the esters studies there was a linear decrease in activity coefficient between 17% and 80% ethanol.

Other studies have also shown the effect that wood extractives can have on the solubility of aroma compounds. Results demonstrated that not only do wood extractives decrease the size of ester agglomerates that form (Conner et al., 1994) but that it also decreases the alcohol concentration at which those micelles will start to form (Conner et al., 1999).

Another study examined the effect of ethanol on headspace concentration of more than just esters. Authors Boothroyd, Linforth and Cook (2012) examined the effect of ethanol at three different concentrations (5%, 23% and 40% ABV) of 14 different compounds. Their study showed what the effect of ethanol on headspace concentration is compound dependent. Several compounds such as pyrazine, 2-methylpyrazine, 2-acetylthiazole, and furfural were minimally affected by changes in ethanol concentrations. Other compounds such as β-damascenone and ethyl octanoate were highly affected by ethanol concentration. While no sensory data was collected to supplement this data, it can be seen from the analytical data that at each ethanol concentration there is a different ratio of aroma compounds, this suggests that there will be a different aroma perception at each of these concentrations. Further work to link the analytical data with what a consumer or panelist perceives is necessary.

While there has been some work into how ethanol concentration effects flavor perception there is still much work that needs to be done. First, a better understanding of the dynamic system of flavor release is required. Continued work using APCI-MS for different ethanol concentrations should be done to see if the same phenomena observed at 12% alcohol are repeatable at 23% and 40% ABV. Additionally, there is a great need to be able to link the analytical data collected with sensory data.

2.8 Figures

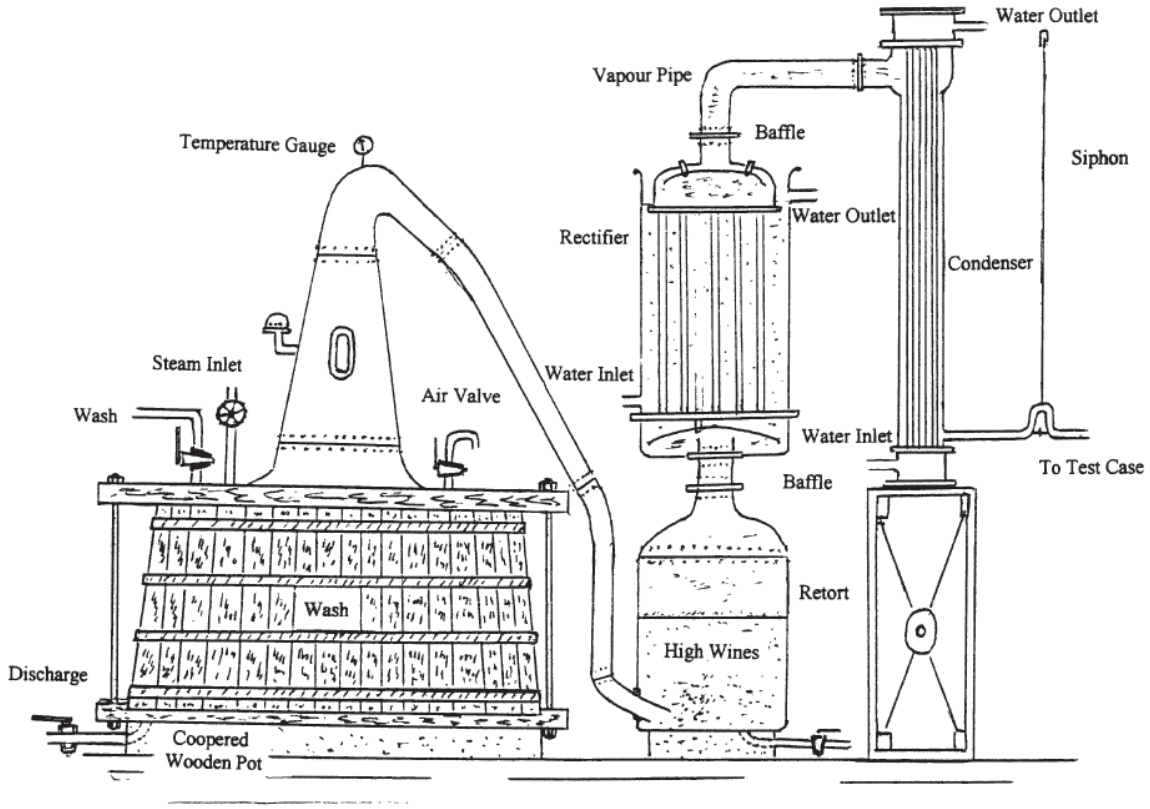


Figure 2.1 Traditional single pot distillation for rum production (with permission Nicol, 2003)

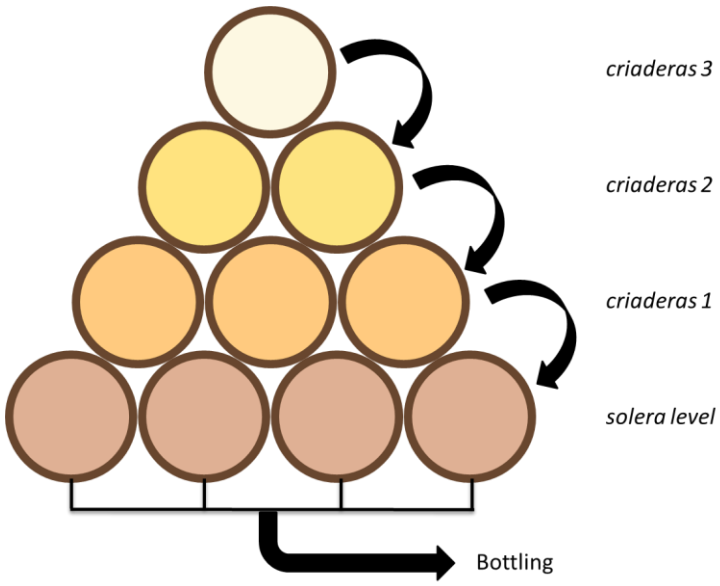


Figure 2.2 Diagram of the solera aging system for rum

2.9 References

Acree, T. E., & Barnard, J. (1994). Gas chromatography-olfactometry and CharmAnalysis. *Trends in Flavour Research*, *35*, 211–220.

Arroyo, R. (1939). El Aroma del Ron. *Revista de Agricultura, Indistria Y Comercio de Puerto Rico*, *31*, 448–450.

Ayala, L. K. (2001). *The Rum Experience*. Texas, USA: Rum Runner Press Inc.

Aznar, M., Tsachaki, M., Linforth, R. S. T., Ferreira, V., & Taylor, A. J. (2004). Headspace analysis of volatile organic compounds from ethanolic systems by direct APCI-MS. *International Journal of Mass Spectrometry*, *239*, 17–25. http://doi.org/10.1016/j.ijms.2004.09.001

Barty-King, H., & Massel, A. (1983). *Rum: Yesterday and Today*. London: Heidelberg Publishers Ltd.

Batiz, H., & Rosado, E. (1978). A Single Column Gas Chromatographic Method for the Direct Trace Analysis of High Boiling Components in Rums. *The Journal of Agriculture of University of Puerto Rico*, *62*(4), 330–343.

Blue, A. D. (2004). Rum. In *The Complete Book of Spirits: A Guide to Their History, Production, and Enjoyment* (1st ed., pp. 69–103). New York: Harer Collins Publishers.

Bober, A., & Haddaway, L. W. (1963). Gas Chromatographic Identification of Alcoholic Beverages. *Journal of Gas Chromatography*, *1*(12), 8–13.

Boothroyd, E. L., Linforth, R. S. T., & Cook, D. J. (2012). Effects of Ethanol and Long-Chain Ethyl Ester Concentrations on Volatile Partitioning in a Whisky Model System. *Journal of Agricultural and Food Chemistry*, *60*, 9959–9966. http://doi.org/10.1021/jf3022892

Broom, D. (2016). *Rum - The Manual*. London: Mitchell Beazley.

Burnside, E. E. (2012). *Characterization of Volatiles in Commercial and Self-Prepared Rum Ethers and Comparison with Key Aroma Compounds of Rum*. University of Illinois at Urbana-Champaign. Retrieved from https://www.ideals.illinois.edu/handle/2142/34368

Business Monitor International Research. (2016). *United States - Food & Drink Report*. Retrieved from http://search.ebscohost.com/login.aspx?direct=true&db=bth&AN=113556469&site=eds-live

Capone, S., Tufariello, M., & Siciliano, P. (2013). Analytical characterisation of Negroamaro red wines by Aroma Wheels". *Food Chemistry*, *141*, 2906–2915. http://doi.org/10.1016/j.foodchem.2013.05.105

Civille, G. V., Lapsley, K., Huang, G., Yada, S., & Seltsam, J. (2010). Development of an Almond Lexicon To Assess the Sensory Properties of Almond Varieties. *Journal of Sensory Studies*, *25*, 146–162. http://doi.org/10.1111/j.1745-459X.2009.00261.x

Conner, J. M., Birkmyre, L., Paterson, A., & Piggott, J. R. (1998). Headspace Concentrations of Ethyl Esters at Different Alcoholic Strengths. *Journal of the Science of Food and Agriculture*, *77*, 121–126.

Conner, J. M., Paterson, A., & Piggott, J. R. (1994). Agglomeration of Ethyl Esters in Model Spirit Solutions and Malt Whskies. *Journal of Science of Food and Agriculture*, *66*, 45–53.

Conner, J. M., Paterson, A., & Piggott, J. R. (1999). Release of distillate flavour compounds in Scotch malt whisky. *Journal of the Science of Food and Agriculture*, *79*, 1015–1020.

D'Angelo, M., Onori, G., & Santucci, A. (1994). Self-Association of Monohydric Alcohols in Water: Compressibility and Infrared Absorption Measurements. *The Journal of Chemical Physics*, *100*(4), 3107–3113. http://doi.org/10.1063/1.466452

de Souza, M. D. C. A., Vásquez, P., del Mastro, N. L., Acree, T. E., & Lavin, E. H. (2006). Characterization of Cachaça and Rum Aroma. *Journal of Agricultural and Food Chemistry*, *54*, 485–488. http://doi.org/10.1021/jf0511190

Delavante, M. P. (2004). Rum - The Commercial and Technical Aspects. In J. H. Bryce & G. G. Stewart (Eds.), *Distilled Spirits: Tradition and innovation* (pp. 209–214). Nottingham, UK: Nottingham University Press.

Drake, M. a, McInvale, S. C., Gerard, P. D., Cadwallader, K. R., & Civille, G. V. (2001). Development of a Descriptive Language for Cheddar Cheese. *Journal of Food Science*, *66*(9), 1422–1427.

Eberle, S. (2014, June). Rum's Handcrafted Renaissance. *Outside*. Retrieved from https://www.outsideonline.com/1924131/rums-handcrafted-renaissance

Escalona-Buendia, H., Piggott, J. R., Conner, J. M., & Paterson, A. (1998). Effect of ethanol strength on the release of higher alcohols and aldehydes in model solutions. *Developments in Food Science*, *40*(C), 615–620.

Fahrasmane, L. (2014). Rum. In C. W. Bamforthm & R. E. Ward (Eds.), *The Oxford Handbook of Food Fermentations* (pp. 277–303). New York: Oxford University Press.

Foss, R. (2012). *Rum: A Global History*. London: Reaktion Books.

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*, 637–645. http://doi.org/10.1021/acs.jafc.5b05426

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*, 9041–9053. http://doi.org/10.1021/acs.jafc.6b04046

Freedman, B. (2016, May). Is High-End Rum the New Whiskey? *Forbes*. Retrieved from https://www.forbes.com/sites/brianfreedman/2016/05/19/is-high-end-rum-the-new-whiskey/#45b3ad364c7f

Gately, I. (2008). *Drink: A Cultural History of Alcohol*. New York: Gotham Books.

Global Rum Insights - Market Forecasts, Product Innovation and Consumer Trends. (2016). Retrieved January 1, 2017, from http://www.just-drinks.com/market-research/global-rum-insights-market-forecasts-product-innovation-and-consumer-trends_id260118.aspx?utm_source=pr_newswire&utm_medium=press_release&utm_campaign=none&utm_term=just_drink/iwsr&utm_content=rum

Global Rum Market: Leading Brands Based on Sales Volume 2015. (2017). Retrieved January 1, 2017, from https://www.statista.com/statistics/259739/leading-rum-brands-worldwide-based-on-sales-volume/

Global Rum Market Set to Decline Over the Next Five Years. (2017, February 14). *PR Newswire Europe*. London. Retrieved from http://www.marketwatch.com/story/global-rum-market-set-to-decline-over-the-next-five-years-2017-02-14-3203148

Global Spirits. (2016). *MarketLine Industry Profile*.

Gómez, S. M. (2002). *Rum Aroma Descriptive Analysis*. Louisiana State University. Retrieved from http://etd.lsu.edu/docs/available/etd-1114102-110301/

Gonzáles Gordon, M. M. (1990). The Solera System. In J. Doxat (Ed.), *Sherry: The Noble Wine* (pp. 141–153). London: Quiller Press.

Hopkins, A. (2014). World's Largest Rum Markets. Retrieved January 1, 2017, from https://www.thespiritsbusiness.com/2014/03/worlds-largest-rum-markets/5/

Hopkins, A. (2015). Super-Premium Rums Set for Growth. Retrieved January 1, 2017, from https://www.thespiritsbusiness.com/2015/11/super-premium-rum-set-for-50-growth/

Irani, D. (2013, November). Renaissance! Rum is Not Just the Favourite Drink of Pirates. *The Economic Times*. Retrieved from http://economictimes.indiatimes.com/magazines/brand-equity/renaissance-rum-is-not-just-the-favourite-drink-of-pirates/articleshow/26421641.cms

Jeffers, H. P. (1997). *High Spirits*. New York: Lyons & Burford, Publishers.

Jolly, N. P., & Hattingh, S. (2001). A Brandy Aroma Wheel for South African Brandy. *South African Journal of Enology and Viticulture*, *22*(1), 16–21.

Kleinert, M., Bongartz, A., Raemy, E., & Wadenswil. (2009). Development of a Flavour Wheel for Breads. *Getreide, Mehl Und Brot*, *63*(1), 60–69.

Koch, I. S., Muller, M., Joubert, E., van der Rijst, M., & Næs, T. (2012). Sensory characterization of rooibos tea and the development of a rooibos sensory wheel and lexicon. *Food Research International*, *46*, 217–228. http://doi.org/10.1016/j.foodres.2011.11.028

Labeling and advertising of distilled spirits, Title 27 Code of Federal Regulations, Pt. 5 Section 5:22. 1969 ed.

Lawless, L. J. R., Hottenstein, A., & Ellingsworth, J. (2012). The McCormick Spice Wheel: A Systematic and Visual Approach to Sensory Lexicon Development. *Journal of Sensory Studies*, *27*, 37–47. http://doi.org/10.1111/j.1745-459X.2011.00365.x

Lee, K.-Y. M., Paterson, A., Piggott, J. R., & Richardson, G. D. (2001). Origins of Flavour in Whiskies and a Revised Flavour Wheel: a Review. *Journal of the Institute of Brewing*, *107*(5), 287–313. http://doi.org/10.1002/j.2050-0416.2001.tb00099.x

Leppänen, O., Denslow, J., & Ronkainen, P. (1979). A Gas Chromatographic Method for the Accurate Determination of Low Concentration of Volatile Sulfur Compounds in Alcoholic Beverages. *Journal of the Institute of Brewing*, *85*, 350–353.

Liebich, H. M., Koeing, W. A., & Bayer, E. (1970). Analysis of the Flavor of Rum by Gas-Liquid Chromatography and Mass Spectrometry. *Journal of Chromatographic Science*, *8*, 527–533. Retrieved from http://chromsci.oxfordjournals.org/content/8/9/527.short

Lurton, L., Ferrari, G., & Snakkers, G. (2012). Cognac: production and aromatic characteristics. In J. Piggott (Ed.), *Alcoholic Beverages: Sensory Evaluation and Consumer Research* (pp. 242–266). Oxford: Woodhead Publishing Limited. http://doi.org/10.1016/B978-0-85709-051-5.50011-0

Maarse, H., & tem Noever de Brauw, M. C. (1966). The Analysis of Volatile Components of Jamaica Rum. *Journal of Food Science*, *31*(6), 951–955. Retrieved from http://onlinelibrary.wiley.com/doi/10.1111/j.1365-2621.1966.tb03275.x/full

Macinnis, P. (2002). *Bittersweet - The Story of Sugar*. Crows Nest, Australia: Allen & Unwin.

Magnani, B. D. (2009). *Estudo Comparativo das Características Sensoriais do Rum e da Cachaça Estudo Comparativo das Características Sensoriais do Rum e da Cachaça*. Universidade Estadual Paulista.

Mariani, J. F. (1983). *The Dictionary of American Food & Drink*. New Haven & New York: Ticknor & Fields.

Miles, E. (2015). Rum. In *Craft Spirit World - A guide to artisan spirit-makers and distillers you need to try* (pp. 70–79). New York: Dog "n" Bone Books.

Minnick, F. (2017). *Rum Curious: The Indispensable Tasting Guide to the World's Spirit*. Minneapolis, MN:

Voyageur Press.

Mojet, J., & de Jong, S. (1994). The sensory wheel of virgin olive oil. *Grasas Y Aceites*, *45*(1–2), 42–47.

Monsalve, J. O., López, C., & Zapata, J. (2016). Characterization of aroma compounds in colombian rums by HS-SPME-GC-MS-O. *Revista Colombiana de Química*, *45*(2), 48–54.

Ng, L.-K. (1999). Analysis of Vodkas and White Rums by SPME-GC-MS. In J. Pawliszyn (Ed.), *Applications of Solid Phase Microextraction* (pp. 393–406). Cambridge, UK: The Royal Society of Chemistry. http://doi.org/10.1039/9781847550149-00393

Nicol, D. A. (2003). Rum. In A. G. H. Lea & J. R. Piggott (Eds.), *Fermented Beverage Production* (Second, pp. 263–287). New York: Kluwer Academic/Plenum Publishers.

Padgett, T. (2014, April 25). Rum Renaissance Revives The Spirit's Rough Reputation. *NPR- the Salt*. Retrieved from http://www.npr.org/sections/thesalt/2014/04/25/306826984/rum-renaissance-revives-the-spirits-rough-reputation

Padgett, T. (2017, April). Rum's Renaissance: Why Rum is having its Cognac Moment. *American Magazine*. Retrieved from https://www.americamagazine.org/politics-society/2017/04/18/rums-renaissance-why-rum-having-its-cognac-moment

Pérez-Cacho, P. R., Galán-Soldevilla, H., Mahattanatawee, K., Elston, A., & Rouseff, R. L. (2008). Sensory Lexicon for Fresh Squeezed and Processed Orange Juices. *Food Science and Technology International*, *14*(Suppl. 5), 131–141. http://doi.org/10.1177/1082013208094723

Pino, J. A. (2007). Characterization of rum using solid-phase microextraction with gas chromatography–mass spectrometry. *Food Chemistry*, *104*, 421–428. http://doi.org/10.1016/j.foodchem.2006.09.031

Pino, J. A., & Roncal, E. (2016). Validation of a HS-SPME-GC Method for Determining Higher Fatty Esters and Oak Lactones in White Rums. *Food Analytical Methods*, *9*, 1958–1962. http://doi.org/10.1007/s12161-015-0368-3

Pino, J. A., Tolle, S., Gök, R., & Winterhalter, P. (2012). Characterisation of odour-active

compounds in aged rum. *Food Chemistry*, *132*, 1436–1441. http://doi.org/10.1016/j.foodchem.2011.11.133

Pino, J., Martí, M. P., Mestres, M., Pérez, J., Busto, O., & Guasch, J. (2002). Headspace solid-phase microextraction of higher fatty acid ethyl esters in white rum aroma. *Journal of Chromatography A*, *954*, 51–57.

Reader, H. P., & Dominguez, M. (2003). Fortified Wines - Sherry, Port and Madeira. In A. G. H. Lea & J. R. Piggott (Eds.), *Fermented Beverage Production* (Second, pp. 157–194). New York: Kluwer Academic/Plenum Publishers.

Rogers, A. (2014). *Proof - The Science of Booze*. New York: Houghton Mifflin Harcourt.

Schmelzle, A. (2009). The Beer Aroma Wheel. *Brewing Science*, *62*, 26–32. Retrieved from http://www.scribd.com/doc/201188460/Aroma-Wheel#scribd

Shoup, M. E. (2017). Could rum be the dark horse of spirits? Rum author and importer sees it chip away at whiskey's supremacy. Retrieved May 22, 2017, from http://www.beveragedaily.com/Markets/Rum-might-chip-away-Whiskey-s-supremacy-due-to-price-increase?utm_source=newsletter_daily&utm_medium=email&utm_campaign=11-May-2017&c=gZqft5FYEog%2FwSvsxu8NFQ%3D%3D&p2=

Smith, F. H. (2005). *Caribbean Rum: A Social and Economic History*. Gainsville, FL: University of Florida Press.

Smith, G. D., & Roskrow, D. (2012). *Whiskeyopus*. New York: DK Publishing.

Spirits in the United States. (2016). *MarketLine Industry Profile*.

Stephenson, T. (2017). *The Curious Bartender's Rum Revolution*. Ryland Peters & Small.

Stevens, R., & Martin, G. (1965). Gas Chromatographic Identification of Ethyl Esters of Fatty Acids in Domestic and Imported Rums. *Journal of the Association of Official Agricultural Chemists*, *48*(4), 802–805.

Street, P. (2011). US Alcoholic Beverage Market - Overview. Retrieved November 8, 2015, from

http://www.parkstreet.com/industry/alcoholic-beverage-market-overview/

Swartz, K. (2016, February). 8 Trends The Drove the Distilled Spirits Market in 2015. Retrieved January 1, 2017, from http://www.beveragedynamics.com/2016/02/02/8-trends-that-drove-the-distilled-spirits-market-in-2015/

Taylor, A. J., Tsachaki, M., Lopez, R., Morris, C., Ferreira, V., & Wolf, B. (2010). Odorant Release from Alcoholic Beverages. *ACS Symposium Series*, *1036*, 161–175. http://doi.org/10.1021/bk-2010-1036.ch012

ter Heide, R., Schaap, H., Wobben, H. J., de Valosis, P. J., & Timmer, R. (1981). Flavor Constituents in Rum. In *The Quality of Foods and Beverages* (pp. 183–200).

Timmer, R., ter Heide, R., Wobben, H. J., & de Valois, P. J. (1971). Phenolic Compounds in Rum. *Journal of Food Science*, *36*, 462–463.

Tsachaki, M., Aznar, M., Linforth, R. S. T., & Taylor, A. J. (2006). Dynamics of flavour release from ethanolic solutions. *Developments in Food Science*, *43*, 441–444. http://doi.org/10.1016/S0167-4501(06)80104-4

Tsachaki, M., Gady, A.-L., Kalopesas, M., Linforth, R. S. T., Athès, V., Marin, M., & Taylor, A. J. (2008). Effect of Ethanol, Temperature, and Gas Flow Rate on Volatile Release from Aqueous Solutions under Dynamic Headspace Dilution Conditions. *Journal of Agricultural and Food Chemistry*, *56*, 5308–5315. http://doi.org/10.1021/jf800225y

Tsachaki, M., Linforth, R. S. T., & Taylor, A. J. (2005). Dynamic Headspace Analysis of the Release of Volatile Organic Compounds from Ethanolic Systems by Direct APCI-MS. *Journal of Agricultural and Food Chemistry*, *53*, 8328–8333. http://doi.org/10.1021/jf051202n

Ward, C. (2015, May). Rum's Time. *Market Watch*. Retrieved from http://marketwatchmag.com/rum-may-2015/

Williams, A. A. (1972). Flavour Effects of Ethanol in Alcoholic Beverages. *The Flavour Industry*, *3*(12), 604–607.

Williams, A. A., & Rosser, P. R. (1981). Aroma enhancing effects of ethanol. *Chemical Senses*, *6*(2),

149–153. http://doi.org/10.1093/chemse/6.2.149

Williams, I. (2005). *Rum: A Social and Sociable History of the Real Spirit of 1776*. New York: Nation Books.

Wobben, H. J., Timmer, R., ter Heide, R., & de Valois, P. J. (1971). Nitrogen Compounds in Rum and Whiskey. *Journal of Food Science*, *36*, 464–465.

Chapter 3: Identification of Odor-Active Compounds in a Selection of Premium Rums

3.1 Abstract

Rum is one of the most diverse distilled spirits on the market. Despite this great product variability, previous research into the odor-active constituents of rum has only focused on only one or two rums as representative of the entire class. Therefore, the present study evaluated nine rums, seven premium and two mixing, to gain a better understanding of overall rum flavor, particularly in terms better defining the flavor chemistry of premium rums. Fifty-nine odor-active regions, encompassing sixty-four compounds were identified in the nine rum samples. Aroma extract dilution analysis was performed on all samples to gain a better understanding of the key potent odorants in rum. The overall most potent odorants contributing to rum flavor include acetal, 2-/3-methyl-1-butanol, β-damascenone, 2-phenethyl alcohol, *cis*-whiskey lactone/4-methylguaiacol, eugenol, sotolon, syringol, isoeugenol, vanillin, ethyl vanillate, and syringaldehyde. Mixing rums were found to contain the same odor-active compounds as premium rums but with less potency. Meanwhile, premium rums contained additional odor-active compounds not present in the mixing rums. Additionally, the profile of compounds encompassing rum aroma varied from sample to sample.

3.2 Introduction

Rum is a distilled spirit produced from any sugar cane by-product, typically molasses. Rum has a limited standard of identity, allowing for more variation within the product category than most other traditional spirits. Rum manufacturers are free to produce rum using whatever starting material (cane juice, cane syrup or molasses), fermentation style (wild fermentation or culture started), distillation methods (pot or column distillation), barrels used for maturation (new oak, whiskey, sherry, wine, etc.), and maturation length they find appropriate.

The earliest studies of rum aroma focused on the identification of all volatile compounds (Batiz & Rosado, 1978; Bober & Haddaway, 1963; Liebich, Koeing, & Bayer, 1970; Maarse & tem Noever de

Brauw, 1966; Ng, 1999; Nykanen, Puputti, & Suomalainen, 1968; Pino et al., 2002; Pino, 2007; Stevens & Martin, 1965; ter Heide, Schaap, Wobben, de Valosis, & Timmer, 1981; Timmer, ter Heide, Wobben, & de Valois, 1971; Wobben, Timmer, ter Heide, & de Valois, 1971). While these studies provided insight into the compounds that are present in rums, they gave no indication about which volatile compounds contribute to its odor. De Souza and others (2006) were the first to identify odor-active constituents in rum. Twenty odor-active compounds were identified with β-damascenone, acetal, ethyl 2-methylbutyrate, and ethyl 3-methylbutyrate being the most potent odorants. However, no quantitative data was provided at that time. Pino was next to identify odorants in rums and was the first to quantitate the compounds present (J. A. Pino, Tolle, Gök, & Winterhalter, 2012). He identified nineteen odor-active compounds and found ethyl butyrate, ethyl hexanoate, β-damascenone, *cis*-whiskey lactone, and vanillin to be the most potent odorants in the rum aroma. Franitza and colleagues (2016a) later identified forty odor-active compounds in two commercial rums, with the most potent odorants in rum A as *cis*-whiskey lactone, vanillin, decanoic acid, 2-/3-methyl-1-butanol, eugenol and sotolon, while rum B was characterized by ethyl cyclohexanoate, ethyl butanoate, acetal, ethyl 2-methylbutyrate and decanoic acid. Another recent study evaluated the odorants in nine Colombian rums using HS-GC-MS-O, identifying 46 odor-active compounds (Monsalve, Lopez, & Zapata, 2016). No quantitation of the identified volatiles was performed. Franitza also went on to study the production process of rum following 44 compounds and how their concentrations increased or decreased during fermentation, distillation, and maturation (Franitza, Granvogl, & Schieberle, 2016b).

While a significant amount of research has been done on rum aroma, the previous studies have only focused on one or two rum samples, except the Colombian rum study. Due to the considerable variation in production styles of rum, it is difficult to say that the previously evaluated rums encompass the totality of rum as a class. The goal of this study was to identify the odor-active compounds in a variety of premium aged rums and several mixing rums, in order to gain a better understanding of the important odorants in premium aged rums and how they are differentiated from mixing rums.

3.3 Materials and Methods

Materials

Nine rums, seven premium and two mixing rums, were chosen for analysis based on expert ratings, awards received and product availability (Table 3.1). The nine selected rums were purchased at a local liquor store (Champaign, IL). All nine rums had reported ethanol concentration of 40% alcohol by volume (ABV). Mention of the brand name of these rums does not imply any research contact or sponsorship and is not for advertisement or endorsement purposes.

De-odorized water used for volatile extraction was prepared by boiling deionized-distilled water to two-thirds of its original volume.

Chemicals

Dichloromethane and anhydrous sodium sulfate were purchased from Fisher Scientific Co. (Fair Lawn, NJ) and used for volatile extraction.

Reference Standard Compounds

The following chemicals were used as authentic standards to confirm the identification of odor compounds: acetaldehyde and isobutanol and were obtained from Fisher (Fair Lawn, NJ); 2-methylpropanal, ethyl propanoate, 2,3-butanedione, ethyl-3-methylbutyrate, hexanal, isoamyl acetate, ethyl hexanoate, ethyl octanoate, methional, phenyl acetaldehyde, *p*-cresol, eugenol, and *Z*-6-dodecene-γ-lactone were obtained from Aldrich (Milwaukee, WI); 3-methylbutanal, ethyl 2-methylpropanoate, ethyl butyrate, ethyl-2-methylbutyrate, ethyl pentanoate, heptanal, 2-methyl-1-butanol, 3-methyl-1-butanol, 1-octen-3-one, (*E*)-2-nonenal, 3-methylbutyric acid, mixture of *cis*-&-*trans* whiskey lactone, 2-phenethyl alcohol, guaiacol, 4-propyl guaiacol, syringol, and ethyl vanillin were obtained from Sigma-Aldrich (St. Louis, MO); acetic acid, ethyl 3-phenylpropanoate, 4-methyl guaiacol, 4-ethyl guaiacol, *m*-cresol, sotolon, vanillin, syringaldehyde were obtained from SAFC (St. Louis, MO); isoeugenol and ethyl vanillate were obtained from Alfa Aeasar (Lancaster, UK); 2-methylbutanal and 1-octen-3-ol were obtained from Bedoukian (Danbury CT); acetal (1,1-diethoxyethane) was obtained from Acros Organics (NJ); β-damascenone was obtained from Firmenich (Switzerland); ethyl acetate was obtained from Applied Biosystems Inc. (Foster City, CA).

Ethyl cyclohexancarboxylate was synthesized as follows below.

Synthesis of *Ethyl Cyclohecancarboxylate*

Cyclohexanecarboxylic acid (1.28 g; 10 mmol), ethanol (4.6 g, 100 mmol) and 2 drops of concentrated H_2SO_4 were added to a 22-mL glass vial. The vial was sealed with a PTFE-lined silicon cap and then heated at 100°C for 2 h. After cooling the vial to room temperature the reaction mixture was diluted 10 mL of pentane and extracted with a saturated aqueous Na_2CO_3 solution (2 x 5 mL). The pentane layer was washed with saturated aqueous NaCl (2 x 5 mL) and dried over anhydrous Na_2SO_4. The target compound (0.91 g) was recovered after removal of the pentane using a gentle stream of N_2 gas.

Methods

Direct Solvent Extraction

Nine rums, seven premium and two mixing rums, were pipetted (10mL) into individual 50mL screwcap centrifuge tubes. To reduce the alcohol by volume ratio to 10% ethanol, 30mL of deodorized water was added. The tubes were sealed with PTFE-lined caps and shaken for 5 minutes by hand. Dichloromethane (2mL) was added and the mixture shaken for an additional 5 minutes. The tubes were then centrifuged at 3500 RMP for 5 minutes (IEC HN-SI; Damon/IEC Division, Needham Heights, Massachusetts) to separate the solvent layers. The bottom phase (dichloromethane) was transferred into a 15mL conical test tube. The extraction with dichloromethane was repeated two more times, and the extracts were pooled. The pooled extract was dried with sodium sulfate (2g) to remove any excess water. The final dried extract was condensed to 0.5 mL using a gentle stream of nitrogen gas and stored at -20° C prior to analysis.

GCO Parameters

The gas chromatography-olfactometry (GCO) system used for analysis of the rum extracts consisted of a 6890N GC (Agilent Technologies, Inc., Wilmington, DE) equipped with a FID and olfactory detection port (OD2, Gerstel, Germany). One µL of extract was injected into a CIS-4 inlet (Gerstel, Germany) in the cold splitless mode (-50° C for 0.10 min, then increased at 12° C/sec to a final temperature of 260° C). Polar separation was performed using a RTX®-Wax column (15 m length x 0.53 mm i.d. x 1.0 µm film thickness; Restek; Bellefonte, PA), while non-polar separation was

performed using RTX®-5MS column (15 m length x 0.53 mm i.d. x 1.0 µm film thickness; Restek) to aid in identification. Helium was used as the carrier gas at 5.0 mL/minute. Post-separation, the flow was split using a deactivated, uncoated fused silica gel column between the FID (250° C) and the olfactory port (transfer line 250° C). Oven temperature was programmed as follows: initial temperature, 40° C (5 min hold), ramp rate 10° C/min, final temperature, 225° C (30 min hold).

GC-MS Parameters

The GC-MS system used for analysis of rum extracts consisted of a 6890N GC equipped with a 5973N mass spectrometer (Agilent Technologies Inc.). One µL of spiked extract was injected into a CIS-4 inlet (Gerstel, Germany) in the cold splitless mode (-50° C for 0.10 min, then increased at 12° C/sec to a final temperature of 260° C). Separations were performed using a RTX®-Wax column (30 m length x 0.53 mm i.d. x 1.0 µm film thickness; Restek; Bellefonte, PA). Helium was used as the carrier gas at 5.0 mL/minute. FID temperature was 250° C. Oven temperature was programmed as follows: initial temperature, 40° C (5 min hold), ramp rate 4° C/min, final temperature, 225° C (30 min hold). To aid in identification, analysis was also conducted using a RTX®-5MS column (30 m length x 0.53 mm i.d. x 1.0 µm film thickness; Restek).

Identification of Compounds

The rum extracts were subject to evaluation by both GCO and GC-MS. The retention index (RI) was calculated for each aroma active compound based on comparing its retention time (RT) to those of standard n-alkanes (van Den Dool & Kratz, 1963). The RI is calculated using the equation:

$$RI = 100n + 100n_{diff}\left[\frac{\left(t_{r(unknown)} - t_{r(n)}\right)}{\left(t_{r(N)} - t_{r(n)}\right)}\right]$$

where the difference in retention time between the unknown ($t_{r(unknown)}$) and the lower alkane ($t_{r(n)}$), is divided by the difference between the retention time of the upper alkane ($t_{r(N)}$) and the lower alkane, then multiplied by 100 times the difference in carbon numbers of the two alkanes (n_{diff}), and added to 100 times the number of carbons in the lower alkane(n). Odor-active compounds were tentatively identified based on three criteria: 1) comparison of RI on two different stationary phase columns (RTX-5 and wax) against literature values for known compounds, 2) comparison of the odor properties against published values, and 3) comparison of electron

ionization mass spectra (EI-MS) from the GC-MS to the EI-MS spectra in the National Institute of Standards and Technology (NIST) database. Compounds were considered positively identified when these comparisons were made against data from authentic reference standard analyzed under identical conditions.

Aroma Extract Dilution Analysis

Starting with a 0.5 mL aroma extract, AEDA was performed on a stepwise dilution series in dichloromethane. For this, 100 μL of the 0.5mL concentrated extract was diluted into 100 μL of dichloromethane serially to obtain 1:2 (FD=2), 1:4 (FD=4), 1:8 (FD=8), 1:16 (FD=16), 1:32 (FD=32), 1:64 (FD=64), 1:128 (FD=128), 1:256 (FD=256), 1:512 (FD=512), 1:1024 (FD=1024), 1:2048 (FD=2048), 1:4096 (FD=4095), and 1:8192 (FD=8192), dilution ratios. Each dilution was stored in a 1.5 mL septum-capped Target DP vial (National Scientific, Rockwood, TN) at -20° C prior to analysis. Dilution series were evaluated in order, starting with the most concentrated sample and subsequent dilutions were evaluated until no odorants were detected. The last dilution a compound was perceived was noted, corresponding to the compounds dilution factor. Due to time constraints, multiple panelists performed AEDA. The final flavor dilution (FD) factors were determined by converting individual FD factors to log2 values, averaging the results from two panelists rounding up to the nearest whole number and finally converting the values back to FD factors.

3.4 Results and Discussion

Nine rum samples, consisting of two mixing rums and seven premium rums were chosen for comprehensive aroma analysis (Table 3.1). Bacardi Superior and Bacardi Gold were chosen to represent the category of mixing rums since Bacardi is the number one seller of rum in the United States and the number two rum brand worldwide after McDowell's No. 1 Celebration (an Indian rum brand) ("Leading rum brands worldwide in 2015, based on sales volume (in million 9 liter cases)," 2017). The seven premium rums were chosen by comparing the review score on the Rum Howler blog (an industry expert), the number of awards and medals received by the company, making sure that a variety of different rums (in terms of production style) were evaluated and that the rum was able to be purchased at a local store.

Identification of Odorants and Aroma Extract Dilution Analysis

All rum samples were extracted and analyzed by GCO on two separate columns to identify the odor-active compounds present in the nine rum samples. Identification of the odor-active regions was determined by comparison of the retention index (RI) on two columns (RTX-Wax and RTX-5) to literature values, odor property matching that of literature, comparison of mass spectrum of the compounds determined by EI-MS to a library of known compounds and verification with an authentic standard. AEDA was performed on all rum samples to determine the relative potency of the identified compounds. FD factors are calculated on the basis of the compound's odor activity value (OAV) in air. Compounds perceived at higher dilutions are assumed to have a greater impact on the overall aroma of rum. It is important to note that OAV's for compounds are highly dependent on the matrix and while the compound may be perceived easily in air, it may be below its OAV is an alcoholic matrix.

Most Potent Odorants in Individual Rums

The intensity and order of potent odorants was found to vary between rum samples, as was the number of potent odorants detected. The total number of odor regions perceived for each rum and the most potent odorants (FD≥32) are reported below for each rum. The complete list of compounds identified and corresponding FD factors for all rums can be found in Table 3.2.

Odor-Active Compounds in Bacardi White Rum

Nineteen odor-active regions encompassing 22 compounds were detected in the BW rum. The region with the highest FD factor was identified as vanillin (FD=128), followed by acetal and 2-/3-methyl-1-butanol (FD=32). All other regions had FD factors of 8 or less.

Odor-Active Compounds in Bacardi Gold Rum

Thirty-three odor-active regions were detected in the BG rum. The regions with the highest FD factors were found to be 2-phenethyl alcohol, (*E*)-isoeugenol, and vanillin (FD=128). The next highest regions were 2-/3-methylbutanal and β-damascenone (FD=64) followed by *cis*-whiskey lactone/4-methylguaiacol, and sotolon (FD=32).

Odor-Active Compounds in Appleton Estate Rum

Forty-three odor-active regions were detected in AE rum. The regions with the highest FD factor were 2-/3-methyl-1-butanol, and 2-phenethyl alcohol (FD=512). The next most potent regions were *cis*-whiskey lactone/4-methylguaiacol (FD=256), acetal, sotolon, and vanillin (128), followed by (*E*)-isoeugenol and syringaldehyde (FD=64).

Odor-Active Compounds in Ron Abuelo 7 year Rum

Forty-four odor-active regions were detected in RA7. The region with the highest FD factor was vanillin (1024). This was followed by 2-phenethyl alcohol (FD=256), and 2-/3-methyl-1-butanol, *cis*-whiskey lactone/4-methylguaiacol (FD=128). Medium potent odorants consisted of acetal, sotolon, syringol, and ethyl vanillate (FD=64) and syringaldehyde (FD=32).

Odor-Active Compounds in Appleton Estate 12 year Rum

Forty-five odor-active regions were detected in AE12. The two most potent regions were determined to be vanillin (FD=2048) and (*E*)-isoeugenol (FD=512). The next most potent regions were 2-phenethyl alcohol (FD=128), followed by eugenol, ethyl vanillate, and unknown 59 (FD=64). Acetal, 2-/3-methyl-1-butanol, *cis*-whiskey lactone/4-methylguaiacol, and sotolon regions were also found to have a medium odor potency (FD=32).

Odor-Active Compounds in El Dorado 12 Year Rum

Fifty odor-active regions were detected in ED12. The most potent odorant was found to be vanillin (FD=512), followed by *cis*-whiskey lactone/4-methylguaiacol (FD=256) 2-phenethyl alcohol, and syringol (FD=128). Medium potent odor regions were determined to be 2-/3-methyl-1-butanol, *trans*-whiskey lactone/ethyl 3-phenylpropanoate (FD=64), sotolon, and (*E*)-isoeugenol (FD=32).

Odor-Active Compounds in Diplomatico Reserva 12 year Rum

Forty-four odor-active regions were detected in DR12 rum. The most potent odorants were determined to be vanillin (FD=4096), followed by ethyl vanillin (FD=2048), 2-/3-methyl-1-butanol (FD=1024), and 2-phenethyl alcohol (FD=512). (*E*)-Isoeugenol, unknown 59 (FD=256) and acetal (FD=128) were also found to have high potency. Medium potent odorants were determined to be

sotolon and syringaldehyde (FD=64) followed by ethyl butyrate, β-damascenone, *trans*-whiskey lactone/ethyl 3-phenylpropanoate, *cis*-whiskey lactone/4-methylguaiacol and ethyl vanillate (FD=32).

Odor-Active Compounds in Ron Zacapa Rum

Forty-five odor-active regions were detected in RZ. The most potent odorants were determined to be vanillin (FD=4096), 2-phenethyl alcohol (FD=2048), 2-/3-methyl-1-butanol, and *cis*-whiskey lactone/4-methylguaiacol (FD=1024). Medium potent odorants were determined to be β-damascenone (FD=64) followed by guaiacol, *m*-cresol, sotolon, (*E*)-isoeugenol, syringaldehyde and unknown 59 (FD=32).

Odor-Active Compounds in Dictador Insolent XO Rum

Thirty-six odor-active regions were detected in RZ. The region with the highest FD factor was ethyl vanillin (2048) followed by *cis*-whiskey lactone/4-methylguaiacol (512), vanillin (256), and 2-phenethyl alcohol (128). Regions with medium potency were 2-/3-methyl-1-butanol (FD=64), unknown 40, and isoeugenol (FD=32).

Overall, 59 odor-active regions, consisting of 64 compounds were detected in the nine rum samples. FD factors for all nine rums are shown in Table 3.2. Of those 59 regions, 11 were detected in all nine rums including acetal, ethyl butyrate, ethyl 2-methylbutyrate, 2-/3-methyl-1-butanol, *trans*-whiskey lactone/ethyl 3-phenylpropanoate, 2-phenethyl alcohol, *cis*-whiskey lactone/4-methylguaiacol, ethyl vanillin, vanillin, syringaldehyde and unknown 59 (Wax RI-2951, campfire). Twelve additional regions were detected in all rums except BW consisting of acetaldehyde, 2-/3-methylbutanal, ethyl 2-methylpropanoate, (*Z*)-2-nonenal, unknown 32 (Wax RI-1724, fruity, spice), β-damascenone, eugenol, sotolon, syringol, (*E*)-isoeugenol, unknown 51 (Wax RI-2421, woody), and ethyl vanillate. The absence of these compounds in BW suggests that they are formed during the maturation process, either through extraction or reactions within the distillate, or that these compounds are lost during the charcoal filtration step used to remove the color from BW rum. Additionally, these twenty-three regions encompassed all the most potent odorants (FD≥64) detected in the nine rum samples. Vanillin was found to be the most potent odorant in most rum samples except AE (2-phenethyl alcohol and 2-/3-methyl-1-butanol) and DX (ethyl vanillin). The overall most potent odorants contributing to rum flavor include acetal, 2-/3-methyl-1-butanol, β-

damascenone, 2-phenethyl alcohol, *cis*-whiskey lactone/4-methylguaiacol, eugenol, sotolon, syringol, (*E*)-isoeugenol, vanillin, ethyl vanillate, and syringaldehyde.

Unknowns accounted for fourteen of the detected odor-active regions. None of the unknowns are perceived at FD factors higher than 16 in any of the samples with the exception of unknown 59 (Wax RI-2951, Sac-5 RI-1832, campfire). This compound was found in every sample, with DR12 having the highest perception of the odorant (FD=256). Unknown 59 could not be identified despite having a significant peak. Electron ionization (EI)-MS (Figure 3.1) suggests the compound has a molecular weight of 226. However, no confirmed matches were found from searching the NIST database. Further research is required to identify this compound. The relatively high abundance of this compound suggests it may contribute to woody and smoky perceptions in rum.

Of the 50 odorants identified in the present study, 40 were previously identified as odor-active in rum (Burnside, 2012; de Souza et al., 2006; Franitza et al., 2016a, 2016b; J. A. Pino et al., 2012). In total, 10 compounds were identified for the first time as odor-active in rum, specifically: acetaldehyde, ethyl acetate, 1-octene-3-ol, (*Z*)-2-nonenal, *m*-cresol, syringol, (*E*)-isoeugenol, *Z*-6-dodecene-γ-lactone, ethyl vanillin, and syringaldehyde. The majority of these compounds have been previously identified in rum (Batiz & Rosado, 1978; Liebich et al., 1970; Maga, 1989; Pino, 2007; Pino, Marbot, Perez, & Nunez de Villavicencio, 1999; Pino et al., 2012; ter Heide et al., 1981). However, this is the first study to identify (*Z*)-2-nonen-al, (*Z*)-6-dodecene-γ-lactone and ethyl vanillin in any capacity in rum. (*Z*)-6-Dodecene-γ-lactone has previously been identified in Bourbon whiskey (Poisson & Schieberle, 2008) and white wine (Guth, 1997) and (*Z*)-2-nonenal has previously been detected in wood extracts (de Simón, Esteruelas, Muñoz, Cadahía, & Sanz, 2009). The presence of ethyl vanillin in the rum samples was not expected. Ethyl vanillin is a synthetic compound that is typically used as artificial vanilla. Ethyl vanillin was most likely added to the rum samples to increase vanilla aroma which is permissible by the Alcohol and Tobacco Tax Trade Bureau (*Limited Ingredients*, 2016). Under the regulation, ethyl vanillin and vanillin can be added to distilled beverages as long as the total concentration does not exceed 40ppm of vanillin and ethyl vanillin, and the rum does not need to be labeled as artificial.

Comparison of premium and mixing rums

Mixing rums were found to contain the same odorants as the premium rums with the exception of ethyl propanoate and 2,3-butandione which were the only two odorants to be detected exclusively in the mixing rums. All compounds detected in BW were also detected at the same or higher dilution factors in BG except heptanal and unknown 55 (Wax RI-2578, fresh/floral). The mixing rums contained less odor-active compounds. These compounds were also present in lower abundance, as indicated by the lower dilution factors, compared to the premium rum samples. All compounds detected in the mixing rums, except for the two previously mentioned, are found in at least two premium rums, with the majority of detected compounds found in all premium rums.

Premium rums were found to have at least ten additional odor-active regions compared to the mixing rums, with the exception of DX (only 36 odor-active regions). Due to the large-scale of Bacardi rum production, continuous column distillation is used. This process removes more of the volatile compounds produced during fermentation than a traditional pot still. Additionally, the increase in the number of odorants perceived in the premium rums could be a result of the extended time spent in the casks compared to the mixing rums. The extended time in the cask allows for the extraction of more oak extractives as well as allowing time for more reactions to occur between compounds in the distillate.

Premium rums all contained the following 23 compounds: acetaldehyde, acetal, 2-/3-methylbutanal, ethyl 2-methylpropanoate, ethyl butyrate, ethyl 2-methylbutyrate, 2-/3-methyl butan-1-ol, (*Z*)-2-nonenal, unknown 32 (fruity/spicy), β-damascenone, *trans*-whiskey lactone/ethyl 3-phenylpropanoate, 2-phenethyl alcohol, *cis*-whiskey lactone/4-methylguaiacol, eugenol, sotolon, syringol, (*E*)-isoeugenol, unknown 51 (woody), ethyl vanillin, vanillin, ethyl vanillate, syringaldehyde, and unknown 59 (campfire). Additional compounds were perceived in at least two samples with the exception of (*E*)-2-nonenal which was only found in ED12. Additionally, the potency and abundance of compounds varied from rum to rum. These variations are likely attributed to differences in production style. However, it is difficult to draw conclusions as to how specific difference in production methodologies may change the volatile profile of rum with the present information. A more thorough investigation into how production practices alter final rum is needed.

Origins of Odorants Found in Rums

Odorants present in the final rums can come from a variety of sources. These include coming from the initial molasses or cane juice, formation during fermentation, created from reactions occurring during distillation and/or aging, or extracted from the wood barrels.

The starting material, either molasses, cane juice or cane syrup, contributes more than just fermentable sugar to the final rum product. Franitza and others (2016b) followed odor-active compounds during the production process of rum, demonstrating that all odor-active compounds identified in the final rum product were present in the initial molasses, at some concentration, with the exception of *cis*- & *trans*-whiskey lactone. Other studies have also identified acetic acid, damascenone, guaiacol, 2-phenethyl alcohol, *p*-cresol, sotolon, syringol, isoeugenol, and vanillin in sugar cane molasses (Abe, Nakatani, Yamanishi, & Muraki, 1978a, 1978b; Tokitomo, Kobayashi, Yamanishi, & Muraki, 1980). Kobatashi (1989a) demonstrated sotolon to be a key odorant in raw sugar cane aroma.

Ethanol is the main by-product and reason for fermentation; however, numerous other odor-active compounds are also generated from the yeast and bacteria. The main compounds generated during fermentation are alcohols, acids, and esters. *Saccharomyces cerevisiae* and *Schizosaccharomyces pombe* help to generate propanol, butanol, isobutanol, propanoic acid, butyric acid, isobutyric acid, 3-methyl butanoic acid, and hexanoic acid (Fahrasmane, Parfait, Jouret, & Galzy, 1985). Formation of ethyl acetate, isoamyl acetate, and acetic acid by yeast has also been demonstrated (Nordström, 1963; B. L. Nykänen, Nykänen, & Suomalainen, 1977; L. Nykänen & Nykänen, 1977). Ethyl esters are formed enzymatically by activating the corresponding acids to acyl-CoA, which then reacts with ethanol. (Nordström, 1963). Ethyl 2-methylbutanoate is formed enzymatically from the esterification of 2-methyl-1-butanol with activated acetic acid (Matheis, Granvogl, & Schieberle, 2016). In alcoholic beverages, only the (S)-isomer exists as 2-methylbutanol is formed from (S)-isoleucine. 2-Methyl butan-1-ol is partially formed from the reduction of 2-methylbutanal according to the Ehrlich mechanism by oxidation of 2-methylbutanol to 2-methylbutanoic acid, followed by esterification with ethanol. However, this cannot be the only mechanism of formation as both (R) and (S) enantiomers of 2-methylbutanal have been found in alcoholic beverages. 2-methylbutanal can also be formed through Strecker-type degradations of L-isoleucine.

Aside from being present in the initial molasses used for fermentation, β-damascenone significantly increases after distillation (Franitza et al., 2016b). The formation of β-damascenone in alcoholic beverages is still unclear, although it is hypothesized that precursors could be generated during fermentation and then converted to β-damascenone through acid hydrolysis (Sefton, Skouroumounis, Elsey, & Taylor, 2011).

Maturation also has a significant impact on the final aroma of rum. Compounds formed during maturation come from three main pathways: 1)extracted directly from the wood, 2) decomposition of the wood macromolecules and 3) reactions that occur in the barrel between wood extractive, distillate components or both (Mosedale, 1995). Compounds directly extracted from the wood include compounds such as 2-phenethyl alcohol, 4-propylguaiacol, *m*-cresol, and *cis*- & *trans*-whiskey lactone (Cutzach, Chatonnet, Henry, & Dubourdieu, 1997; Maga, 1989; Mosedale, 1995). *Cis*- & *trans*-whiskey lactones were confirmed as only coming from wood extractives by Franitza and others (Franitza et al., 2016b), as the whiskey lactones were not detected in any of the steps prior to maturation.

Charring of the barrels has also been shown to form the precursors for (*E*)-2-nonenal and 1-octen-3-one which are then generated through auto-oxidative reactions, which are then extracted by ethanol into the distillate (Chatonnet & Dubourdieu, 1998). Whiskey lactone has been shown to be generated during barrel charring (Conner, Paterson, & Piggott, 1993).

The decomposition of wood macromolecules can be initiated by two methods. The first is through extraction of the lignin into the distillate, a process known as ethanolysis (Baldwin, Black, Andreasen, & Adams, 1967; Mosedale & Puech, 1998). The lignin is then broken down into sub-units of either coniferyl alcohol, sinapyl alcohol, and coumaryl alcohol. These lignin sub-units can also be formed through pyrolysis of the lignin during barrel charring (Conner et al., 1993; Piggott & Conner, 2003). The sub-units can further react and breakdown to form guaiacol, 4-ethylguaiacol, 4-vinylguaiacol, eugenol, isoeugenol and vanillin from coniferyl alcohol; syringaldehyde and syringol from coumaryl alcohol; and *p*-cresol from sinapyl alcohol (Baldwin et al., 1967; Cutzach et al., 1997; Genthner, 2014; Maga, 1989).

Chemical reactions that occur, typically oxidation and acetal formation, in the distillate during aging can account for the formation compounds such as acetaldehyde and acetic acid (Piggott & Conner,

2003). Esterification is one of the most frequent reactions that takes place between wood extractive such as aliphatic acids and compounds originally from the distillate including the formation of ethyl esters such as ethyl acetate, ethyl octanoate, ethyl hexanoate, and ethyl vanillate due to the significant amount of ethanol present (Maga, 1989; Piggott & Conner, 2003).

Sotolon was initially demonstrated to be formed from glutamic acid and pyruvate in raw sugar cane were the glutamic acid oxidized to α-keto glutarate and then condensed with the pyruvate (Kobayashi, 1989). It was later demonstrated that sotolon was formed from α-ketobutyric acid and acetaldehyde in wine model systems (Thuy, Elisabeth, Pascal, & Claudine, 1995). Sotolon concentration has been shown to increase over time in both Madeira wine and port (Câmara, Alves, & Marques, 2006; Silvia Ferreira, Barbe, & Bertrand, 2003). Other reaction mechanisms have been suggested sotolon could be formed from the condensation of diacetyl and hydroxyacetaldehyde (Silvia Ferreira et al., 2003). The most likely pathway in the aldol condensation between 2-ketobutyric acid and acetaldehyde, as has also demonstrated in dry white wines, and results have shown that 2-ketobutyric acid can be formed by strains of *Saccharomyces cerevisiae* (Pons, Lavigne, Landais, Darriet, & Dubourdieu, 2010).

The effect of wood maturation on the generation of these compounds in rum was demonstrated in Franitza's (2016b) recent study following the production process of rum, were the concentrations of vanillin, guaiacol, 4-ethylguaiacol, 4-propylguaiacol, *p*-cresol, sotolon and *cis*- & *trans*-whiskey lactone all increased during maturation.

Conclusion

A total of 10 compounds were identified as odor-active compounds for the first time in rum. The compounds (*Z*)-2-nonenal, (*Z*)-6-dodecene-γ-lactone and ethyl vanillin were identified for the first ever in any rum sample. In summary, clear differences exist between mixing and premium rums, primarily in number and potency of odorants as well as with the premium rum class. However, the 23 odorants identified in all premium samples suggest they are the key components of rum flavor. Differences in production practices are the most likely reason for variations between samples. Quantitative studies to confirm the contribution of the identified compound to the overall aroma of rum have been undertaken and will be discussed in Chapter 4.

3.5 Tables and Figure

Table 3.1 Product and manufacturing information for rums analyzed

Code	Rum	Age*	Country of Origin	Barrels Used	Manufacturer
BW	Bacardi Superior[M]	1 year	Puerto Rico	White Oak[F]	Bacardi Limited
BG	Bacardi Gold[M]	2 years	Puerto Rico	Toasted Oak[F]	Bacardi Limited
AE	Appleton Estate V/X[M]	5-10 years[B]	Jamaica	Whiskey Barrels	J. Wary & Nephew Ltd.
RA7	Ron Abuelo: Reserva Superior[M]	7 years	Panama	Small Oak Barrels	Varela Hermanos
AE12	Appleton Estate Extra[M]	12 years	Jamaica	American Oak Barrels[P]	J. Wary & Nephew Ltd.
DR12	Diplomatica Reserva Exclusiva [C]	12 years	Venezuela	Small Oak Casks[P]	Destilería Unidas S.A
ED12	El Dorado: Finest Demerara Rum[M]	12 years	Guyana	Bourbon Oak Casks[+]	Demerara Distillers Limited
RZ	Ron Zacapa (Centenario) XO: Solera Gran Reserva Especial[C]	6-25 years[S]	Guatemala	American Whiskey, Sherry, Pedro Ximenez Wines and Cognac	Rum Creation and Products, Inc.
DX	Dictador XO Insolent[C]	21 years[S]	Columbia	Jerez and Port Barrels[A, R]	Dictador

*Age declared on bottle, [M] Produced from molasses, [C] Produced from sugar cane honey, [B] Blend of rums, [S] aged using Solera system, [F] Rum charcoal filtered, [P] Distilled using copper pot stills, [+] Combination of wooden and metal coffee stills and wooden pot stills, [A] Distilled in stainless steel alembic, [R] Barrels recharred

Table 3.2 Odor-active compounds identified by AEDA of nine rums

			RI[a]		Flavor Dilution Factor[b,c]								
No.	Compound	Odor Description[d]	WAX	RTX 5	BW	BG	AE	RA7	AE12	DR12	ED12	RZ	DX
1	acetaldehyde[e]	fruity, sweet	712	<500	-[f]	1	2	8	2	2	4	1	2
2	2-methylpropanal[e]	chocolate	906	592	-	-	1	-	2	2	-	1	2
3	ethyl acetate	plastic	922	629	-	-	-	-	1	-	1	2	-
4	acetal[e]	melon	927	720	32	16	128	64	32	128	16	2	16
5a,b	2-/3-methylbutanal[e]	chocolate	930	669	-	2	16	2	4	2	4	8	1
6	ethyl propanoate[e]	cherry	960	711	2	2	-	-	-	-	-	-	-
7	ethyl 2-methylpropanoate[e]	fruity	968	752	-	4	8	8	8	1	4	2	2
8	2,3-butanedione[g]	sweaty/cheesy	983	598	1	1	-	-	-	-	-	-	-
9	unknown	plastic	998		1	2	2	-	4	1	4	-	-
10	unknown	pungent, plastic, fruity	1010		-	1	-	-	4	2	1	-	-
11	unknown	solvent, painty	1014		-	-	-	2	2	-	4	4	-
12	ethyl butyrate[e]	fruity	1041	803	1	4	2	4	2	32	2	1	8
13	ethyl 2-methylbutyrate[e]	melon	1057	844	1	1	16	8	8	1	8	1	2
14	unknown	fruity	1061		2	16	4	4	2	2	4	2	-
15	ethyl 3-methylbutyrate[e]	fruity	1075	852	1	4	1	1	-	-	2	-	-
16	hexanal[h]	green	1087	807	-	-	-	-	-	-	1	-	1
17	isobutanol[e]	chocolate	1101	653	-	-	-	1	1	4	1	2	-
18	isoamyl acetate[e]	fruity	1122	884	-	-	-	-	-	1	1	2	-
19	ethyl pentanoate[e]	fruity	1145	900	-	-	-	1	-	1	1	-	1
20	heptanal[g]	fruity	1197	900	1	-	-	-	-	1	1	-	-
21a,b	2-/3-methyl-1-butanol[e]	chocolate	1212	731	32	64	512	128	32	1024	64	1024	64
22	ethyl hexanoate[e]	floral	1239	1001	-	-	-	-	1	1	2	1	1
23	1-octen-3-one[h]	mushroom, earthy	1303	980	1	2	1	1	-	1	1	2	1
24	ethyl cyclohexanecarboxylate[g]	fruity	1422	1126	-	-	16	2	-	2	2	2	-
25	ethyl octanoate[e]	earthy, soil	1436	1195	-	2	2	4	-	-	-	-	-
26	acetic acid[e]	fruity, vinegar	1448	630	-	-	1	1	4	2	-	2	2
27	methional[g]/1-octene-3-ol[h]	potato/mushroom	1460	902/980	-	-	1	4	2	2	-	4	-

Table 3.2 (cont.) Odor-active compounds identified by AEDA of nine rums

			RI[a]		Flavor Dilution Factor[b,c]								
No.	Compound	Odor Description[d]	WAX	RTX 5	BW	BG	AE	RA7	AE12	DR12	ED12	RZ	DX
28	*(Z)*-2-nonenal[g]	laundry, floral	1502	1148	-	1	2	16	8	2	8	4	2
29	*(E)*-2-nonenal[g]	hay	1536	1141	-	-	-	-	-	-	2	-	-
30	phenyl acetaldehyde[h]	floral	1636		-	-	-	-	2	2	2	-	1
31	3-methylbutyric acid[g]	cheesy	1661	856	-	-	8	2	1	-	1	16	2
32	unknown	fruity/spicy	1724		-	8	8	4	2	1	4	16	2
33	unknown	floral	1798		-	-	-	-	1	-	2	-	-
34	β-damascenone[e]	applesauce	1813	1380	-	64	32	16	16	32	8	64	1
35	guaiacol[e]	spices/cloves	1844	1084	-	1	8	2	4	-	2	32	-
36a,b	*trans*-whiskey lactone[e]/ ethyl 3-phenylpropanoate[h]	floral	1876	1290/1350	8	16	8	8	8	32	64	8	8
37	2-phenethyl alcohol[e]	roses	1903	1109	8	128	512	256	128	512	128	2048	128
38a,b	*cis*-whiskey lactone[e]/ 4-methylguaiacol[e]	coconut, potpourri	1939	1311/1182	2	32	256	128	32	32	256	1024	512
39	unknown	spicy, cloves	1961		-	-	1	-	-	-	1	4	-
40	unknown	cotton candy	1998		-	-	32	2	-	1	4	2	32
41	4-ethylguaiacol[e]	spices, floral	2016	1270	-	-	2	2	8	4	1	-	4
42	unknown	sweat BO	2033		-	-	4	-	-	-	2	2	-
43	*p*-cresol[e]	skunky/barnyard	2070	1076	-	-	16	1	2	4	-	1	-
44	*m*-cresol[e]	burnt plastic	2076	1076	-	-	16	8	2	8	-	32	1
45	4-propylguaiacol[h]	nutmeg	2095	-	-	8	8	4	4	-	4	4	-
46	eugenol[e]	baking spices	2152	1367	-	8	16	16	64	2	16	16	16
47	sotolon[g]	curry	2167	1103	-	32	128	64	32	64	32	32	8
48	syringol[e]	smoky, spices	2243	1344	-	8	32	8	16	8	128	8	1
49	(*E*)-isoeugenol[e]	floral, cloves	2326	1462	-	128	64	64	512	256	32	32	32
50	*Z*-6-dodecene-*γ*-lactone[g]	floral, stale	2379	1653	-	-	-	1	8	-	-	1	-
51	unknown	woody	2421		-	4	1	2	2	1	2	8	1
52	unknown	dirty floral	2476		-	-	1	2	1	4	1	1	-

Table 3.2 (cont.) Odor-active compounds identified by AEDA of nine rums

			RI[a]		Flavor Dilution Factor[b,c]								
No.	Compound	Odor Description[d]	WAX	RTX 5	BW	BG	AE	RA7	AE12	DR12	ED12	RZ	DX
53	ethyl vanillin[e]	vanilla	2492	1430	4	8	1	4	8	2048	16	4	2048
54	vanillin[e]	vanilla	2534	1396	128	128	128	1024	2048	4096	512	4096	256
55	unknown	fresh/floral	2578		4	-	1	8	1	-	2	16	16
56	ethyl vanillate[e]	vanilla	2606	1560	-	16	4	64	64	32	16	8	8
57	unknown	band-aid	2850		-	-	-	2	4	4	4	-	2
58	syringaldehyde[e]	vanilla	2916	1656	2	16	64	32	16	64	8	32	16
59	unknown	campfire	2951	1832	4	4	16	8	64	256	2	32	8

[a] Retention indexes determined from GCO data. [b] "BW" is Bacardi White, "BG" is Bacardi Gold, "AE" is Appleton Estate V/X, "RA7" is Ron Abuelo 7 year, "AE12" is Appleton Estate 12 year, "DR12" is Diplomatico Reserva Exclusica, "ED12" is El Dorado 12 year, "RZ" is Ron Zacapa Centurio, "DX" is Dictador XO Insolent. [c] FD factors were determined on a RTX-wax column and were determined from average $\log_2$ FD factors [n=2] after rounding up to the nearest whole number. [d] Odor properties determined by GCO. [e] Compound positively identified based on retention index on both RTX-wax and RTX-5 columns, odor property, mass spectral data, and reference standard compound. [f] Not detected. [g] Compound tentatively identified based on retention index on both RTX-wax and RTX-5 columns, odor property, and reference standard compound. [h] Compound tentatively identified based on retention index on RTX-wax column, odor property, and reference standard compound.

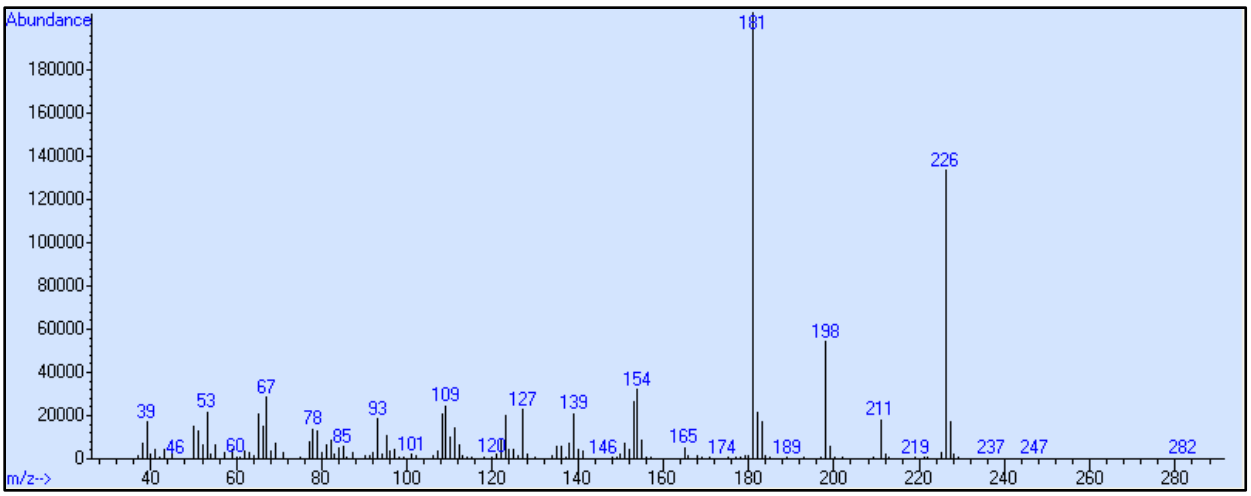


Figure 3.1 EI-Mass spectrum of unknown 59

3.6 References

Abe, E., Nakatani, Y., Yamanishi, T., & Muraki, S. (1978a). Studies on the "Sugary Flavor" of Raw Cane Sugar. I. *Proceedings of the Japan Academy. Ser. B: Physical and Biological Sciences*, *54*(B), 542–547. http://doi.org/10.2183/pjab.54.542

Abe, E., Nakatani, Y., Yamanishi, T., & Muraki, S. (1978b). Studies on the "Sugary Flavor" of Raw Cane Sugar. III. *Proceedings of the Japan Academy. Ser. B: Physical and Biological Sciences*, *54*(B), 457–462. http://doi.org/10.2183/pjab.54.542

Baldwin, S., Black, R. A., Andreasen, A. A., & Adams, S. L. (1967). Aromatic Congener Formation in Maturation of Alcoholic Distillates. *Journal of Agricultural and Food Chemistry*, *15*(3), 381–385. http://doi.org/10.1021/jf60151a012

Batiz, H., & Rosado, E. (1978). A Single Column Gas Chromatographic Method for the Direct Trace Analysis of High Boiling Components in Rums. *The Journal of Agriculture of University of Puerto Rico*, *62*(4), 330–343.

Bober, A., & Haddaway, L. W. (1963). Gas Chromatographic Identification of Alcoholic Beverages. *Journal of Gas Chromatography*, *1*(12), 8–13.

Burnside, E. E. (2012). *Characterization of Volatiles in Commercial and Self-Prepared Rum Ethers and Comparison with Key Aroma Compounds of Rum*. University of Illinois at Urbana-Champaign. Retrieved from https://www.ideals.illinois.edu/handle/2142/34368

Câmara, J. S., Alves, M. A., & Marques, J. C. (2006). Changes in volatile composition of Madeira wines during their oxidative ageing. *Analytica Chimica Acta*, *563*(1–2 SPEC. ISS.), 188–197. http://doi.org/10.1016/j.aca.2005.10.031

Chatonnet, P., & Dubourdieu, D. (1998). Identification of Substances Responsible for the "Sawdust" Aroma in Oak Wood. *Journal of the Science of Food and Agriculture*, *76*, 179–188. http://doi.org/10.1002/(SICI)1097-0010(199802)76:2<179::AID-JSFA924>3.0.CO;2-6

Conner, J. M., Paterson, A., & Piggott, J. R. (1993). Changes in Wood Extractives from Oak Cask Staves through Maturation of Scotch Malt Whisky. *Journal of the Science of Food and Agriculture*, *62*,

169–174. http://doi.org/10.1002/jsfa.2740620210

Cutzach, I., Chatonnet, P., Henry, R., & Dubourdieu, D. (1997). Identification of Volatile Compounds with a "Toasty" Aroma in Heated Oak Used in Barrelmaking. *Journal of Agricultural and Food Chemistry*, *45*, 2217–2224. http://doi.org/10.1021/jf960947d

de Simón, B. F., Esteruelas, E., Muñoz, Á. M., Cadahía, E., & Sanz, M. (2009). Volatile Compounds in Acacia, Chestnut, Cherry, Ash, and Oak Woods, with a View to Their Use in Cooperage. *Journal of Agricultural and Food Chemistry*, *57*, 3217–27. http://doi.org/10.1021/jf803463h

de Souza, M. D. C. A., Vásquez, P., del Mastro, N. L., Acree, T. E., & Lavin, E. H. (2006). Characterization of Cachaça and Rum Aroma. *Journal of Agricultural and Food Chemistry*, *54*, 485–488. http://doi.org/10.1021/jf0511190

Fahrasmane, A., Parfait, A., Jouret, C., & Galzy, P. (1985). Production of Higher Alcohols and Short Chain Fatty-Acids By Different Yeasts Used in Rum Fermentations. *Journal of Food Science*, *50*, 1427–1436. http://doi.org/10.1111/j.1365-2621.1985.tb10492.x

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*, 637–645. http://doi.org/10.1021/acs.jafc.5b05426

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*, 9041–9053. http://doi.org/10.1021/acs.jafc.6b04046

Genthner, E. R. (2014). *Identification of Rotundone as an Important Contributor to the Flavor of Oak Aged Spirits*. University of Illinois at Urbana Champaign. Retrieved from https://www.ideals.illinois.edu/handle/2142/16898

Guth, H. (1997). Identification of Character Impact Odorants of Different White Wine Varieties. *Journal of Agricultural and Food Chemistry*, *45*, 3022–3026.

Kobayashi, A. (1989). Sotolon: Identification, Formation, and Effect on Flavor. In *Flavor Chemistry: Trends and Developments (ACS 388)* (Vol. 388, pp. 49–59). American Chemical Society. http://doi.org/10.1021/bk-1989-0388.ch005

Leading rum brands worldwide in 2015, based on sales volume (in million 9 liter cases). (2017). Retrieved March 16, 2017, from https://www.statista.com/statistics/259739/leading-rum-brands-worldwide-based-on-sales-volume/

Liebich, H. M., Koeing, W. A., & Bayer, E. (1970). Analysis of the Flavor of Rum by Gas-Liquid Chromatography and Mass Spectrometry. *Journal of Chromatographic Science*, *8*, 527–533. Retrieved from http://chromsci.oxfordjournals.org/content/8/9/527.short

Limited Ingredients. (2016). *Alcohol and Tobacco Tax and Trade Bureau*. Retrieved from https://www.ttb.gov/ssd/limited_ingredients.shtml

Maarse, H., & tem Noever de Brauw, M. C. (1966). The Analysis of Volatile Components of Jamaica Rum. *Journal of Food Science*, *31*(6), 951–955. Retrieved from http://onlinelibrary.wiley.com/doi/10.1111/j.1365-2621.1966.tb03275.x/full

Maga, J. A. (1989). The Contribution of Wood to the Flavor of Alcoholic Beverages. *Food Reviews International*, *5*(1), 39–99. http://doi.org/10.1080/87559128909540844

Matheis, K., Granvogl, M., & Schieberle, P. (2016). Quantitation and Enantiomeric Ratios of Aroma Compounds Formed by an Ehrlich Degradation of L-Isoleucine in Fermented Foods. *Journal of Agricultural and Food Chemistry*, *64*, 646–652. http://doi.org/10.1021/acs.jafc.5b05427

Monsalve, J. O., Lopez, C., & Zapata, J. (2016). Characterization of aroma compounds in Colombian rums by HS-SPME-GC-MS-O. *Revista Colombiana de Química*, *45*(2), 48–54. http://doi.org/http://dx.doi.org/10.15446/rev.colomb.quim.v45n2.60406.

Mosedale, J. R. (1995). Effects of oak wood on the maturation of alcoholic beverages with particular reference to whisky. *Forestry*, *68*(3), 203–230. http://doi.org/10.1093/forestry/68.3.203

Mosedale, J. R., & Puech, J.-L. (1998). Wood maturation of distilled beverages. *Trends in Food Science & Technology*, *9*, 95–101. http://doi.org/10.1016/S0924-2244(98)00024-7

Ng, L.-K. (1999). Analysis of Vodkas and White Rums by SPME-GC-MS. In J. Pawliszyn (Ed.), *Applications of Solid Phase Microextraction* (pp. 393–406). Cambridge, UK: The Royal Society of Chemistry. http://doi.org/10.1039/9781847550149-00393

Nordström, K. (1963). Formation of Esters from Acids by Brewer's Yeast I. Kinetic Theory and Basic Experiments. *Journal of the Institute of Brewing*, *69*, 310–322.

Nykänen, B. L., Nykänen, I., & Suomalainen, H. (1977). Distribution of Esters Produced During Sugar Fermentation Between the Yeast Cell and the Medium. *Journal of the Institute of Brewing*, *83*, 32–34.

Nykänen, L., & Nykänen, I. (1977). Production of Esters by Different Yeast Strains in Sugar Fermentations. *Journal of the Institute of Brewing*, *83*, 30–31.

Nykanen, L., Puputti, E., & Suomalainen, K. (1968). Composition of the Aroma in Some Brands of Whisky and Rum Analysed by Customary Methods and by Gas Chromatography. *Kemian Teollisuus*, *25*(5), 399–404.

Piggott, J. R., & Conner, J. M. (2003). Whiskies. In A. G. . Lea & J. R. Piggott (Eds.), *Fermented Beverage Production* (2nd ed., pp. 239–262). New York: Kluwer Academic/Plenum Publishers.

Pino, J. A. (2007). Characterization of rum using solid-phase microextraction with gas chromatography–mass spectrometry. *Food Chemistry*, *104*, 421–428. http://doi.org/10.1016/j.foodchem.2006.09.031

Pino, J. A., Marbot, R., Perez, J., & Nunez de Villavicencio, M. (1999). Application of Multivariate Statistical Methods to Differentiation of Rum Aged in Two Types of Oak Barrels. *Journal of Food Quality*, *22*, 183–191. Retrieved from %5C%5CRobsrv-05%5Creference manager%5CArticles%5C8919.pdf

Pino, J. A., Tolle, S., Gök, R., & Winterhalter, P. (2012). Characterisation of odour-active compounds in aged rum. *Food Chemistry*, *132*, 1436–1441. http://doi.org/10.1016/j.foodchem.2011.11.133

Pino, J., Martí, M. P., Mestres, M., Pérez, J., Busto, O., & Guasch, J. (2002). Headspace solid-phase microextraction of higher fatty acid ethyl esters in white rum aroma. *Journal of Chromatography A*, *954*, 51–57.

Poisson, L., & Schieberle, P. (2008). Characterization of the Most Odor-Active Compounds in an American Bourbon Whisky by Application of the Aroma Extract Dilution Analysis. *Journal of*

Agricultural and Food Chemistry, *56*, 5813–5819.

Pons, A., Lavigne, V., Landais, Y., Darriet, P., & Dubourdieu, D. (2010). Identification of a Sotolon Pathway in Dry White Wines. *Journal of Agricultural and Food Chemistry*, *58*, 7273–7279. http://doi.org/10.1021/jf100150q

Sefton, M. a, Skouroumounis, G. K., Elsey, G. M., & Taylor, D. K. (2011). Occurrence, Sensory Impact, Formation, and Fate of Damascenone in Grapes, Wines, and Other Foods and Beverages. *Journal of Agricultural and Food Chemistry*, *59*, 9717–46. http://doi.org/10.1021/jf201450q

Silvia Ferreira, A. C., Barbe, J., & Bertrand, A. (2003). 3-Hydroxy-4,5-dimethyl-2(5H)-furanone: A key Odorant of the Typical Aroma of Oxidative Aged Port Wine. *Journal of Agricultural and Food Chemistry*, *51*, 4356–4363. http://doi.org/10.1021/jf0342932

Stevens, R., & Martin, G. (1965). Gas Chromatographic Identification of Ethyl Esters of Fatty Acids in Domestic and Imported Rums. *Journal of the Association of Official Agricultural Chemists*, *48*(4), 802–805.

ter Heide, R., Schaap, H., Wobben, H. J., de Valosis, P. J., & Timmer, R. (1981). Flavor Constituents in Rum. In *The Quality of Foods and Beverages* (pp. 183–200).

Thuy, P. T., Elisabeth, G., Pascal, S., & Claudine, C. (1995). Optimal Conditions for the Formation of Sotolon from α-Ketobutyric Acid in the French "Vin Jaune." *Journal of Agricultural and Food Chemistry*, *43*(10), 2616–2619. http://doi.org/10.1021/jf00058a012

Timmer, R., ter Heide, R., Wobben, H. J., & de Valois, P. J. (1971). Phenolic Compounds in Rum. *Journal of Food Science*, *36*, 462–463.

Tokitomo, Y., Kobayashi, A., Yamanishi, T., & Muraki, S. (1980). Studies on the "Sugary Flavor" of Raw Cane Sugar. II. *Proceedings of the Japan Academy. Ser. B: Physical and Biological Sciences*, *56*, 452–456.

van Den Dool, H., & Kratz, P. D. (1963). A Generalization of the Retention Index System Including Linear Temperature Programmed Gas—Liquid Partition Chromatography. *Journal of Chromatography*, *11*, 463–471.

Wobben, H. J., Timmer, R., ter Heide, R., & de Valois, P. J. (1971). Nitrogen Compounds in Rum and Whiskey. *Journal of Food Science*, *36*, 464–465.

Chapter 4: Quantitation of Odor-Active Compounds in a Selection of Premium Rums and Use of Chemometrics to Correlate Analytical and Sensory Analysis

4.1 Abstract

Thirty-four of 50 odor-active compounds identified in the previous study in mixing and premium rums were quantitated. Results revealed the same compounds were present in all rums analyzed, except the Bacardi White rum and the compound ethyl vanillin; however, they varied in their concentration accounting for flavor differences among rums. Sixteen compounds were determined to be the most important components of overall rum flavor since they were detected in all nine rum samples with odor activity values > 1. These consisted of 2-methyl propanal, acetal, 3-methyl butanal, 2-methyl butanal, ethyl 2-methylpropanoate, ethyl butanoate, ethyl 2-methylbutanoate, ethyl 3-methylbutanoate, 3-methyl-1-butanol, 2-methyl-1-butanol, ethyl hexanoate, β-damascenone, guaiacol, *cis*-oak lactone, and vanillin. Premium rums tended to have higher concentrations and subsequently higher OAVs than mixing rums for most compounds, except for Dictador XO Insolent 21 year rum, in which concentrations for some compounds were lowest among all rums. Chemometrics was employed to gain a better understanding of the drivers of aroma variations in the rums analyzed. Vanillin and ethyl vanillate, were found to be driving factors of sweet-like aroma attributes including brown sugar, caramel, maple and vanilla aromas. Meanwhile, roasted aroma was driven by a decrease of several compounds rather than by an increase or decrease in any single odorant.

4.2 Introduction

Rum is a complex and diverse spirit, produced from sugarcane by-products including sugarcane juice, syrup or molasses. Rum's minimum standard of identity allows for a variety of manufacturing practices to be used in its production. Key differences in production styles include variations in staring material, yeast and bacteria used for fermentation, length of fermentation, distillation

apparatus, aging system, barrel type and maturation length. The resulting rums span from light one-year aged white rums, to heavy Jamaican style 50 year old rum. The breadth of rum types available make it difficult to identify the key constituents of overall rum flavor. Previous studies on rum flavor have only focused on the evaluation of one or two rum samples, making it difficult to define the entire category (Burnside, 2012; de Souza, Vasquez, Del Mastro, Acree, & Lavin, 2006; Franitza, Granvogl, & Schieberle, 2016a, 2016b; Pino, Tolle, Gök, & Winterhalter, 2012). Additionally, only three of these studies have quantitated the odor-active compounds identified in rum (Franitza et al., 2016a, 2016b; Pino et al., 2012) and only the studies by Franitza have used stable isotope dilution analysis for compound quantitation. In our previous study (Chapter 3), the key aroma compounds were identified for a variety of premium rums and a set of mixing rums on the basis of flavor dilution factors determined by application of aroma extract dilution analysis. A total of 59 odor-active regions, encompassing 50 identifiable compounds and 14 unknown regions.

Chemometrics is the use of statistics to analyze chemical data (Beebe, Pell, & Seasholtz, 1998). Chemometrics can be used in one of two ways, either by creating a calibration for use in predicting and/or identifying future samples or to help identify patterns in complex datasets (Beebe et al., 1998; Roberts & Cozzolino, 2016). A number of different methods exist for both types of analyses. Model creation methods include artificial neural networks, multiple linear regression, principle components regressions and partial least squares discrimination analysis. Pattern recognition analysis includes hierarchical cluster analysis and principal components analysis (PCA). Partial least square discriminant analysis and PCA are by far the most often methods used in the correlation of sensory and analytical data (Seisonen, Vene, & Koppel, 2016).

In the present study, principal components analysis was selected, as the goal of this research was to evaluate the relationship between sensory and analytical data, and not to create a model system. The purpose of PCA is to reduce the number of variables to the fewest number of factors possible (Beebe et al., 1998; Brereton, 2007, 2009). These new factors are then plotted instead of the original variable measurements allowing for easier visualization and interpretation of the data.

Chemometrics has been used extensively to evaluate food systems and to better understand the complexity of food matrices as illustrated by Roberts and Cozzolino (2016) in their recent review article. Focusing specifically on flavor chemistry, a significant number of studies have used chemometrics to correlate sensory and analytical data (Seisonen et al., 2016). Alcoholic beverages

that have been investigated using chemometrics include beer (da Silva et al., 2012; Dong et al., 2014), whiskey (Wiśniewska, Śliwińska, Dymerski, & Wardencki, 2017), and rice wine (Jung, Lee, Lim, Kim, & Park, 2014; Mimura, Isogai, Iwashita, Bamba, & Fukusaki, 2014), with the majority of studies focused on wine (Andreu-Sevilla, Mena, Martí, García Viguera, & Carbonell-Barrachina, 2013; Aznar, López, Cacho, & Ferreira, 2003; González Álvarez, González-Barreiro, Cancho-Grande, & Simal-Gándara, 2011; Green, Parr, Breitmeyer, Valentin, & Sherlock, 2011; Liu et al., 2015; Niu et al., 2011; Robinson et al., 2011; Vilanova, Genisheva, Masa, & Oliveira, 2010; Xiao et al., 2014). Chemometrics has also been used to profile rum (Sampaio, Reche, & Franco, 2008) and cachaça, a Brazilian sugarcane spirit similar to rum (Granato, de Oliveira, Caruso, Nagato, & Alaburda, 2014). Most studies focused on the differentiation of the two beverages (Cardoso et al., 2004; P. P. de Souza et al., 2007; Todeschini et al., 2007). These studies used mineral concentration, electrospray ionization-mass spectrometry, and concentrations of selected compounds consisting mainly of higher alcohol and phenolic compounds as variables to differentiate the rum and cachaça samples. However, to date chemometrics has not been implemented to correlate the sensory attributes and volatile aroma components of rum or cachaça.

The goal of this research was two-fold. The first aim was to first quantitate the odor-active compounds identified in our previous study (Chapter 3). The second aim was to use chemometrics to correlate the analytical data (concentrations, odor activity values, and flavor dilutions factors) with sensory aroma intensity ratings for the same rum samples determined in a previous study (Chapter 6) in order to gain a better understanding of how sensory attributes are affected by changes in concentration of odor-active compounds.

4.3 Materials and Methods

Materials

The nine selected rums were purchased at a local liquor store (Champaign, IL) (Table 3.1). All nine rums had reported ethanol concentration of 40% alcohol by volume (ABV). Mention of the brand name of these rums does not imply any research contact or sponsorship, and is not for advertisement or endorsement purposes.

Chemicals

Dichloromethane, ethyl acetate, hydrochloric acid, calcium chloride, potassium hydroxide, sodium chloride and sodium sulfate were purchased from Fisher Scientific Co. (Fair Lawn, NJ); 3,4-dihydroxy-5-methoxybenzaldehyde, d_6-dimethylfulate and d_6-ethanol were purchased from Aldrich (Milwaukee, WI) and used for volatile extraction and synthesis of isotopic standards. De-odorized water was prepared by boiling deionized-distilled water to two-thirds of its original volume.

Deodorized water and 190 proof ethanol (Decon Labs, Inc. USP grade, King of Prussia, PA) were used to create the 40% ABV mimic matrix.

Standard Compounds

The following chemicals were used as authentic standards to determine response factors for quantitation with isotopes and relevant odor thresholds: 2-methylpropanal, ethyl propanoate, ethyl-3-methylbutyrate, isoamyl acetate, ethyl hexanoate, ethyl octanoate, *p*-cresol, and eugenol, were obtained from Aldrich (Milwaukee, WI); acetaldehyde, 3-methylbutanal, ethyl 2-methylpropanoate, ethyl butyrate, ethyl-2-methylbutyrate, ethyl pentanoate, 2-methyl-1-butanol, 3-methyl-1-butanol, mixture of *cis*-&-*trans* whiskey lactone, 2-phenethyl alcohol, guaiacol, syringol, isoeugenol, and ethyl vanillin were obtained from Sigma-Aldrich (St. Louis, MO); acetic acid, 4-methylguaiacol, 4-ethylguaiacol, *m*-cresol, sotolon, vanillin, syringaldehyde were obtained from SAFC (St. Louis, MO); ethyl vanillate was obtained from Alfa Aeasar (Lancaster, UK); 2-methylbutanal was obtained from Bedoukian (Danbury CT); acetal (1,1-diethoxyethane) was obtained from Acros Organics (NJ); isobutanol was obtained from Fisher (Fair Lawn, NJ); and β-damascenone was obtained from Firmenich (Switzerland).

Isotopes for Quantitation

The following compounds were purchased to be used as isotopically labeled standards quantitation: d_7-ethyl butanoate, d_{11}-ethyl hexanoate, d_3-guaiacol, and d_3-*p*-cresol were purchased from C/D/N Isotopes Inc., (Pointe- Claire, Quebec, Canada), and d_8-*m*-cresol was purchased from Sigma-Aldrich (St. Louis, MO).

Isotopically labeled standards not available for purchased were synthesized according to the published procedure in parentheses: d_2-2-methyl propanal, d_2-3-methyl butanal, d_2-2-methylbutanal

(Lapsongphon, Yongsawatdigul, & Cadwallader, 2015; Steinhaus & Schieberle, 2005) d_2-isoamyl acetate, d_2-*cis*- & *trans*-whiskey lactone, d_2-4-methylguaiacol, d_3-vanillin, d_5-ethyl vanillate (Lahne, 2010), d_2-isobutanol (Lahne, 2010; Steinhaus & Schieberle, 2005), d_2-3-methyl-1-butanol (Steinhaus & Schieberle, 2005), d_2-2-methyl-1-butanol (Kelley, 2014; Steinhaus & Schieberle, 2005), d_4-ethyl octanoate (Genthner, 2014), d_4-β-damascenone (Kotseridis, Baumes, & Skouroumounis, 1998; Lahne, 2010), $^{13}C_2$-2-phenethyl alcohol (Lahne, 2010; Schuh & Schieberle, 2006), d_5-4-ethylguaiacol (Lahne, 2010; Rayne & Eggers, 2007), d_3-eugenol (Kulkarni, Kadam, Mane, Desai, & Wadgoankar, 1999; Lahne, 2010; Schneider & Rolando, 1992), d_3-syringol (Lahne, 2010; Schneider & Rolando, 1992), d_3-*(E)*-isoeugenol (Lorjaroenphon, 2012), d_{10}-acetal and d_3-syringaldehyde (below).

Structures for all labeled isotopes mentioned above are shown in Figure 4.1.

Synthesis of d_{10}-Acetal

d_{10}-acetal was synthesized following the procedure by Adkins and Nissen (1941). d_6-Ethanol (1.26mL) and anhydrous calcium chloride (0.2g) were added to a 50mL screw top test tube and cooled in an ice bath. Next, freshly distilled acetaldehyde (0.46mL) was slowly pipetted down the side of the tube, to form a layer on top of the alcoholic calcium chloride. The test tube was capped and shaken vigorously for 2 minutes. The mixture was then allowed to stand for one day at room temperature with intermittent shaking. The reaction was checked by GC-MS to determine that it had gone to completion. Once the reaction was complete, the top layer (acetal) was pipetted off into a separatory funnel, and the acetal was washed 3x with 2mL of water.

Synthesis of d_5-Ethyl Esters

d_5-Ethyl propanoate was synthesized as follows. Propionic acid (0.74 g; 10 mmol), d_6-ethanol (0.158 g, 3 mmol; Aldrich, ≥99.5% atom %D) and 2 drops of concentrated H_2SO_4 were added to a 22-mL glass vial. The vial was sealed with a PTFE-lined silicon cap and then heated at 100°C for 2 h. After cooling the vial to room temperature the reaction mixture was diluted 10 mL of pentane and extracted with a saturated aqueous Na_2CO_3 solution (2 x 5 mL). The pentane layer was washed with saturated aqueous NaCl (2 x 5 mL) and dried over anhydrous Na_2SO_4. The target compound (0.21 g) was recovered after removal of the pentane using a gentle stream of N2 gas:

d$_5$-Ethyl 2-methylbutanoate, *d*$_5$-ethyl 2-methylpropanoate, *d*$_5$-ethyl 3-methylbutanoate were synthesized following the same procedure.

Synthesis of *d*$_3$-Syringaldehyde

d$_3$-Syringaldehyde was synthesized following the procedure by Lahne (2010). First 0.501 g (3 mmol) of 3,4-dihydroxy-5-methoxybenzaldehyde was dissolved in aqueous 40% KOH (5mL) under a nitrogen purge in a screw-capped test tube (PTFE-top) equipped with a stir bar. Then, over the course of 30 minutes (5-6 drops every 5 minutes), 0.35 mL (0.42 g, 3.2 mmol) of *d*$_6$-dimethylsulfate was added to the reaction tube after which the reaction mixture became yellow and cloudy. The vial was then capped and stirred for 2 hours. The reaction was checked for completion by removing 5-6 drops of the mixture, adding it to a vial containing 1 mL aqueous 1N HCl and 0.5 mL ethyl acetate, and analyzing the ethyl acetate layer by GC-MS. The reaction was continued, adding 0.08 mL (0.096 g, 0.73 mmol) d$_6$-dimethylsulfate and letting the reaction stir overnight until nearly all starting material had been consumed. The reactions was stopped by acidifying the mixture to ~pH 1 and extracted with ethyl acetate (1 x 10mL, 4 x 5 mL). The ethyl acetate layer was washed with saturated NaCl and then dried over anhydrous Na_2SO_4. The solution was concentrated to ~10 mL using a vigreux column and the remaining solvent was then removed under a stream of nitrogen. The final product was weighed for a final yield of 0.5734 g.

Methods

Stable Isotope Dilution Analysis (SIDA)

Isotopically labeled (^{2}H or ^{13}C) standard compounds were used for the quantitation of compounds determined to be potent odorants by AEDA. For analysis by direct solvent extraction, the rum samples (10 mL) were spiked with a known concentration of the isotope for each compound of interest. Next, deodorized water (30 mL) was added to dilute the alcohol concentration to ~10%ABV and the samples were then shaken for 5 minutes. Dichloromethane (2 mL) was added to each sample to extract the isotopes and target compounds. The samples were shaken for an additional 5 minutes and then centrifuged at 3500 RPM to separate the aqueous and organic layers. The bottom layer (dichloromethane) was transferred to a 15 mL conical test tube. The sample was extracted two more times and the extracts were pooled. The extract was then dried over sodium

sulfate and the sample concentrated to 0.5 mL under a gentle stream of nitrogen. The samples were stored at -20 °C until analyzed.

GC-MS Analysis

Solutions for analysis by GC-MS were prepared for both mass spectra and labeled:unlabeled mass ratio calibration. Each solution was analyzed by GC-MS in cold-splitless mode (-50°C for 0.10 min, then increased at 12°C/sec to 260°C, with 1.10 min valve-delay), using the same stationary columns (Stabiwax column and RTX-5 column) as for the analysis of the samples.

The GC-MS system used for quantitation consisted of a 6890 GC/5973N mass selective detector (Agilent Technologies Inc.). Two µL of spiked extract was injected into a CIS-4 inlet (Gerstel, Germany) in the cold splitless mode (-50°C for 0.10 min, then increased at 12°C/sec to a final temperature of 260°C). Separations were performed using a Stabilwax column (30 m length x 0.25 mm i.d. x 0.25 µm film thickness; Restek; Bellefonte, PA). Helium was used as the carrier gas at 0.7 mL/minute. Oven temperature was programmed as follows: initial temperature, 35 °C (5 min hold), ramp rate 4 °C/min, final temperature, 225 °C (30 min hold). For each compound the key identifying ions were scanned for during the run using selection ion monitoring (SIM) mode. Table 4.1 contains the list of compounds quantitated along with their ions analyzed and the response factor from the standard curve.

For each compound a response factor was determined by plotting the ratio of the mass of the standard of interest / mass of corresponding isotope vs the ratio of the area count of the standard/ area count of the isotope. The response factor was then calculated from 1 over the slope:

$$Rf = \frac{1}{slope}$$

For each compound, the area of the selected mass ion on the chromatogram was integrated using Enhanced Data Analysis Software (Agilent Technologies, USA). The mass ratio of the labeled:unlabeled compound is plotted against the chromatogram area of the selected mass ion, using the slope of the line to calculate the response factor for each compound. Standard curve data from all compounds quantitated can be found in Appendix A. The response factor used to calculate the actual concentration of the compound in the sample using the following equation:

$$concentration_{unlabeled} = \frac{area_{unlabeled}}{area_{labeled}} * Rf * mass_{labeled} / sample\ volume$$

where the area of the target compounds is divided by the area of the isotope, then multiplied by the response factor, multiplied by the mass of the isotope in the samples (determined by multiplying the volume of isotope spiked by the concentration of the solution) and finally divided by the volume of sample initially spiked with the isotope.

Headspace Solid-Phase Microextraction (HS-SPME)

Headspace solid-phase microextraction (HS-SPME) was used to quantitate the highly volatile aroma compounds. Rum (0.5 mL) was pipeted into a 20 mL glass headspace vial containing 0.5 g of sodium chloride and 1.5 mL of deodorized water. The samples were then spiked with the isotope solutions. Samples were analyzed by GC-MS using an auto-sampler. Samples were equilibrated at 60°C for 10 minutes and then the headspace volatiles were extracted by placing a triple phase SPME fiber (divinylbenzene/carboxen/polydimethylsiloxane) (Supelco; Bellefonte, PA) to extract the volatiles for 5 minutes at 60°C. The SPME fiber was then removed and the volatiles desorbed into a Gerstal CS4 injection port (splitless injection at 260°C with 4 minute valve-delay).

Quantitation of Strecker Aldehydes

Strecker aldehydes (methylpropanal, 3-methylbutanal, and 2-methylbutanal) were quantitated by SIDA using HS-SPME-GC-MS. The conditions for SPME extraction and desorption were the same as above. The GC-MS parameters were as follows: separations were performed using an RXi-5ms column (30 m length x 0.25 mm i.d. x 0.25 μm film thickness; Restek; Bellefonte, PA). Helium was used as the carrier gas at 1.0 mL/minute. Oven temperature was programmed as follows: initial temperature, 30° C (5 min hold), ramp rate 6° C/min, final temperature, 225° C (30 min hold). Other GC-MS conditions were the same as earlier described.

Quantitation of Acetal

Additionally, acetal was quantitated using direct injection methodology. The rum samples (1 mL) were spiked with a known concentration of the isotope immediately before injection and then shaken for one minute. Then, a 1 μL sample was injected into the GC-MS using hot, splitless injection (260°C with 1.10 minute valve-delay) and separations performed using a RTX-5 column.

(30 m length x 0.25 mm i.d. x 0.25 μm film thickness; Restek; Bellefonte, PA). Helium was used as the carrier gas at 0.5 mL/minute. Oven temperature was programmed as follows: initial temperature, 35° C (5 min hold), ramp rate 6° C/min, final temperature, 225° C (30 min hold). Other GC-MS conditions were the same as earlier described.

Quantitation of Ethyl Vanillin

Ethyl vanillin was quantitated using internal standard methodology. The rum samples were extracted following the same procedure used for SIDA, spiking the samples with a known concentration of d_3-vanillin. A standard curve comparing mass ratios and area ratios for selected ions of ethyl vanillin to d_3-vanillin were constructed and can be found in Appendix A.

Quantitation of Acetaldehyde and Acetic Acid

Acetaldehyde and acetic acid were quantitated using external standard calibration. The GC-FID system used for quantitation consisted of a 6890N GC (Agilent Technologies Inc.) equipped with a flame ionization detector (FID). Two μL of straight rum was injected using a 7683 autosampler and injector (Agilent Technologies Inc.) into a split/splitless inlet in the hot split mode (260° C, 5:1 split ratio). Separations were performed using a Stabiwax-DA column (30 m length x 0.32 mm i.d. x 0.5 μm film thickness; Restek; Bellefonte, PA). Helium was used as the carrier gas at 2.0 mL/minute. FID temperature was 250°C. Oven temperature was programmed as follows: initial temperature, 35 °C (5 min hold), ramp rate 10 °C/min, final temperature, 225 °C (20 min hold).

Calibration solutions were prepared by spiking known amounts of acetaldehyde or acetic acid into a 40% ABV mimic matrix. Standard curves for acetaldehyde and acetic acid can be found in Appendix A.

Determination of Odor Thresholds

All procedures and recruitment material was approved by the Institutional Review Board (IRB) at the University of Illinois Urbana-Champaign (IRB Protocol Number: 17508), Appendix B.

Odor thresholds of ethyl vanillate, isoeugenol, and syringaldehyde were determined in 40% ABV ethanolic matrix. Odor purity of the samples was checked prior to threshold determination by

running the most concentrated dilution by GCO. Samples were determined odor pure if no other odorants were detected at that concentration.

A series of seven samples was prepared for sensory evaluation for each compound. A stock solution of each compound was prepared by dissolving the compounds of interest in 100 mL a 40% ABV ethanolic matrix. The solution was pipetted (20 mL) into a 125 mL Teflon bottle. A 1:3 dilution was prepared by adding 20 mL of 40% ABV ethanolic matrix to a Teflon bottle and then adding 10 mL of the stock solution. The remaining five solutions in the series were prepared in the same manner, taking 10 ml of the previous solution for the dilution. The final volume in each bottle was 20 mL.

Odor thresholds were determined by sensory evaluation through the use of the 3-alternative forced choice (3-AFC) method, according to the American Society for Testing and Materials (ASTM) method for determining odor thresholds (ASTM E679-04, 2011) using an ascending concentration series. A minimum of seven panelists were used for each threshold determination. For each concentration level, panelists were presented with one bottle containing the compound of interest and two blanks (20 ml 40% ABV ethanolic matrix in a Teflon bottle). Panelists started with the least concentrated sample and evaluated samples in ascending order. Samples were covered with aluminum foil and labeled with a random three-digit code prior to analysis. Panelists were asked to sniff the bottles in the order indicated on the sheet and then select which of the samples was stronger than the other two. Panelists evaluated the series in duplicate with a five-minute break between replications. The concentrations used for each dilution series and panelists results can be found in Appendix C.

Statistical Analysis of Quantitation Data

Statistical analysis of the data was performed using Statistical Analysis System (SAS)® (Version 9.4, SAS Institute Inc., Cary, NC, USA). Analysis of variance (ANOVA) was conducted on each compounds quantitated to determine the presence of overall significant differences ($p<0.05$) using the PROC GLM function for variations aroma concentration between the nine rums. The calculated probabilities were compared to significance levels $\alpha=0.05$, 0.01 and 0.001. Fisher's least significant difference (LSD) test was conducted on all attributes determined as significant by ANOVA. Cluster analysis was also conducted using SAS software using the PROC CLUSTER function on the mean quantitation and OAV data separately.

Chemometric Analysis

Principle component analysis (PCA) was employed to compare the analytical and sensory results. Sensory scores for the aroma attributes evaluated in the nine rum samples obtained from previous descriptive analysis panel (Chapter 6) were used. The sensory scores were compared to multiple analytical results: concentrations, odor activity values and FD factors (Chapter 3). Odor activity values and FD factors were pre-process prior to evaluation. OAV were pre-processed by removing all compounds that had OAVs less than 1 for all rum samples. For FD factors, only odor-active regions that contained at least one FD factor of 8 or higher were used for statistical analysis.

Statistical analysis was performed using SAS. Principle component analysis (PCA) was conducted using the PROC CORR function followed by the PROC FACTOR function. Microsoft® Excel® 2016 (Version 16: Microsoft Corporation, Redmond, WA) was used to create a visual representation of the data to allow further examination of the relationship of the rums to individual attributes that characterized the samples. Pearson correlations were calculated using the same SAS software, with significance determined at α=0.1, 0.05, and 0.01.

4.4 Results and Discussion

Quantitation of Potent Odorants in Mixed and Premium Rum

Stable isotope dilution analysis (SIDA) was used for accurate quantitation of selected odor-active compounds in rums. SIDA is a highly accurate method of quantitation for volatile compounds as isotopically labeled compounds are used as the internal standards. The isotopes differ only from the target compounds by the replacement of carbon atoms (^{12}C) with heavy carbon atoms (^{13}C) or by replacement of hydrogen atoms (^{1}H) with deuterium atoms (^{2}H). As a result, the physical and chemical properties of the isotopes are the same as the corresponding standard. Therefore, the isotope and standard will interact with the matrix and extraction solvents in the same way. Losses of the two compounds will be the same, and the ratio established when the internal standard is added to the sample will be the same as when the extract is analyzed. All isotopes used in this study (Figure 4.1) were labeled with deuterium except for 2-phenethyl alcohol which was labeled with heavy carbon (^{13}C).

A total of 34 odor-active compounds positively identified in the previous study (Chapter 3) were selected for quantitation by SIDA or external standard calibration (Table 4.2). All compounds quantitated were found in all nine rum samples regardless if they were detected by AEDA with the exception of 4-ethylguaiacol and eugenol, which were not detected in BW. This is to be expected as they are compounds generated during wood aging (Cutzach, Chatonnet, Henry, & Dubourdieu, 1997; Maga, 1989). Additionally, ethyl vanillin was only detected in DR12 and DX. ANOVA was performed for each compound quantitated, revealing significant differences in concentration across the nine rums for all compounds. Calculated F-values can be found in (Table 4.3), and mean separation by Fisher's Least Significant Difference test was performed on all compounds with concentrations found to be statistically different between rums.

The most abundant compounds in all nine rums were 3-methyl-1-butanol, isobutanol, acetaldehyde, acetic acid, 2-methyl-1-butanol and acetal. This is in agreement with the previous studies by Franitza (2016a, 2016b), who also found these compounds to be the most abundant in rum, with the exception of acetaldehyde which was not quantitated in that study. Interestingly, while these compounds varied in concentration among the rums, the relative order of abundance was relatively similar. In BW, BG, AE and RZ the compounds descended in concentration in the order as listed above. RA7, AE12 and ED12 had the same order of descending compound except acetic acid was the most abundant compound in these three rums. The order of abundance for DR12 and DX were similar to the concentration order of RA7, AE12, and ED12 except the order of 2-methyl-1-butanol, acetaldehyde, and acetal varied. Aside from these compounds, the order of other compounds varied among rums. Syringaldehyde, 2-phenethyl alcohol, *cis*-whiskey lactone, vanillin and ethyl propanoate appeared as the next 7 most abundant compounds in all nine rums. The least abundant compounds in all samples tended to be 4-ethylguaiacol, 4-methylguaiacol, *m*-cresol, and *p*-cresol. Other compounds present in low abundance included β-damascenone, eugenol, ethyl 2-methylbutanoate, and ethyl pentanoate.

Ethyl vanillin was only detected in two samples, DR12 and DX. Ethyl vanillin is a synthetic flavor compound commonly used as artificial vanilla and its presence in rum was not expected. However, the Alcohol and Tobacco Tax and Trade Bureau (TTB) lists ethyl vanillin as one of four compound on its limited ingredients list (*Limited Ingredients*, 2016). Compounds on this list can be added to distilled beverages without having to claim them on the label or identifying the product as imitation. As long as ethyl vanillin is present at concentrations less than 16 ppm, and the "total vanillin"

concentration (sum of the concentration of vanillin plus 2.5 times the ethyl vanillin concentration) is less than 40 ppm the final rum can still be called a natural product. The "total vanillin" concentrations of both DX and DR12 are well under this limit, 8.75 ppm and 5.24 ppm respectively.

Comparing compounds across rums, AE12 and ED12 has the highest concentrations for the majority of odorants. Overall, the aged rums tended to have the highest concentration of all compounds with the exception of DX. BW, BG and DX which consistently had the lowest concentrations of all compounds quantitated. Interestingly, DX had the highest concentration of ethyl butanoate and β-damascenone among all nine rums. It is difficult to say why the compound concentration of DX is so low in comparison to the other aged rums. The low concentrations in DX might be a result of maturation by the solera system or the extended aging period (21 years) of the rum, as many of the volatiles may have been lost to evaporation over time. A more detailed investigation into the production process of DX would be required to better explain the overall low compound abundance in this rum.

BW and BG were expected to have the lowest concentration of many of the compounds This is due to the fact that the two mixing rums spent the least amount of time in barrels and were distilled by continuous column distillation which removes more fermentation-derived odor-active compounds compared with other distillation methods such as pot distillation. It was hypothesized that the mixing rums may have higher concentrations of the more volatile compounds such as acetaldehyde or the Strecker aldehydes that may be lost due to evaporation over time in the aged rums but this was not the case.

Cluster analysis was performed using the quantitations data (Figure 4.2). BG and BW were found to be the most similar to each other as the distance between the two rums is smallest of any cluster pairing and less than half of the distance to the next cluster. As was expected, the aged rums (RA7, AE12, DR12, ED12, and RZ) were grouped together, with the exception of DX, which was grouped with the younger aged rums (BW, BG, AE). Groupings within the aged rums revealed no other significant correlations between quantitation data and the disclosed production processes (Table 3.1). The grouping of DX with the younger rums in most likely related to the fact that overall the concentration for most compounds was significantly lower than the other aged rums.

Calculation of OAVs

Calculation of odor activity values (OAVs) is necessary to better understand the impact of odorants on the final rum flavor. While compound concentration reveals how much is present in the sample, it gives no indication as to how important the compound is to the overall aroma. Some compounds may be present in high concentrations but have a minimal impact on the overall aroma while other compounds may be low threshold potent odorants, where they have low concentrations but high impact factors. An odor detection threshold is the concentration a compound required for it to be perceived in a matrix. Since compounds will react differently in different matrices, it is best to determine thresholds in a matrix as similar to the final product as possible. Research has shown that odor thresholds do change with changes in ethanol concentration. Therefore, thresholds determined in a 40:60 (v/v) ethanol/water matrix were used when possible. OAVs are calculated by dividing the concentration of the compound in the matrix by the concentration needed to detect the compound in the matrix. Compounds with OAVs over 1 are assumed to impact the overall flavor perception of the food or beverage.

The calculated OAVs for the nine rum samples are presented in Table 4.4. The number of compounds with OAVs greater than 1 varied among rums. The number of compounds present at concentrations above their thresholds was 17 for BW, 19 for BG, 23 for AE, 23 for RA7, 25 for AE12, 23 for DR12, 22 for ED12, 24 for RX, and 19 for DX. The order of compound potency varied among rums as well as OAVs for a single compound across all nine rum samples. For example, the OAV of 2-methylpropanal in AE12 was 488 whereas it was only 6 in DX. Significant difference is OAVs were also seen among rums for 3-methylbutanal (OAVs of 12 to 432), ethyl 2-methylpropanoate (OAVs of 3 to 154), ethyl 2-methylbutanoate (OAVs of 18 to 369), ethyl 3-methylbutanoate (OAVs of 9 to 149), β-damascenone (OAVs of 34 to 439), and vanillin (OAVs of 15 to 217).

Of the 34 compounds quantitated, 26 of the compounds had OAVs greater than 1 in at least one of the rums. Fifteen of the compounds had OAVs greater than 1 in all nine samples, specifically: 2-methylpropanal, acetal, 3-methylbutanal, 2-methylbutanal, ethyl 2-methylpropanoate, ethyl butanoate, ethyl 2-methylbutanoate, ethyl 3-methylbutanoate, 3-methyl-1-butanol, 2-methyl-1-butanol, ethyl hexanoate, β-damascenone, guaiacol, *cis*-whiskey lactone, and vanillin. When excluding the mixing rums, ethyl octanoate and eugenol also have OAVs above 1 for all premium rums.

Additionally, these compounds contained the highest OAV values across all rum samples as all compounds with OAVs of 10 or greater were among these 17 compounds. The most potent odorants were β-damascenone for BG (OAV 90), RA7 (OAV 272), DR12 (OAV 143), and DX (OAV 439), 2-methylpropanal for BW (OAV 52), AE (OAV 400) and AE12 (OAV 488), 3-methylbutanal for ED12 (OAV 288) and ethyl 2-methylpropanoate (OAV 154).

4-Methylguaiacol, *p*-cresol, *m*-cresol, ethyl vanillate and syringaldehyde all had OAVs less than 0.01 in all rums. Syringol, *trans*-whiskey lactone and (*E*)-isoeugenol had OAVs less than 1 for all rums. While these compounds may not have a direct impact on the aroma of rum, compounds with high abundance such as syringaldehyde, ethyl vanillate, (*E*)-isoeugenol and *trans*-whiskey lactone, may affect the partitioning of other compounds into the headspace and may be necessary for the creation of an accurate model system.

The variation in odorants with OAVs greater than 1 is likely the cause of the differences perceived in rum aroma within the category. While there seems to be a core set of compounds important to all rums, the relative differences in concentration differentiate them from each other. The only compounds that specifically defines a set of rums is ethyl vanillin in DR12 and DX. The inclusion of ethyl vanillin in these samples is likely the result of the addition to the rums during the manufacturing process as discussed previously. The most significant differences observed between premium and mixing rums were the OAVs for *cis*-whiskey lactone and vanillin. Noticeable differences also existed for ethyl octanoate and acetic acid.

Cluster analysis was also performed on the nine rums using the OAV results (Figure 4.3). Interestingly, the rums were grouped differently than when using the quantitation data (Figure 4.2). BW and BG are still grouped together as the most similar to each other, with the smallest distance between clusters. AE and AE12 are also grouped together, although while they are grouped as more similar to each other, they are not as closely related as the other seven rums are to themselves as indicated by the distance between clusters. The aged rums are no longer clearly separated from the other rums and DX is grouped much farther away from the mixing rums despite its overall low concentration of volatiles.

Comparison to previous studies

Of the 34 compounds quantitated, 24 had previous been quantitated in rum after being identified as odor-active constituents (Franitza et al., 2016a, 2016b; Pino et al., 2012). Ten compounds, acetaldehyde, 2-methylpropanal, ethyl propanoate, 4-methyl guaiacol *m*-cresol, syringol, isoeugenol, ethyl vanillin, and syringaldehyde were quantitated for the first time in rum. However, only acetaldehyde, 2-methylpropanal, ethyl propanoate and ethyl vanillin were found to have OAVs over 1. While these other compounds may not have a direct impact on the aroma of rum, they may have an impact on flavor release based on their interactions with other compounds present in the matrix.

The concentrations of all compounds are of similar magnitude to those reported in other rum studies (Franitza et al., 2016a, 2016b; Pino et al., 2012). Significant variation does exists with respect to concentrations between studies, but as demonstrated in this study, these differences are most likely attributed to variations among products. OAVs were also found to be of similar magnitude to previous studies. Pino found β-damascenone to have the highest OAV in the rum sample analyzed, followed by ethyl butanoate, vanillin, ethyl hexanoate, guaiacol, *cis*-whiskey lactone, ethyl 2-methylpropanoate, ethyl octanoate, ethyl decanoate, 4-propyl guaiacol, eugenol, acetal, ethyl 2-methylbutanoate, γ-nonalactone, 4-ethylguaiacol, 2-phenethyl alcohol, isoamyl acetate and 2-phenethyl acetate, which all had an OAVs greater than 1 (Pino et al., 2012). These results are similar to the present study, although the OAVs of β-damascenone and ethyl butanoate reported in the previous study were much higher than any of the rums analyzed in this present study.

Franitza's analysis of two rum samples found only 14 compounds in rum A and 12 compounds in rum B to have OAVs above 1 of the 37 compounds quantitated (Franitza et al., 2016a). Rum A, their aged rum sample, contained vanillin, 2-methylbutanoate, β-damascenone, 3-methylbutanal, 2,3-butandione, ethyl butanoate, acetal, and *cis*-whiskey lactone at OAVs well over 1 (OAVs $\geq$ 5). These compounds were also found to be the most important in the aged rums in the present study. Rum B, the lower quality rum, contained 2,3-butandione, 3-methylbutanal, ethyl butanoate, ethyl 2-methylbutanote, ethyl pentanoate, β-damascenone, and acetal at high OAVs. Franitza found the OAVs to be much higher for 3-methylbutanal and ethyl butanoate in the lower quality rum compared to the aged rum, while in our study the aged rums tended to have higher concentrations of all compounds. The lower OAVs in Rum A could be due to the fact that the rum was aged in a

solera system, as we also observed lower compound concentrations and OAVs for DX solera aged rum as well.

Franitza's (2016b) more recent study following the production process of rum. They observed an increase in concentration and OAVs for many of the compounds. This difference might be attributed to different aging practices as in that study - the rum was single cask aged for 3 years in contrast to the rum aged by the solera system in their previous study. β-Damascenone was found to have the highest OAV (3280), followed by 3-methylbutanal, 2,3-butandione, ethyl 2-methylbutaonate, vanillin, ethyl butanoate, 2-methylbutanal, guaiacol, acetal, sotolon, ethyl octanoate, 2-methyl-1-butanol, ethyl 3-methylbutanoate, 4-ethyguaiacol, 3-methyl-1-butanol, ethyl hexanoate, 4-propylphenol, isoamyl acetate, 4-ethylphenol and 3-methyl butyric acid, which were all found to have OAVs of 5 or greater. The present study also found many of these compounds to have OAV's above 1 with β-damascenone, 3-methylbutanal, ethyl 2-methylbutanoate, vanillin, and ethyl butanoate also having relatively high OAV's in the present study.

Chemometrics

Although pre-processing can be a useful tool in chemometrics, only exclusion of certain variables was applied, and no data transformation was employed other than what was done by SAS. Preliminary analyses were done on unmanipulated and autocorrected (application of mean centering followed by variance scaling (dividing by standard deviation)), revealed no significant differences in the data analysis.

Four different PCA analyses were performed to correlate the aroma sensory attributes obtained from a previous descriptive analysis panel study (Chapter 6, Table 6.3) to various analytical measurements, specifically: 1) quantitation data, 2) odor activity values, 3) flavor dilution factors of 8 or greater, and 4) flavor dilution factors of 16 or greater. These different analytical measurements were selected to evaluate which measurement may be most appropriate for correlating the analytical and sensory data.

Aroma intensity ratings and quantitation data was correlated and the results can be seen in Figure 4.4. Pearson correlation coefficients used to create the PCA plot are given in Table 4.5. The first principal component (PC1) accounted for 44.6% of the variation, with the second principal component (PC2) accounting for 23.0% of the variation. Visually apparent in the graph, the aroma

attributes are clustered into two distinct groups with roasted aroma in the middle. One group contains vanilla, caramel, chocolate, brown sugar, coconut and maple aromas and the other contains smoky, phenolic, alcohol and citrus aromas. Many of the odor-active compounds quantitated were not significantly correlated to any of the aroma attributes. As expected, ethyl vanillin was highly correlated ($p<0.01$) to the sweet aroma attributes including brown sugar, caramel, maple, vanilla and chocolate aroma while being negatively correlated to alcohol, phenolic and citrus aroma. β-Damascenone was also significantly correlated ($p<0.1$) to brown sugar aroma and maple aroma. Ethyl vanillin has a sweet, vanilla odor and it is logical that the high levels present in DX and DR12 would increase perceptions of those sweet-like aroma attributes. Additionally, ethyl butyrate was significantly correlated to maple aroma and negatively correlated to both citrus and alcohol aroma. 2-Methylpropanal and ethyl propanoate were significantly correlated to phenolic aroma, which is interesting as the compounds have chocolate and fruity aromas, respectively, when perceived by alone. Additionally, acetic acid was correlated to coconut aroma. Finally roasted aroma has significant negative correlation with acetal, ethyl propanoate, ethyl 2-methylbutanoate, ethyl 3-methylbutanoate, ethyl pentanoate, *trans*-whiskey lactone, *cis*-whiskey lactone, (*E*)-isoeugenol, ethyl vanillate, and syringaldehyde.

Aroma data was also correlated with OAV data. The PCA results can be seen in Figure 4.5 and the Pearson correlation coefficients are provided in Table 4.6. The first principal component (PC1) accounted for 38.9% of the variation, with the second principal component (PC2) accounting for 26.6% of the variation. Compounds that had OAVs of less than 1 for all nine rums were not used for the analysis as those compounds are not expected to significantly impact the overall aroma perception of the rum. Similar to the correlation with quantitation data, roasted aroma was negatively correlated ($p<0.1$) to acetal, ethyl propanoate, ethyl 2-methylbutanoate, ethyl 3-methylbutanoate, 2-methyl-1-butanol, 3-methyl-1-butanol, ethyl octanoate, 2-phenethyl alcohol, 4-ethylguaiacol and eugenol. Additionally, phenolic aroma was correlated to methylpropanal and 2-methylbutanal. β-Damascenone was again correlated to brown sugar and maple aroma as well as coconut aroma while negatively correlated to citrus aroma. Interestingly, ethyl vanillin had no significant correlation with any of the aroma attribute when the results were converted to OAVs, however, vanillin had a number of significant correlations. Vanillin was correlated to brown sugar, caramel, vanilla, roasted and chocolate aroma and negatively correlated to phenolic aroma. Finally,

ethyl hexanoate was correlated to brown sugar, caramel, and maple aroma, while negatively correlated to alcoholic aroma.

Finally, the aroma attributes were correlated to flavor dilution factors. Two different levels of FD factors were chosen as cut off for evaluation to see how changes in selected variables may affect the outcome of the correlation. The first cutoff was that compounds had to be perceived at an FD factor of 8 or greater in at least one of the rum samples. Any compounds that did not meet this criterion were removed from the analysis. The PCA results can be seen in Figure 4.6 and the Pearson correlation coefficients are provided in Table 4.7. The first principal component (PC1) accounted for 27.6% of the variation, with the second principal component (PC2) accounting for 19.8% of the variation. Similar to the correlations with the quantitation data, ethyl vanillin was highly correlated to brown sugar, caramel, maple, vanilla and chocolate aroma while negatively correlation to citrus, phenolic, alcohol and smoky aroma. However, unlike the quantitation and OAV correlations roasted aroma did not have as many significant correlations. Roasted aroma was correlated to ethyl butanoate and syringaldehyde while negatively correlated to eugenol and (*Z*)-6-dodecen-γ-lactone. In contrast, smoky aroma was significantly correlated with a number of compounds, where no significant correlation were observed in the first two PCA plots. Smoky aroma was positively correlated to 2-/3-methylbuatnal, ethyl 2-methylpropanoate, ethyl-2-methylbutanoate, ethyl cyclohexanoate, *p*-cresol, 4-propylguaiacol, and sotolon, while negatively correlated to ethyl vanillin. Ethyl butanoate was another compound with numerous correlations including positive correlations with caramel, vanilla, roasted and chocolate aromas and a negative correlation with phenolic aroma.

Aroma attributes were then correlated to compounds with FD factors of 16 or greater in at least one of the rum samples. The PCA results can be seen in Figure 4.7, and the Pearson correlation coefficients are provided in Table 4.8. The first principal component (PC1) accounted for 29.3% of the variation, with the second principal component (PC2) accounting for 21.3% of the variation. Moving the cutoff to an FD factor of 16 or greater in at least one of the rums eliminated acetaldehyde, ethyl 2-methylpropanoate, 4-ethylguaiacol, 4-propyl guaiacol, isoeugenol and (*Z*)-6-dodecen-γ-lactone from the analysis. Interestingly, the removal of these compounds caused no change in the significant correlation or even the correlation coefficients other than the removal of those linked to compounds omitted from the analysis. The results suggest that the cutoff for FD factors to consider in correlation to sensory results does not have a huge impact on the overall

correlations other than to remove possible correlations that may exist between those lower perceived compounds and the aroma attributes being evaluated.

Comparing the four PCAs to each other, the correlations using the quantitation and OAV data accounted for the most variation amongst the samples (68.6% and 65.5% respectively). The correlations with FD factors only account for about half of the variation (47.7% for FD ≥ 8 and 50.6% for FD ≥ 16). All four analyses had the aroma attributes clustered into two distinct groups, brown sugar, caramel, chocolate, coconut, maple and vanilla aromas in one group and alcohol, citrus, phenolic and smoky aromas in the other. Of interest is that fact that ethyl vanillin was highly correlated with brown sugar, caramel, chocolate, maple and vanilla aromas in all PCA except the correlation with OAVs. In that PCA plot, vanillin was significantly correlated to those attributes, and ethyl vanillin had no significant correlations. The other main difference was that the quantitation and OAV PCA plots saw significant correlations with roasted aroma, while for the FD factors PCA showed significant correlations with smoky aroma. Interestingly, roasted aroma seems to be better defined by the lack of certain compounds rather than the presence of others as indicated by the significant number of negative correlations.

While results show that the the analytical variables selected to correlate with sensory attributes has an impact on the final results, all four PCA's saw similar correlations. Based on the present study, OAV and quantitation data should be further pursued when correlating sensory and analytical results as both PCAs accounted for over 65% of the data variation.

Overall, the number of correlations are not as significant or insightful as may have been initially thought. The lack of significant correlations suggests that the changes in sensory perceptions are more complex, determined by changes in multiple variables. While flavors may be affected by changes in a single compound, the reality of the situation is that the concentrations of all compounds differ simultaneously relative to each other from rum to rum. Therefore, changes in sensory perception that may be caused my synergies between compounds are difficult to detect and understand, requiring a significant amount of work to tease out the relationships of how compounds interact together.

Additionally, evaluation of a greater number and variety of rums may provide greater insights into how changes in volatile composition change sensory perception. Nine rums is a relatively small number of samples, much smaller than the number of variables evaluated. Increasing the number of

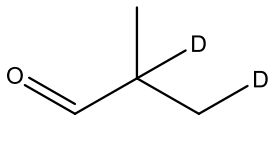
samples may increase the power of the chemometric analysis to better tease out relationships between sensory perceptions and volatile concentrations.

4.5 Tables and Figures

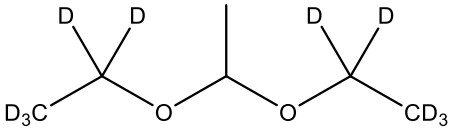
Table 4.1 Compounds, isotopes, selected ions, and response factors used for stable isotope dilution analysis

No.[b]	Target	Isotope	Selected Ion (m/z)[a] Unlabeled	Labeled	R_f[c]
1	acetaldehyde		-[d]	-	1.253
2	2-methylpropanal	d_2-2-methylpropanal	72	74	0.579
4	acetal	d_{10}-acetal	103	113	0.819
5a	3-methylbutanal	d_2-3-methylbutanal	71	73	0.488
5b	2-methylbutanal	d_2-2-methylbutanal	86	88	0.518
6	ethyl propanoate	d_5-ethyl propanoate	57	62	1.136
7	ethyl 2-methylpropanoate	d_5-ethyl 2-methylpropanoate	116	121	1.220
12	ethyl butanoate	d_7-ethyl butanoate	71	78	0.553
13	ethyl 2-methylbutanoate	d_5-ethyl 2-methylbutanoate	102	107	0.980
15	ethyl 3-methylbutanoate	d_2-ethyl 3-methylbutanoate	115	117	0.122
17	isobutanol	d_2-isobutanol	74	76	0.656
18	isoamyl acetate	d_2-isoamyl acetate	70	72	0.166
19	ethyl pentanoate	d_5-ethyl pentanoate	88	93	0.812
21a	3-methyl-1-butanol	d_2-3-methyl-1-butanol	70	72	0.711
21b	2-methyl-1-butanol	d_2-2-methyl-1-butanol	70	72	0.478
22	ethyl hexanoate	d_{11}-ethyl hexanoate	99	110	2.018
25	ethyl octanoate	d_4-ethyl octanoate	127	131	0.580
26	acetic acid		-[d]	-	0.743
34	β-damascenone	d_4-β-damascenone	69	73	0.261
35	guaiacol	d_3-guiacol	124	127	1.384
36a	*trans*-whiskey lactone	d_2-*trans*-whiskey lactone	99	101	0.342
37	2-phenethyl alcohol	$^{13}C_2$-2-phenethyl alcohol	91	93	1.177
38a	*cis*-whiskey lactone	d_2-*cis*-whiskey lactone	99	101	1.366
38b	4-methylguaiacol	d_3-4-methylguaiacol	123	125	0.393
41	4-ethylguaiacol	d_5-4-ethylguaiacol	152	157	0.763
43	*p*-cresol	d_3-*p*-cresol	108	111	0.704
44	*m*-cresol	d_8-*m*-cresol	108	115	0.446
46	eugenol	d_3-eugenol	164	167	0.760
48	syringol	d_3-syringol	154	157	0.789
49	*(E)*-isoeugenol	d_3-*(E)*-isoeugenol	164	167	0.283
53	ethyl vanillin	d_3-vanillin	166	155	0.416
54	vanillin	d_3-vanillin	152	155	0.229
56	ethyl vanillate	d_5-ethyl vanillate	196	201	0.380
58	syringaldehyde	d_3-syringaldehyde	182	185	0.603

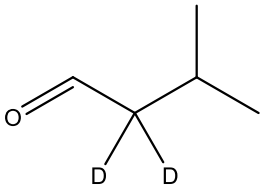
[a]Ions used for quantitation. [b]Numbers correspond to identification of compounds in Table 3.2. [c]Respose factors determined by analyzing the area ratios of target and for a variety of mass ratios (5:1, 2:1, 1:1, 1:2, 1:5). [d]Compound quantitated by direct injection using external calibration.



d$_2$-methylpropanal



d$_{10}$-acetal



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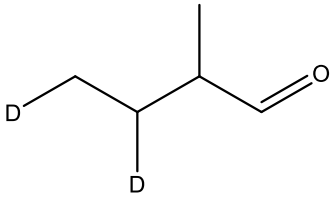
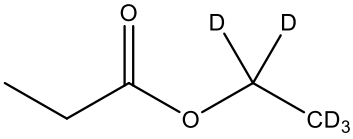
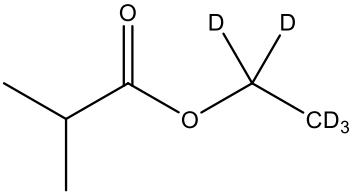


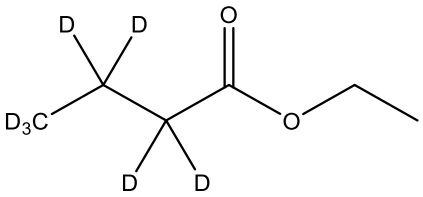
d$_2$-2-methylbutanal



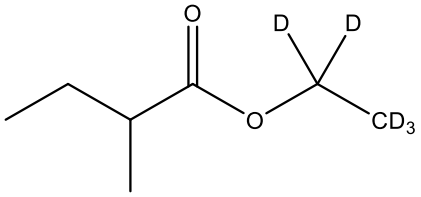
d$_5$-ethyl propanoate



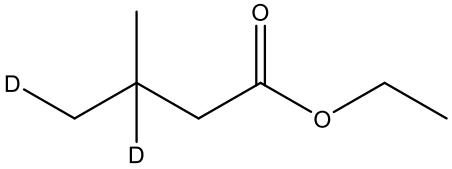
d$_5$-ethyl 2-methylpropanoate



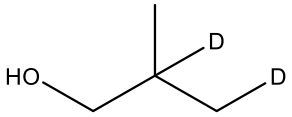
d$_7$-ethyl butanoate



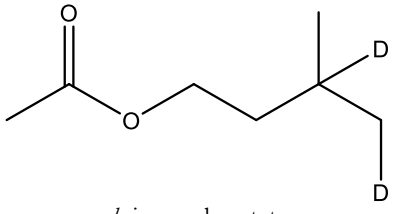
d$_5$-ethyl 2-methylbutanoate



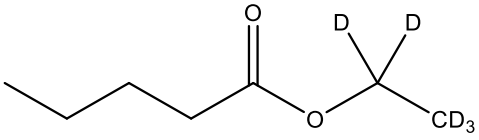
d$_2$-ethyl 3-methylbutanoate



d$_2$-isobutanol

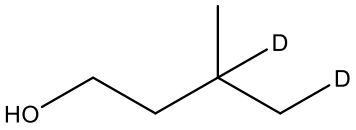


d$_2$-isoamyl acetate

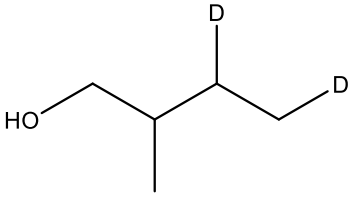


d$_5$-ethyl pentanoate

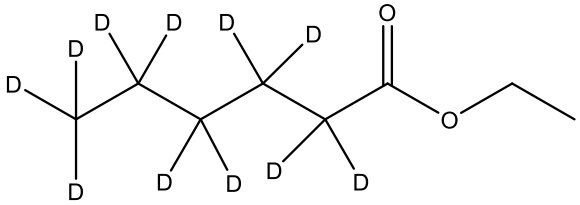
Figure 4.1 Isotopically labeled standards used for quantitation



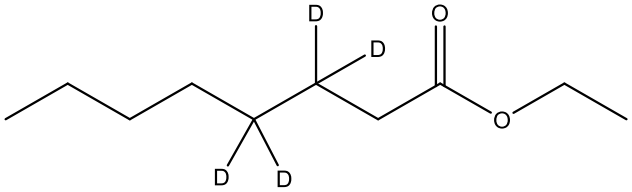
d_2-3-methyl-1-butanol



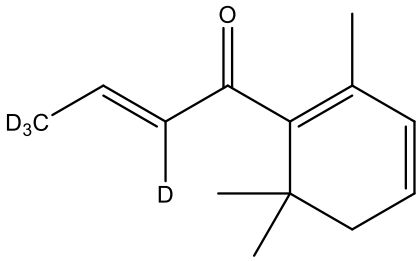
d_2-2-methyl-1-butanol



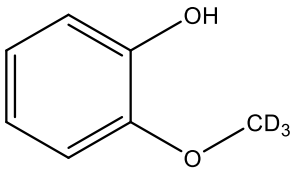
d_{11}-ethyl hexanoate



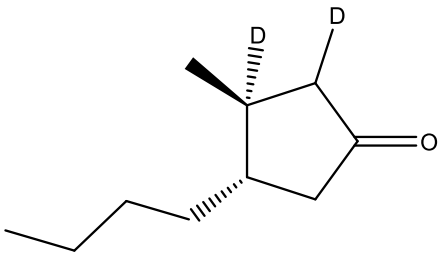
d_4-ethyl octanoate



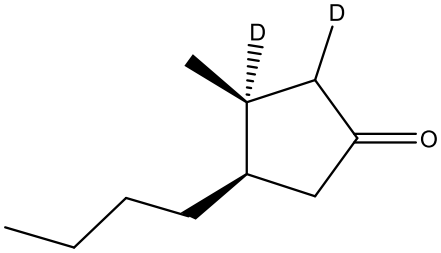
d_4-β-damascenone



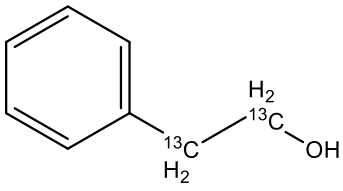
d_3-guaiacol



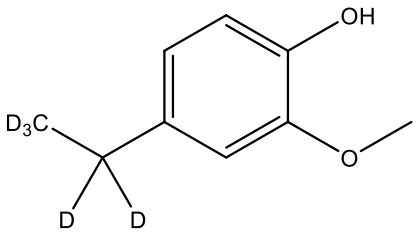
d_2-*trans*-whiskey lactone



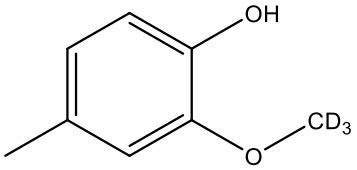
d_2-*cis*-whiskey lactone



$^{13}C_2$-2-phenethyl alcohol

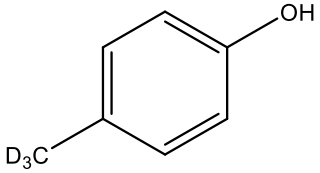


d_5-4-ethylguaiacol

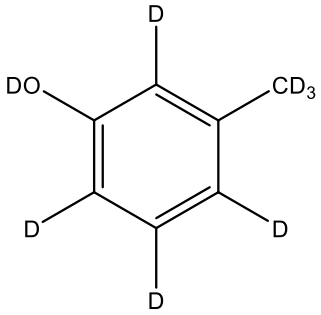


d_3-4-methylguaiacol

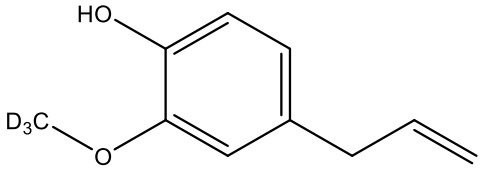
Figure 4.1 (cont.) Isotopically labeled standards used for quantitation



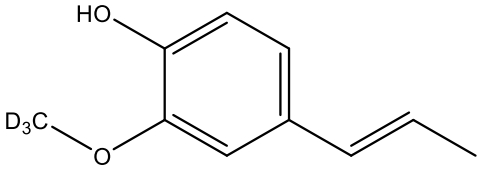
d$_3$-*p*-cresol



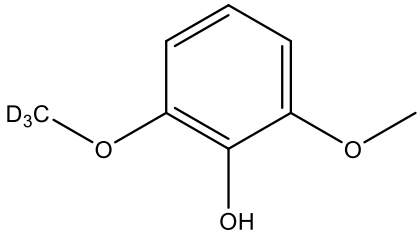
d$_3$-*m*-cresol



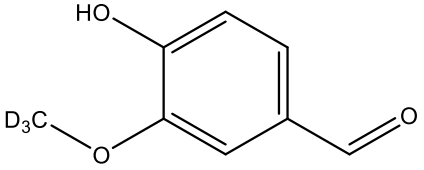
d$_3$-eugenol



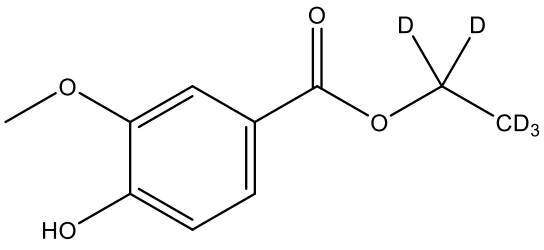
d$_3$-*(E)*-isoeugenol



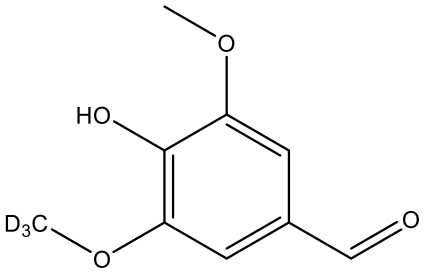
d$_3$-syringol



d$_3$-vanillin



d$_5$-ethyl vanillate



d$_3$-syringaldehyde

Figure 4.1 (cont.) Isotopically labeled standards used for quantitation

Table 4.2 Concentrations of the most important aroma compounds in nine rums

No.	Compound	Concentration ug/L (ppb) (±%RSD)†								
		BW	BG	AE	RA7	AE12	DR12	ED12	RZ	DX
1	acetaldehyde[α]	42700 (± 12.4)[f]	57500 (± 11.7)[e]	116000 (± 1.4)[b]	86100 (± 6.6)[c]	143000 (± 9.7)[a]	93100 (± 8.7)[c]	73300 (± 8.5)[d]	113000 (± 5.7)[b]	28000 (± 9.0)[g]
2	2-methylpropanal[β]	307 (± 5.0)[d]	206 (± 2.9)[d,e]	2360 (± 5.4)[b]	303 (± 0.78)[d]	2880 (± 5.2)[a]	182 (± 10.7)[e]	784 (± 4.6)[c]	104 (± 5.5)[e,f]	38.0 (± 10.1)[f]
4	acetal[γ]	11100 (± 5.2)[h]	15400 (± 3.6)[f]	25500 (± 2.4)[e]	28000 (± 2.0)[d]	44600 (± 1.0)[a]	13500 (± 1.9)[g]	37600 (± 1.1)[b]	35200 (± 1.8)[c]	7500 (± 1.9)[i]
5a	3-methylbutanal[β]	126 (± 7.9)[f]	225 (± 0.87)[e]	422 (± 3.8)[c]	358 (± 4.3)[d]	1210 (± 2.5)[a]	369 (± 7.4)[d]	806 (± 6.8)[b]	34.7 (± 5.7)[d]	63.0 (± 6.9)[g]
5b	2-methylbutanal[β]	160 (± 10.3)[e]	137 (± 4.8)[e,f]	1230 (± 6.2)[b]	219 (± 6.2)[d]	1520 (± 3.7)[a]	83.9 (± 4.2)[f,g]	487 (± 6.8)[c]	57.3 (± 3.1)[g]	39.8 (± 7.1)[g]
6	ethyl propanoate[β]	273 (± 10.3)[f]	306 (± 11.7)[f]	1080 (± 3.5)[c]	793 (± 5.2)[d]	1890 (± 9.2)[a]	737 (± 9.5)[d]	1430 (± 9.2)[b]	595 (± 2.9)[e]	861 (±2.3)[d]
7	ethyl 2-methylpropanoate[β]	70.5 (± 4.9)[f]	133 (± 3.4)[d]	156 (±2.7)[c]	117 (± 3.1)[e]	270 (± 1.2)[b]	55.0 (± 4.5)[g]	143 (± 1.2) [c,d]	692 (± 3.2)[a]	12.6 (± 11.3)[h]
12	ethyl butanoate[β]	123 (± 5.8)[g]	208 (± 3.2)[f]	366 (± 5.2)[d]	156 (± 8.1)[g]	547 (± 6.5)[c]	279 (± 9.1)[e]	608 (± 6.2)[b]	223 (± 3.0)[f]	650 (± 0.41)[a]
13	ethyl 2-methylbutanoate[β]	7.54 (± 6.2)[e]	17.7 (± 3.6)[d]	29.6 (± 7.0)[b]	18.9 (± 8.9)[d]	81.1 (± 6.6)[a]	8.23 (± 4.5)[e]	26.0 (± 3.3)[c]	10.3 (± 3.4)[e]	3.89 (± 6.5)[f]
15	ethyl 3-methylbutanoate[β]	20.6 (± 10.3)[f]	60.5 (± 7.4)[d,e]	93.2 (± 1.2)[c]	70.8 (± 10.5)[d]	238 (± 9.8)[a]	45.7 (± 6.9)[e]	127 (± 8.7)[b]	64.8 (± 4.7)[d]	14.6 (± 7.6)[f]
17	isobutanol[β]	84000 (± 3.9)[e]	104000 (± 8.9)[e]	177000 (± 9.4)[d]	209000 (± 11.6)[c,d]	235000 (± 5.7)[b,c]	212000 (± 5.5)[b,c,d]	494000 (± 10.0)[a]	247000 (± 5.7)[b]	31100 (± 1.8)[f]
18	isoamyl acetate[δ]	118 (± 2.8)[g,h]	123 (± 5.3)[g]	853 (± 4.3)[b]	189 (± 5.1)[f]	502 (± 2.4)[e]	737 (± 2.2)[c]	1070 (± 2.5)[a]	537 (± 1.6)[d]	88.9 (± 8.5)[h]
19	ethyl pentanoate[β]	7.58 (± 9.3)[f,g]	10.5 (± 9.1)[e,f]	23.5 (± 9.2)[c]	20.9 (± 5.7)[c,d]	83.8 (± 11.9)[a]	11.0 (± 4.3)[e,f]	36.6 (± 6.1)[b]	15.6 (± 7.8)[d,e]	3.23 (± 10.2)[g]
21a	3-methyl-1-butanol[β]	134000 (± 0.50)[h]	166000 (± 3.8)[g]	271000 (± 9.2)[e]	238000 (± 1.5)[f]	367000 (± 0.78)[d]	393000 (± 4.3)[c]	415000 (± 0.99)[b]	539000 (± 0.59)[a]	46400 (± 0.96)[i]
21b	2-methyl-1-butanol[β]	14500 (± 4.1)[f]	17300 (± 8.5)[f]	36000 (± 4.1)[e]	30500 (± 9.0)[e]	56100 (± 5.1)[d]	211000 (± 3.1)[*, a]	65800 (± 11.3)[c]	79200 (± 4.1)[b]	5480 (± 9.3)[g]
22	ethyl hexanoate[δ]	246 (± 7.7)[f]	371 (± 5.0)[d,e]	524 (± 6.0)[c]	350 (± 2.8)[e]	1280 (± 2.5)[b]	466 (± 7.3)[c,d]	1580 (± 9.8)[a]	485 (± 2.6)[c]	108 (± 6.6)[g]
25	ethyl octanoate[δ]	70.9 (± 3.6)[g]	69.8 (± 7.2)[*, g]	564 (± 2.9)[c]	313 (± 0.82)[d]	818 (± 3.3)[b]	309 (± 1.6)[d]	1800 (± 2.1)[a]	761 (± 9.0)[b]	288 (± 7.0)[h]
26	acetic acid[α]	15400 (± 7.7)[g]	24200 (± 4.4)[g]	110000 (± 10.9)[f]	628000 (± 4.69)[b]	372000 (± 0.81)[d]	785000 (± 3.5)[a]	765000 (± 6.7)[a]	502000 (± 3.4)[c]	164000 (± 8.5)[e]
34	β-damascenone[δ]	3.38 (± 2.1)[h]	8.99 (± 7.0)[g]	36.5 (± 2.0)[b]	27.2 (± 5.6)[c]	23.8 (± 0.96)[d]	14.3 (± 4.6)[f]	15.7 (± 6.67)[e]	9.60 (± 8.1)[g]	43.9 (± 1.2)[a]
35	guaiacol[δ]	89.3 (± 4.8)[e]	37.6 (± 5.4)[f]	90.3 (± 5.3)[e]	255.3 (± 8.4)[c]	347 (± 5.4)[a]	151 (± 2.6)[d]	309 (± 3.6)[b]	104 (± 7.4)[e]	8.00 (± 7.6)[g]
36a	*trans*-whiskey lactone[δ]	5.63 (± 5.2)[h]	8.91 (± 3.4)[g,h]	36.5 (± 4.2)[e]	74.9 (± 4.8)[c]	126 (± 3.9)[b]	21.7 (± 3.5)[f]	140.9 (± 3.5)[a]	60.8 (± 6.4)[d]	13.7 (± 2.0)[g]
37	2-phenethyl alcohol[δ]	882 (± 0.85)[g]	944 (± 2.5)[*, g]	1330 (± 1.1)[e]	2420 (± 0.69)[d]	2700 (± 2.8)[c]	1170 (± 0.62)[f]	4360 (± 1.7)[a]	3510 (± 2.5)[b]	748 (± 0.007)[h]
38a	*cis*-whiskey lactone[δ]	125 (± 3.9)[i]	268 (± 1.6)[h]	1270 (± 3.9)[e]	3020 (± 3.5)[c]	4920 (± 0.92)[b]	707 (± 4.6)[f]	5350 (± 2.5)[a]	2210 (± 3.5)[d]	464 (± 2.5)[g]
38b	4-methylguaiacol[ε,δ]	1.16 (± 11.2)[g]	4.33 (± 0.62)[*, f]	7.08 (± 7.3)[c,d]	1.69 (± 1.51)[*, a]	13.1 (± 8.3)[b]	5.64 (± 11.2)[e]	8.09 (± 3.7)[c]	6.79 (± 3.5)[d,e]	1.53 (± 3.7)[g]

Table 4.2 (cont.) Concentrations of the most important aroma compounds in nine rums

		Concentration ug/L (ppb) (±%RSD)[a]								
No.	Compound	BW	BG	AE	RA7	AE12	DR12	ED12	RZ	DX
41	4-ethylguaiacol[δ]	N.D.[g]	1.12 (± 9.1)[f]	17.6 (± 7.6)[b]	11.0 (± 10.22)[d]	32.2 (± 1.1)[a]	17.0 (± 0.51)[b]	5.20 (± 1.6)[e]	14.4 (± 3.5)[c]	0.831 (± 6.1)[f,g]
43	*p*-cresol[δ]	1.72 (± 1.2)[c]	0.870 (± 0.22)[*,f]	1.63 (± 4.3)[c]	2.24 (± 6.4)[*, a]	1.97 (± 1.1)[b]	1.13 (± 6.7) [e]	0.902 (± 8.9)[f]	1.09 (± 6.98)[e]	1.07 (± 6.1)[*, d]
44	*m*-cresol[δ]	1.08 (± 8.82)[d]	1.21 (± 6.4)[d]	1.08 (± 3.7)[d]	2.54 (± 3.7)[b]	3.57 (± 1.6)[a]	1.00 (± 4.2)[d]	3.77 (± 8.7)[a]	1.68 (± 2.02)[c]	0.402 (± 9.2)[e]
46	eugenol[δ]	ND	31.6 (± 4.3)[c]	31.4 (± 5.0)[c]	39.8 (± 1.8)[b]	24.0 (± 3.3)[d]	14.2 (± 6.6)[f]	94.0 (± 1.4)[a]	24.4 (± 3.8)[d]	16.9 (± 2.1)[e]
48	syringol[δ]	6.44 (± 0.24)[e,f]	4.79 (± 8.3)[f]	9.87 (± 7.5)[d]	16.30 (± 4.5)[c]	43.50 (± 6.2)[a]	9.19 (± 5.7)[d]	30.30 (± 3.9)[b]	9.90 (± 7.8)[d]	6.74 (± 5.9)[e]
49	(*E*)-isoeugenol[δ]	2.23 (± 6.1)[*,e]	118 (± 10.6)[c]	99.2 (± 8.9)[c]	46.7 (± 8.1)[d]	678 (± 7.8)[a]	36.4 (± 5.0)[d,e]	385 (± 6.1)[b]	46.7 (± 8.06)[d]	7.84 (± 10.3)[d,e]
53	ethyl vanillin[ε]	N.D.	N.D.	N.D.	N.D.	N.D.	873 (± 6.4)	N.D.	N.D.	3020 (± 3.4)
54	vanillin[δ]	322 (± 1.7)[g]	325 (± 1.7)[g]	1180 (± 0.50)[f]	2270 (± 1.0)[d]	4470 (± 2.3)[b]	3050 (± 4.1)[c]	4780 (± 3.4)[a]	1940 (± 0.26)[e]	1200 (± 5.3)[f]
56	ethyl vanillate[δ]	111 (± 1.1)[g]	126 (± 0.93)[f,g]	271 (± 0.71)[d]	582 (± 4.8)[c]	1430 (± 6.1)[a]	177 (± 5.0)[e,f]	1080 (± 1.6)[b]	218 (± 1.3)[d,e]	40.3 (± 6.6)[h]
58	syringaldehyde[δ]	713 (± 2.8)[h]	1040 (± 4.8)[*,g]	2020 (± 2.4)[e]	3880 (± 3.8)[c]	8580 (± 1.6)[a]	1590 (± 0.22)[f]	6910 (± 1.6)[b]	2970 (± 3.08)[*,d]	461 (± 1.2)[i]

[†]Mean values of triplicates. [α]Calculated using external standard methodology and direct injection. [β]Calculated using HS-SPME in combination with SIDA. [γ]Calculated by direct injection in combination with SIDA. [δ]Calculated using extraction and liquid injection in combination with SIDA. [ε]Calculated using extraction in combination with internal standard methodology. [+]N.D., not detected *Mean values of duplicate rather than triplicate. [a,b,c,d,e,f,g,h,i] indicate values statistically different across rums. ‡ Chirality determined in previous paper: (S)-Ethyl 2-methylbutanoate > 99%, (S)-2-methylbutanol >99% (Franitza et al., 2016a) ^No difference detected.

Table 4.3 ANOVA F-ratios for quantitation data

No.	Compound	Rum	Pr
1	acetaldehyde	82.59	<0.0001
2	2-methylpropanal	750.34	<0.0001
4	acetal	2066.08	<0.0001
5a	3-methylbutanal	1011	<0.0001
5b	2-methylbutanal	777.27	<0.0001
6	ethyl propanoate	124.78	<0.0001
7	ethyl 2-methylpropanoate	1942.4	<0.0001
12	ethyl butanoate	275	<0.0001
13	ethyl 2-methylbutanoate	403.2	<0.0001
15	ethyl 3-methylbutanoate	163	<0.0001
17	isobutanol	122.41	<0.0001
18	isoamyl acetate	1322	<0.0001
19	ethyl pentanoate	144.21	<0.0001
21a	3-methyl-1-butanol	662.55	<0.0001
21b	2-methyl-1-butanol	483	<0.0001
22	ethyl hexanoate	233	<0.0001
25	ethyl octanoate	854	<0.0001
26	acetic acid	528	<0.0001
34	β-damascenone	866	<0.0001
35	guaiacol	372	<0.0001
36a	*trans*-whiskey lactone	870	<0.0001
37	2-phenethyl alcohol	1989	<0.0001
38a	*cis*-whiskey lactone	2656	<0.0001
38b	4-methylguaiacol	219	<0.0001
41	4-ethylguaiacol	1037	<0.0001
43	*p*-cresol	117	<0.0001
44	*m*-cresol	218	<0.0001
46	eugenol	2075	<0.0001
48	syringol	429	<0.0001
49	(*E*)-isoeugenol	326	<0.0001
54	vanillin	1268	<0.0001
56	ethyl vanillate	734	<0.0001
58	syringaldehyde	3145	<0.0001

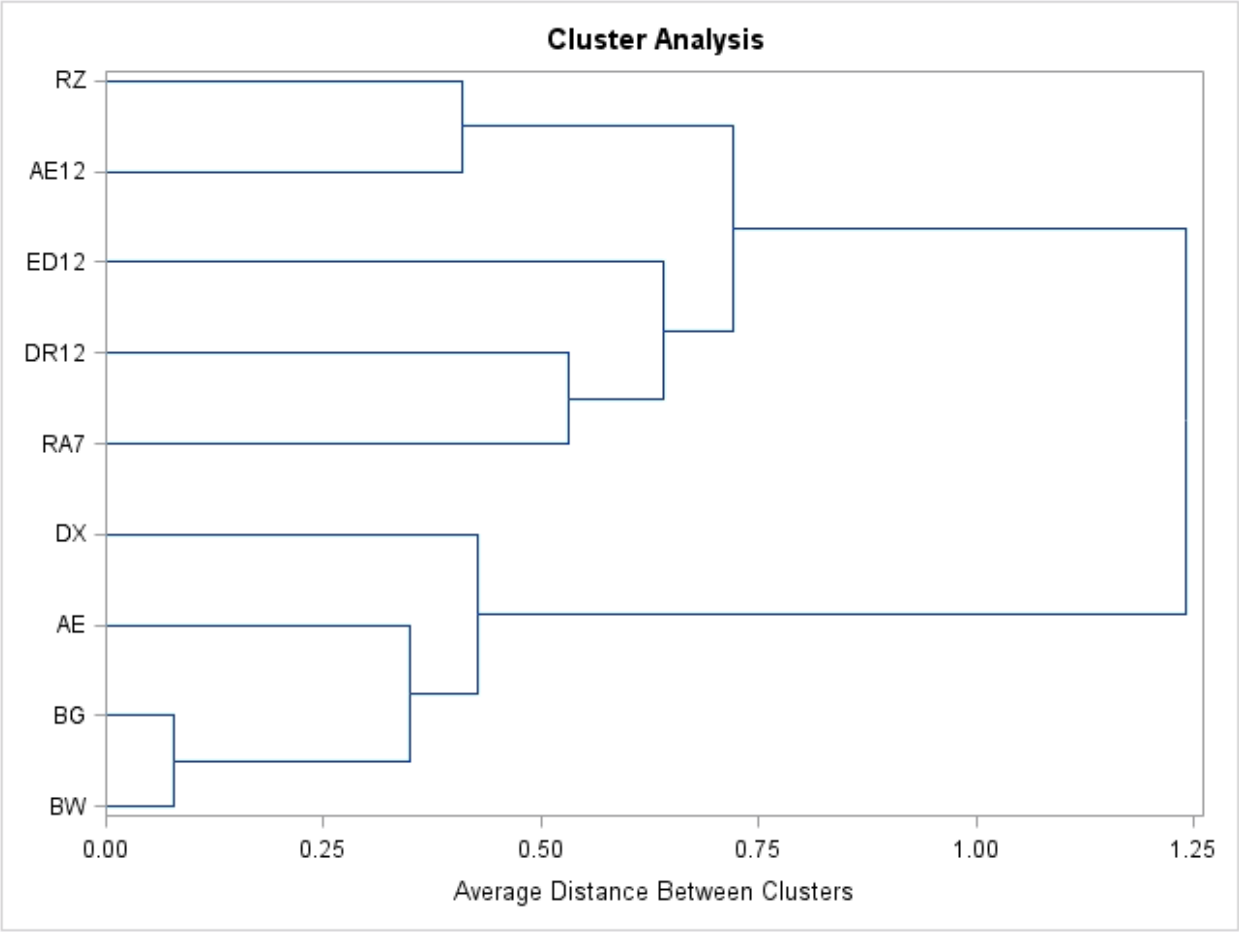


Figure 4.2 Cluster analysis of nine rums based on quantitation data

Table 4.4 Odor activity values and odor thresholds for most important compounds in rum

			OAV[a]								
No.	Compound	Threshold (ug/L)	BW	BG	AE	RA7	AE12	DR12	ED12	RZ	DX
1	acetaldehyde	192000[b]	0.2	0.3	1	0.4	1	0.5	0.4	1	0.1
2	2-methylpropanal	5.9[c]	52	35	400	51	488	31	133	18	6
4	acetal	719[d]	15	21	35	39	62	19	52	49	10
5a	3-methylbutanal	2.8[d]	45	80	151	128	432	132	288	12	23
5b	2-methylbutanal	33[e]	5	4	37	7	46	3	15	2	1
6	ethyl propanoate	3452[d]	0.1	0.1	0.3	0.2	1	0.2	0.4	0.2	0.2
7	ethyl 2-methylpropanoate	4.5[d]	16	30	35	26	60	12	32	154	3
12	ethyl butanoate	9.5[d]	13	22	39	16	58	29	64	23	68
13	ethyl 2-methylbutanoate	0.22[d]	34	80	135	86	369	37	118	47	18
15	ethyl 3-methylbutanoate	1.6[d]	13	38	58	44	149	29	79	41	9
17	isobutanol	160000[e]	1	1	1	1	1	1	3	2	0.2
18	isoamyl acetate	245[d]	0.5	1	3	1	2	3	4	2	0.4
19	ethyl pentanoate	11[e]	1	1	2	2	8	1	3	1	0.3
21a	3-methyl-1-butanol	56100[d]	2	3	5	4	7	7	7	10	1
21b	2-methyl-1-butanol	6100[e]	2	3	6	5	9	35	11	13	1
22	ethyl hexanoate	30[d]	8	12	17	12	43	16	53	16	4
25	ethyl octanoate	147[d]	0.5	0.5	4	2	6	2	12	5	2
26	acetic acid	230000[e]	0.1	0.1	0.5	3	2	3	3	2	1
34	β-damascenone	0.1[d]	34	90	365	272	238	143	157	96	439
35	guaiacol	9.2[d]	10	4	10	28	38	16	34	11	1
36a	*trans*-whiskey lactone	790[f]	<0.1	<0.1	<0.1	0.1	0.2	<0.1	0.2	0.1	<0.1
37	2-phenethyl alcohol	2600[d]	0.3	0.4	1	1	1	0.5	2	1	0.3
38a	*cis*-whiskey lactone	67[f]	2	4	19	45	73	11	80	33	7
38b	4-methylguaiacol	315[b]	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1

Table 4.4 (cont.) Odor activity values and odor thresholds for most important compounds in rum

			OAV[a]								
No.	Compound	Threshold (ug/L)	BW	BG	AE	RA7	AE12	DR12	ED12	RZ	DX
41	4-ethylguaiacol	6.9[d]	-[*]	0.2	3	2	5	2	1	2	0.1
43	*p*-cresol	81.5[g]	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
44	*m*-cresol	680[h]	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
46	eugenol	7.1[d]	-	4	4	6	3	2	13	3	2
48	syringol	570[i]	<0.1	<0.1	<0.1	<0.1	0.1	<0.1	0.1	<0.1	<0.1
49	(*E*)-isoeugenol	1860[j]	<0.1	0.1	0.1	<0.1	0.4	<0.1	0.2	<0.1	<0.1
53	ethyl vanillin	100[h]	-	-	-	-	-	9	-	-	30
54	vanillin	22[d]	15	15	54	103	203	139	217	88	55
56	ethyl vanillate	796000[j]	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
58	syringaldehyde	6490000[j]	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1

[a]Odor activity values were calculated by dividing the concentrations (Table 4.2) by the respective odor threshold. [b]Willner et al. 2013 (40% v/v ethanol/water matrix). [c] Uselmann and Schieberle 2015 (40% v/v ethanol/water matrix). [d]Poisson and Schieberle 2008 (40% v/v ethanol/water matrix). [e]Franitza et al., 2016b (40% v/v ethanol/water matrix). [f]Otsuka, Zenibayashi, Itoh, & Totsuka, 1974 (30% v/v ethanol/water matrix). [g]Franitza et al., 2016a (40% v/v ethanol/water matrix). [h]Fazzalari, 1978 (water). [i]López, Aznar, Cacho, & Ferreira, 2002 (10% v/v ethanol/water matrix). [j]Odor thresholds were determined in 40% v/v ethanol/water matrix. [*] - indicates compound not quantifed

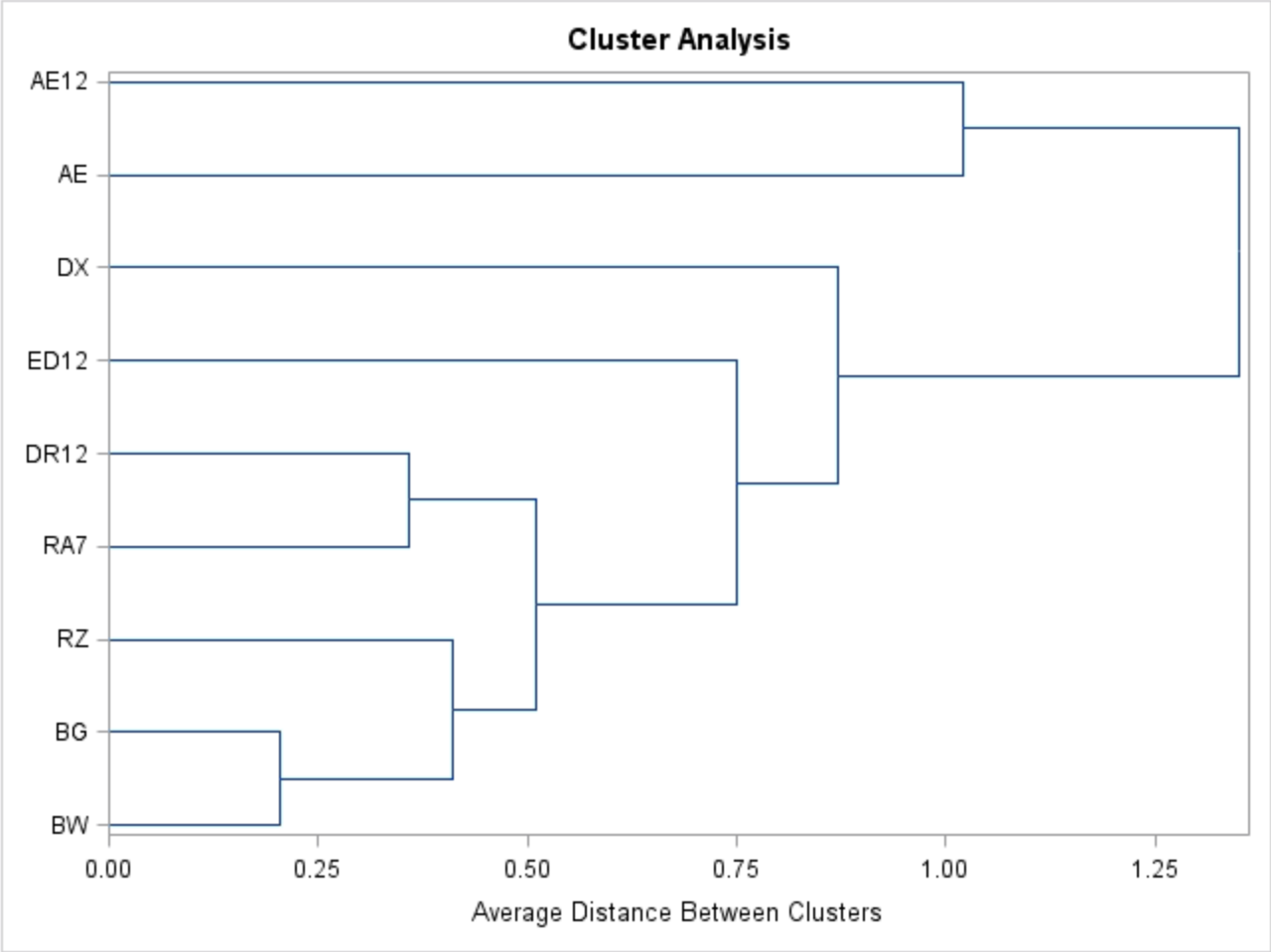


Figure 4.3 Cluster analysis of nine rums based on OAV data

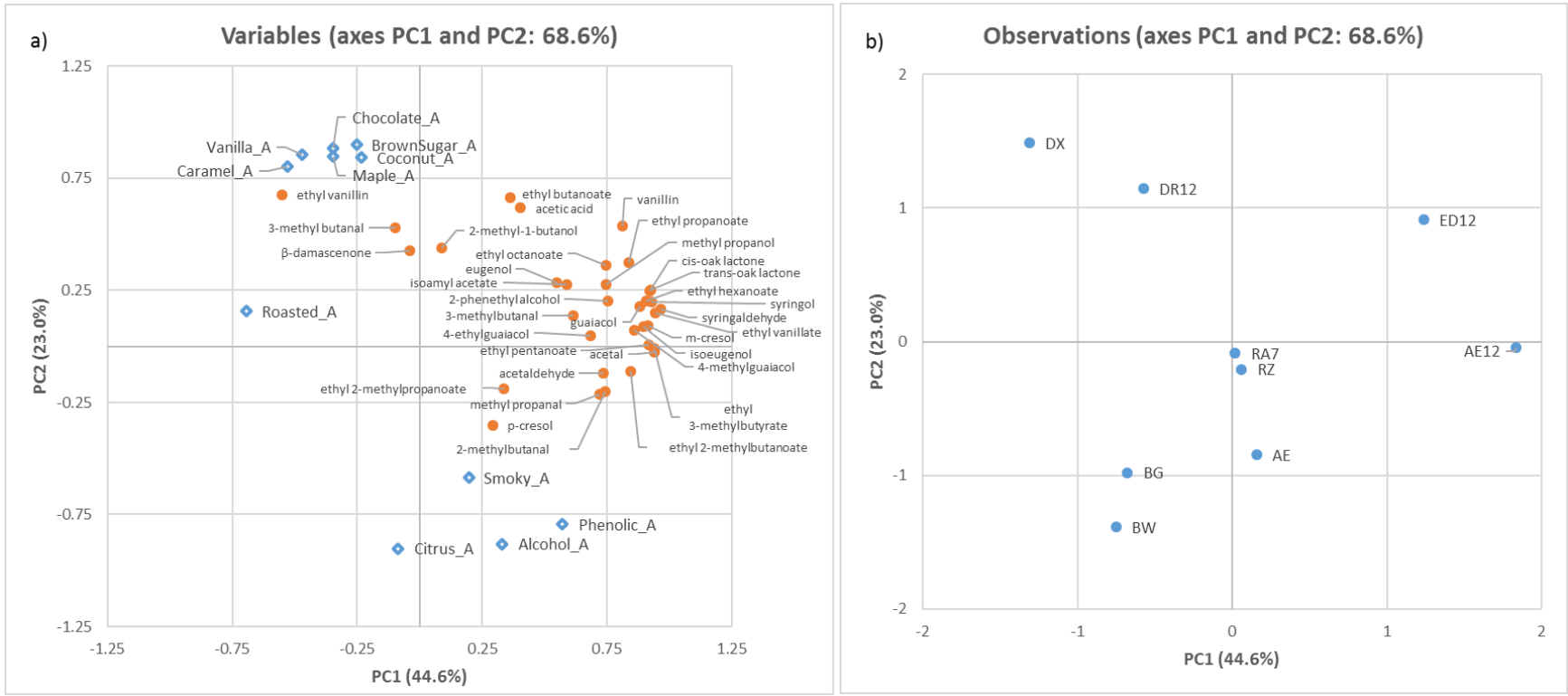


Figure 4.4 Principal component analysis of quantitation and sensory data
a) sensory and analytical variables used to create the model b) rum samples used to create model

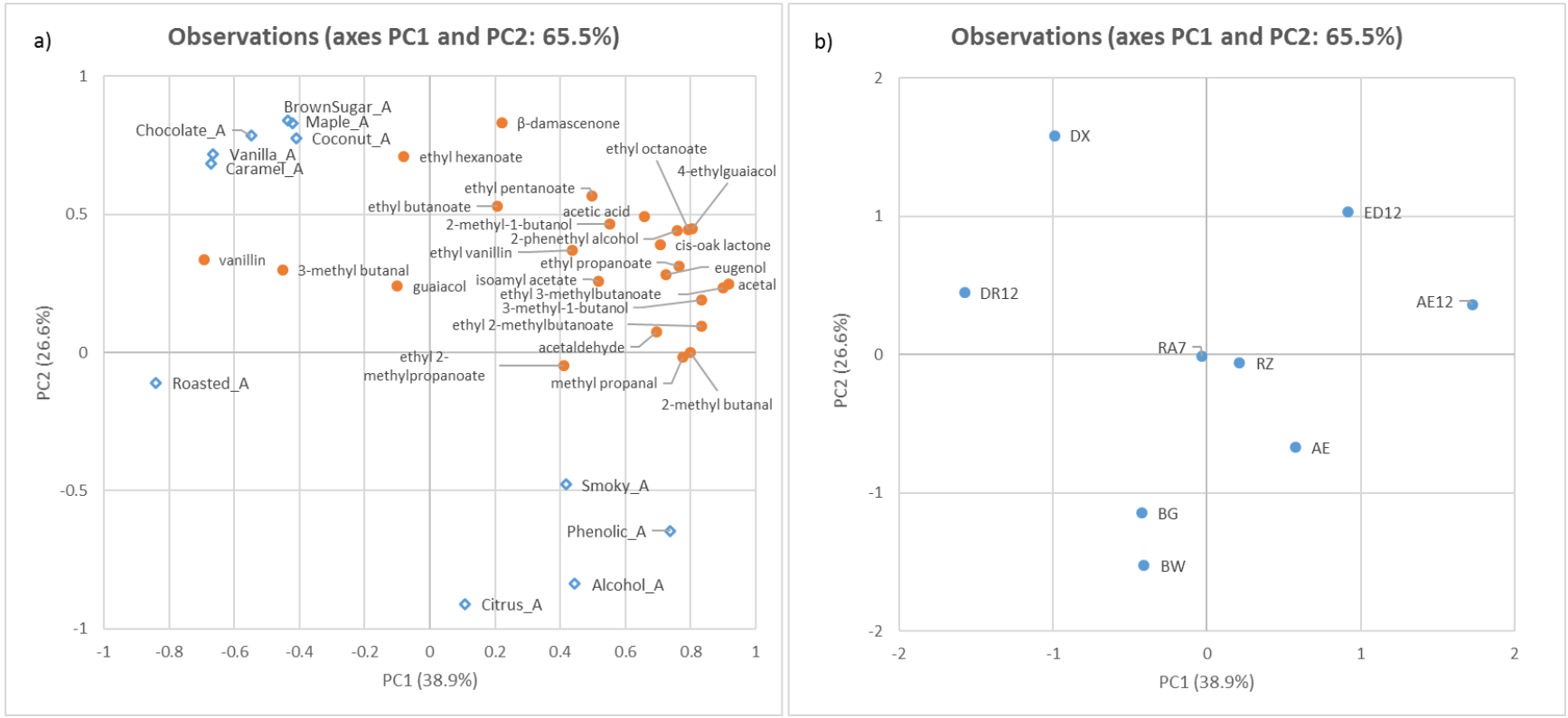


Figure 4.5 Principal component analysis of odor activity values and sensory data
a) sensory and analytical variables used to create the model b) rum samples used to create model

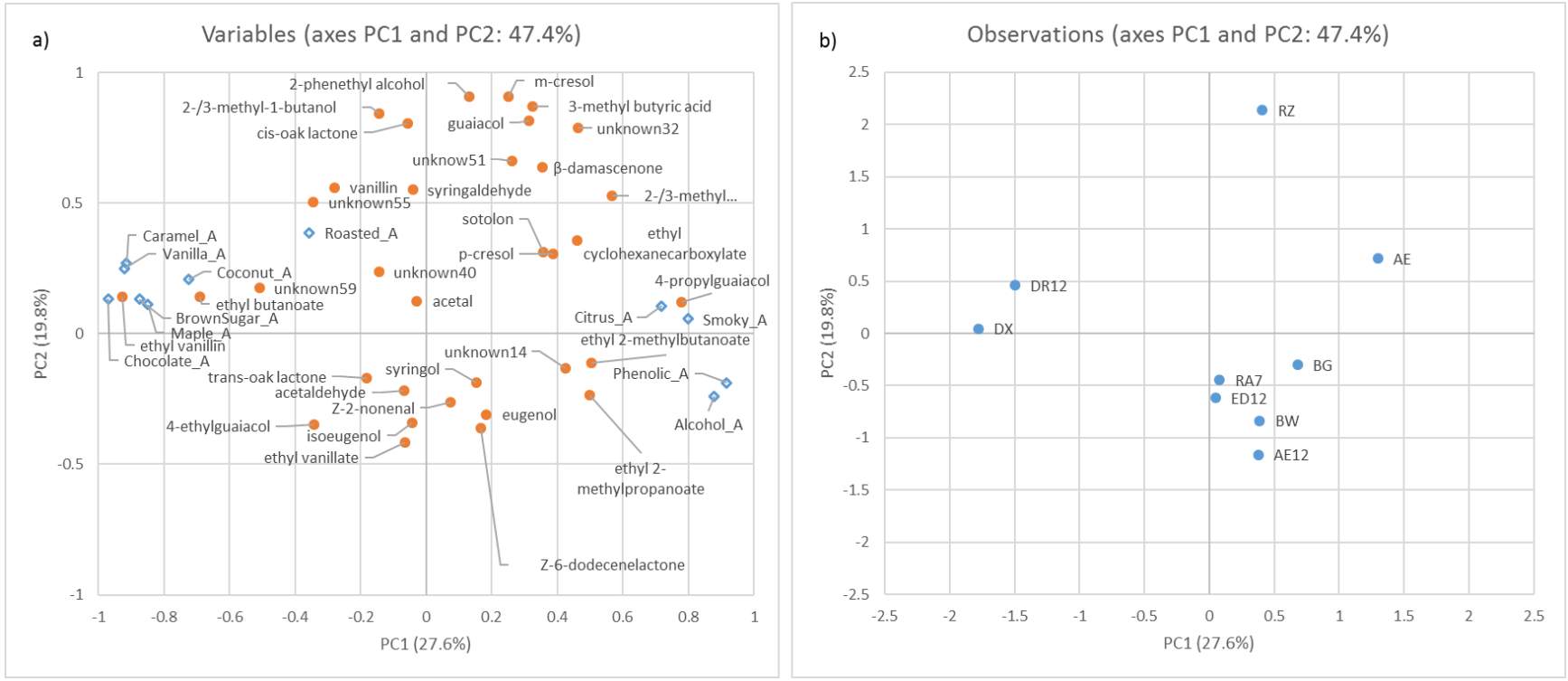


Figure 4.6 Principal component analysis of flavor dilution factors ≥ 8 and sensory data
a) sensory and analytical variables used to create the model b) rum samples used to create model

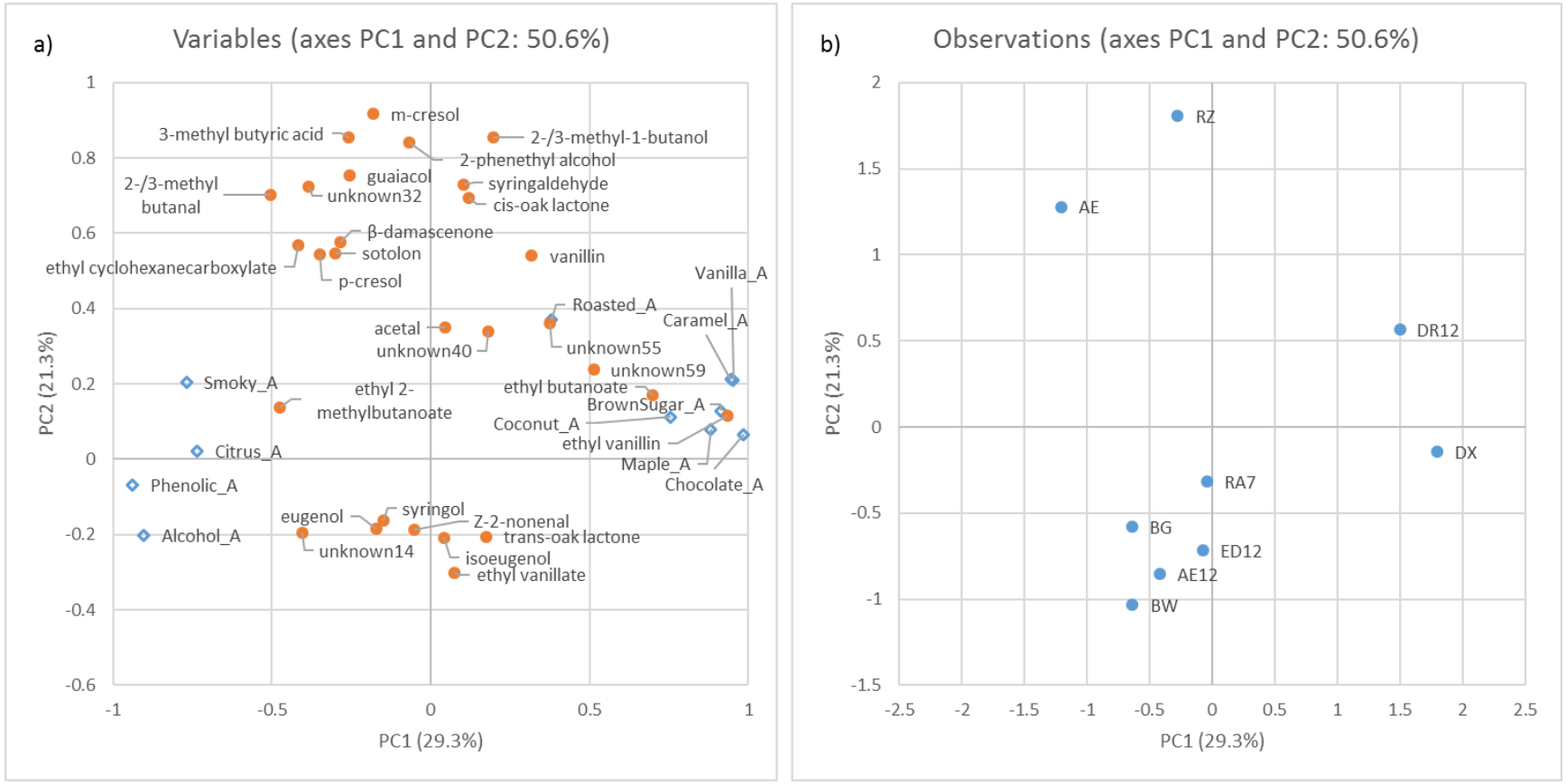


Figure 4.7 Principal component analysis of flavor dilution factors ≥ 16 and sensory data
a) sensory and analytical variables used to create the model b) rum samples used to create model

Table 4.5 Pearson correlation coefficients for quantitation and sensory (aroma) data

Attributes	Brown Sugar Aroma	Caramel Aroma	Maple Aroma	Vanilla Aroma	Coconut Aroma	Citrus Aroma	Phenolic Aroma	Alcohol Aroma	Smoky Aroma	Roasted Aroma	Chocolate Aroma
acetaldehyde	-0.162	-0.350	-0.328	-0.318	-0.388	0.043	0.532	0.280	0.248	-0.331	-0.285
2-methylpropanal	-0.263	-0.446	-0.277	-0.447	-0.582	-0.067	0.668**	0.284	0.488	-0.530	-0.400
acetal	-0.233	-0.500	-0.325	-0.456	-0.160	-0.002	0.538	0.314	0.191	-0.692**	-0.344
3-methylbutanal	0.320	0.392	0.215	0.488	0.388	-0.363	-0.486	-0.335	-0.409	0.519	0.462
2-methylbutanal	-0.262	-0.458	-0.275	-0.454	-0.561	-0.079	0.668**	0.290	0.494	-0.549	-0.406
ethyl propanoate	0.192	-0.094	0.145	-0.050	0.005	-0.544	0.231	-0.142	0.061	-0.605*	0.064
ethyl 2-methylpropanoate	-0.244	-0.248	-0.272	-0.296	-0.148	0.376	0.304	0.183	0.002	-0.347	-0.210
ethyl butanoate	0.496	0.360	0.593*	0.362	0.368	-0.732**	-0.266	-0.596*	-0.122	-0.366	0.446
ethyl 2-methylbutanoate	-0.184	-0.426	-0.239	-0.432	-0.506	-0.051	0.576	0.299	0.188	-0.715**	-0.288
ethyl 3-methylbutanoate	-0.168	-0.433	-0.247	-0.410	-0.366	-0.095	0.541	0.279	0.170	-0.708**	-0.273
methylpropanol	-0.105	-0.308	-0.221	-0.176	0.281	-0.205	0.190	0.133	0.081	-0.257	-0.150
isoamyl acetate	-0.048	-0.157	-0.148	-0.035	0.148	-0.292	0.187	-0.016	0.281	0.035	-0.101
ethyl pentanoate	-0.135	-0.400	-0.207	-0.388	-0.369	-0.134	0.520	0.235	0.069	-0.759**	-0.214
3-methyl-1-butanol	-0.100	-0.202	-0.271	-0.131	0.058	0.030	0.218	0.116	-0.060	-0.141	-0.084
2-methyl-1-butanol	0.323	0.334	0.095	0.426	0.253	-0.273	-0.305	-0.257	-0.397	0.477	0.403
ethyl hexanoate	-0.159	-0.385	-0.221	-0.302	-0.012	-0.209	0.352	0.172	0.091	-0.550	-0.189
ethyl octanoate	-0.025	-0.216	-0.042	-0.126	0.305	-0.332	0.156	-0.049	0.091	-0.432	-0.062
acetic acid	0.403	0.212	0.183	0.348	0.602*	-0.490	-0.302	-0.259	-0.386	0.090	0.365
β-damascenone	0.595*	0.456	0.667**	0.444	0.292	-0.690**	-0.274	-0.564	0.182	-0.044	0.363
guaiacol	-0.057	-0.373	-0.214	-0.276	0.001	-0.261	0.342	0.225	-0.071	-0.565	-0.141
***trans*-whiskey lactone**	-0.034	-0.339	-0.115	-0.262	0.115	-0.290	0.311	0.116	0.022	-0.674**	-0.132
2-phenethyl alcohol	-0.110	-0.325	-0.184	-0.250	0.254	-0.103	0.231	0.124	-0.012	-0.515	-0.152
***cis*-whiskey lactone**	-0.026	-0.339	-0.110	-0.263	0.112	-0.292	0.310	0.121	0.016	-0.683**	-0.131
4-methylguaiacol	-0.130	-0.302	-0.215	-0.280	-0.321	-0.078	0.445	0.154	0.145	-0.501	-0.175
4-ethylguaiacol	0.047	-0.151	-0.117	-0.135	-0.347	-0.163	0.383	0.081	0.048	-0.350	-0.055

Table 4.5 (cont.) Pearson correlation coefficients for quantitation and sensory (aroma) data

Attributes	Brown Sugar Aroma	Caramel Aroma	Maple Aroma	Vanilla Aroma	Coconut Aroma	Citrus Aroma	Phenolic Aroma	Alcohol Aroma	Smoky Aroma	Roasted Aroma	Chocolate Aroma
***p*-cresol**	-0.196	-0.391	-0.272	-0.390	-0.403	0.033	0.494	0.359	0.155	-0.396	-0.325
***m*-cresol**	-0.183	-0.482	-0.281	-0.403	-0.013	-0.119	0.404	0.311	0.032	-0.680	-0.264
eugenol	-0.024	-0.225	-0.050	-0.104	0.406	-0.253	0.050	0.077	0.279	-0.196	-0.160
syringol	-0.024	-0.318	-0.099	-0.276	-0.115	-0.294	0.367	0.116	-0.061	-0.756	-0.089
(*E*)-isoeugenol	-0.121	-0.359	-0.162	-0.342	-0.284	-0.153	0.427	0.189	0.033	-0.735**	-0.166
ethyl vanillin	0.816***	0.897***	0.933***	0.837***	0.577	-0.666*	-0.815***	-0.912***	-0.485	0.238	0.848***
vanillin	0.245	-0.024	0.101	0.074	0.275	-0.525	0.026	-0.154	-0.248	-0.409	0.202
ethyl vanillate	-0.083	-0.389	-0.165	-0.333	-0.114	-0.247	0.406	0.199	0.015	-0.737**	-0.170
syringaldehyde	-0.080	-0.384	-0.175	-0.326	-0.071	-0.222	0.398	0.188	0.001	-0.731**	-0.165

*, **, *** stand for significance at $p<0.1$, $p<0.05$, and $p<0.01$ respectively.

Table 4.6 Pearson correlation coefficients for odor activity values and sensory (aroma) data

Attributes	Brown Sugar Aroma	Caramel Aroma	Maple Aroma	Vanilla Aroma	Coconut Aroma	Citrus Aroma	Phenolic Aroma	Alcohol Aroma	Smoky Aroma	Roasted Aroma	Chocolate Aroma
acetaldehyde	-0.140	-0.254	-0.094	-0.316	-0.338	0.045	0.486	0.076	0.387	-0.555	-0.268
2-methylpropanal	-0.251	-0.434	-0.247	-0.442	-0.570	-0.079	0.658*	0.262	0.491	-0.559	-0.391
acetal	-0.181	-0.450	-0.215	-0.432	-0.114	-0.050	0.496	0.232	0.195	-0.791**	-0.304
3-methylbutanal	0.320	0.393	0.215	0.488	0.388	-0.362	-0.487	-0.335	-0.409	0.520	0.462
2-methylbutanal	-0.250	-0.450	-0.253	-0.450	-0.548	-0.092	0.661*	0.273	0.493	-0.575	-0.398
ethyl propanoate	0.016	-0.229	-0.035	-0.235	-0.307	-0.267	0.395	0.050	-0.029	-0.735**	-0.047
ethyl 2-methylpropanoate	-0.228	-0.232	-0.231	-0.290	-0.133	0.360	0.291	0.153	0.010	-0.389	-0.199
ethyl butanoate	0.312	0.183	0.181	0.281	0.200	-0.557	-0.116	-0.292	-0.154	0.016	0.311
ethyl 2-methylbutanoate	-0.167	-0.409	-0.199	-0.425	-0.491	-0.068	0.563	0.269	0.193	-0.753**	-0.276
ethyl 3-methylbutanoate	-0.124	-0.390	-0.145	-0.392	-0.328	-0.136	0.505	0.204	0.177	-0.807***	-0.240
isoamyl acetate	-0.230	-0.320	-0.153	-0.275	0.300	0.000	0.163	0.092	0.137	-0.435	-0.219
ethyl pentanoate	0.160	0.037	0.293	0.059	0.332	-0.461	0.002	-0.318	0.307	-0.356	0.046
3-methyl-1-butanol	-0.113	-0.372	-0.145	-0.384	-0.387	-0.147	0.501	0.202	0.053	-0.821***	-0.192
2-methyl-1-butanol	0.125	0.016	0.218	-0.036	0.201	-0.166	0.062	-0.245	-0.012	-0.601*	0.077
ethyl hexanoate	0.639*	0.637*	0.818***	0.557	0.537	-0.580	-0.556	-0.787**	-0.315	-0.205	0.627
ethyl octanoate	-0.073	-0.304	-0.047	-0.259	0.064	-0.292	0.283	0.041	0.092	-0.702**	-0.123
acetic acid	-0.032	-0.228	-0.046	-0.143	0.269	-0.334	0.183	-0.042	0.103	-0.463	-0.072
β-damascenone	0.608*	0.364	0.593*	0.404	0.724**	-0.697**	-0.407	-0.536	-0.368	-0.368	0.494
guaiacol	0.388	0.258	0.187	0.362	0.109	-0.489	-0.112	-0.213	0.130	0.418	0.216
2-phenethyl alcohol	0.044	-0.277	0.032	-0.241	0.093	-0.366	0.264	0.047	-0.037	-0.812***	-0.071
***cis*-whiskey lactone**	-0.102	-0.346	-0.118	-0.250	0.270	-0.257	0.266	0.097	0.289	-0.472	-0.234
4-ethylguaiacol	-0.012	-0.325	-0.080	-0.255	0.127	-0.307	0.297	0.097	0.018	-0.708**	-0.120
eugenol	0.094	-0.141	0.095	-0.185	-0.283	-0.256	0.386	-0.035	0.194	-0.683**	-0.079

Table 4.6 (cont.) Pearson correlation coefficients for odor activity values and sensory (aroma) data

Attributes	Brown Sugar Aroma	Caramel Aroma	Maple Aroma	Vanilla Aroma	Coconut Aroma	Citrus Aroma	Phenolic Aroma	Alcohol Aroma	Smoky Aroma	Roasted Aroma	Chocolate Aroma
ethyl vanillin	-0.017	-0.227	-0.055	-0.098	0.425	-0.263	0.041	0.085	0.260	-0.180	-0.156
vanillin	0.615*	0.704**	0.468	0.757**	0.398	-0.470	-0.657*	-0.571	-0.535	0.687**	0.705**

*, **, *** stand for significance at $p<0.1$, $p<0.05$, and $p<0.01$ respectively.

Table 4.7 Pearson correlation coefficients for FD factors ≥ 8 and sensory (aroma) data

Attributes	Brown Sugar Aroma	Caramel Aroma	Maple Aroma	Vanilla Aroma	Coconut Aroma	Citrus Aroma	Phenolic Aroma	Alcohol Aroma	Smoky Aroma	Roasted Aroma	Chocolate Aroma
acetaldehyde	0.300	0.013	0.167	0.124	0.453	-0.404	-0.124	-0.020	0.058	-0.053	0.051
acetal	0.114	0.098	-0.038	0.187	-0.094	-0.228	0.034	-0.017	0.306	0.576	-0.007
2-/3-methylbutanal	-0.264	-0.294	-0.254	-0.277	-0.283	0.092	0.472	0.182	0.752**	0.004	-0.432
ethyl 2-methylpropanoate	-0.094	-0.383	-0.162	-0.344	-0.282	-0.094	0.484	0.326	0.590	-0.395	-0.408
ethyl butanoate	0.575	0.646*	0.401	0.713**	0.366	-0.419	-0.619*	-0.482	-0.484	0.715**	0.640*
ethyl 2-methylbutanoate	-0.181	-0.400	-0.196	-0.331	-0.211	-0.206	0.520	0.235	0.752**	-0.242	-0.447
unknown14	-0.377	-0.313	-0.378	-0.310	-0.306	0.581	0.163	0.533	0.427	0.218	-0.450
2-/3-methyl-1-butanol	0.176	0.284	0.030	0.313	0.155	0.009	-0.191	-0.211	-0.140	0.510	0.226
ethyl cyclohexanecarboxylate	-0.213	-0.229	-0.208	-0.183	-0.231	-0.008	0.382	0.157	0.806***	0.230	-0.404
(*Z*)-2-nonenal	0.158	-0.172	0.019	-0.088	0.268	-0.280	0.091	0.116	-0.021	-0.385	-0.053
3-methylbutyric acid	-0.123	-0.077	-0.101	-0.120	-0.016	0.227	0.186	-0.004	0.220	-0.078	-0.155
unknown32	-0.237	-0.183	-0.224	-0.216	-0.065	0.442	0.195	0.198	0.346	-0.005	-0.302
β-damascenone	-0.209	-0.099	-0.283	-0.122	-0.224	0.561	0.098	0.290	0.237	0.293	-0.240
guaiacol	-0.173	-0.129	-0.178	-0.177	-0.048	0.320	0.201	0.066	0.058	-0.172	-0.149
***trans*-whiskey lactone**	0.080	0.010	0.016	0.146	0.486	-0.326	-0.202	-0.106	-0.084	0.127	0.121
2-phenethyl alcohol	-0.020	0.053	-0.070	0.025	0.089	0.232	0.010	-0.061	-0.062	0.063	0.017
***cis*-whiskey lactone**	0.201	0.259	0.279	0.203	0.361	-0.041	-0.209	-0.370	-0.115	-0.094	0.220
unknown40	0.356	0.393	0.519	0.357	0.191	-0.451	-0.217	-0.507	0.358	0.162	0.218
4-ethylguaiacol	0.487	0.298	0.412	0.282	-0.064	-0.585*	-0.075	-0.374	-0.309	-0.347	0.422
***p*-cresol**	-0.156	-0.163	-0.176	-0.129	-0.329	-0.037	0.370	0.120	0.721**	0.254	-0.328
***m*-cresol**	-0.065	-0.025	-0.125	-0.040	0.001	0.212	0.132	0.009	0.146	0.097	-0.102
4-propylguaiacol	-0.458	-0.536	-0.459	-0.520	-0.423	0.439	0.542	0.576	0.839***	-0.098	-0.683**
eugenol	0.057	-0.190	0.034	-0.230	-0.312	-0.205	0.368	0.037	-0.012	-0.794**	-0.044
sotolon	-0.052	-0.146	-0.170	-0.060	-0.150	-0.081	0.274	0.170	0.687**	0.349	-0.302
syringol	-0.117	-0.261	-0.113	-0.143	0.322	-0.272	0.119	0.051	0.247	-0.202	-0.163

Table 4.7 (cont.) Pearson correlation coefficients for FD factors ≥ 8 and sensory (aroma) data

Attributes	Brown Sugar Aroma	Caramel Aroma	Maple Aroma	Vanilla Aroma	Coconut Aroma	Citrus Aroma	Phenolic Aroma	Alcohol Aroma	Smoky Aroma	Roasted Aroma	Chocolate Aroma
(*E*)-isoeugenol	0.132	-0.021	-0.007	-0.030	-0.377	-0.151	0.189	0.040	-0.216	-0.334	0.111
(*Z*)-6-dodecenelactone	-0.033	-0.242	-0.095	-0.289	-0.439	-0.062	0.411	0.146	-0.149	-0.751**	-0.066
unknow51	-0.117	-0.085	-0.143	-0.129	0.027	0.412	0.050	0.127	-0.035	-0.131	-0.108
ethyl vanillin	0.845***	0.945***	0.828***	0.941***	0.577	-0.671**	-0.869***	-0.876***	-0.603*	0.544	0.917***
vanillin	0.279	0.282	0.083	0.300	0.160	-0.078	-0.205	-0.228	-0.514	0.155	0.372
unknown55	0.414	0.460	0.526	0.373	0.481	-0.193	-0.434	-0.531	-0.382	-0.126	0.442
ethyl vanillate	0.246	-0.049	0.047	0.000	-0.025	-0.255	0.075	0.096	-0.218	-0.328	0.089
syringaldehyde	0.244	0.247	0.083	0.315	0.036	-0.193	-0.088	-0.151	0.264	0.613*	0.102
unknown59	0.409	0.444	0.197	0.506	0.146	-0.305	-0.362	-0.320	-0.459	0.516	0.492

*, **, *** stand for significance at $p<0.1$, $p<0.05$, and $p<0.01$ respectively.

Table 4.8 Pearson correlation coefficients for FD factors ≥ 16 and sensory (aroma) data

Attributes	Brown Sugar Aroma	Caramel Aroma	Maple Aroma	Vanilla Aroma	Coconut Aroma	Citrus Aroma	Phenolic Aroma	Alcohol Aroma	Smoky Aroma	Roasted Aroma	Chocolate Aroma
acetal	0.114	0.098	-0.038	0.187	-0.094	-0.228	0.034	-0.017	0.306	0.576	-0.007
2-/3-methylbutanal	-0.264	-0.294	-0.254	-0.277	-0.283	0.092	0.472	0.182	0.752**	0.004	-0.432
ethyl butanoate	0.575	0.646*	0.401	0.713**	0.366	-0.419	-0.619*	-0.482	-0.484	0.715**	0.640*
ethyl 2-methylbutanoate	-0.181	-0.400	-0.196	-0.331	-0.211	-0.206	0.520	0.235	0.752**	-0.242	-0.447
unknown14	-0.377	-0.313	-0.378	-0.310	-0.306	0.581	0.163	0.533	0.427	0.218	-0.450
2-/3-methyl-1-butanol	0.176	0.284	0.030	0.313	0.155	0.009	-0.191	-0.211	-0.140	0.510	0.226
ethyl cyclohexanecarboxylate	-0.213	-0.229	-0.208	-0.183	-0.231	-0.008	0.382	0.157	0.806***	0.230	-0.404
(*Z*)-2-nonenal	0.158	-0.172	0.019	-0.088	0.268	-0.280	0.091	0.116	-0.021	-0.385	-0.053
3-methylbutyric acid	-0.123	-0.077	-0.101	-0.120	-0.016	0.227	0.186	-0.004	0.220	-0.078	-0.155
unknown32	-0.237	-0.183	-0.224	-0.216	-0.065	0.442	0.195	0.198	0.346	-0.005	-0.302
β-damascenone	-0.209	-0.099	-0.283	-0.122	-0.224	0.561	0.098	0.290	0.237	0.293	-0.240
guaiacol	-0.173	-0.129	-0.178	-0.177	-0.048	0.320	0.201	0.066	0.058	-0.172	-0.149
***trans*-whiskey lactone**	0.080	0.010	0.016	0.146	0.486	-0.326	-0.202	-0.106	-0.084	0.127	0.121
2-phenethyl alcohol	-0.020	0.053	-0.070	0.025	0.089	0.232	0.010	-0.061	-0.062	0.063	0.017
***cis*-whiskey lactone**	0.201	0.259	0.279	0.203	0.361	-0.041	-0.209	-0.370	-0.115	-0.094	0.220
unknown40	0.356	0.393	0.519	0.357	0.191	-0.451	-0.217	-0.507	0.358	0.162	0.218
***p*-cresol**	-0.156	-0.163	-0.176	-0.129	-0.329	-0.037	0.370	0.120	0.721**	0.254	-0.328
***m*-cresol**	-0.065	-0.025	-0.125	-0.040	0.001	0.212	0.132	0.009	0.146	0.097	-0.102
eugenol	0.057	-0.190	0.034	-0.230	-0.312	-0.205	0.368	0.037	-0.012	-0.794**	-0.044
sotolon	-0.052	-0.146	-0.170	-0.060	-0.150	-0.081	0.274	0.170	0.687**	0.349	-0.302
syringol	-0.117	-0.261	-0.113	-0.143	0.322	-0.272	0.119	0.051	0.247	-0.202	-0.163
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vanillin	0.279	0.282	0.083	0.300	0.160	-0.078	-0.205	-0.228	-0.514	0.155	0.372
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syringaldehyde	0.244	0.247	0.083	0.315	0.036	-0.193	-0.088	-0.151	0.264	0.613*	0.102
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*, **, *** stand for significance at $p<0.1$, $p<0.05$, and $p<0.01$ respectively.

4.6 References

Adkins, H., & Nissen, B. H. (1941). Acetal. *Organic Syntheses*, *1*, 1. https://doi.org/10.15227/orgsyn.003.0001

Andreu-Sevilla, A. J., Mena, P., Martí, N., García Viguera, C., & Carbonell-Barrachina, Á. A. (2013). Volatile composition and descriptive sensory analysis of pomegranate juice and wine. *Food Research International*, *54*(1), 246–254. https://doi.org/10.1016/j.foodres.2013.07.007

Aznar, M., López, R., Cacho, J., & Ferreira, V. (2003). Prediction of Aged Red Wine Aroma Properties from Aroma Chemical Composition . Partial Least Squares Regression Models. *Journal of Agricultural and Food Chemistry*, *51*, 2700–2707. https://doi.org/10.1021/jf026115z

Beebe, K. R., Pell, R. J., & Seasholtz, M. B. (1998). *Chemometrics - A Practical Guide*. New York: John Wiley & Sons, Inc.

Brereton, R. G. (2007). Pattern Recognition. In *Applied Chemometrics for Scientitsts* (pp. 145–191). West Sussex, England: John Wiley& Sons, Ltd.

Brereton, R. G. (2009). Exploratory Data Analysis. In *Chemometrics for Pattern Recognition* (pp. 47–106). John Wiley& Sons, Ltd.

Burnside, E. E. (2012). *Characterization of Volatiles in Commercial and Self-Prepared Rum Ethers and Comparison with Key Aroma Compounds of Rum*. University of Illinois at Urbana-Champaign. Retrieved from https://www.ideals.illinois.edu/handle/2142/34368

Cardoso, D. R., Andrade-Sobrinho, L. G., Leite-Neto, A., Reche, R. V., Isique, W. D., Ferreira, M. M. C., … Franco, D. W. (2004). Comparison between Cachaca and Rum Using Pattern Recognition Methods. *Journal of Agricultural and Food Chemistry*, *52*, 3429–3433. https://doi.org/10.1021/jf035262+

Cutzach, I., Chatonnet, P., Henry, R., & Dubourdieu, D. (1997). Identification of Volatile Compounds with a "Toasty" Aroma in Heated Oak Used in Barrelmaking. *Journal of Agricultural and Food Chemistry*, *45*, 2217–2224. https://doi.org/10.1021/jf960947d

da Silva, G. A., Maretto, D. A., Bolini, H. M. A., Teófilo, R. F., Augusto, F., & Poppi, R. J. (2012).

Correlation of quantitative sensorial descriptors and chromatographic signals of beer using multivariate calibration strategies. *Food Chemistry*, *134*, 1673–1681. https://doi.org/10.1016/j.foodchem.2012.03.080

de Souza, M. D. C. A., Vásquez, P., del Mastro, N. L., Acree, T. E., & Lavin, E. H. (2006). Characterization of Cachaça and Rum Aroma. *Journal of Agricultural and Food Chemistry*, *54*, 485–488. https://doi.org/10.1021/jf0511190

de Souza, P. P., Augusti, D. V, Catharino, R. R., Siebald, H. G. L., Eberlin, M. N., & Augusti, R. (2007). Differentiation of Rum and Brazilian Artisan Cachaca via Electrostray Ionization Mass Spectrometry Fingerprinting. *Journal of Mass Spectrometry*, *42*, 1294–1299. https://doi.org/10.1002/jms.1197

Dong, J. J., Li, Q. L., Yin, H., Zhong, C., Hao, J. G., Yang, P. F., … Jia, S. R. (2014). Predictive analysis of beer quality by correlating sensory evaluation with higher alcohol and ester production using multivariate statistics methods. *Food Chemistry*, *161*, 376–382. https://doi.org/10.1016/j.foodchem.2014.04.006

Fazzalari, F. A. (Ed.). (1978). *Compilation of Odor and Taste Threshold Values Data*. Baltimore, MD: American Society for Testing and Materials.

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*, 637–645. https://doi.org/10.1021/acs.jafc.5b05426

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*, 9041–9053. https://doi.org/10.1021/acs.jafc.6b04046

Genthner, E. R. (2014). *Identification of Rotundone as an Important Contributor to the Flavor of Oak Aged Spirits*. University of Illinois at Urbana Champaign. Retrieved from https://www.ideals.illinois.edu/handle/2142/16898

González Álvarez, M., González-Barreiro, C., Cancho-Grande, B., & Simal-Gándara, J. (2011). Relationships between Godello white wine sensory properties and its aromatic fingerprinting

obtained by GC–MS. *Food Chemistry*, *129*, 890–898. https://doi.org/10.1016/j.foodchem.2011.05.040

Granato, D., de Oliveira, C. C., Caruso, M. S. F., Nagato, L. A. F., & Alaburda, J. (2014). Feasibility of different chemometric techniques to differentiate commercial Brazilian sugarcane spirits based on chemical markers. *Food Research International*, *60*, 212–217. https://doi.org/10.1016/j.foodres.2013.09.044

Green, J. A., Parr, W. V., Breitmeyer, J., Valentin, D., & Sherlock, R. (2011). Sensory and chemical characterisation of Sauvignon blanc wine: Influence of source of origin. *Food Research International*, *44*(9), 2788–2797. https://doi.org/10.1016/j.foodres.2011.06.005

Jung, H., Lee, S. J., Lim, J. H., Kim, B. K., & Park, K. J. (2014). Chemical and sensory profiles of makgeolli, Korean commercial rice wine, from descriptive, chemical, and volatile compound analyses. *Food Chemistry*, *152*, 624–632. https://doi.org/10.1016/j.foodchem.2013.11.127

Kelley, L. E. (2014). *Analysis of Potent Odorants in Spearmint Oils*. University of Illinois at Urbana-Champaign. Retrieved from https://www.ideals.illinois.edu/handle/2142/50415

Kotseridis, Y., Baumes, R., & Skouroumounis, G. K. (1998). Synthesis of labelled [2 H 4] β-damascenone , [2 H 2] 2-methoxy-3-isobutylpyrazine, [2 H 3]α-ionone, and [H]β-ionone, quantification in grapes , juices and wines. *Journal of Chromatography A*, *824*, 71–78.

Kulkarni, P. P., Kadam, A. J., Mane, R. B., Desai, U. V., & Wadgoankar, P. P. (1999). Demethylation of Methyl Aryl Ethers using Pyridine Hydrochloride in Solvent-free Conditions under Microwave Irradiation. *Journal of Chemical Research*, *S*, 394–395. Retrieved from http://pubs.rsc.org/EN/content/articlehtml/1999/jc/a901278h

Lahne, J. (2010). *Aroma Characterization of American Rye Whiskey by Chemical and Sensory Assays*. University of Illinois at Urbana-Champaign. Retrieved from https://www.ideals.illinois.edu/handle/2142/16713

Lapsongphon, N., Yongsawatdigul, J., & Cadwallader, K. R. (2015). Identification and Characterization of the Aroma-Impact Components of Thai Fish Sauce. *Journal of Agricultural and Food Chemistry*, *63*, 2628–2638. https://doi.org/10.1021/jf5061248

Limited Ingredients. (2016). *Alcohol and Tobacco Tax and Trade Bureau*. Retrieved from https://www.ttb.gov/ssd/limited_ingredients.shtml

Liu, J., Toldam-Andersen, T. B., Petersen, M. A., Zhang, S., Arneborg, N., & Bredie, W. L. P. (2015). Instrumental and sensory characterisation of Solaris white wines in Denmark. *Food Chemistry*, *166*, 133–142. https://doi.org/10.1016/j.foodchem.2014.05.148

López, R., Aznar, M., Cacho, J., & Ferreira, V. (2002). Determination of minor and trace volatile compounds in wine by solid-phase extraction and gas chromatography with mass spectrometric detection. *Journal of Chromatography A*, *966*, 167–177. https://doi.org/10.1016/S0021-9673(02)00696-9

Lorjaroenphon, Y. (2012). *Identification and Characterization of Potent Odorants Responsible for Typical and Storage-Induced Flavors of Cola-Flavored Carbonated Beverages*. University of Illinois at Urbana-Champaign. Retrieved from https://www.ideals.illinois.edu/handle/2142/31932

Maga, J. A. (1989). The Contribution of Wood to the Flavor of Alcoholic Beverages. *Food Reviews International*, *5*(1), 39–99. https://doi.org/10.1080/87559128909540844

Mimura, N., Isogai, A., Iwashita, K., Bamba, T., & Fukusaki, E. (2014). Gas chromatography/mass spectrometry based component profiling and quality prediction for Japanese sake. *Journal of Bioscience and Bioengineering*, *118*(4), 406–414. https://doi.org/10.1016/j.jbiosc.2014.04.006

Niu, Y., Zhang, X., Xiao, Z., Song, S., Eric, K., Jia, C., … Zhu, J. (2011). Characterization of odor-active compounds of various cherry wines by gas chromatography-mass spectrometry, gas chromatography-olfactometry and their correlation with sensory attributes. *Journal of Chromatography B: Analytical Technologies in the Biomedical and Life Sciences*, *879*(23), 2287–2293. https://doi.org/10.1016/j.jchromb.2011.06.015

Otsuka, K., Zenibayashi, Y., Itoh, M., & Totsuka, A. (1974). Presence and Significance of Two Diastereomers of β-Methyl-γ- octalactone in Aged Distilled Liquors. *Agricultural and Biological Chemistry*, *38*(3), 485.

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

https://doi.org/10.1016/j.foodchem.2011.11.133

Poisson, L., & Schieberle, P. (2008). Characterization of the Key Aroma Compounds in an American Bourbon Whisky by Quantitative Measurements, Aroma Recombination, and Omission Studies. *Journal of Agricultural and Food Chemistry*, *56*(14), 5820–6. https://doi.org/10.1021/jf800383v

Rayne, S., & Eggers, N. J. (2007). Quantitative determination of 4-ethylphenol and 4-ethyl-2-methoxyphenol in wines by a stable isotope dilution assay. *Journal of Chromatography A*, *1167*, 195–201. https://doi.org/10.1016/j.chroma.2007.08.049

Roberts, J. J., & Cozzolino, D. (2016). An Overview on the Application of Chemometrics in Food Science and Technology—An Approach to Quantitative Data Analysis. *Food Analytical Methods*, *9*(12), 3258–3267. https://doi.org/10.1007/s12161-016-0574-7

Robinson, A. L., Adams, D. O., Boss, P. K., Heymann, H., Solomon, P. S., & Trengove, R. D. (2011). The relationship between sensory attributes and wine composition for Australian Cabernet Sauvignon wines. *Australian Journal of Grape and Wine Research*, *17*, 327–340. https://doi.org/10.1111/j.1755-0238.2011.00155.x

Sampaio, O. M., Reche, R. V., & Franco, D. W. (2008). Chemical Profile of Rums as a Function of their Origin. The Use of Chemometric Techniques for their Identificatio. *Journal of Agricultural and Food Chemistry*, *56*, 1661–8. https://doi.org/10.1021/jf0726841

Schneider, S., & Rolando, C. (1992). One Step Synthesis of Vanillin d3 (4-hydroxy-3-(methoxy d3)-benzaldehyde). *Journal of Labelled Compounds and Radiopharmaceuticals*, *31*(6), 489–492.

Schuh, C., & Schieberle, P. (2006). Characterization of the Key Aroma Compounds in the Beverage Prepared from Darjeeling Black Tea : Quantitative Differences between Tea Leaves and Infusion and Infusion. *Journal of Agricultural and Food Chemistry*, *54*, 916–924.

Seisonen, S., Vene, K., & Koppel, K. (2016). The current practice in the application of chemometrics for correlation of sensory and gas chromatographic data. *Food Chemistry*, *210*, 530–540. https://doi.org/10.1016/j.foodchem.2016.04.134

Steinhaus, M., & Schieberle, P. (2005). Characterization of Odorants Causing an Atypical Aroma in White Pepper Powder (Piper nigrum L.) Based on Quantitative Measurements and Orthonasal Breakthrough Thresholds Pipernigrum. *Journal of Agricultural and Food Chemistry*, *53*, 6049–6055. https://doi.org/10.1021/jf0506030

Todeschini, R., Ballabio, D., Rojas, C., Manganaro, A., Mauri, A., Consonni, V., & Tripaldi, P. (2007). Evaluation of Multivariate Classification and Variable Selection for the Distinction of Cachaça and Rum Samples. *Alimentos Ciencia E Ingeniería*, *16*(2), 113–115.

Uselmann, V., & Schieberle, P. (2015). Decoding the Combinatorial Aroma Code of a Commercial Cognac by Application of the Sensomics Concept and First Insights into Differences from a German Brandy. *Journal of Agricultural and Food Chemistry*, *63*, 1948–1956. https://doi.org/10.1021/jf506307x

Vilanova, M., Genisheva, Z., Masa, A., & Oliveira, J. M. (2010). Correlation between volatile composition and sensory properties in Spanish Albariño wines. *Microchemical Journal*, *95*, 240–246. https://doi.org/10.1016/j.microc.2009.12.007

Willner, B., Granvogl, M., & Schieberle, P. (2013). Characterization of the Key Aroma Compounds in Bartlett Pear Brandies by Means of the Sensomics Concept. *Journal of Agricultural and Food Chemistry*, *61*, 9563–9593.

Wiśniewska, P., Śliwińska, M., Dymerski, T., & Wardencki, N. (2017). Comparison of an Electronic Nose Based on Ultrafast Gas Chromatography, Comprehensive Two-Dimensional Gas Chromatography, and Sensory Evaluation for an Analysis of Type of Whisky. *Journal of Chemistry*, 1–13. https://doi.org/https://doi.org/10.1155/2017/2710104 Research

Xiao, Z., Liu, S., Gu, Y., Xu, N., Shang, Y., & Zhu, J. (2014). Discrimination of Cherry Wines Based on Their Sensory Properties and Aromatic Fingerprinting using HS-SPME-GC-MS and Multivariate Analysis. *Journal of Food Science*, *79*(3). https://doi.org/10.1111/1750-3841.12362

Chapter 5: Novel Creation of a Rum Flavor Lexicon Through the Use of Web-Based Material

5.1 Abstract

Flavor lexicons help both manufacturers and consumers communicate the intricacies of flavor nuances they experience within a product. Lexicon development typically requires the use of a trained sensory panel to evaluate a representative sample set of the product category to generate terms that describe certain product attributes. In the case of rum, there is considerable variation in terms of style, flavor characteristics, and the sheer number of rums produced making it difficult to create a lexicon in this manner. Furthermore, sensory fatigue from the high alcohol content can also hinder lexicon development. This is the first study to create a rum flavor lexicon using web-based material (comprising blogs, company descriptions and review websites) to minimize the time and cost and to allow for the inclusion of a greater number of rum products. Reviews for over one thousand different rums were utilized, comprising evaluations that described an array of rums, including white, gold, aged and agricole. Each evaluation was coded for aroma, aroma-by-mouth, and taste attributes using NVivo™ software to amass the sensory terms. Word frequency analysis was conducted on coded attributes. The analysis yielded 147 terms, sorted into 22 different categories. The most prominent terms included vanilla, oak, caramel, fruity, molasses and baking spices.

Results of this study demonstrate that web-based material can be used for products containing a large variation and where significant sensory fatigue is an issue to create a lexicon provided enough evaluations of the product exist. The developed lexicon will aid in term generation for future descriptive analysis panels on rum, as well as provide a standardized language for use in the rum industry when training and evaluating samples for quality assurance as well as marketing.

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5.2 Introduction

Flavor lexicons are standardized vocabularies that aid in the communication of the perceived sensory attributes in foods and beverages. An established vocabulary provides terminology to describe flavor perceptions in a consistent manner. Lexicons aid in communication between researchers, product developers and manufacturers for use in quality assurance and product assessment, as well as to aid marketers in articulating the subtle flavor perceptions to consumers. Lexicons typically contain terminology for multiple sensory perceptions encompassed in the term flavor, including aroma, aroma-by-mouth, taste, mouthfeel and trigeminal sensations.

Lexicons have been developed for a variety of different food products including spices (Lawless, Hottenstein, & Ellingsworth, 2012), cheese (Drake, McInvale, Gerard, Cadwallader, & Civille, 2001), bread (Kleinert, Bongartz, Raemy, & Wadenswil, 2009), olive oil (Mojet & de Jong, 1994), almonds (Civille, Lapsley, Huang, Yada, & Seltsam, 2010), tea (Koch, Muller, Joubert, van der Rijst, & Næs, 2012) and orange juice (Pérez-Cacho, Galán-Soldevilla, Mahattanatawee, Elston, & Rouseff, 2008). Additionally, a number of lexicons have been developed for alcoholic beverages including beer (Clapperton, Dalgiesh, & Meilgaard, 1976; Meilgaard, Dalgliesh, & Clapperton, 1979; Parker, 2012), brandy (Jolly & Hattingh, 2001), cognac (Lurton, Ferrari, & Snakkers, 2012), distilled beverages (Mc Donnell, Hulin-Bertaud, Sheehan, & Delahunty, 2001), whisky (Lee, Paterson, Piggott, & Richardson, 2001; Piggott & Jardine, 1979; Swan, Howie, & Burtles, 1981) and wine (Noble et al., 1984, 1987). The wine flavor wheel is one of the most well-known lexicons, recognized by connoisseurs and consumers alike. Standardized terms, definitions, and references for a product allow users to describe and verbalize the differences among products within a category (Lawless & Civille, 2013).

Typical development of a lexicon requires the use of a trained sensory panel. Panelists generally undergo numerous hours of training on evaluating different food products through descriptive analysis (Lawless & Civille, 2013) . To develop a complete lexicon, samples that encompass all of the diverse aspects of a product category need to be evaluated. This can include not only products from different manufacturers but also products produced in various geographical regions or having different maturities to develop a comprehensive lexicon (Drake et al., 2001). Once the products to

be evaluated have been selected, panelists will generate terms to describe their perceptions, determine appropriate chemical or food product references, and develop specific definitions for each attribute. After the initial term generation, terms that are redundant are removed from the list. Once the terms and references have been determined, the lexicon will be organized into a comprehensive list. The developed lexicon can then be validated to demonstrate that the terms are effective for distinguishing relevant product characteristics within the category (Lawless & Civille, 2013). Panelists start by scaling the attributes according to the selected references. Each sample is then evaluated by the panelists with each attribute being rated in comparison to its corresponding reference. The compiled data allow researchers to identify how products within the category differ from each other.

Once a lexicon has been developed, it can be converted into a flavor wheel which provides a visual representation of the generated terms (Lawless & Civille, 2013). Terms are typically grouped by category, with the grouping identified in the inner circle and the specific term listed along the outside. The completed wheel can be used to train new panelists by aiding with term selection and communication with other scientists, consumers, or marketers.

A limited number of sensory studies have been conducted on rum. A vocabulary for evaluating distilled spirits was developed using a white rum along with white tequila, vodka, gin, grappa, and pear acquavite (Mc Donnell et al., 2001). Term development generated 100 initial terms which were then reduced to 30 final terms for use in qualitative descriptive analysis. De Souza and others (de Souza, Vásquez, del Mastro, Acree, & Lavin, 2006) used descriptive sensory analysis to compare the aroma profiles of cachaça and rum on the basis of 10 aroma attributes. Franitza and others (Franitza, Granvogl, & Schieberle, 2016a, 2016b) have recently published two papers where aroma profile analysis was used to compare model aroma recombinates to the original rum samples. These studies are limited in scope as they each evaluated only one or two rums, with a primary focus on the flavor chemistry of the products rather than on their sensory profiles. The most comprehensive sensory study on rum to date is a master's thesis by Gómez (Gómez, 2002) where 33 terms were generated through the evaluation of 15 different rums. However, this vocabulary is incomplete as demonstrated by their later descriptive analysis panel which utilized terms that were not part of the initial vocabulary (Gómez, 2002). The main emphasis of these studies has been to develop terminology to aid in evaluating one or a specific subgroup of rum samples rather than to gain a comprehensive understanding of rum flavor across the entire category.

Currently, there is no published flavor lexicon for rum. Rum is an extremely complex product category due to its limited standards of identity. The only production requirement is that the distillate must be produced from a sugarcane by-product (Labeling and advertising of distilled spirits, 27 C.F.R. § 5.22 1969). Since rum can be produced from a variety of sugarcane products, be distilled in multiple ways, and aged in any type of barrel the manufacturer desires, there is a significant amount of variation amongst products classified as rum. Rums are typically grouped into several categories including white, gold, aged, agricole, flavored and spiced rums (Ayala, 2001). White rums are typically aged in either stainless steel tanks or wood casks for 1 to 2 years and then filtered through charcoal. Gold rums are typically aged for 1 to 3 three years in wood casks. Aged rums are those that have been aged for at least 3 years or more. Agricole rums are produced from pure sugar cane juice rather than molasses and are produced predominately in the French West Indies. Flavored and spiced rums are rums blended with fruits and spices during production and should not be compared with rums produced in the traditional manner. Due to the enormous variation in the product category and the sensory fatigue panelists would experience from the high alcohol content of the product, a rum lexicon developed in the traditional way would be both expensive and time intensive.

Web-based materials are increasingly available, with more content being added to the internet on a daily basis. The ease of access allows enthusiasts and connoisseurs of spirits and alcoholic beverages, such as rum, to publish their opinions and reviews online. Additionally, companies readily market their product through the use of descriptive terminology. Compiling the terms already being used by consumers and the rum industry provides an excellent starting point for the creation of a flavor lexicon. A similar approach has recently been used to create a flavor wheel for Chenin Blanc wine, where the researchers used the terminology found in the John Platter wine guide to construct the wheel (Valente, 2016).

With this in mind, the objective of this study was to evaluate a new method for lexicon creation of rum through the use of web-based materials. Rum products have numerous product descriptions and reviews available online. Use of web-based material allowed for the collection of data on a wide variety of rum products, more than could feasibly be evaluated with traditional methods.

5.3 Materials and Methods

Selection of Web-based Material

Web-based material consisting of blogs, company descriptions and review websites, were chosen based on the following criteria: use of qualitative flavor descriptors and website organization. Web-material was found through the use of Google™ search using keywords such as "rum blogs" and "rum reviews." Blogs and websites that provided only reviews and/or ratings for rums but no qualitative flavor descriptions were excluded from the study. Company web pages were sought for each rum reviewed on other websites. All companies that had web pages and product descriptions were included. Seventeen websites and 57 company descriptions were selected for analysis (Table 5.1). Only reviews available through June 2015 were included. All evaluations were captured as PDFs and imported into NVivo™ (NVivo qualitative data analysis software; QSR International Pty Ltd. Version 10, 2014).

Evaluation of Web-Based Material for Sensory Terms

Each rum evaluation was coded by hand for aroma (orthonasal perception), aroma-by-mouth (retronasal perception), and taste (consisting of basic tastes, mouthfeel and trigeminal) attributes. Only qualitative descriptors were coded. Subjective descriptors such as good, bad, excellent, and mature were excluded. Once all evaluations were coded, word frequency analysis was conducted in NVivo on the collected attributes. Any descriptor that appeared at least ten times throughout the entire dataset was selected for the preliminary lexicon. This was a natural cutoff in the data as there were still sensory relevant terms and each term encompassed 0.05% of the total terms coded.

Categorization of Flavor Terms

A sorting exercise was performed to categorize the terms. Ten individuals, 3 male, and 7 female, 23-29 years of age were selected from University of Illinois students based on availability and interest in participating on the sorting panel. Each person was given a bag containing all of the selected terms written on paper slips. Participants were instructed to sort the terms into categories as they saw fit, based solely on their knowledge of the presented terms. Panelists were allowed to ask for definitions of terms they did not know. They were also instructed to group redundant terms and remove terms they felt were coded by mistake or not relevant to flavor perceptions such as palate, little, slightly,

and sip. Once the participants had sorted all of the terms, they were asked to label and write a brief description for each category they constructed. The data were visually analyzed by the panel facilitator who compiled the categories developed from panelists into one comprehensive lexicon. Terms that were grouped together consistently by multiple assessors were placed together in the final lexicon. Terms that were sorted into multiple categories by panelists with no clear majority were placed into their final grouping based on the organization of previous alcoholic beverage flavor wheels (Noble and others 1984, 1987; Jolly and Hattingh 2001; Lee and others 2001).

5.4 Results and Discussion

Rum reviews from 17 different websites as well as product descriptions from 57 different companies were compiled for data analysis. Over 3,000 individual reviews were coded for 1,053 different products which encompassed white, gold, aged, and agricole rums. Flavored and spiced rums were not included in this analysis as additional flavoring agents are added to these products to change the flavor of the rum. Initially, 267 individual terms were selected through the word frequency analysis. The ten most frequently used terms to describe rum flavor were vanilla, sweet, spices, oak, caramel, fruity, dry, smooth, sugar, and molasses. These ten words comprised 28.48% of the total descriptors coded.

The selected terms were given to participants for categorization. Through this exercise, a number of terms were eliminated from the lexicon as they were either duplicate words that had multiple spellings or endings such as fruit, fruits, and fruity or words that were not useful attribute descriptors such as deep and tones. Terms which could be considered compound terms, or terms composed of multiple attributes, were not eliminated from the lexicon. The individual categorizations were then combined based on how often terms were grouped together. After term categorization, a final lexicon consisting of 147 terms sorted into 22 categories was created (Table 2). Descriptors were not identified as positive or negative with regard to overall flavor quality. All terms remained as they appeared in the web-based material with the exception of brine which was replaced with salty for the lexicon. The final lexicon is a compilation of the most prevalent terms currently used to describe rum flavor. It is expected that only a subset of these terms would be required to describe an individual rum.

Rum Flavor Wheel

The terms selected for the lexicon were organized into a flavor wheel for ease of use (Figure 1). The rum flavor wheel is split into two tiers, with 22 first tier descriptors and 125 second-tier descriptors. The innermost tier consists of the broader terms, while the outer wheel contains more precise terminology within each inner category. Terms that are more similar are located closer to each other on the wheel.

All of the first tier descriptors have been used in other alcoholic beverage lexicons as category groupings except for chocolate, coffee and confections (Clapperton and others 1976; Meilgaard and others 1979; Shortreed 1979; Noble and others 1984, 1987; Langstaff and Lewis 1993; Jolly and Hattingh 2001; Lee and others 2001; Le Barbe 2003; Lurton and others 2012). Terms associated with sugary products are typically categorized as sweet-associated rather than categorized under sugar as we have done (Shortreed 1979; Jolly and Hattingh 2001; Lee and others 2001; Le Barbe 2003). All of the categories have been used in at least two other lexicons except alcoholic beverages and dairy products. The whisky flavor wheel published by Lee and others (2001) is the only lexicon to include other alcoholic beverages as a category which they label "previous use." Additionally, mouthfeel and trigeminal sensations tend to be grouped together when found on previous flavor wheels (Clapperton and others 1976; Meilgaard and others 1979; Shortreed 1979; Noble and others 1984, 1987; Langstaff and Lewis 1993; Jolly and Hattingh 2001; Lee and others 2001; Le Barbe 2003; Lurton and others 2012). Meanwhile, chocolate and coffee terms have not previously been used as a category, although they are found as second tier terms (Clapperton and others 1976; Noble and others 1984, 1987; Jolly & Hattingh 2001; Le Barbe 2003; Lurton and others 2012). Chocolate has previously been grouped under caramel, smoky, sweet associated and vanilla, while coffee has been grouped under caramel, smoky, toasted, and woody.

Terms Most Common to Rum Categories

The abundance of data collected using web-based material allows for the identification of not only the terms used to describe rum as an entire class but also demonstrates how the various categories of rum differ from each other. Rums categorized as white, gold, and a variety of age statement types including 2-5 years, 5-10 years, 10-20 years, and 20 plus years were able to be analyzed. The 15 most prevalent aroma and aroma-by-mouth terms in each categorization can be found in Table 3. These

data indicate that all rums appear to be characterized by vanilla, caramel, fruity and spices. White rums seem to be further characterized by coconut, floral, banana and mineral notes compared to the other categories; whereas, woody, tobacco, toffee and chocolate notes seem to increase as a function of age. Previous sensory profiles of rums also show the terms vanilla, caramel, fruity and terms related to spices as key attributes to describe rum flavor along with alcoholic/ethanolic and woody (Gómez 2002; De Souza and others 2006; Franitza and others 2016a, b). Previous studies have not focused on aroma differences as a result of maturation, making this the first study to provide insight into how rum aroma profiles may change as a result of maturation.

Discussion of the Rum Lexicon

The use of web-based material for term generation provides an excellent starting point for lexicon development. The final lexicon contains many terms that overlap with already published lexicons for alcoholic beverages. All of the category descriptors except trigeminal, chocolate, leather, dairy and coffee as well as more than half the individual terms have been used in previous lexicons for alcoholic beverages (Piggott and Jardine 1979; Swan and others 1981; Noble and others 1984; Jolly and Hattingh 2001; Lee and others 2001; Mc Donnell and others 2001; Schmelzle 2009). The substantial overlap of terminology indicates that appropriate descriptors were coded for and used to develop the wheel. The terms not previously used in flavor lexicons are likely to be descriptors that are unique to rum.

A similar data mining approach has recently been used to construct a flavor wheel for Chenin Blanc wines (Valente 2016). The researchers collected terms from the John Platter Wine Guide over a seven year period. The guide annually rates the wines produced by the vineyards in South Africa, enabling them to amass terms from 2746 wines. Our approach is similar in that both studies are collecting potential terms from previously published reviews. Our study further expands the use of data mining, as we have evaluated reviews from multiple online sources rather than just a single publication. Both studies demonstrate that preexisting data can be used to construct a valid flavor lexicon.

While the current practice for lexicon development makes use of a descriptive analysis panel, original flavor wheels for beverages such as wine and beer were developed through the use of experts in the field who suggested terms to be included in the lexicon (Clapperton and others 1976;

Noble and others 1987). This collaboration led to the creation of lexicons which adequately described the beverage class. A similar approach was followed here, where reviews from rum experts, enthusiasts, and connoisseurs were collected and evaluated to create the lexicon. While the reviewers did not specifically propose terms, we used their descriptors in the development of the rum lexicon.

A limiting factor of the lexicon is that web-reviewers do not adequately define the terms they use in their descriptions. As a result, no precise definitions or references for terms were collected to create this lexicon. While definitions are helpful for a better grasp of the accurate perception of an attribute, many flavor wheels do not contain definitions for their terms. This is true for many whisky wheels (Jackson 1989; MacLean 1997) as well as the McCormick Spice Wheel (Lawless and others 2012). While definitions are helpful, they are not essential for the wheel to be useful. Many times panelists identify that a sample contains a familiar attribute but are not able to articulate what they perceive without the visual cue to accompany the perception. Having a lexicon accessible to them gives panelists a selection of words to choose from, instead of forcing them to generate the term from memory. Additionally, a majority of the terms included in the rum lexicon have inherent meanings for panelists such as the aroma of caramel, clove or banana.

While definitions are not always a necessity for connoisseurs or expert judges, they are essential if the terms are to be used as part of a descriptive analysis panel. Definitions, as well as specific references, will need to be developed and selected in order for a panel to consistently rate the terms across samples. Defining terms through the use of a descriptive analysis panel would be beneficial to clarify the meaning of the terms with respect to how they are perceived in rum. This would be especially useful for the trigeminal and mouthfeel terms, as people tend to be less familiar with those sensations compared to terms which describe food products.

Another limiting factor of the rum lexicon is the use of compound terms. During typical lexicon development, panelists are discouraged from using terms that combine multiple attributes and prompted to break those terms apart into singular attributes. However, this is not the case for web reviewers, they describe what they perceive, and sometimes the attributes are combined to form a complex term that is more easily identifiable than the individual attributes. For example, our wheel contains the term mocha which combines the aromas of chocolate and coffee, and even those attributes could be considered compound terms as well. Praline is another compound term of nutty

and caramel. Additional compound terms encompassed in the rum lexicon include marzipan, crème brûlée, tea, cigar, fruitcake, and gingerbread. Regardless, compound terms have been used in other lexicons as well. Most notably, coffee and tea are typically included in lexicons (Noble and others 1984, 1987; Jolly and Hattingh 2001; Lee and others 2001; Le Barbe 2003; Lurton and others 2012) even though entire lexicons have been created to characterize those products (Seo and others 2009; Koch and others 2012; Muller and Joubert 2013; Theron and others 2014; Spencer and others 2016). These terms are most likely included in lexicons as they are easy for evaluators to identify since the combination of aromas has a characteristic profile that people encounter on a regular basis. The terms marzipan and cigar (box) have been included in the whisky (Lee and others 2001) and cognac (Lurton and others 2012) flavor wheels, respectively. Additionally, the whisky (Lee and others 2001), sparkling wine (Le Barbe 2003), and brandy (Jolly and Hattingh 2001) flavor lexicons include alcoholic beverages such as sherry and port as attributes.

It should be noted that to the best of our knowledge this is the first attempt to create a flavor lexicon for rum. Even though over 3,000 reviews were utilized for this analysis, it is expected that the lexicon will need to be modified over time, similar to the case for the wine and beer lexicons and most recently the coffee lexicon (Meilgaard and other 1979; Noble and others 1987; Spencer and others 2016). The beer terminology wheel was altered after discussions at the annual meetings of the European and American brewing societies (Meilgaard and others 1979). Participants were able to submit suggestions by mail in order to refine the lexicon to better meet the practical needs of brewers' societies (Meilgaard and others 1979). The wine aroma wheel also allowed for feedback from experts in the field leading to the addition of several terms, reorganization of the wheel, and the addition of chemical or food references for each term (Noble and others 1987). The new coffee wheel utilized industry experts to develop the lexicon terms, followed by statistical analysis of term sorting (Spencer and others 2016). These modifications have allowed the lexicons to change to be better aligned with the needs of these ever-changing industries.

Conclusion

While the rum wheel includes terms utilized by companies and avid spirit enthusiasts, it is likely that there are missing terms that may be identified by a trained panel. Validation of the wheel using a descriptive analysis panel would be a first step in the refinement process. Additionally, this wheel

only includes terms which describe the finished rum products. The wheel would likely need to be expanded if it were to be used during the production process.

The developed rum flavor lexicon provides manufacturers and retailers with an initial vocabulary to describe rums. This will allow the same perceptions to be communicated consistently and provide terminology for attributes that people may not have been able to previously articulate. The next step would be to define the different terms using a descriptive analysis panel so that each term has a standard reference and definition that can then be used to train new people for quality assurance. This rum lexicon will be used to aid in the development of terms for a descriptive analysis panel by providing a bank of terms for the panel to assess when generating terms.

5.5 Tables and Figure

Table 5.1 Web-based material used to create the rum flavor lexicon

Name of Blog	Type	Website Address
Best of Luxury	Blog	http://www.bestofluxury.com/rankings-of-best-rum-liquors
Bilgemunky	Blog	http://www.bilgemunky.com/category/pirate-reviews/rum/
Dowd's Tasting Notes	Blog	http://dowdtastingnotes.blogspot.com/
El Machete's Rum Reviews	Blog	http://macheterum.blogspot.com/
Fahrenheit 173	Blog	http://fahrenheit173.com/ratings/rum/?search=&top=all&origin=all&type=w
Got Rum	Blog	http://www.gotrum.com/rumreviews
Proof66	Blog	http://www.proof66.com/liquor/rum.html
Refined Vices Blog	Blog	https://refinedvices.com/rum-reviews/
Rob's Rum Guide	Blog	http://www.robsrum.com/
Rum Dood	Blog	http://rumdood.com/rum-reviews/
Rum Ratings	Blog	https://www.rumratings.com/brands
Scottes' Rum Pages	Blog	https://scottesrum.com/category/all-rum-reviews/
Spirits Review	Blog	http://spiritsreview.com/class/rum/
Tastings	Blog	http://www.tastings.com/Home.aspx
The Rum Howler	Blog	https://therumhowlerblog.com/rum-reviews/
The Rum Shop	Blog	http://www.rumshop.net/
The Rumelier	Blog	http://www.therumelier.com/index.html
Admiral Rodney	Company	http://www.saintluciarums.com/admiral-rodney.html
A.H. Riise	Company	https://www.ahriiserum.com/products.html
Amrut	Company	http://www.amrutdistilleries.com/validated/pages/opdr.html
Angostura	Company	http://www.angostura.com/Brands/
Antigua Distillery Cavalier	Company	http://www.antiguadistillery.com/our-range.html
Appleton Estate	Company	http://www.appletonestate.com/en/our-rum/
Atlantico	Company	http://www.atlanticorum.com/services3
Bacardi	Company	https://www3.bacardi.com/us/en/our-rums/
Ron Barcelo	Company	http://www.ronbarcelo.com/initial.html
Brugal	Company	https://www.brugal-rum.com/our-rum/
Cana Brava	Company	http://www.canabravarum.com/
Clarke's Court	Company	http://www.clarkescourtrum.com/products/aged
Rhum Clement	Company	http://rhumclementusa.com/index.php
Chairman's	Company	http://www.saintluciarums.com/chairmans-reserve.html
Cockspur	Company	http://www.cockspurrum.com/concocktions/
Cruzan	Company	http://www.cruzanrum.com/rum-collection/
Deadhead	Company	http://deadheadrum.com/the-rum.html
Dictador	Company	http://www.dictador.com/dictador-rums.html
Diplomatico	Company	http://www.rondiplomatico.com/rums
Don Pancho Origenes	Company	http://origenesdonpancho.com/?age-verified=cd956f803a
Don Papa	Company	http://www.donpaparum.com/the-goods.html
Dos Maderas	Company	http://www.rondosmaderas.com/en/index.php
El Dorado	Company	http://theeldoradorum.com/our-portfolio
Facundo	Company	http://www.facundorum.com/the-rum-collection/
Flor de Cana	Company	http://flordecana.com/eng/products
Gosling's	Company	http://www.goslingsrum.com/our-products/
Green Island	Company	http://greenislandrum.com/products.html
Havana Club	Company	http://havana-club.com/en/cuban-rum/havana-club-rum
Kirk and Sweeney	Company	http://www.3badge.com/kirkandsweeney/
Koloa	Company	http://koloarum.com/rums/
Montanya	Company	http://www.montanyarum.com/home-rums/
Mount Gay	Company	http://www.mountgayrum.com/
Neisson	Company	http://www.neisson.fr/-rubrique14-.html?lang=en
New Grove	Company	http://www.newgrove.mu/#
Newfoundland Screech	Company	http://screechrum.com/#products
Opthimus	Company	http://spiritimportsinc.com/brands/opthimus/
Penny Blue	Company	http://indianoceanrum.com/pennybluerum/
Plantation	Company	http://www.plantationrum.com/rums-plantation#vintages
Rhum Agricole Bologne	Company	http://www.rhumbologne.fr/en/rums.html
Rhum Barbancourt	Company	barbancourtrhum.com/the-rhums/

Table 5.1 (cont.) Web-based material used to create the rum flavor lexicon

Name of Blog	Type	Website Address
Rhum J.M	Company	http://www.rhumjmusa.com/index.php
Ron Abuelo	Company	http://www.ronabuelopanama.com/category/brand/?lang=en&lang=en
Ron Matusalem	Company	http://www.matusalem.com/en.html
Rum Nation	Company	http://www.rumnation.com/en/
Saint James	Company	http://www.saintjames-rum.com/#!/gamme
Santa Teresa	Company	https://ronsantateresa.com/us/#/we-make-rum
Sergeant Classick	Company	http://sgtclassick.com/default.asp
St. Barth	Company	http://www.rhumstbarth.com/collection-rhum.asp
Tanduay	Company	http://tanduay.com/brands/tanduay-rhum-5-years/
The Real McCoy	Company	http://www.realmccoyspirits.com/therum
TOZ	Company	http://www.saintluciarums.com/toz.html
Trois Rivieres	Company	http://www.plantationtroisrivieres.com/3-rivieres/the-collection/id/1319
Wild Geese	Company	http://thewildgeesecollection.com/rum/our-rum/
Yacuro	Company	http://www.calderonglobaltrade.com/en/ron_yacuro/

Table 5.2 Categorization of terms generated from web-material used to create the flavor wheel

First Tier	Second Tier	First Tier	Second Tier	First Tier	Second Tier
Sugar	Candied	Woody	Barrel	Citrus	Lemon
	Honey		Cedar		Lime
	Honeycomb		Oak		Marmalade
	Maple		Sandalwood		Orange
	Marshmallow				
	Marzipan	Nutty	Almond	Alcoholic	Arrack
	Molasses		Hazelnut		Bourbon
	Nougat		Pecan		Brandy
	Sugarcane		Walnut		Cognac
	Syrup				Sherry
	Treacle	Leather	Saddle		Whiskey
					Wine
Caramel	Brown	Earthy	Cigar		
	Butterscotch		Musty	Medicinal	Alkali
	Caramelized		Peat		Copper
	Cola		Root		Metallic
	Crème Brulee		Sap		Mineral
	Praline		Tobacco		Rubber
	Toffee				Tar
		Vegetal	Floral		
Dairy	Buttery		Fresh	Tastes	Bitter
	Cream		Grass		Salty
	Custard		Green		Sweet
			Herbal		
Chocolate	Cocoa		Minty	Mouthfeel	Astringent
	Fudge		Tea		Buttery
					Creamy
Coffee	Mocha	Fruity	Apple		Crisp
			Apricot		Dry
Confections	Fruitcake		Cherry		Heavy
	Gingerbread		Currants		Oily
	Meringue		Dates		Rough
			Figs		Sharpness
Baking Spices	Allspice		Grapes		Silky
	Cardamom		Peaches		Smooth
	Cinnamon		Pear		Supple
	Clove				Syrupy
	Ginger	Dried Fruit	Dried Apricot		Thick
	Licorice		Dried Dates		Velvety
	Mace		Dried Currants		
	Nutmeg		Dried Figs	Trigeminal	Bite
	Peppery		Prunes		Burn
	Vanilla		Raisin		Harsh
					Hot
Roasted	Burnt	Tropical Fruit	Banana		Pungent
	Charred		Coconut		Sharp
	Smoky		Mango		Warm
	Toasted		Pineapple		Tannins

Table 5.3 Top 15 descriptors for each category of rum

White	Gold	2-5 years	5-10 years	10-20 years	20+ years
Vanilla	Vanilla	Spices	Vanilla	Vanilla	Vanilla
Banana	Spices	Vanilla	Oak	Oak	Spices
Citrus	Sugar	Caramel	Caramel	Spices	Oak
Caramel	Caramel	Oak	Spices	Caramel	Fruity
Fruity	Oak	Fruity	Fruity	Fruity	Caramel
Coconut	Fruity	Molasses	Sugar	Molasses	Orange
Oak	Molasses	Sugar	Molasses	Toffee	Sugar
Spices	Banana	Tobacco	Cinnamon	Sugar	Toffee
Molasses	Toffee	Orange	Tobacco	Orange	Woody
Sugar	Woody	Toffee	Toffee	Tobacco	Molasses
Butterscotch	Nutty	Banana	Orange	Cinnamon	Cinnamon
Cream	Tobacco	Coconut	Butterscotch	Woody	Tobacco
Floral	Orange	Cinnamon	Leather	Banana	Chocolate
Mineral	Honey	Butterscotch	Banana	Chocolate	Honey

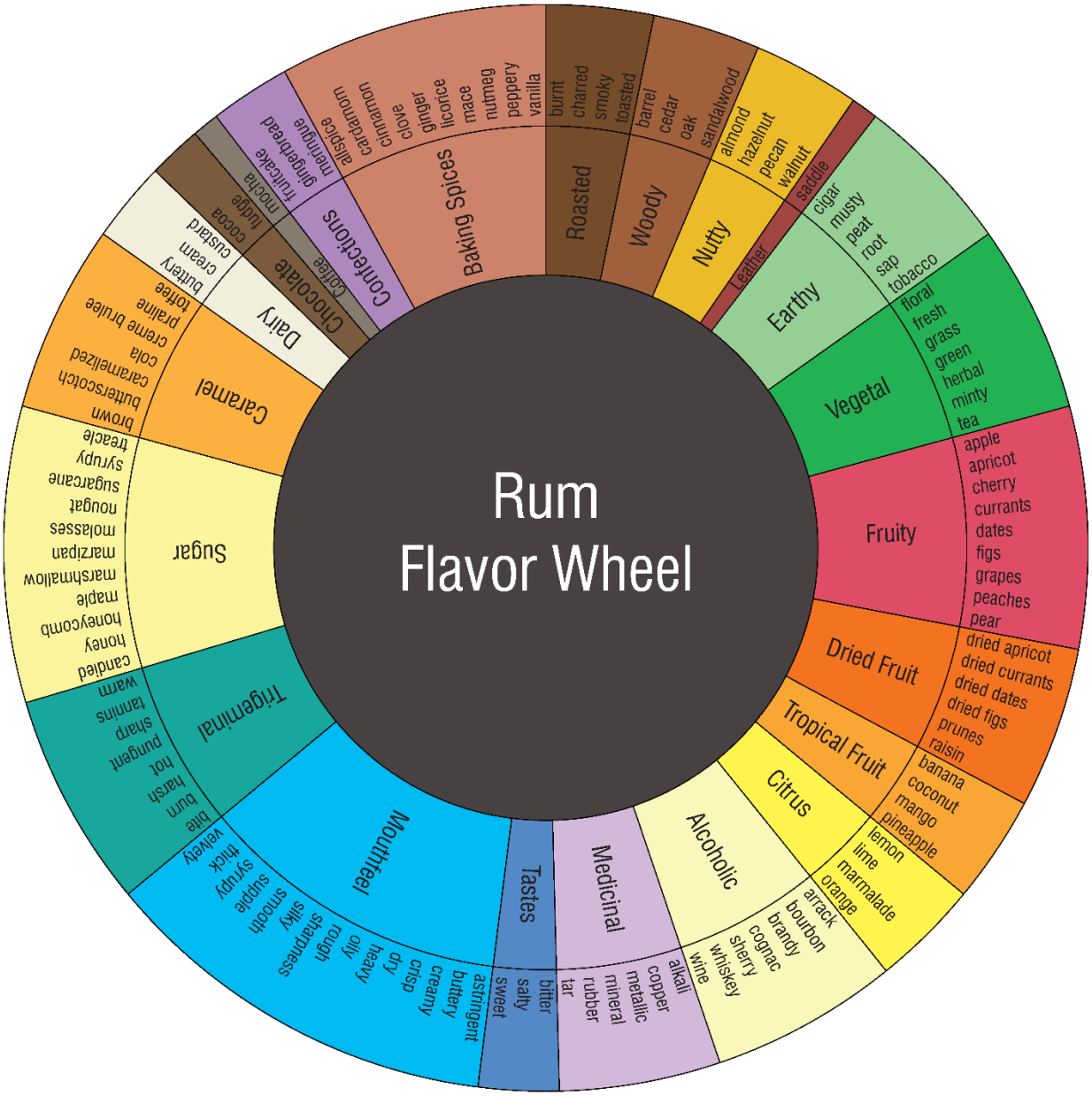


Figure 5.1 Rum flavor wheel developed from web-based material describing white, gold and aged rums

5.6 References

Ayala, L. K. (2001). *The Rum Experience*. Texas, USA: Rum Runner Press Inc.

Civille, G. V., Lapsley, K., Huang, G., Yada, S., & Seltsam, J. (2010). Development of an Almond Lexicon To Assess the Sensory Properties of Almond Varieties. *Journal of Sensory Studies*, *25*, 146–162. https://doi.org/10.1111/j.1745-459X.2009.00261.x

Clapperton, J. F., Dalgiesh, C. E., & Meilgaard, M. C. (1976). Progress Towards an International System of Beer Flavour Terminology. *Journal of the Institute of Brewing*, *82*, 7–13.

de Souza, M. D. C. A., Vásquez, P., del Mastro, N. L., Acree, T. E., & Lavin, E. H. (2006). Characterization of Cachaça and Rum Aroma. *Journal of Agricultural and Food Chemistry*, *54*, 485–488. https://doi.org/10.1021/jf0511190

Drake, M. a, McInvale, S. C., Gerard, P. D., Cadwallader, K. R., & Civille, G. V. (2001). Development of a Descriptive Language for Cheddar Cheese. *Journal of Food Science*, *66*(9), 1422–1427.

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*, 637–645. https://doi.org/10.1021/acs.jafc.5b05426

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*, 9041–9053. https://doi.org/10.1021/acs.jafc.6b04046

Gómez, S. M. (2002). *Rum Aroma Descriptive Analysis*. Louisiana State University. Retrieved from http://etd.lsu.edu/docs/available/etd-1114102-110301/

Jolly, N. P., & Hattingh, S. (2001). A Brandy Aroma Wheel for South African Brandy. *South African Journal of Enology and Viticulture*, *22*(1), 16–21.

Kleinert, M., Bongartz, A., Raemy, E., & Wadenswil. (2009). Development of a Flavour Wheel for Breads. *Getreide, Mehl Und Brot*, *63*(1), 60–69.

Koch, I. S., Muller, M., Joubert, E., van der Rijst, M., & Næs, T. (2012). Sensory characterization of

rooibos tea and the development of a rooibos sensory wheel and lexicon. *Food Research International*, *46*, 217–228. https://doi.org/10.1016/j.foodres.2011.11.028

Labeling and advertising of distilled spirits, Title 27 Code of Federal Regulations, Pt. 5 Section 5:22. 1969 ed.

Lawless, L. J. R., & Civille, G. V. (2013). Developing Lexicons: A Review. *Journal of Sensory Studies*, *28*(4), 270–281. https://doi.org/10.1111/joss.12050

Lawless, L. J. R., Hottenstein, A., & Ellingsworth, J. (2012). The McCormick Spice Wheel: A Systematic and Visual Approach to Sensory Lexicon Development. *Journal of Sensory Studies*, *27*, 37–47. https://doi.org/10.1111/j.1745-459X.2011.00365.x

Lee, K.-Y. M., Paterson, A., Piggott, J. R., & Richardson, G. D. (2001). Origins of Flavour in Whiskies and a Revised Flavour Wheel: a Review. *Journal of the Institute of Brewing*, *107*(5), 287–313. https://doi.org/10.1002/j.2050-0416.2001.tb00099.x

Lurton, L., Ferrari, G., & Snakkers, G. (2012). Cognac: production and aromatic characteristics. In J. Piggott (Ed.), *Alcoholic Beverages: Sensory Evaluation and Consumer Research* (pp. 242–266). Oxford: Woodhead Publishing Limited. https://doi.org/10.1016/B978-0-85709-051-5.50011-0

Mc Donnell, E., Hulin-Bertaud, S., Sheehan, E. M., & Delahunty, C. M. (2001). Development and Learning Process of a Sensory Vocabulary for the Odor Evaluation of Selected Distilled Beverages Using Descriptive Analysis. *Journal of Sensory Studies*, *16*(2001), 425–445.

Meilgaard, M. C., Dalgliesh, C. E., & Clapperton, J. F. (1979). Beer Flavour Terminology. *Journal of the Institute of Brewing*, *85*, 38–42.

Mojet, J., & de Jong, S. (1994). The sensory wheel of virgin olive oil. *Grasas Y Aceites*, *45*(1–2), 42–47.

Noble, A. C., Arnold, R. A., Buechsenstein, J., Leach, E. J., Schmidt, J. O., & Stern, P. M. (1987). Modification of a Standardized System of Wine Aroma Terminology. *American Journal of Enology and Viticulture*, *38*(2), 143–146.

Noble, A. C., Arnold, R. A., Masuda, B. M., Pecore, S. D., Schmidt, J. O. S., & Stern, P. M. (1984). Progress Towards a Standardized System of Wine Aroma Terminology. *American Journal of*

Enology and Viticulture, *35*(2), 107–109. https://doi.org/10.1073/pnas.0703993104

Parker, D. K. (2012). Beer: production, sensory characteristics and sensory analysis. In J. Piggott (Ed.), *Alcoholic Beverages: Sensory Evaluation and Consumer Research* (pp. 133–158). Oxford: Woodhead Publishing Limited. https://doi.org/10.1016/B978-0-85709-051-5.50006-7

Pérez-Cacho, P. R., Galán-Soldevilla, H., Mahattanatawee, K., Elston, A., & Rouseff, R. L. (2008). Sensory Lexicon for Fresh Squeezed and Processed Orange Juices. *Food Science and Technology International*, *14*(Suppl. 5), 131–141. https://doi.org/10.1177/1082013208094723

Piggott, J. R., & Jardine, S. P. (1979). Descriptive Sensory Analysis of Whisky Flavour. *Journal of the Institute of Brewing*, *85*(2), 82–85. https://doi.org/10.1002/j.2050-0416.1979.tb06830.x

Swan, J. S., Howie, D., & Burtles, S. M. (1981). Sensory and Instrumental Studies of Scotch Whisky Flavour. *The Quality of Foods and Beverages*, 201–223. https://doi.org/10.1016/B978-0-12-169101-1.50020-3

Valente, C. C. (2016). *Understanding South African Chenin Blanc wine by using data mining techniques applied to published sensory data*. Stellenbosch University. Retrieved from http://scholar.sun.ac.za/handle/10019.1/98866

Chapter 6: Characterization of Sensory Differences in Premium Rums Through the Use of Descriptive Analysis Panel

6.1 Abstract

Rum is a highly diverse distilled spirit due to the numerous variations in methods used in its products resulting from its limited standard of identify. This large product variation makes it difficult to define typical rum flavor. Overall, sensory studies evaluating rum flavor are limited. The little sensory work that has been done typically only focuses on one or two rum samples and only aroma perception of rums has been evaluated. A comprehensive sensory analysis of premium rums is lacking.

The aims of this study were to 1) identify and quantify the sensory differences between seven premium rums and two mixing rums and 2) validate the developed rum flavor lexicon (Chapter 5). Results showed that the use of the rum flavor lexicon aided in sensory term generation, as 17 additional terms were generated after the wheel was provided to panelists. Thirty-eight sensory terms were generated and evaluated by the panel. Only five of the finalized terms were not found on the flavor wheel. Twenty attributes were found to be significantly different between rums. DX and DR12 were significantly different from the other seven rums, with higher perceptions of brown sugar, caramel, vanilla, and chocolate aroma, caramel, maple, and vanilla aroma-by-mouth and caramel aftertaste. The other seven rums had similar aroma profiles, with the mixing rums having the lowest intensities for brown sugar, caramel, vanilla attributes.

6.2 Introduction

Rum is a complex and ill-defined spirit. With its only standard of identity being that it is produced from a sugarcane by-product, numerous production variations have been developed. These differences in production methods include variations in starting material, the length and type of fermentation, distillation apparatus, type of barrels used for aging and length of maturation. The

resulting rum products are highly varied, making it difficult to identify and describe typical rum flavor.

Sensory descriptive analysis (DA) methods enable the identification and quantification of sensory differences between food samples (Lawless & Heymann, 1999b; Powers, 1988; Stone & Sidel, 1993; Zook & Pearce, 1988). A number of different DA methods exist including Flavor Profile (Cairncross & Sjöström, 1950; Caul, 1957), Quantitative Descriptive Analysis® (QDA) (Stone, 1992; Stone, Sidel, Oliver, Woolsey, & Singleton, 1974), Spectrum™ Descriptive Analysis (Muñoz & Civille, 1992), and Free-Choice Profiling (Williams & Langron, 1984). The QDA and spectrum methods are the two most frequently used for descriptive analysis of products. QDA requires the use of a trained sensory panel to evaluate the products (Stone & Sidel, 1993; Stone et al., 1974; Zook & Pearce, 1988). Panelists are trained over multiple sessions, usually spanning several weeks. Panel training consists of term generation, identification of appropriate references for the generated terms, development of a specific definition for each term, scaling of the references, and practice rating the samples using the developed references and reference scores (Stone & Sidel, 1993). During final sample evaluations, panelists rate the samples multiple times in individual in booths using a line scale with verbal anchors. Finally, statistical analysis is performed on the collected data set. The Spectrum method is similar to QDA although panelists undergo more intense training and use a predetermined list of sensory attributes and references to describe the products (Lawless & Heymann, 1999b; Muñoz & Civille, 1992). Another key difference is that panelists use a numerical 15 point scale rather than a line scale. Both methods use panelists as trained instruments to quantify the sensory of differences between the products.

Research characterizing the sensory properties of rum is limited. Previous studies have only evaluated one modality (aroma) or only characterized one or two rum samples (de Souza, Vásquez, del Mastro, Acree, & Lavin, 2006; Franitza, Granvogl, & Schieberle, 2016a, 2016b; Gómez, 2002; Magnani, 2009). De Souza and others (de Souza et al., 2006) were the first to evaluate rum flavor. They performed a limited descriptive analysis panel where 10 terms were generated to describe the aroma differences between rum and cachaça. Results indicated that rum is higher in caramel and vanilla aroma attributes while cachaça was higher in grassy, sulfury, vinegar, spicy, citrus, alcohol and melon attributes.

Aroma profile analysis has also been used to characterize several rum samples. The first study evaluated the aroma of two rum samples, a 15 year old solera system rum and a cheap (mixing) rum (Franitza et al., 2016a). Only six attributes were chosen to describe the samples, ethanolic, malty, butter-like, fruity, clove-like, and vanilla-like. Franitza then went on to characterize the flavor changes that occur during the rum making process (Franitza et al., 2016b). Four different steps in the production process were analyzed: the starting material (molasses), the mash, distillate and final rum. Eight aroma attributes were evaluated, adding caramel-like and baked apple-like to their previous descriptors.

Only one study has evaluated all sensory modalities (aroma, aroma-by-mouth, taste, mouthfeel, and aftertaste) for rum (Magnani, 2009). Magnani used QDA to characterize the sensory difference between two rum and two cachaça samples using 17 sensory attributes. The results indicated that cachaça was higher in woody and sweet aroma and aroma-by-mouth as well as higher viscosity, body and golden color.

While these studies give a basic insight into the defining sensory characteristics of rum, they give little insight into the variations that exist in flavor between rum samples across the larger category. These sensory studies focused on one or two samples or followed the production process of a single type of rum. Due to the huge amount of variation amongst rums, sensory evaluation of a greater number of rums are needed to gain a comprehensive understanding of rum as an entire class.

The most complete sensory study to date was a descriptive analysis panel done by Gomez (Gómez, 2002). Nine commercially available rums and one experimental sample were evaluated for 22 sensory attributes and 4 chemical aroma sensations. Rums samples were chosen to include a variety of raw materials, processing protocols, production regions and price points. All rum samples were able to be distinguished from each other with samples having significant differences in woody, ethanol, caramel, honey, smoke, vanilla, banana, prune, cardboard and ocean-like aroma attributes. This study was the first to demonstrate the significant variation in rum aroma across a larger and more complete rum sample set.

The previous work has begun to identify the characterizing sensory attributes of rum flavor as well as differences that exist within the broader rum category. However, the large variation of products in

the market requires more sensory analysis of rum samples to gain a better understanding of overall rum flavor.

The aim of this study was to evaluate and quantify the sensory differences of a variety of premium aged rums and mixing rums as well as to validate the developed rum flavor lexicon (Chapter 5) (Ickes, Lee, & Cadwallader, 2017). It was hypothesized that mixing rums would be easily distinguishable from the premium rums. Additionally, that many of the terms used to describe the difference in rum flavor would be found on the rum flavor wheel.

6.3 Materials and Methods

Materials

Nine commercially available rums, previously analyzed in chapters 3 & 4, were purchased at the local liquor store (Champaign, IL). All nine rums, (Bacardi Superior [BW], Bacardi Gold [BG], Appleton Estate V/X [AE], Appleton Estate Extra [AE12], Ron Abuelo: Añejo 7 years [RA7], Diplomatica Reserva Exclusiva [DR12], El Dorado 12 year old [ED12], Ron Zacapa (Centenario) XO: Solera Gran Reserva Especial [RZ], Dictador XO Insolent [DX]) had reported ethanol concentration of 40% alcohol by volume (ABV). Mention of the brand name of these rums does not imply any research contact or sponsorship and is not for advertisement or endorsement purposes. Before testing, 20 mL of each sample was measured into a black double old-fashion glass (Threshold, Target, USA) and covered with a glass petri dish no more than one hour before the panel assessment.

Attribute references were prepared daily and placed into 2 or 4 oz. lidded plastic soufflé cups (Dart Container Corporation, Mason, MI) and labeled with the reference identity. References were not prepared more than 24 h prior to evaluation. A complete list of attributes, definitions, references, reference scores and preparation procedures can be found in Table 6.1. Product information for references can be found in Appendix I.

The following materials were purchased for initial panelist taste screening: caffeine (Fisher Scientific, Fair Lawn, NJ), citric acid (Ball, Hearthmark, LLC dba Jarden Home Brands, Daleville, IN), sodium

chloride (Morton Salt, Morton Salt, Inc., Chicago, IL), and sucrose (C&H Pure Cane Sugar, Domino Foods, Inc., Yonkers, NY). Additionally, the following compounds were used for aroma screening: ethyl butyrate, eugenol, oak lactone, 2-phenethyl alcohol, and vanillin. All compounds were food grade and purchased from Sigma-Aldrich (St. Louis, MO).

Subject Recruitment

All materials related to panelist recruitment and compensation were approved by the Institutional Review Board (IRB) at the University of Illinois Urbana-Champaign (IRB Protocol Number: 16854), Appendix D. Panelists were recruited through the departmental listserve and by word of mouth. Potential panelists completed an initial recruitment questionnaire to screen for availability and familiarity with distilled beverages (Appendix E). After passing the initial questionnaire, potential panelists then completed a sensory screening for basic taste perception and aroma identification. Potential panelists were required to identify several basic taste solutions: caffeine (0.024% wt/vol), citric acid (0.05% wt/vol), sodium chloride (0.1% wt/vol), and sucrose (0.7% wt/vol). The solutions (10mL) were placed into 1 oz. lidded plastic cups. Panelists were also screened for their ability to detect and correctly identify odorants common to rum: ethyl butyrate (1.03 mg/mL), eugenol (6.00 mg/mL), oak lactone (0.0396 mg/mL), 2-phenethyl alcohol (1.05 mg/mL), and vanillin (2.46 mg/mL). The odorants were spiked (10μL, 2 μL, 10 μL, 10 μL, and 5 μL respectively) onto an odorless cotton ball and placed into a 5.5oz lidded plastic cup. All samples were labeled with random three digit codes. The ballot used for screening can be found in Appendix F. Panelists were also required to present a valid form of identification at the screening to verify that they were over 21 years of age. Panelists were selected if they achieved at least 70% acuity on the aroma identification and were available at the time selected for the panel. Panelists granted informed consent (Appendix G) before the start of the study.

Descriptive Analysis Procedure

The panel methodology was a hybrid of the Quantitative Descriptive Analysis® (Stone, 1992) and the Spectrum™ method (Meilgaard, Civille, & Carr, 2007; Muñoz & Civille, 1992). The nine samples were evaluated by eight panelists, 4 male and 4 female, ages 23-66, over a total of 23 days. On the first day of panel, panelists were introduced to the specific descriptive analysis (DA) method used in this study. The first six sessions (1 h each) consisted of term and reference generation, followed by

reference refinement. The panelists were presented with three random rum samples each day and asked to generate terms for the attributes they perceived in the samples for aroma, aroma-by-mouth, mouthfeel, taste and aftertaste modalities. Through group discussion, panelists identified the terms to be used, determined corresponding references and developed a precise definition for each attribute. The first three days of the panel consisted of free term generation, where the panelists were unaided in the identification of the attributes present in the sample. During days 4-6 panelists were provided with the rum flavor wheel previously developed (Chapter 5, Figure 5.1) to aid in term generation.

After the terms and references were established, panelists then spent five sessions (1 hour each) determining the reference intensities of each attribute. Panelists were asked to scale the references based on a 15 point scale, where zero is no perception of a given attribute and 15 is the strongest perception of that attribute in the rum samples. Determined reference scores can be found in Table 6.1.

Panelists then spent six days practicing scoring the rums, using the references as anchor points for the scale, to aid in panel uniformity. On one of the days, panelists conducted individual booth practice sessions in Bevier Hall on the University of Illinois at Urbana-Champaign campus for two thirty-minute sessions using the Compusense five (Version 5.0: Guelph ON, Canada) data acquisition system. Panelists were routinely provided with their scoring results from the previous day to help identify and correct for attributes they were rating inconsistently with the rest of the group.

The panel concluded with 5 days of individual booth testing. Panelists attended two 30 minute sessions per day, evaluating two samples at each session. Panelists were provided with their reference tray when they arrived and encouraged to evaluate all references before proceeding into the booth for testing. Rum samples were presented in black double old fashions glasses covered with a petri dish and labeled with random three-digit codes. Samples were evaluated under red lighting using the Compusense five software. Sample presentation was randomized between all panelists. Panelists were free to leave the booth at any time to come and re-evaluate a reference.

A more detailed, day-by-day description of the DA panel can be found in Appendix O.

Statistical Analysis

Statistical analysis of the data was performed using Statistical Analysis System (SAS)® (Version 9.4, SAS Institute Inc., Cary, NC, USA). Analysis of variance (ANOVA) was conducted on each of the 38 attributes evaluated during the DA panel to determine the presence of overall significant differences ($p<0.05$) using the PROC GLM function for variations within the rums, panelists, replications and their corresponding interactions: rum-by-panelist (Rum x P), rum-by-replication (Rum x Rep), and replications-by-panelist (Rep x P). The calculated probabilities were compared to significance levels $\alpha=0.05$, 0.01 and 0.001. When significant Rum x P interactions existed, adjusted F-ratios were calculated using Microsoft® Excel® 2016 (Version 16: Microsoft Corporation, Redmond, WA) by dividing the rum mean square by the Rum x P interaction mean square and calculating the new probability using the F.DIST function. Fisher's least significant difference (LSD) test was conducted on all attributes determined as significant by ANOVA.

Principal component analysis (PCA) biplots were produced using SAS and Microsoft Excel to create a visual representation of the data to allow further examination of the relationship of the rums to individual attributes that characterized the samples. Pearson correlations were calculated using the same SAS software, with significance determined at $\alpha=0.05$, 0.01, and 0.001. Cluster analysis was also conducted using SAS software using the PROC CLUSTER function.

6.4 Results and Discussion

Term Generation and Lexicon Validation

The descriptive analysis panel was conducted to describe and quantify the sensory differences perceived in the nine rum samples, two mixing and 7 premium rums, whose volatile composition had previously been analyzed (Chapters 3 & 4). Additionally, the descriptive analysis panel provided validation for the rum lexicon that was previously developed through the use of web-based material (Chapter 5).

During the term generation phase of the panel, panelists were allowed to generate terms freely for the first three days, without the aid of the flavor lexicon. This initial term generation provided terms

that panelists were able to identify on their own. Initially 52 terms were generated consisting of 25 aroma, 16 aroma-by-mouth, 6 mouthfeel, 1 taste, and 4 aftertaste terms. Panelists were then provided with the flavor wheel to aid in the generation of additional terms to adequately describe the flavor of the rums being evaluated. After the panelists were presented with the flavor wheel (Figure 5.1), an additional 17 terms were generated, including 12 aroma, 4 aroma-by-mouth and 1 aftertaste. No additional taste or mouthfeel terms were generated. Of those additional terms generated, 14 of the 17 terms are found on the flavor wheel. The addition of caramel aftertaste is likely not due to the aid of the flavor wheel, but rather refinement of the panel's ability to detect and perceive different intensities of odorants as caramel was a term that had initially been generated in the aroma and aroma-by-mouth modalities during the first three days of the panel.

At the conclusion of the term generation phase of the panel, 69 terms had been generated. Of the generated terms 53 were unique attributes. The other 16 terms appeared in multiple modalities, usually under aroma, aroma-by-mouth and aftertaste. Of the unique terms generated, 37 appear on the flavor lexicon.

Throughout the reference refinement and scaling portions of the panel, panelists were encouraged to reduce the number of terms to be evaluated. Terms were removed if they were no longer perceived in the samples, panelists could not uniformly identify the attribute in the samples, or the attribute intensity did not differ among samples. The panelists decided on a final set of 38 attributes (Table 6.1) to describe the rum samples, consisting of 27 unique terms.

Of the final 38 terms used for evaluation, all but five terms can be found directly on the rum flavor wheel. Of those five remaining terms, similar forms of three of the terms can be found in the lexicon. Alcohol appears as alcoholic, and brown spice is synonymous with baking spices. Brown sugar has both of its components (sugar and brown) found on the wheel under sugar and caramel categories, respectively. Only two terms were not found on the wheel in any form: phenolic and slick. When creating the rum lexicon, it was postulated that terms had been missed from the lexicon and would need to be added as time went on. Phenolic, slick and brown sugar are three terms that should be considered for addition to the lexicon.

Many words included in the lexicon were not selected for the descriptive analysis panel. There are several reasons for this occurrence. First, the rums selected, primarily premium aged rums, are only a

selection of all the varieties of rum available. There are numerous variations of rum flavor due to limited regulation requirements. As a result, the terms not included in the DA panel will likely be used to describe the other categories and types of rums. Second, due to the large number of terms generated to describe rum flavor, the terms needed to be simplified and condensed where possible so that the panelists could consistently and accurately identify the differences among samples. Attributes that were difficult to detect or did not differ among the rum samples were excluded from the final evaluation. However, the large overlap between the final terms selected and the created rum lexicon demonstrate that using web-material is a valid way to create a lexicon and can be used for the evaluation of a variety of rums.

Descriptive Analysis Panel Results

The descriptive analysis panel was used to characterize and quantify the sensory differences between rum samples. Panelists generated 38 terms to describe the samples. The generated terms, term definitions, selected references, reference scores and reference preparations can be found in Table 6.1. Reference scores are an average of individual panelist's ratings.

Analysis of variance (ANOVA) was conducted on all 38 attributes identified and rated by the panelists, and the results are shown in Table 6.2. In general, panelists results were uniform, indicating the high amount of training they received.

Sample replications were not a significant ($p>0.05$) source of variation for the majority of attributes except citrus aroma, roasted aroma, caramel aroma-by-mouth and roasted aroma-by-mouth. The lack of variation shows that panelists were able to consistently rate the samples between replications. Significant variation ($p<0.05$) did exist for panelists for all attributes except astringent mouthfeel. This type of variation is typical of descriptive analysis panels and is most likely attributed to panelists only using a portion of the scale or not uniformly using the scale (Lawless & Heymann, 1999b; Stone et al., 1974). Rep x P interactions were not significant ($p>0.05$) for most attributes except caramel aroma, cherry aroma, almond aroma, cherry aftertaste, vanilla aroma-by-mouth, cherry aroma-by-mouth, and walnut aroma-by-mouth. Lack of significant interaction indicates that the panelists were able to agree on the intensity of attributes in the samples across replications. No significant ($p>0.05$) Rum x Rep interactions were found, indicating that while the panelists may have used the scale differently from each other, they rated the rum samples similarly across replications.

Across all nine rum samples, 24 of the attributes were found to be significantly ($p<0.05$) different. Significant ($p<0.05$) Rum x P interactions existed for 17 of the attributes. These interactions indicate that panelists did not agree on the order of attribute intensity across the rum samples. Adjusted F-values were calculated for attributes that had significant Rum x P interactions to account for this variation. The adjusted F-values are shown in Table 6.2. Of the adjusted F-values, five of the attributes (caramel aroma, maple aroma, vanilla aroma, phenolic aroma, and caramel aroma-by-mouth) were shown to be statistically ($p<0.05$) different among rum samples. After adjusted F-values were calculated, twenty terms were determined to be significantly different including brown sugar aroma, caramel aroma, maple aroma, vanilla aroma, alcohol aroma, citrus aroma, coconut aroma, roasted aroma, smoky aroma, phenolic aroma, chocolate aroma, warming mouthfeel, slick mouthfeel, bitter taste, brown spice aftertaste, caramel aftertaste, caramel aroma-by-mouth, maple aroma-by-mouth, vanilla aroma-by-mouth, and coconut aroma-by-mouth.

Defining Attributes

Mean separation analysis by Fisher's Least Significant Difference (LSD) test was performed on the attributes that were significantly different among rum samples, and results are shown in Table 6.3. Rums were able to be differentiated into multiple groupings for each attribute except chocolate aroma which had two distinct groups. Significant overlap between rum groupings existed. DX had the highest intensity score for caramel aroma, and maple aroma and both attributes were significantly different ($p<0.05$) compared to the other 8 rums. DX and DR12 had the highest scores for brown sugar aroma, vanilla aroma, chocolate aroma, caramel aftertaste, caramel aroma-by-mouth, maple aroma-by-mouth, and vanilla aroma-by-mouth. DX, DR12, RA7, ED12, and RZ were highest in coconut aroma and coconut aroma-by-mouth. DX, DR12, ED12, and RZ were highest in brown spice aftertaste, while DX, DR12, RA7 and ED12 were highest in slick mouthfeel. Interestingly, DX, DR12, AE, and BG were highest in roasted aroma while AE had the highest smoky aroma intensity which was significantly different ($p<0.05$) from the other 8 rums. Additionally, AE12, AE, and BW were highest in phenolic aroma. BW, BG, AE, AE12, RZ, and RA7 had the highest scores for bitter taste and warming mouthfeel. BW, BG, AE, and RZ had the highest citrus aroma. Finally, DX had the lowest alcohol aroma and was significantly different from all other rums except DR12.

BW had the lowest intensity ratings for brown sugar aroma, caramel aroma, vanilla aroma, maple aroma, chocolate aroma, slick mouthfeel, brown spice aftertaste, caramel aftertaste, caramel aroma-by-mouth, maple aroma-by-mouth, vanilla aroma-by-mouth and coconut aroma-by-mouth. It makes sense that BW , a clear white rum, would have the lowest intensity of these attributes as the terms are typically associated with aging with the except coconut.

The higher number of aroma terms generated and evaluated and subsequently identified as being significant between rums, suggests that aroma differences are easier to perceive that in-mouth perceptions. This could potentially be a result of the high alcohol concentration.

Spider plots (Figure 6.1 and 6.2) of the results were constructed to better visualize the differences between samples. Both the spider plots and LSD results illustrate that DX and DR12 are significantly different from the other rums in terms of caramel aroma, vanilla aroma, chocolate aroma, caramel aftertaste, caramel aroma-by-mouth, maple aroma-by-mouth, and vanilla aroma-by-mouth. Interestingly, when the DX and DR12 rums are removed from the spider plot (Figure 6.3), the remaining rums all have similar intensity profiles to each other. However, there are still attributes that are significantly different among the rums.

A potential reason for the higher intensities of caramel, maple and vanilla attributes in the DX and DR12 rums is that they were the only two rums found to contain ethyl vanillin (Chapter 4). Ethyl vanillin is an artificial compound not found in nature. It is most likely added to these rums sometime during maturation or the bottling process. While it seems peculiar for a naturally produced product to contain a synthetic compound, the Alcohol and Tobacco Tax and Trade Bureau (TTB) lists ethyl vanillin as one of four compounds on its limited ingredients list (*Limited Ingredients*, 2016). This list identifies compounds that can be added to distilled beverages without the need to label the product as imitation. As long as ethyl vanillin is present at concentrations less than 16 ppm, and the "total vanillin" concentration (determined by adding the concentration of vanillin with 2.5 times the ethyl vanillin concentration) is less than 40 ppm the final rum can still be called a natural product. The "total vanillin" concentrations of both DX and DR12 are well under this limit, 8.75 ppm and 5.24 ppm respectively.

The Pearson correlation coefficients are given in Table 6.5. The attributes brown sugar aroma, caramel aroma, maple aroma, vanilla aroma, coconut aroma, chocolate aroma, brown spice

aftertaste, caramel aftertaste, caramel aroma-by-mouth, maple aroma-by-mouth, vanilla aroma-by-mouth, and coconut aroma-by-mouth were all positively correlated with each other ($p<0.05$). The terms are all negatively correlated ($p<0.05$) to alcohol aroma, citrus aroma, phenolic aroma, warming mouthfeel and bitter taste, with the exception of coconut aroma-by-mouth and warming mouthfeel which were not correlated ($p>0.05$). Additionally, alcohol aroma, phenolic aroma, warming mouthfeel and bitter taste were all positively correlated with each other. Citrus aroma was positively correlated to alcohol aroma and warming mouthfeel. Slick mouthfeel was negatively correlated to citrus aroma and positively correlated to caramel aroma-by-mouth and vanilla aroma-by-mouth. Finally, chocolate aroma is negatively correlated to smoky aroma.

Principal component analysis was also conducted to help reduce the complexity of the data and gain a better visual representation of the data (Figure 6.4) (Lawless & Heymann, 1999a). The covariance matrix was chosen for sample evaluation since the samples were all scored by a trained panel (Jolliffe, 2014). The first five factors have eigenvalues greater than 1 (Appendix J), and the total variance of the products was explained in 8 factors. The first factor contained the majority of variation between the samples (88.4%), with the second factor only containing 3.6% of the variation. This indicates that the second factor was not significant in differentiating the rum samples. This is also illustrated by the factor correlations (Appendix K). Principal component 1 (PC1) contrasted samples high in brown sugar, caramel, maple, vanilla, and chocolate aromas, brown spice and caramel aftertastes, caramel, maple, vanilla and coconut aftertastes with samples high in alcohol, citrus, and phenolic aromas, warming mouthfeel, and bitter taste. These correlations are similar to those indicated by the Pearson correlations. Principal component 2 (PC2) was minimally loaded with the main distinguishing attribute being slick mouthfeel ($r=0.75$), as well as partially by citrus aroma ($r=-0.36$) and smoky aroma ($r=0.31$).

Using the resulting mean intensity ratings calculated from ANOVA, cluster analysis was performed (Figure 6.5). DX and DR12 are more closely related to each other than any of the other seven rums since the distances between the two rums is less than half the distance between that cluster and the other seven rums. In the grouping of 7 rums there are two distinct clusters, one containing RZ, RA7 and ED12 and a second cluster containing BW, BG, AE, and AE12 rums.

While it was expected that the Bacardi rums would be grouped more closely together, it is interesting that they are also grouped with the Appleton Estate rums. AE and BG were grouped as most similar

to each other. It was hypothesized that the mixing rums (BW and BG) would be significantly different from the premium rums. However, BW, BG, AE, and AE12 are consistently grouped together for multiple attributes. Additionally, they tend to have the lowest intensity scores for brown sugar aroma, caramel aroma, maple aroma, vanilla aroma, coconut aroma, brown spice aftertaste, caramel aftertaste, caramel aroma-by-mouth, maple aroma-by-mouth, vanilla aroma-by-mouth, and coconut aroma-by mouth.

The overall DA panel results indicate that as rums mature in the barrels, the brown sugar, caramel, maple, and vanilla attributes across all modalities increase with age. Additionally, alcohol aroma citrus aroma, phenolic aroma, and warming mouthfeel tend to decrease with age. However, while overall trends are visible, clear patterns do not emerge. The rums that are clearly different from the others are DX and DR12 with their higher caramel, maple and vanilla attributes. Even though the remaining rums have similar profiles to each other, they can still be differentiated on a number of attributes, demonstrating the complexity and variation present in rum products.

Comparison to Previous Sensory Studies

This was the first sensory study to evaluate premium rums and the first comprehensive study to evaluate the in-mouth perceptions (aroma-by-mouth, taste, mouthfeel, and aftertaste) of rum flavor. Most studies have only evaluated rum aroma (de Souza et al., 2006; Franitza et al., 2016a, 2016b; Gómez, 2002). The only other study to study in mouth perception of rum only evaluated two rum samples with the main focus of the study was to identify the sensory differences between rum and cachaça (Magnani, 2009).

Comparing all six studies, alcohol aroma has been used to differentiate and characterize rum in all studies. Additionally, one or more sweet associated terms have been used in each study: vanilla aroma, caramel aroma or sweet aroma. Brown spice aroma is also a commonly used term ((de Souza et al., 2006; Franitza et al., 2016a, 2016b). While Magnani (2009) also evaluated in-mouth perceptions, only four attributes were evaluated in both studies: wood aroma-by-mouth, alcohol aroma-by-mouth, bitter taste, and warming/burning mouthfeel. Warming/burning mouthfeel has been labeled differently between studies, warming in the current study and residual burning in Maganani's study, but the term definitions were the same. This lack of overlap can be attributed to

difference in objectives between the studies, as Magnani was differentiating rum and cachaça samples while the current study only differentiated rum samples.

The previous five studies evaluated 23 attributes that were not included in this study. Of those terms, 15 are found on the rum flavor wheel. The difference in the terms selected between studies is most likely a result of the rums being evaluated. With the huge variety of rums available, it is reasonable that different attributes would be needed to discriminate different subsets of rum. This demonstrates the complexity of rum flavor across products.

Little product information is typically provided in the literature, making it difficult to compare studies and particularly the samples evaluated against each other. De Souza (2006) does identify the brands used in her study, Bacardi was used as the rum sample, but specific product information was not provided. Gomez (2002) is the only other author to identify the specific rums and brands evaluated. Gomez evaluated two rums also evaluated in the current study, BW and ED12. Four aroma attributes overlapped between the two studies, caramel, vanilla, alcohol and smoky. While Gomez did not find any statistical difference between the two rums for these four attributes, both studies did rate ED 12 as being higher in caramel, vanilla, and smoky aromas. Neither study found alcohol aroma to be significantly different between the rums as indicated by their reversed order in the two studies. The results, while limited, suggest that rum sample can be rated consistently across studies when panelists are trained.

Evaluation of Results and Methodology

While panelists were able to differentiate rums for a number of attributes, the results demonstrate the difficultly in evaluating distilled spirits. The large number of terms chosen by the panel to evaluate the rum samples demonstrates the complexity of rum flavor. Sixty-nine terms were initially generated and 38 of those were selected for the final analysis. However, only 20 of the 38 evaluated terms were found to be significant across samples. This indicates that they panel may have needed more training on the intensity and perception of the attributes not found to be significant. The benefit of additional training is also indicated by the high panelist variation and Rum x P interactions seen in the ANOVA results.

Additionally, it may be beneficial for these terms to be removed before evaluation if their intensity differences among samples were difficult to measure. While the larger number of terms allows us to

better describe the total flavor profile of rum, the evaluation of so many attributes may have made it difficult for panelists distinguish differences between samples. The large number of terms most likely made it difficult for the panelists to remember intensities of the references when evaluating the samples in the booth. Even though panelists were allowed to leave the booth to reevaluate reference at any time, most did not. As a result, they may not have been able to consistently rate the product attributes. Consolidating or reducing the terms such as brown sugar aroma, caramel aroma, and maple aroma into one term may have aided panelists ability to focus on identifying the difference between samples rather than trying to find the individual attributes in each sample.

Furthermore, the high ethanol concentration (40% ABV) may lead to sensory fatigue both during training and booth testing. This fatigue may have made it difficult to accurately quantify the differences between samples. Sensory fatigue of alcoholic beverages has been noted by other studies (Gómez, 2002). While sample presentation was limited to two rums per session and samples order was random, it is probable that sensory fatigue may have occurred between just these two samples or even during the initial evaluation. However, Rum x Rep interactions only existed for caramel aroma, indicating that if sensory fatigue occurred between samples, it did not impact the results. It is more likely that the high alcohol concentration made it difficult to identify differences in attribute intensities between samples and could be a contributing factor as to why so many attributes were not significantly different among samples.

Of the 11 aroma-by-mouth terms initially identified and rated by panelists, only 4 were found to be statistically different between rum samples; caramel, maple, vanilla, and coconut. The high amount of panelists variation could account for the inability to differentiate the intensity of these attributes in the samples. One reason for this could be sensory fatigue and the impact of ethanol on panelist ability to consistently perceive aroma-by-mouth perceptions. Comparing all five modalities, panelists had the most difficulty differentiating the aroma-by mouth attributes. More than half the attributes were not statistically different among rums.

Additionally, panelists reluctance to make full use of the scale may have contributed to the inability to differentiate the rums for many of the attributes. During reference scaling, panelists asked to rate one of the samples as a 15 and base their reference and other rum scores off of that number. However, during booth testing panelists had trouble assigning 15's to samples indicated by the small number of attributes receiving mean intensity scores higher than 10. The panelist's reluctance to use

the full scale could have resulted from improperly scored or inaccurate references, where the reference intensity was scored too low by panelists during scaling. This could have resulted from panelists reluctance to change the intensity of the reference even with prompting by the facilitator. Additionally, panelists could have been reluctant to rate samples highly, expecting a sample with a higher intensity of that attribute to be presented later.

While this panel gives significant insight into the sensory differences between premium rums and mixing rums, it is important to note that this only encompasses a subset of available rum products. It is expected that lower quality rums and particularly white and agricole rums will be defined and differentiated by different sensory terms as indicated from the most frequent terms used to describe those products (Chapter 5). Additionally, DA panels quantify the sensory differences among samples and may not be the best at characterizing the overall flavor of rums. To better evaluate the entirely of rum flavor it may be best to perform a preliminary sensory evaluation and sorting of a larger variety of rum samples using techniques such as Napping to identify similar types of rums and then select one sample from each category to be included in a descriptive analysis panel or aroma profile analysis. This would provide greater insight into the differences between rum across the class.

6.5 Tables and Figures

Table 6.1 List of final attributes, definitions, references, reference scores, and reference preparations determined for the descriptive analysis panel on rum

Modality		Attribute	Definition	Reference	Reference Score	Preparation
Aroma	**Sugar & Spices**	brown sugar	aroma of brown sugar	dark brown sugar	**13.5**	1 packed teaspoon in 2 oz. cup
		caramel	aroma of caramelized sugar	Smucker's caramel syrup	**14**	10 g in 2 oz. cup
		maple	aroma of maple syrup	maple extract	**11.5**	1 3/4 teaspoon in 500 mL volumetric flask, dilute to volume, 10 mL in 2 oz. cup
	Baking Spices	brown spice	aroma of nutmeg	ground nutmeg	**14**	1g in 600 mL of water, stir 5 minutes, 10 mL in 2 oz. cup
		vanilla	aroma of vanilla extract	natural vanilla extract	**10.5**	1/4 teaspoon in 500 mL volumetric flask, dilute to volume, 10 mL in 2 oz. cup
	Alcohol	alcohol	aroma associated with 40% or greater alcohol	190 Proof Ethanol	**11.5**	10 oz. in 2 oz. cup
	Fruit	cherry	aroma of cooked cherries	cherry pie filling	**14.5**	1 cherries and syrup to 5 g in 4 oz. cup
		citrus	aroma of lime zest	lime peel	**12**	soak 0.5 g in 200 mL of hot water for 5 minutes, 10 mL in 2oz cup
		coconut	aroma of toasted coconut	toasted coconut flakes	**14**	0.1 g in 4 oz. cup
		dried fruit	aroma of prunes	prunes	**14.5**	0.8 g (~1/8) prune in a 2 oz. cup
	Nutty	almond	aroma of almonds	almonds	**13.5**	1 whole almond in 4 oz. cup
		walnut	aroma of walnuts	chopped walnuts	**12.5**	1 g in 2 oz. cup
	Woody/ Roasted	roasted	aroma of medium roasted malted barley	brown roasted barley	**15**	0.2 g in a 2 oz. cup
		smoky	aroma associated with a hardwood smoked products	smoked bacon	**15**	0.02 g piece of bacon, just muscle tissue, in a 4 oz. cup
		woody	aroma of a wood barrel	oak wood chips	**11**	1 g in 2 oz. cup
	Medicinal	phenolic	aroma of a Band-Aid	Band-Aid	**13**	1 unwrapped Band-Aid in a 2 oz. cup
	Dairy	butter	aroma of melted butter	melted butter	**13**	2 TBS of better melted over low heat, 0.2 g in a 4 oz. cup
		chocolate	aroma of dark chocolate	baker's chocolate	**13**	0.01 g of shaved chocolate in a 2 oz. cup

Table 6.1 (cont.) List of final attributes, definitions, references, reference scores, and reference preparations determined for the descriptive analysis panel on rum.

Modality	Attribute	Definition	Reference	Reference Score	Preparation
Mouthfeel	astringent	a drying sensation in the mouth associated with a high tannin wine	over-brewed green tea	**8.5**	steep 1 tea bag in 300 mL of boiling water for 5 minutes, place 15 mL in a 2 oz. cup
	slick	a smooth tongue coating	glycerin	**9.5**	20 g of glycerin + 60 g water, ~10 g in a 2 oz. cup
	warming	the increase in temperature perception in the mouth as a result of alcohol concentration	190 Proof Ethanol (1:2 dilution)	**14**	1:2 dilution, 10 mL in 2 oz. cup (alcohol)
Taste	bitter	bitter taste of caffeine solution	caffeine solution	**10**	1 g caffeine in 500 mL of water, 15 mL in each cup
Aftertaste	bitter	aftertaste associated with a caffeine solution	caffeine solution	**11.5**	1 g caffeine in 500 mL of water, 15 mL in each cup
	brown spice	aftertaste associated with brown spices	nutmeg	**14**	1 g in 600 mL of water, stir 5 minutes, 10 mL in 2 oz. cup
	caramel	aftertaste associated with caramel	Smucker's caramel syrup	**13**	caramel solution, 10 g of caramel dissolved in 200 mL of water ~10 mL in a 2 oz. cup
	cherry	aftertaste associated with cooked cherries	cherry pie filling	**13**	1 cherry and syrup to 5 g in 4 oz. cup
	coffee	aftertaste associated with coffee	dark roast coffee	**12**	1 1/2 teaspoons of coffee, in teabag, in 300 mL of boiling water for 5 minutes

Table 6.1 (cont.) List of final attributes, definitions, references, reference scores, and reference preparations determined for the descriptive analysis panel on rum.

Modality		Attribute	Definition	Reference	Reference Score	Preparation
Aroma by Mouth	**Sugar**	caramel	aroma-by-mouth of caramelized sugar	caramel syrup solution	**10**	caramel solution, 10g of caramel dissolved in 200mL of water ~10mL in a 2 oz. cup
		maple	aroma-by-mouth of maple syrup	maple extract	**13**	1 3/4 teaspoon in 500mL volumetric flask, dilute to volume, 10 mL in 2oz cup
	Baking Spices	brown spice	aroma-by-mouth of nutmeg	ground nutmeg	**15**	1g in 600mL of water, stir 5 minutes, 10mL in 2 oz. cup
		vanilla	aroma-by-mouth of vanilla extract	natural vanilla extract	**11**	1/4 teaspoon in 500mL volumetric flask, dilute to volume, 10 mL in 2oz cup
	Alcohol	alcohol	aroma-by-mouth associated with 40% or greater alcohol	Everclear	**14**	10 oz. in 2 oz. cup
	Fruit	cherry	aroma-by-mouth of cooked cherries	cherry pie filling	**13**	1 cherries and syrup to 5g in 4 oz. cup
		coconut	aroma-by-mouth of toasted coconut	toasted coconut flakes	**14**	1g in 2 oz. cup
	Nutty	walnut	aroma-by-mouth of walnuts	chopped walnuts	**13.5**	3g in 2 oz. cup
	Woody/ Roasted	roasted	aroma-by-mouth of medium roasted malted barley	brown roasted barley	**15**	0.2 g in a 2oz cup
		smoky	aroma-by-mouth associated with a hardwood smoked products	liquid smoke	**14.5**	0.5g in 1000mL volumetric flask, dilute to volume, 10 mL in 2oz cup
		woody	aroma-by-mouth of a wood barrel	oak wood chips	**8**	1g in 2 oz. cup

Table 6.2 Analysis of variance (ANOVA) F-ratios for sensory attributes rated for nine rum samples[+]

Modality	Attribute	Rum	Panelist	Rep	Rum x P†	Rum x Rep†	Rep x P†	Adjusted Sample F
Aroma	brown sugar	7.44***	5.53***	0.11	1.30	0.78	1.67	
	caramel	31.87***	9.07***	2.88	2.01**	2.15*	2.86*	15.82***
	maple	13.15***	7.73***	0.00	1.71*	1.31	1.80	7.67**
	brown spice	1.48	6.60***	2.54	2.45***	1.26	2.04	0.61
	vanilla	11.64***	6.00***	0.14	1.89**	2.09	0.92	6.16*
	alcohol	3.62**	5.82***	0.04	1.05	0.77	0.87	
	cherry	1.77	19.85***	0.48	2.05**	1.24	2.43*	0.86
	citrus	3.52***	16.91***	4.41*	1.09	0.68	1.26	
	coconut	4.15***	6.11***	0.10	1.33	0.96	0.74	
	dried fruit	1.26	8.54***	2.57	2.25**	1.28	1.88	0.67
	almond	5.16***	16.84***	0.01	2.44***	0.99	2.42*	2.12
	walnut	1.49	5.56***	1.26	0.91	0.31	1.08	
	roasted	2.40*	7.37***	4.30*	0.98	0.73	1.48	
	smoky	3.83**	2.51*	0.70	1.06	1.75	0.71	
	woody	0.99	4.88***	0.79	1.55	1.31	1.04	
	phenolic	9.00***	9.14***	0.69	2.22**	1.48	0.49	4.06**
	butter	7.44***	7.30***	0.73	2.14**	1.46	0.92	3.48
	chocolate	4.65***	5.79***	0.04	1.27	0.44	1.36	
Mouthfeel	astringent	1.48	1.03	3.22	1.38	0.25	1.31	
	warming	2.65*	5.29***	0.03	0.92	0.74	1.29	
	slick	3.18**	9.34***	0.51	1.20	0.51	0.53	
Taste	bitter	3.47**	3.05**	0.04	1.22	1.67	1.31	
Aftertaste	brown spice	3.73**	5.54***	2.52	2.33***	0.85	0.57	1.60
	caramel	23.19***	5.28***	1.89*	1.40	1.59	1.35	
	cherry	0.77	14.10***	0.86	2.52***	1.18	2.71*	0.30
	coffee	1.90	5.35***	0.60	1.09	0.79	1.77	
Aroma by Mouth	caramel	29.65***	14.34***	5.54	2.05**	1.42	1.22	14.48***
	maple	8.02***	5.84***	0.50	1.20	1.08	1.04	
	brown spice	3.32**	12.07***	0.67	3.10***	1.79	1.84	1.07
	vanilla	12.22***	12.59***	1.44	1.31	0.88	2.40*	
	alcohol	2.65*	4.68***	0.32	1.18	2.01	0.74	
	cherry	0.72	17.17***	0.02	2.02**	0.59	4.61***	0.26
	coconut	7.50***	5.35***	1.95	2.46***	0.99	1.11	3.05
	walnut	1.39	31.99***	0.01	1.71*	1.08	3.03*	0.82
	roasted	0.88	9.02***	8.65**	1.28	1.45	1.06	
	smoky	1.37	7.86***	1.03	1.18	1.18	1.43	
	woody	0.93	6.13***	0.21	1.89**	0.86	0.80	0.49

[+]F-rations are shown as a source of variation. *, **, *** stand for significance at $p<0.05$, $p<0.01$, and $p<0.001$ respectively.
†Rum x P, Rep x P, and Rum x Rep represent the interaction between rum samples and panelists, replications and panelists, and rum samples and replications, respectively.

Table 6.3 Mean intensity rating for significant aroma, mouthfeel, taste, aftertaste and aroma-by-mouth attributes of the nine rum samples†

Modality	Attribute	BW*	BG*	AE*	RA7*	AE12*	DR12*	ED12*	RZ*	DX*
Aroma	brown sugar	3.06^{D}	$4.69^{C,D}$	$4.69^{C,D}$	$6.71^{B,C}$	5.88^{C}	$8.38^{A,B}$	5.75^{C}	5.63^{C}	9.94^{A}
	caramel	3.06^{E}	$5.31^{C,D}$	$4.25^{D,E}$	$5.88^{C,D}$	$4.44^{D,E}$	11.19^{B}	$4.88^{C,D}$	6.44^{C}	13.75^{A}
	maple	3.21^{D}	$4.81^{C,D}$	$4.88^{C,D}$	$6.38^{B,C}$	5.75^{C}	7.81^{B}	$6.00^{B,C}$	5.63^{C}	12.31^{A}
	vanilla	4.44^{C}	$6.13^{B,C}$	$5.75^{B,C}$	7.19^{B}	$5.43^{B,C}$	11.06^{A}	6.81^{B}	6.81^{B}	11.81^{A}
	alcohol	9.69^{A}	9.75^{A}	$9.06^{A,B}$	$9.00^{A,B}$	$8.88^{A,B}$	$7.25^{B,C}$	$8.38^{A,B}$	$8.38^{A,B}$	5.56^{C}
	citrus	$4.50^{A,B}$	4.81^{A}	$3.31^{A,B,C}$	$2.94^{B,C,D}$	$2.94^{B,C,D}$	$2.31^{C,D}$	$2.28^{C,D}$	$4.13^{A,B}$	1.50^{D}
	coconut	$2.50^{C,D}$	$2.94^{B,C,D}$	$2.69^{C,D}$	$4.94^{A,B}$	2.19^{D}	5.06^{A}	5.75^{A}	$4.31^{A,B,C}$	6.06^{A}
	roasted	$2.69^{B,C}$	$3.44^{A,B}$	$3.31^{A,B}$	2.88^{B}	1.19^{C}	4.50^{A}	$2.44^{B,C}$	$2.63^{B,C}$	$3.00^{A,B}$
	smoky	$2.19^{B,C}$	3.38^{B}	5.44^{A}	$2.63^{B,C}$	$2.06^{B,C}$	1.00^{C}	$2.75^{B,C}$	$2.00^{B,C}$	1.25^{C}
	phenolic	$7.50^{A,B}$	5.63^{B}	8.19^{A}	5.38^{B}	8.06^{A}	2.69^{C}	5.50^{B}	5.81^{B}	1.31^{C}
	chocolate	1.50^{B}	1.63^{B}	1.13^{B}	2.25^{B}	2.31^{B}	4.06^{A}	2.31^{B}	2.44^{B}	4.69^{A}
Mouthfeel	warming	$8.56^{A,B,C}$	$9.25^{A,B}$	$8.81^{A,B,C}$	$8.69^{A,B,C}$	9.38^{A}	$7.69^{B,C,D}$	$7.63^{C,D}$	$8.56^{A,B,C}$	6.50^{D}
	slick	4.44^{D}	$5.81^{C,D}$	$7.18^{A,B,C}$	$6.38^{A,B,C}$	$6.13^{B,C,D}$	8.00^{A}	$7.81^{A,B}$	$6.00^{C,D}$	$6.69^{A,B,C}$
Taste	bitter	$8.06^{A,B}$	$7.81^{A,B,C}$	$8.31^{A,B}$	$7.75^{A,B,C}$	8.94^{A}	$6.50^{C,D}$	$6.94^{B,C,D}$	$8.13^{A,B}$	5.75^{D}
Aftertaste	brown spice	4.75^{D}	$6.31^{B,C}$	$5.50^{C,D}$	$6.56^{B,C}$	$6.13^{B,C,D}$	$7.56^{A,B}$	$7.56^{A,B}$	$6.88^{A,B,C}$	8.19^{A}
	caramel	1.50^{D}	$2.88^{C,D}$	$2.75^{C,D}$	4.13^{C}	4.00^{C}	10.31^{A}	6.13^{B}	$4.38^{B,C}$	10.75^{A}
Aroma By Mouth	caramel	3.00^{E}	$3.88^{D,E}$	$4.56^{D,E}$	6.88^{B}	$5.19^{B,C}$	12.19^{A}	7.25^{B}	$6.63^{B,C}$	11.13^{A}
	maple	2.75^{C}	$3.88^{B,C}$	$4.00^{B,C}$	5.31^{B}	5.13^{B}	8.19^{A}	6.00^{B}	5.69^{B}	9.69^{A}
	vanilla	4.31^{D}	$5.56^{C,D}$	$6.81^{B,C}$	7.56^{B}	$6.88^{B,C}$	11.31^{A}	8.56^{B}	$7.00^{B,C}$	11.00^{A}
	coconut	1.31^{D}	$3.38^{B,C}$	$2.56^{C,D}$	5.06^{A}	$2.63^{C,D}$	5.25^{A}	$4.81^{A,B}$	$4.31^{A,B}$	5.56^{A}

†Superscripts of the same letter within an attribute indicate no significant difference by Fisher's Least Significant Difference (LSD) test at $\alpha=0.05$

*"BW" is Bacardi White, "BG" is Bacardi Gold, "AE" is Appleton Estate V/X, "RA7" is Ron Abuelo 7 year, "AE12" is Appleton Estate 12 year, "DR12" is Diplomatico Reserva Exclusica, "ED12" is El Dorado 12 year, "RZ" is Ron Zacapa Centurio, "DX" is Dictador XO Insolent

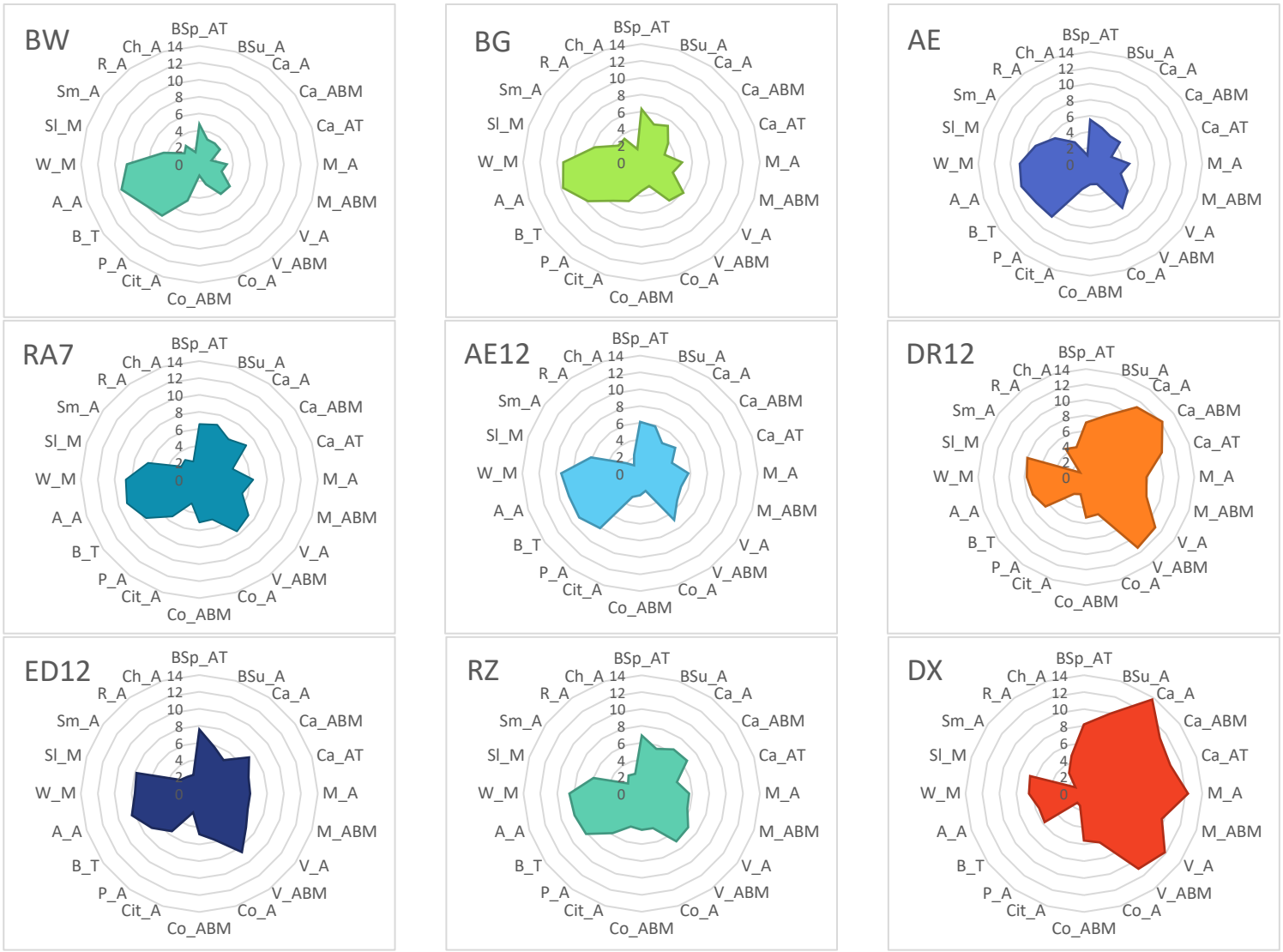


Figure 6.1 Spider plots of mean significant attribute intensities for all nine rum samples.
"BW" is Bacardi White, "BG" is Bacardi Gold, "AE" is Appleton Estate V/X, "RA7" is Ron Abuelo 7 year, "AE12" is Appleton Estate 12 year, "DR12" is Diplomatico Reserva Exclusica, "ED12" is El Dorado 12 year, "RZ" is Ron Zacapa Centurio, "DX" is Dictador XO Insolent. "A" is aroma, "M" is mouthfeel, "T" is taste, "AT" is aftertaste, "ABM" is aroma-by-mouth, "BSp" is brown spice, "BSu" is brown sugar, "Ca" is caramel, "M" is maple, "V" is vanilla, "Co" is coconut, "Cit" is citrus, "P" is phenolic, "B" is Bitter, "A" is alcohol, "W" is warming, "Sl" is slick, "Sm" is smoky, "R" is roasted, and "Ch" is chocolate.

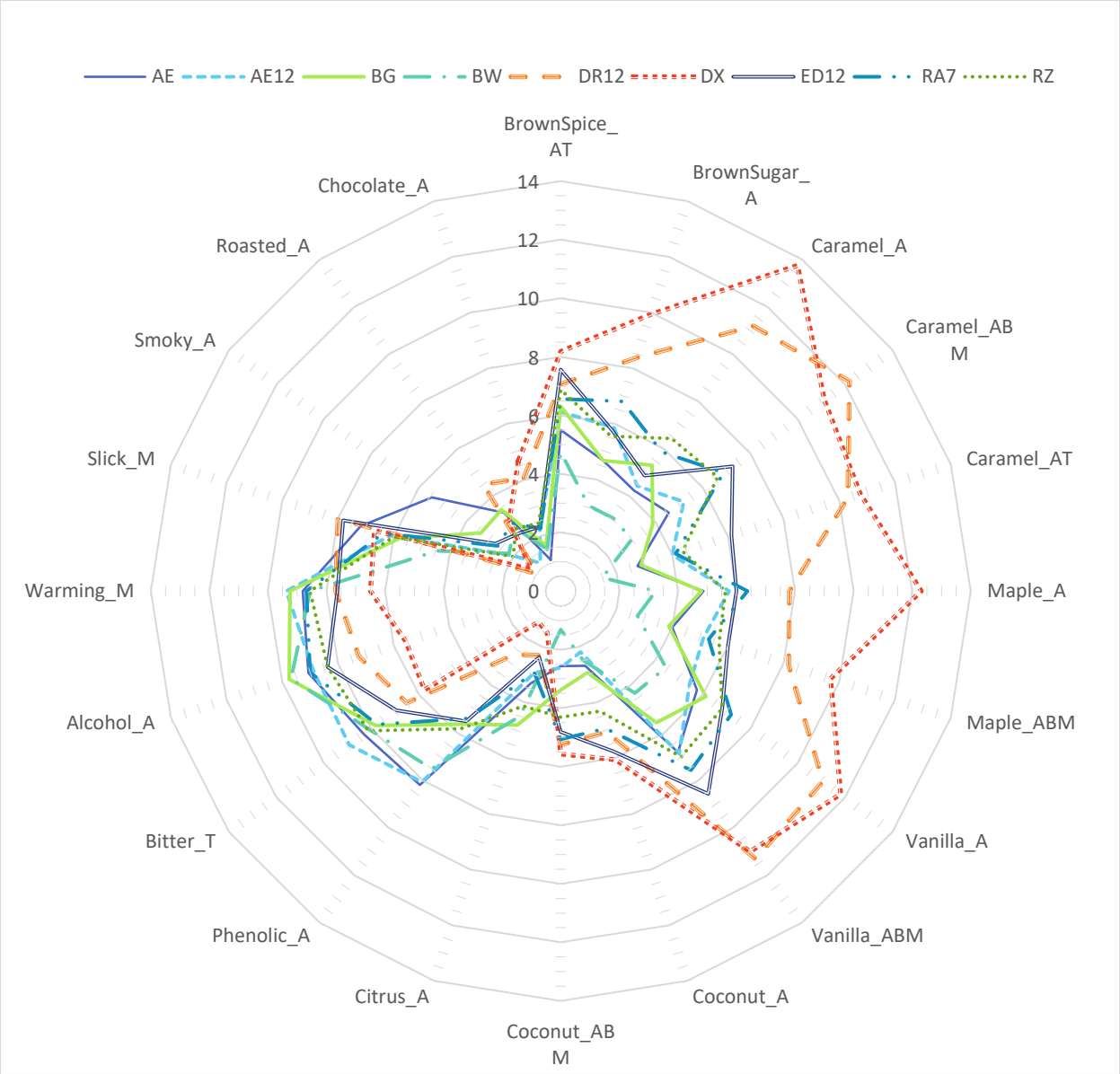


Figure 6.2 Overlaid spider plot of mean significant attribute intensities for all nine rum samples.
"BW" is Bacardi White, "BG" is Bacardi Gold, "AE" is Appleton Estate V/X, "RA7" is Ron Abuelo 7 year, "AE12" is Appleton Estate 12 year, "DR12" is Diplomatico Reserva Exclusica, "ED12" is El Dorado 12 year, "RZ" is Ron Zacapa Centurio, "DX" is Dictador XO Insolent. A is aroma, M is mouthfeel, T is taste, AT is aftertaste, ABM is aroma-by-mouth

Figure 6.3 Spider plot of mean significant attribute intensities for seven rum samples, excluding Diplomatica Reverva 12 year and Dictador Insolent

"BW" is Bacardi White, "BG" is Bacardi Gold, "AE" is Appleton Estate V/X, "RA7" is Ron Abuelo 7 year, "AE12" is Appleton Estate 12 year, "DR12" is Diplomatico Reserva Exclusica, "ED12" is El Dorado 12 year, "RZ" is Ron Zacapa Centurio, "DX" is Dictador XO Insolent. A is aroma, M is mouthfeel, T is taste, AT is aftertaste, ABM is aroma-by-mouth

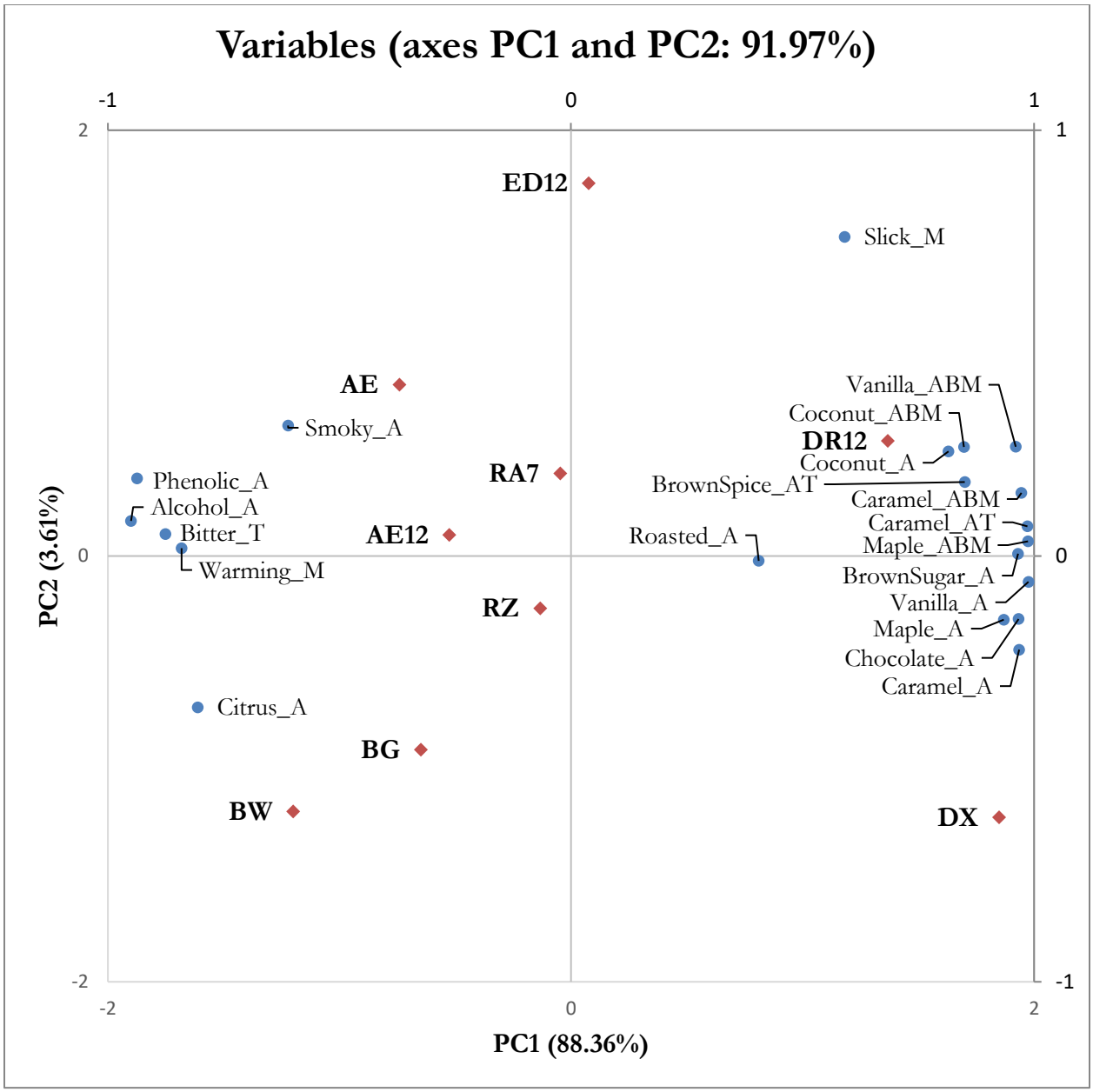


Figure 6.4 Principal component analysis biplot of significant attributes present on principal component 1 (PC1) and 2 (PC2) by the covariance matrix of mean significant attribute intensity rating across all nine rum samples

"BW" is Bacardi White, "BG" is Bacardi Gold, "AE" is Appleton Estate V/X, "RA7" is Ron Abuelo 7 year, "AE12" is Appleton Estate 12 year, "DR12" is Diplomatico Reserva Exclusica, "ED12" is El Dorado 12 year, "RZ" is Ron Zacapa Centurio, "DX" is Dictador XO Insolent. A is aroma, M is mouthfeel, T is taste, AT is aftertaste, ABM is aroma-by-mouth.

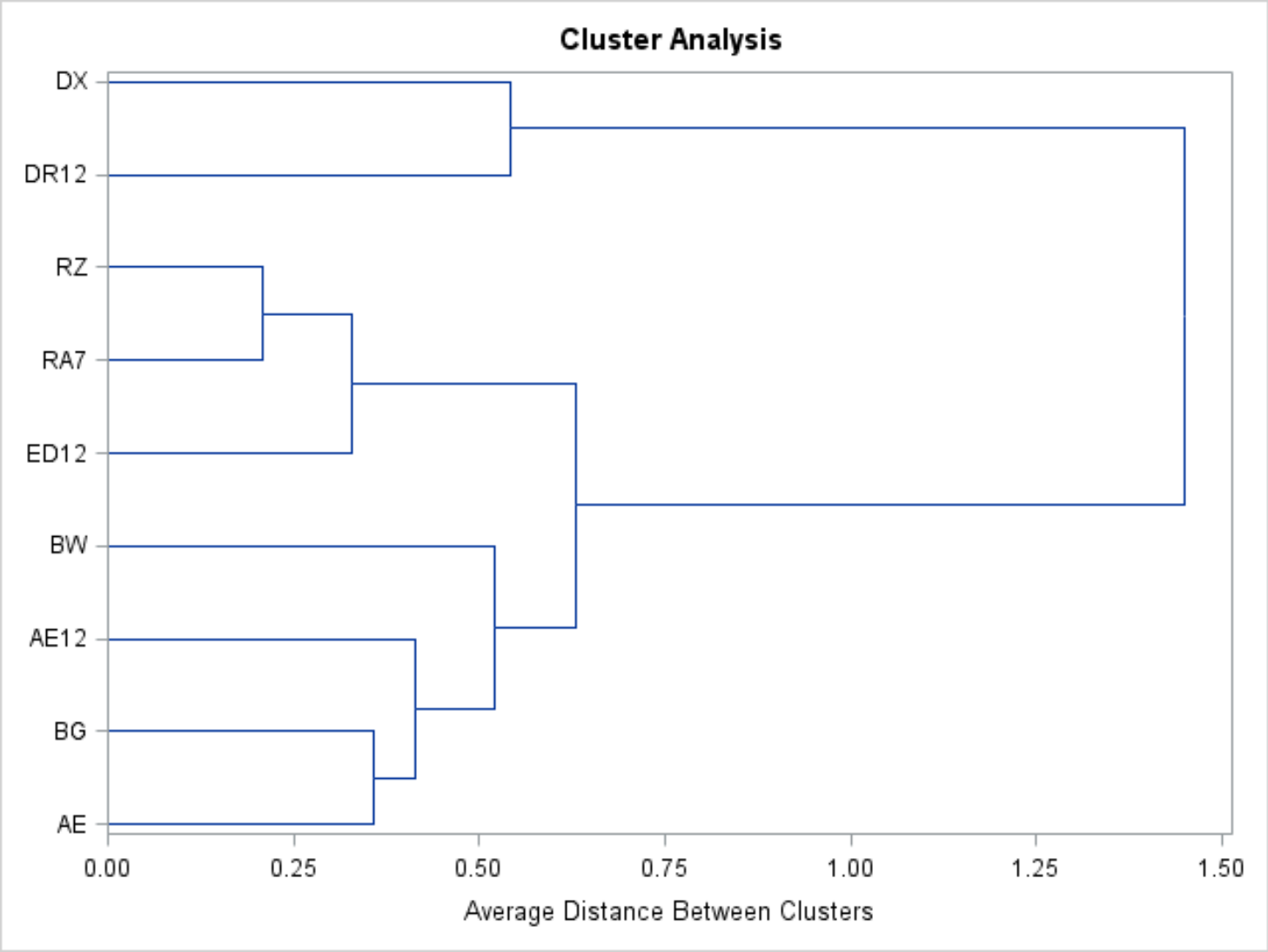


Figure 6.5 Cluster analysis constructed using mean significant attribute intensities for all nine rums
"BW" is Bacardi White, "BG" is Bacardi Gold, "AE" is Appleton Estate V/X, "RA7" is Ron Abuelo 7 year, "AE12" is Appleton Estate 12 year, "DR12" is Diplomatico Reserva Exclusica, "ED12" is El Dorado 12 year, "RZ" is Ron Zacapa Centurio, "DX" is Dictador XO Insolent

Table 6.4 Pearson correlation coefficients for significant attributes for all nine rum samples

Attributes	BrownSugar A	Caramel A	Maple A	Vanilla A	Alcohol A	Citrus A	Coconut A	Roasted A	Smoky A	Phenolic A
BrownSugar_A	**1.000**									
Caramel_A	0.932**	**1.000**								
Maple_A	0.955***	0.932**	**1.000**							
Vanilla_A	0.945**	0.983***	0.910**	**1.000**						
Alcohol_A	-0.916**	-0.935**	-0.956***	-0.921**	**1.000**					
Citrus_A	-0.842**	-0.681*	-0.812**	-0.741*	0.820**	**1.000**				
Coconut_A	0.752*	0.701*	0.729*	0.773*	-0.743*	-0.700*	**1.000**			
Roasted_A	0.273	0.466	0.194	0.525	-0.237	-0.048	0.312	**1.000**		
Smoky_A	-0.565	-0.598	-0.511	-0.570	0.567	0.364	-0.465	-0.001	**1.000**	
Phenolic_A	-0.867**	-0.940**	-0.861**	-0.950***	0.847**	0.606	-0.827**	-0.522	0.635	**1.000**
Chocolate_A	0.936**	0.953***	0.913**	0.945**	-0.940**	-0.752*	0.726*	0.280	-0.772*	-0.908**
Warming_M	-0.730*	-0.794*	-0.811**	-0.813**	0.885**	0.740*	-0.838**	-0.325	0.488	0.827**
Slick_M	0.565	0.436	0.439	0.565	-0.490	-0.705*	0.582	0.377	0.026	-0.414
Bitter_T	-0.764*	-0.845**	-0.801**	-0.881**	0.821**	0.662	-0.850**	-0.535	0.487	0.933**
BrownSpice_AT	0.833**	0.759*	0.827*	0.790*	-0.803**	-0.711*	0.878**	0.130	-0.482	-0.812**
Caramel_AT	0.933**	0.936**	0.892**	0.966***	-0.936**	-0.823**	0.783*	0.392	-0.628	-0.902**
Caramel_ABM	0.928**	0.912**	0.841**	0.960***	-0.894**	-0.805**	0.806**	0.448	-0.623	-0.882**
Maple_ABM	0.969***	0.942**	0.945**	0.954***	-0.966***	-0.838**	0.800**	0.271	-0.619	-0.888**
Vanilla_ABM	0.934**	0.880**	0.858**	0.938**	-0.897**	-0.881**	0.792*	0.397	-0.497	-0.830**
Coconut_ABM	0.844**	0.753*	0.756*	0.821**	-0.718*	-0.674*	0.922	0.351	-0.450	-0.835**

A is aroma, M is mouthfeel, T is taste, AT is aftertaste, ABM is aroma-by-mouth. *, **, *** stand for significance at $p<0.05$, $p<0.01$, and $p<0.001$ respectively.

Table 6.4 (cont.) Pearson correlation coefficients for significant attributes for all nine rum samples

Attributes	Chocolate A	Warming M	Slick M	Bitter T	BrownSpice AT	Caramel AT	Caramel ABM	Maple ABM	Vanilla ABM	Coconut ABM
BrownSugar_A										
Caramel_A										
Maple_A										
Vanilla_A										
Alcohol_A										
Citrus_A										
Coconut_A										
Roasted_A										
Smoky_A										
Phenolic_A										
Chocolate_A	**1.000**									
Warming_M	-0.802**	**1.000**								
Slick_M	0.424	-0.444	**1.000**							
Bitter_T	-0.813**	0.933**	-0.487	**1.000**						
BrownSpice_AT	0.789*	-0.729*	0.608	-0.757*	**1.000**					
Caramel_AT	0.961***	-0.838**	0.642	-0.867**	0.830**	**1.000**				
Caramel_ABM	0.935**	-0.788*	0.672*	-0.819**	0.798**	0.976***	**1.000**			
Maple_ABM	0.966***	-0.823**	0.596	-0.818**	0.881**	0.977***	0.958***	**1.000**		
Vanilla_ABM	0.895**	-0.782*	0.775*	-0.804**	0.821**	0.972***	0.978***	0.957***	**1.000**	
Coconut_ABM	0.752*	-0.659	0.654	-0.745*	0.916**	0.803**	0.849**	0.839**	0.839**	**1.000**

A is aroma, M is mouthfeel, T is taste, AT is aftertaste, ABM is aroma-by-mouth. *, **, *** stand for significance at $p<0.05$, $p<0.01$, and $p<0.001$ respectively.

6.6 References

Cairncross, W. E., & Sjöström, L. B. (1950). Flavor Profile - a new approach to flavor problems. *Food Technology*, *4*, 308–311.

Caul, J. F. (1957). The Profile Method of Flavor Analysis. *Advances in Food Research*, *7*, 1–40.

de Souza, M. D. C. A., Vásquez, P., del Mastro, N. L., Acree, T. E., & Lavin, E. H. (2006). Characterization of Cachaça and Rum Aroma. *Journal of Agricultural and Food Chemistry*, *54*, 485–488. https://doi.org/10.1021/jf0511190

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*, 637–645. https://doi.org/10.1021/acs.jafc.5b05426

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*, 9041–9053. https://doi.org/10.1021/acs.jafc.6b04046

Gómez, S. M. (2002). *Rum Aroma Descriptive Analysis*. Louisiana State University. Retrieved from http://etd.lsu.edu/docs/available/etd-1114102-110301/

Ickes, C. M., Lee, S.-Y., & Cadwallader, K. R. (2017). Novel Creation of a Rum Flavor Lexicon Through the Use of Web-Based Material. *Journal of Food Science*, *82*(5), 1213–1223. https://doi.org/10.1111/1750-3841.13707

Jolliffe, I. (2014). Principal Component Analysis. In *Wiley StatsRef: Statistics Reference Online* (pp. 1–5).

Lawless, H. T., & Heymann, H. (1999a). Data Relationships and Multivariate Applications. In *Sensory Evaluation of Food: Principles and Practices* (pp. 585–601). New York: Springer Science+Business Media, LLC.

Lawless, H. T., & Heymann, H. (1999b). Descriptive analysis. In *Sensory Evaluation of Food: Principles and Practices* (pp. 227–257). New York: Springer Science & Buiness Media, LLC. https://doi.org/10.1007/978-1-4419-6488-5

Limited Ingredients. (2016). *Alcohol and Tobacco Tax and Trade Bureau*. Retrieved from

https://www.ttb.gov/ssd/limited_ingredients.shtml

Magnani, B. D. (2009). *Estudo Comparativo das Características Sensoriais do Rum e da Cachaça Estudo Comparativo das Características Sensoriais do Rum e da Cachaça*. Universidade Estadual Paulista.

Meilgaard, M., Civille, G. V., & Carr, B. T. (2007). The Spectrum Descriptive Analysis Method. In *Sensory Evaluation Techniques* (Fourth Edi, pp. 189–254). Boca Raton, FL: CRC Press/Taylor & Francis.

Muñoz, A. M., & Civille, G. V. (1992). The Spectrum Descriptive Analysis Method. In R. C. Hootman (Ed.), *Manual on Descriptive Analysis Testing for Sensory Evaluation* (pp. 22–34). Baltimore, MD: American Society for Testing and Materials.

Powers, J. J. (1988). Current Practices and Application of Descriptive Methods. In J. R. Piggott (Ed.), *Sensory Analysis of Foods* (2nd ed., pp. 187–266). New York: Elsevier Applied Science.

Stone, H. (1992). Quantitative Descriptive Analysis. In R. C. Hootman (Ed.), *Manual on Descriptive Analysis Testing for Sensory Evaluation* (pp. 15–21). Baltimore, MD: American Society for Testing and Materials.

Stone, H., & Sidel, J. L. (1993). Descriptive Analysis. In S. L. Taylor (Ed.), *Sensory Evaluation Practices* (2nd ed., pp. 202–242). San Diego: Academic Press Inc.

Stone, H., Sidel, J. L., Oliver, S., Woolsey, A., & Singleton, R. (1974). Sensory Evaluation by Quantitative Descriptive Analysis. *Food Technology*, *8*(1), 24–32. https://doi.org/10.1002/9780470385036.ch1f

Williams, A. A., & Langron, S. P. (1984). The Use of Free choice Profiling for the Evaluation of Commercial Ports. *Journal of the Science of Food and Agriculture*, *35*(5), 558–568. https://doi.org/10.1002/jsfa.2740350513

Zook, K. L., & Pearce, J. H. (1988). Quantitative Descriptive Analysis. In H. Moskowitz (Ed.), *Applied Sensory Analysis of Foods: Volume 1* (pp. 43–72). Boca Raton, FL: CRC Press, Inc.

Chapter 7: Effect of Ethanol Concentration on the Flavor Perception of Rum

7.1 Abstract

This is the first sensory study to evaluate the effects of ethanol concentration on the flavor perception of distilled spirits. Dilution series of two rum samples were evaluated to gain insight into the effects of ethanol concentration on the flavor perception of distilled spirits. Rum samples were diluted 1:2 with either pure water to obtain a final sample of 20% ABV or with a 40% ABV solution to account for the flavor dilution effect but keep the ethanol concentration the same as the original samples. A descriptive analysis panel was conducted on both dilution series. Twenty-three attributes were evaluated consisting of eight aroma, four mouthfeel, two taste, five aftertaste and four aroma-by-mouth terms. The results indicated that the original rum samples had the highest intensity for all attributes and the dilution with 40%ABV had the lowest perception except for silky mouthfeel. The flavor profiles of the original sample and the dilutions with water were very similar, with the water dilutions generally having lower attribute intensities. In contrast, the dilution with 40% ABV had significantly different flavor profiles.

7.2 Introduction

Ethanol is arguably the most important component of alcoholic beverages, particularly distilled spirits. Alcoholic beverages span a wide range of alcohol concentrations from beers (3% to 10% ABV) to distilled spirits (usually 40% ABV). Furthermore, ethanol concentration plays an important role in the flavor perception of alcoholic beverages. Molecular structure, flavor partitioning, and sensory perceptions have all been shown to be affected as a function of ethanol concentration.

In terms of the physicochemical properties of ethanol, the water-ethanol structure greatly changes as the system goes from 100% aqueous to 100% ethanolic (Cipiciani, Onori, & Savelli, 1988; Conner, Birkmyre, Paterson, & Piggott, 1998; D'Angelo, Onori, & Santucci, 1994a, 1994b; Franks & Ives, 1966; Onori & Santucci, 1996; Parke & Birch, 1999; Petrillo, Onori, & Sacchetti, 1989; Wakisaka,

Komatsu, & Usui, 2001). In 100% aqueous systems, the water molecules exist in short-range hydrogen bonded structures that are highly fluid, continuously breaking and reforming hydrogen bonds (Franks & Ives, 1966). As the ethanol concentration initially increases, the ethanol molecules are mono-dispersed within the aqueous matrix (Conner et al., 1998; D'Angelo et al., 1994a, 1994b). This behavior continues until the ethanol concentration reaches approximately 15% alcohol-by-volume (ABV). Above this concentration, ethanol molecules begin to form aggregates or micelles (Cipiciani et al., 1988; D'Angelo et al., 1994b; Onori & Santucci, 1996). Once the solution reaches an ethanol concentration of 57% ABV, the final structural shift in the water/ethanol matrix occurs where the water molecules become mono-dispersed within the ethanolic matrix (D'Angelo et al., 1994b).

Previous research on how ethanol concentration affects aroma and sensory perception in alcoholic beverages has mainly approached the problem from an analytical perspective. Additionally, studies have mainly focused on how ethanol affects the headspace concentration of volatiles in static systems. As the ethanol concentration of solutions increases, the headspace concentration has been shown to decrease (Athès, Pena-Lillo, Bernard, Perez-Correa, & Souchon, 2004; Aznar, Tsachaki, Linforth, Ferreira, & Taylor, 2004; Boothroyd, Linforth, & Cook, 2012; Conner et al., 1998; Escalona-Buendia, Piggott, Conner, & Paterson, 1998; Tsachaki, Aznar, Linforth, & Taylor, 2006). The decrease in headspace concentration is typically attributed to an increase in the solubility of aroma compounds as the ethanol concentration increases. While overall decreases in headspace concentration occur, it is important to note volatile compounds are affected differently by the changes in ethanol concentration (Aznar et al., 2004; Boothroyd et al., 2012; Tsachaki et al., 2006). While these studies demonstrate that ethanol can affect the release of aroma compounds in alcoholic beverages, they are not representative of real life systems.

When beverages are consumed, they are not evaluated in equilibrium systems. The glasses are constantly open to the air, allowing solvent evaporation, and exposure to air currents in the room. Additionally, the glass is stirred, either slowly as it is moved for consumption, or deliberately. As a result, the study of dynamic systems allows for better insight into how ethanol concentration may affect sensory perception during the act of consumption.

Evaluation of dynamic systems has mainly been done using atmospheric pressure chemical ionization (APCI)-MS (Taylor et al., 2010; Tsachaki et al., 2008; Tsachaki, Linforth, & Taylor, 2005).

Results from these studies contradict those of the static systems, showing that the headspace concentration increases above ethanolic systems in comparison to aqueous systems under dynamic conditions. This phenomenon is attributed to a combination of the Marangoni effect and Rayleigh-Bénard convection (Taylor et al., 2010; Tsachaki et al., 2006, 2005). Essentially, the bulk solution is stirred through differences in surface tension and density respectively as caused by the evaporation of ethanol (Marangoni, 1865; Rayleigh, 1916). The stirring moves more ethanol and flavor molecules to the surface of the solution for continued evaporation. The results of these studies suggest that alcoholic beverages with higher alcohol concentrations will have increased sensory attribute intensity due to the higher concentration of aroma compounds in the headspace above the samples.

Overall, sensory research exploring the effects of ethanol concentration on the perception of alcoholic beverages is lacking. The majority of studies have evaluated ethanol's effect on wine or wine model systems (Escudero, Campo, Fariña, Cacho, & Ferreira, 2007; Goldner, Zamora, Di Leo Lira, Gianninoto, & Bandoni, 2009; Guth, 1998; Jones, Gawel, Francis, & Waters, 2008; King, Dunn, & Heymann, 2013; Le Berre, Atanasova, Langlois, Etiévant, & Thomas-Danguin, 2007). While these studies demonstrate that ethanol concentration can have an impact on flavor perception in alcohol, the alcohol content of wine is very different from distilled spirits.

To date, the only sensory study to include distilled spirits was done by in the 1970's (Williams, 1972). Williams dealcoholized five different alcoholic beverages and observed the sensory changed compared to the original beverage. The study showed that de-ethanolized whiskey perceived as drier and had less bite than the full alcohol sample. No sensory research had been conducted to provide insights into how ethanol's concentration may affect flavor perception during the consumption of distilled spirits.

While some consumers will only drink distilled spirits neat, others typically dilute their drink before consumption. A common practice is to consume spirits on the rocks, where the ice both cools and dilutes the beverage. Others insist that a small splash of water is needed to open up the flavor. Still others state that distilled spirits need to be diluted to ~23% ABV to get the perception of the beverage. This has been the traditional practice in the whiskey industry for years, and the common reason given for this practice is to reduce the pungency of the alcohol (Smith & Roskrow, 2012).

Descriptive analysis panels allow researchers to identify and quantify the sensory differences between products (Lawless & Heymann, 1999b; Meilgaard, Civille, & Carr, 2007; Stone & Sidel,

1993). Panelists develop terms and corresponding definitions and references for the sensory attributes they perceive in the sample for the modalities of aroma, aroma-by-mouth, taste, mouthfeel, and aftertaste. Panelists rate the determined references and then use those as anchor points on the scale when evaluating the samples. Panelists finally rate the samples in individual booths for all the attributes that were previously identified. The collected data is then subjected to statistical analysis to evaluate the samples using methods such as analysis of variance, and principal component analysis.

The goal of this study was to evaluate using a descriptive analysis panel, the effects of ethanol concentration on the flavor perception of distilled spirits using rum samples by comparing the original sample to a 1:2 dilution with water and a 1:2 dilution with 40% ethanol. It is hypothesized that changes in ethanol concentration will significantly affect the aroma of rum samples. Samples with lower ethanol concentrations are expected to have lower perceived solvent and pungent characteristics. The 40% ABV dilution was expected to be most similar to the original rum sample.

7.3 Materials and Methods

Materials

Two commercially available rums, Ron Abuelo: Añejo 7 years (RA7), and Diplomatica Reserva Exclusiva (DR12), were purchased at a local liquor store (Champaign, IL). Both rums had a reported ethanol concentration of 40% alcohol by volume (ABV). Mention of the brand name of these rums does not imply any research contact or sponsorship and is not for advertisement or endorsement purposes.

Two dilutions of each rum were prepared, a 1:2 (v/v) dilution with 40% ethanol and a 1:2 (v/v) dilution with pure water (Ice Mountian 100% Natural Spring Water, Nestlé Waters North America, Stamford, CT). The 40% ethanol solution was prepared by diluting 190 Proof (95%ABV) ethanol (USP Grade, Decaon Labs, Inc., King of Prussia, PA) with pure water. Prior to testing, 20 mL of each sample was measured into a black double old-fashion glass (Threshold, Target, USA) and covered with a glass petri dish no more than an hour before the panel.

Attribute references were prepared daily and placed into 2 or 4 oz. lidded plastic soufflé cups (Dart Container Corporation, Mason, MI) and labeled with the reference identity. References were not prepared more than 24 hours prior to evaluation. A complete list of attributes, definitions, references, reference scores and preparation procedures can be found in Table 7.1. Product information for references can be found in the Appendix L.

Subject Recruitment

All materials related to panelists recruitment and compensation were approved by the Institutional Review Board (IRB) at the University of Illinois Urbana-Champaign (IRB Protocol Number: 16854), Appendix D. The same panelists that were selected for the rum descriptive analysis panel in chapter 5 were retained for this descriptive analysis panel. Information regarding the recruitment and screening process can be found there.

Descriptive Analysis Procedure

A hybrid of Qualitative Descriptive Analysis® (Stone, 1992) and the Spectrum™ method (Meilgaard et al., 2007; Munoz & Civille, 1992) was used. Two rums were evaluated as a dilution series. At each session, panelists received one dilution series consisting of three samples: straight rum, a 1:2 dilution with 40%ABV ethanol, and a 1:2 dilution with water. On the first day of the panel, the panelists were refreshed about the DA method to be used in the study. The first four sessions (1 hour each) consisted of term and reference generation, followed by reference refinement. Panelists were presented with a dilution series of samples labeled with random three digit codes and asked to generate the attributes they perceived in the rum samples for aroma, aroma-by-mouth, mouthfeel, taste and aftertaste modalities. Panelists were provided with the developed rum flavor wheel to aid in term generation. Through group discussion, panelists identified the terms to be used, developed a precise definition of each attribute and determined a corresponding reference.

After the terms and references were established, panelists then spent two sessions (1 hour each) determining the reference intensities of each attribute. Panelists were asked to scale the references based on a 15 point scale, where zero is no perception of a given attribute and 15 is the strongest perception of that attribute in the rum samples. Panelists then spent six days practicing scoring the rums, using the references as anchor points for the scale to aid in panel uniformity. On one of the days, panelists conducted individual booth practice sessions in Bevier Hall on the University of

Illinois at Urbana-Champaign campus for one thirty minute session using the Compusense five (Version 5.0: Guelph ON, Canada) data acquisition system. Panelists were routinely provided with their scoring results from the previous day to help identify and correct for attributes they were rating inconsistently with the rest of the group.

The panel concluded with two days of individual booth testing. Panelists attended two 30 minute sessions per day, evaluating one dilution series of three samples at each session. Rum samples were presented in black double old fashions glasses covered with a petri dish and labeled with random three-digit codes. Sample presentation was randomized between all panelists. Samples were evaluated under red lighting using the Compusense five software. Panelists were provided with their reference tray when they arrived and encouraged to evaluate all references before proceeding into the booth for testing. Panelists were free to leave the booth at any time to re-evaluate a reference.

A more detailed, day-by-day description of the DA panel can be found in Appendix P.

Statistical Analysis

Statistical analysis of the data was performed using Statistical Analysis System (SAS)® (Version 9.4, SAS Institute Inc., Cary, NC, USA). Analysis of variance (ANOVA) was conducted on each of the 23 attributes evaluated during the DA panel to determine the presence of overall significant differences ($p<0.05$) using the PROC GLM function for variations within the dilutions, panelists, replications and their corresponding interactions: dilution-by-panelist (DxP), dilution-by-replication (DxR), and replications-by-panelist (RxP). Each rum dilution series was analyzed separately. The calculated probabilities were compared to significance levels $\alpha=0.05$, 0.01 and 0.001. When significant DxP interactions existed, adjusted F-ratios were calculated using Microsoft® Excel® 2016 (Version 16: Microsoft Corporation, Redmond, WA) by dividing the dilution mean square by the DxP interaction mean square and calculating the new probability using the F.DIST function. Fisher's least significant difference (LSD) test was conducted on all attributes determined as significant by ANOVA.

Principal component analysis (PCA) biplots were produced using SAS and Microsoft Excel to create a visual representation of the data to allow further examination of the relationship of the rums to individual attributes that characterized the samples. Pearson correlations were calculated using the same SAS software, with significance determined at $\alpha=0.05$, 0.01, and 0.001.

7.4 Results and Discussion

A descriptive analysis panel was performed to characterize the effect ethanol concentration has on aroma perception of alcoholic beverages. A series of three samples was evaluated for each rum consisting of the straight rum (directly from the bottle, 40%ABV), a 1:2 dilution with water (creating a 20%AVB samples) to mimic how samples are routinely evaluated in industry, and a 1:2 dilution with 40% ethanol to account for the flavor dilution effect but keep the alcohol concentration the same. Two different rums were evaluated to assess if the effects were sample specific or applicable to the larger body of distilled spirits. This descriptive analysis panel is the first sensory study to look at the effects of ethanol concentration on flavor perception in distilled beverages.

The panelists generated 23 attributes to describe the two dilution series. The generated terms, term definitions, selected references, reference scores and reference preparations can be found in Table 7.1. Reference scores are an average of individual panelist's ratings. All panelists had previous training evaluating the sensory properties of distilled beverages.

Analysis of variance (ANOVA) was conducted on the dilution series for each rum (DR and RA) separately for all 23 attributes identified and rated by the panelists. The results are shown in Table 7.2 and Table 7.5. Overall, sample replications were not a significant source of error ($p>0.05$) for either the DR12 dilution series (except silky mouthfeel and sweet taste) or the RA7 dilution series (except toasted aroma, woody aroma, sweet taste and plastic aftertaste). This lack of variation shows the panelists were able to rate the sample attributes across replications consistently. Significant variation did exist ($p<0.05$) for all attributes for the DR12 dilution series (except alcohol aroma) and RA7 dilution series. This type of variation is typical of descriptive analysis panels and is most likely a result of panelists not using the entire scale or using different parts of the scale to rate the samples (Lawless & Heymann, 1999b; Stone, Sidel, Oliver, Woolsey, & Singleton, 1974). R x P interactions were not significant ($p>0.05$) for any attributes in the DR12 series nor for most attributes in the RA7 series, except for warming mouthfeel, bitter taste, sweet taste, plastic aftertaste and maple aroma by-mouth. The lack of interaction indicates that panelists were able to agree on the intensity of the attributes in the samples across replications. There were no D x R effects in either series (except slick mouthfeel in RA7 series) indicating that panelists rated the samples similarly across replications.

Significant D x P interactions ($p<0.05$) did exist for DR12 series (except silky mouthfeel, sweet taste, and vanilla aftertaste) and the RA7 series (except toasted aroma, silky mouthfeel, slick mouthfeel, sweet taste, maple aroma-by-mouth and vanilla aroma by mouth). This interaction indicated that panelists were not able to agree on the order of the intensity of the attributes across samples. Adjusted F-vales were calculated for attributes that had significant D x R interaction to account for the variation. The adjusted F-values are shown in Tables 7.2 and 7.5. After the adjusted F-values were calculated, eighteen of the attributes in the DR12 series were determined to be significantly different ($p<0.05$) including alcohol aroma, caramel aroma, maple aroma, vanilla aroma, roasted aroma, woody aroma, astringent mouthfeel, silky mouthfeel, slick mouthfeel, warming mouthfeel, bitter taste, bitter aftertaste, brown spice aftertaste, alcohol aroma-by-mouth, caramel aroma-by-mouth, maple aroma-by-mouth, vanilla aroma-by-mouth, and woody aroma-by-mouth. In the RA7 dilution series sixteen attributes were determined to be significantly different ($p<0.05$) including alcohol aroma, caramel aroma, vanilla aroma, dark fruit aroma, astringent mouthfeel, slick mouthfeel, warming mouthfeel, bitter taste, bitter aftertaste, brown spice aftertaste, vanilla aftertaste, plastic aftertaste, alcohol aroma-by-mouth, caramel aroma-by-mouth, maple aroma-by-mouth, and vanilla aroma-by-mouth. Of the 23 attributes evaluated, all terms (except toasted aroma) were statistically different for at least one of the rum series indicating that proper attributes were chosen for evaluation.

Attribute Differences between Dilutions

The dilution of the rum samples, both with water and ethanol (40% ABV), caused significant changes to the sensory profiles of the rums. The results indicated that rum samples diluted with ethanol had the lowest intensities for all attributes (except silky mouthfeel in the DR12 series).

In the DR12 dilution series, the original undiluted rum was significantly different from DR40 for all attributes, having a higher intensity for all attributes except silky mouthfeel (Table 7.3). Additionally, the two dilutions, DR20 and DR 40, were also significantly different from each other in most attributes, except caramel aroma, maple aroma, vanilla aroma, maple aroma-by-mouth and vanilla aroma by mouth. DR20 had a higher intensity of all attributes except silky mouthfeel. DR and DR20 were not significantly different from each other except for caramel aroma, maple aroma, vanilla aroma and brown spice aftertaste. Selected significant attribute correlations for the DR12 dilution series samples (Table 7.4) include those between astringent mouthfeel and roasted aroma, warming

mouthfeel and alcohol aroma-by-mouth, and a significant negative correlation existed between silky mouthfeel and roasted aroma, astringent mouthfeel, warming mouthfeel and alcohol aroma-by-mouth.

In the RA7 dilution series, the original rum sample (RA) had the highest intensity of the three samples for all attributes (Table 7.6). RA was significantly different from RA40 for all attributes. RA40 had significantly lower attribute intensities compared to RA20 for all attributes except vanilla aroma, vanilla aftertaste, and plastic aftertaste. RA and RA20 were significantly different from each other for alcohol aroma, dark fruit aroma, astringent mouthfeel, caramel aroma-by-mouth, maple aroma-by-mouth and vanilla aroma-by-mouth. Selected significant attribute correlations for the RA7 dilution series samples (Table 7.7) include those between bitter taste and warming mouthfeel and alcohol aroma-by-mouth, slick mouthfeel with brown spice aftertaste, plastic aftertaste and alcohol aroma-by-mouth, and astringent mouthfeel with slick mouthfeel, bitter, brown spice, and plastic aftertaste, and alcohol and maple aroma-by-mouth.

Interestingly, rums diluted with water possessed nearly the same sensory profile as the original rums, with slightly lower attribute intensities as shown in the constructed spider plots (Figures 7.1 and 7.3). In contrast, the results indicate that dilution with ethanol profoundly changes the sensory profile of the rum, especially RA7.

Principal component analysis was also conducted to reduce the complexity of the data and gain a better visual representation of the data (Lawless & Heymann, 1999a). The covariance matrix was chosen for sample evaluation since the samples were all scored by a trained panel (Jolliffe, 2014). For the DR12 dilution series (Figure 7.2), the first factor (PC1) contained the majority of the variation between samples (88.4%) and the second factor (PC2) contained the remaining sample variation (11.6%). The high loading of factor one is also illustrated by the factor correlations (Appendix M). PC1 contrasts samples high in brown sugar, caramel, maple, vanilla, coconut and chocolate aroma, brown spice and caramel aftertaste, caramel, maple, vanilla and coconut aroma-by-mouth, with samples high in alcohol, citrus, and phenolic aroma, warming mouthfeel and bitter taste. PC2 was mainly defined by slick mouthfeel.

Focusing on the RA7 dilution series (Figure 7.4) the first factor contained the majority of the variation as well (94.8%), with the second factor minimally loaded with the remaining variation (5.2%). Factor loading can be found in Appendix N. PC1 contracted samples that were high in all

significant attributes with those that had lower intensities of those attributes. PC2 was defined by samples differentiated in dark fruit aroma.

These results validate the initial hypothesis that the dilution with lower alcohol concentration would have lower attribute intensity, particularly regarding aroma. Previous analytical studies on dynamic systems showed that higher ethanol concentration had higher headspace concentrations of volatiles (Taylor et al., 2010; Tsachaki et al., 2008, 2005). In the current study, the original rum sample at 40% ABV had the highest intensity for all aroma attributes for both rum samples.

However, the results are not as significant as might have been expected, especially since both the alcohol concentration and the congener concentrations were cut in half. No previous work evaluating the effects of ethanol on flavor perception has considered the dilution effect that occurs when a consumer dilutes the beverage. These studies have made replicate model solutions that are identical except for their alcohol concentration (Boothroyd et al., 2012; Tsachaki et al., 2008, 2006, 2005; Tsachaki, Linforth, & Taylor, 2009). Even studies that evaluated wine model systems at various ethanol concentrations spiked the solutions with the same concentration of volatiles after the ethanol dilutions were prepared (Tsachaki et al., 2009). It is likely that the decrease in ethanol concentration decreased the polarity of the system. Additionally, the evaporation effect and subsequent stirring by the Marangoni effect and Rayleigh-Bénard convection (Marangoni, 1865; Rayleigh, 1916) would still occur at 20% ABV, as it has been previously demonstrated in 12% ABV systems (Taylor et al., 2010), and may account for why the aroma attribute intensities did not decrease as much as was expected.

Interestingly, the 40% ABV dilutions were expected to be the closest to the original rums. However, they had the lowest intensity for all attributes (except silky mouthfeel). Furthermore, the 40% ABV dilutions were expected to have the highest perceived intensity of alcohol aroma, alcohol aroma-by-mouth, and warming mouthfeel. While these results are opposite of what we expected, this is the first sensory study to evaluate alcoholic beverages at such high alcohol concentrations. More sensory studies are needed to confirm these results and gain a better understanding of how ethanol affects sensory perceptions at higher alcohol levels.

In mouth sensory perceptions, including mouthfeel and taste, also differed as a result of dilution. Regarding mouthfeel, the warming sensation was the same between the original rums and dilutions with water but significantly decreased in the 40% ABV dilution. This is surprising since previous

research has demonstrated that increased ethanol concentration caused a higher rating of hotness or burning mouthfeel sensation (Demiglio & Pickering, 2008; Jones et al., 2008; Nolden & Hayes, 2015). It was expected that the 40% ABV dilution would have had the highest warming sensation followed by the original rum and then the dilution with water. It may be that ethanol, while one factor contributing to the warming sensation of spirits, may not be the only chemical contributing to that perception. These results are interesting as the ethanol used as the reference for warming mouthfeel was the same ethanol used to dilute the samples.

Additionally, previous research demonstrated that increased ethanol concentration causes a decrease in astringency (Demiglio & Pickering, 2008; Fontoin, Saucier, Teissedre, & Glories, 2008). Interestingly, the 40% ABV dilution did have the lowest perceived astringency, except for the RA7 series, the water dilution was much less intense than the original rum. This difference could be attributed to the fact that previous studies focused on wines. The high concentration of tannins present in wines may alter the perception of astringency differently than distilled spirits when the ethanol concentration changes.

Bitter taste was also shown to be significantly lower for the 40% ethanol dilutions in comparison to the original rums and water dilutions. Previous studies have shown increases in ethanol concentration shown to increase bitterness (Fontoin et al., 2008; Jones et al., 2008; Nolden & Hayes, 2015), which are contrary to our results. The other volatile and non-volatile components dissolved in the rum matrix could account for these differences.

Sweetness was not shown to be significantly different between rum dilutions; however, previous research has shown that sweetness perception increases with ethanol concentration in wines (Nurgel & Pickering, 2006; Zamora, Goldner, & Galmarini, 2006) It is possible that the perceived sweetness of rum is not large enough to enable panelists to perceive changes when the ethanol concentration was changed.

This was the first study to evaluate the sensory effects of ethanol on distilled spirits. Our results showed that the original rums and 1:2 dilutions with water were more similar to one another than expected. The samples were only statistically different for several attributes in each series. These results support the age old industry tradition of diluting distilled spirits to 20% or 23% ABV for blending and evaluation, demonstrating that while the intensity of the attributes decreased in the dilutions, the flavor profiles were very similar. The results for the 40% ABV samples was not

expected, and further research is needed to better understand how ethanol interacts with sensory perceptions at high ethanol concentrations.

7.5 Tables and Figures

Table 7.1. List of final attributes, definitions, references, reference scores, and reference preparations determined for the descriptive analysis panel on ethanol's effect on the flavor perception of rums.

Modality		Attribute	Definition	Reference	Reference Score	Preparation
Aroma		alcohol	aroma associated with ethanol	71 proof alcohol	**11.5**	10 oz. of (125 mL water + 75 ml 190 alcohol) in 2 oz. cup
	sugar	caramel	aroma of caramelized sugar	caramel sauce	**12.5**	2 g in 2 oz. cup
		maple	aroma of maple syrup	maple extract	**13.5**	1 teaspoon in 500 mL volumetric flask, dilute to volume, 10mL in 2 oz. cup
	spices	vanilla	aroma of natural vanilla extract	natural vanilla extract	**11**	1/4 teaspoon in 500 mL volumetric flask, dilute to volume, 10 mL in 2 oz. cup
	fruit	dark fruit	aroma associated with dried dark fruits	prunes	**14**	0.4 g (~1/8) prune in a 2 oz. cup
	woody	roasted	aroma of medium roasted malted barley	roasted barley	**15**	0.2 g in a 2 oz. cup
		toasted	a browned sweet aroma associated with toasted marshmallow	toasted marshmallow	**13**	preheat boiler in oven, cut marshmallow in 1/8's, toast for 30 seconds and place 1/8 marshmallow in 4 oz. cup
		woody	aroma of a wood barrel	wood chips	**10**	0.5 g in 2 oz. cup
Mouthfeel		astringent	a drying sensation in the mouth associated with a high tannin wine	over brewed green tea	**12**	steep 1 tea bag in 300 mL of boiling water for 5 minutes, place ~15mL in a 2oz cup
		silky	an uninhibited flow of liquid over the tongue, with a smooth feeling in the mouth	almond milk	**13**	~15 mL in a 2 oz. cup
		slick	a smooth tongue coating	glycerin dilution	**13.5**	20 g of glycerin + 60 g water, ~10 g in a 2 oz. cup
		warming	the increase in temperature perception in the mouth as a result of alcohol concentration	71 proof alcohol	**14**	10 oz. of (125 mL water + 75 ml 190 alcohol) in 2 oz. cup
Taste		bitter	taste associated with a caffeine solution	caffeine solution	**12.5**	1 g caffeine in 500 mL of hot water, stir until dissolved, ~15 mL in each cup
		sweet	taste associated with a sucrose solution	sugar solution	**11.5**	4 g in 200 mL of water, stir, ~15 mL per cup

Table 7.1 (cont.) List of final attributes, definitions, references, reference scores, and reference preparations determined for the descriptive analysis panel on ethanol's effect on the flavor perception of rums

Modality		Attribute	Definition	Reference	Reference Score	Preparation
Aroma by Mouth		alcohol	aroma-by-mouth associated with 40% or greater alcohol	71 proof alcohol	**14.5**	10 oz. of (125 mL water + 75 ml 190 alcohol) in 2 oz. cup
	sugar	caramel	aroma-by-mouth of caramelized sugar	caramel syrup	**10.5**	caramel solution, 10 g of caramel dissolved in 200 mL of water, ~10 mL in a 2 oz. cup. Make daily
		maple	aroma-by-mouth of maple syrup	maple extract	**12**	1 teaspoon in 500 mL volumetric flask, dilute to volume, 10mL in 2 oz. cup
	spices	vanilla	aroma-by-mouth of natural vanilla extract	vanilla extract	**12.5**	1/4 teaspoon in 500 mL volumetric flask, dilute to volume, 10 mL in 2 oz. cup
		woody	aroma-by-mouth of a woody barrel	wood chips	**10.5**	0.5 g in 2 oz. cup
Aftertaste		bitter	aftertaste associated with a caffeine solution	caffeine solution	**12.5**	1 g caffeine in 500 mL of hot water, stir until dissolved, ~15 mL in each cup
	baking spices	brown spice	aftertaste associated with brown spices such as clove, and nutmeg	nutmeg	**10**	1g in 600 mL of water, stir 5 minutes, filter, 10 mL in 2 oz. cup
		vanilla	aftertaste associated with natural vanilla extract	natural vanilla extract	**10**	1/4 teaspoon in 500 mL volumetric flask, dilute to volume, 10 mL in 2 oz. cup
		plastic	aftertaste associated with PVC plastic	shower curtain	**11**	1 in x 1 in piece, place on tongue

Table 7.2 Analysis of variance (ANOVA) F-ratios for sensory attributes rated for dilutions of Diplomatico Reserva 12-year rum[+]

Modality	Attribute	Dilution	Panelist	Rep	DxP[†]	DxR[†]	RxP[†]	Adjusted Sample F
Aroma	Alcohol	8.54**	2.16	0.12	0.81	1.33	0.12	
	Caramel	5.67*	4.18*	0.14	1.37	3.26	0.79	
	Maple	4.51*	11.48***	0.21	1.48	2.91	1.23	
	Vanilla	5.64*	5.43**	0.5	1.19	1.51	0.7	
	Dark Fruit	1.26	8.29***	0.07	0.82	0.38	0.53	
	Roasted	6.32*	8.15***	0.07	0.71	0.46	1.19	
	Toasted	2.88	2.87*	0.03	0.59	0.52	0.97	
	Woody	8.15**	6.46**	3.02	1.49	2.77	1.62	
Mouthfeel	Astringent	22.04***	5.59**	0.64	0.82	0.28	1.53	
	Silky	22.41***	6.62**	6.67*	3.94**	2.43	0.73	5.69*
	Slick	14.6***	3.81*	0.97	1.81	0.11	2.1	
	Warming	24.47***	3.09*	0.27	0.62	0.12	0.37	
Taste	Bitter	20.56***	5.9**	2.6	1.23	0.87	1.72	
	Sweet	5.31*	11.47***	5.3*	4.67**	1.68	2.69	1.14
Aftertaste	Bitter	21.35***	7.62***	1.75	0.69	1.19	0.19	
	Brown Spice	11.1**	6.32**	0	0.9	0.54	1.05	
	Vanilla	2.3	3.47*	0.1	1.02	0.44	1.01	1.69
	Plastic	7.22**	3.06*	1.56	4.28**	0.48	2.56	
Aroma-by-mouth	Alcohol	36.25***	2.81*	0.06	0.93	0.36	0.35	
	Caramel	7.43**	3.09*	0.04	0.48	0.61	1.29	
	Maple	4.65*	2.88*	2.19	0.53	0.49	0.52	
	Vanilla	3.79*	5.47**	1.51	1.59	1.92	0.59	
	Woody	4.47*	3.29*	4.18	0.72	0.17	0.25	

[+]F-rations are shown as a source of variation. *, **, *** stand for significance at $p<0.05$, $p<0.01$, and $p<0.001$ respectively.
†D x P, R x P, and D x R represent the interaction between dilution samples and panelists, replications and panelists, and dilution samples and replications, respectively.

Table 7.3 Mean intensity rating for significant aroma, mouthfeel, taste, aftertaste and aroma-by-mouth attributes of the Diplomatico Reserva 12 year rum dilution series†

Modality	Attribute	DR*	DR20*	DR40*
Aroma	Alcohol	9.44^{A}	7.94^{A}	5.19^{B}
	Caramel	10.25^{A}	8.31^{B}	7.56^{B}
	Maple	9.63^{A}	7.81^{B}	7.94^{B}
	Vanilla	10.56^{A}	8.44^{B}	8.50^{B}
	Roasted	5.00^{A}	4.88^{A}	3.19^{B}
	Woody	6.38^{A}	5.75^{A}	4.19^{B}
Mouthfeel	Astringent	9.81^{A}	9.31^{A}	5.56^{B}
	Silky	6.63^{B}	6.94^{B}	10.44^{A}
	Slick	8.13^{A}	7.00^{A}	4.56^{B}
	Warming	9.19^{A}	9.06^{A}	3.81^{B}
Taste	Bitter	8.25^{A}	8.50^{A}	4.69^{B}
Aftertaste	Bitter	9.38^{A}	9.71^{A}	5.69^{B}
	Brown Spice	8.38^{A}	7.00^{B}	5.38^{C}
Aroma-by-mouth	Alcohol	10.06^{A}	9.50^{A}	3.81^{B}
	Caramel	9.75^{A}	8.75^{A}	6.94^{B}
	Maple	8.75^{A}	$7.56^{A,B}$	6.44^{B}
	Vanilla	10.19^{A}	$9.06^{A,B}$	8.38^{B}
	Woody	6.63^{A}	6.75^{A}	4.75^{B}

†Superscripts of the same letter within an attribute indicate no significant difference by Fisher's Least Significant Difference (LSD) test at $\alpha=0.05$. *"DR" is Diplomatico Reserva straight rum, "DR20" is 1:2 dilution of Diplomatico Reserva with water to achieve 20% ABV, "DR40" is 1:2 dilution of Diplomatico Reserva with 40% ethanol to achieve 40% ABV

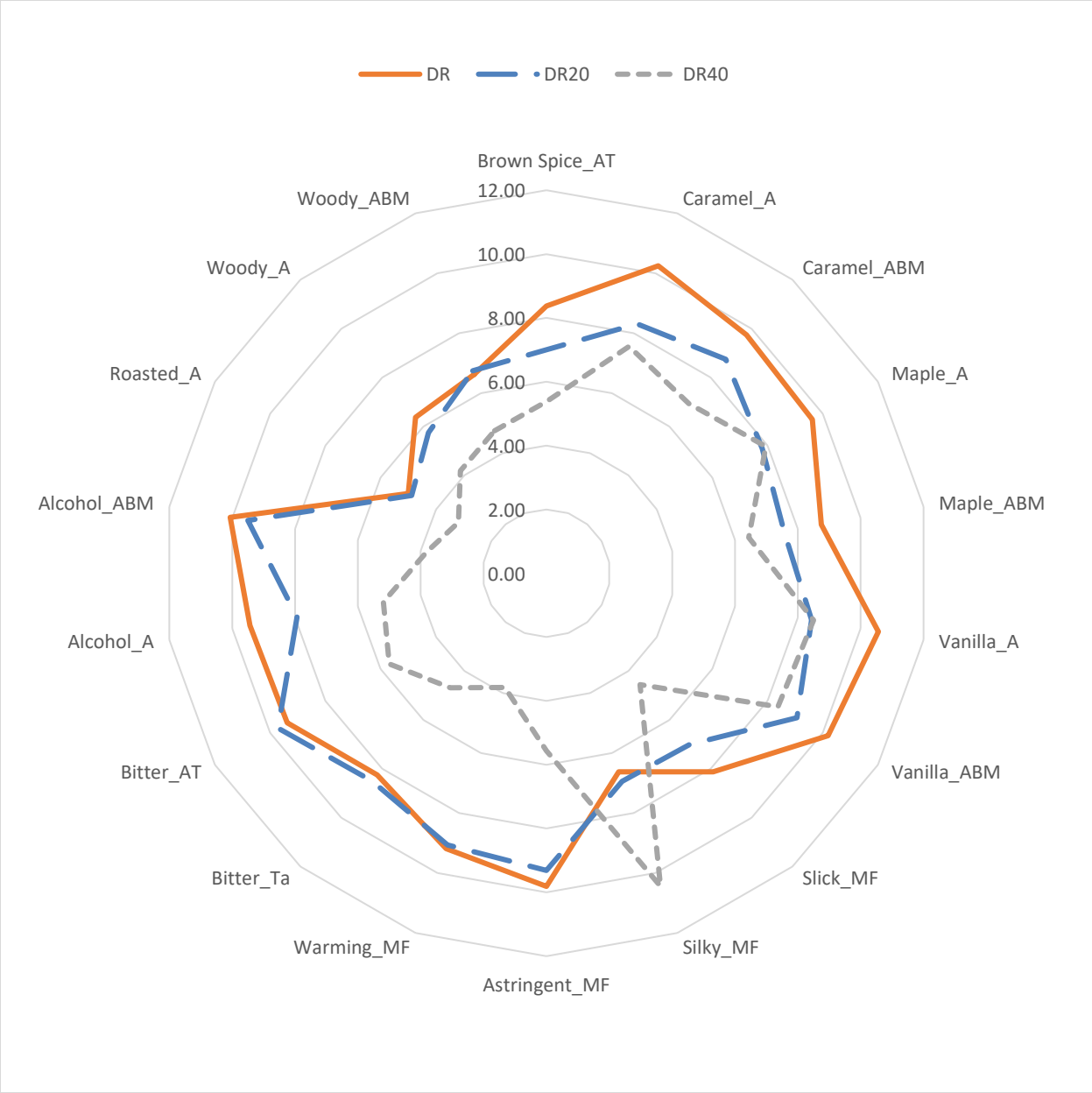


Figure 7.1 Spider plot of mean significant attribute intensities the Diplomatico Reserva 12 year rum dilution series†*

†"DR" is Diplomatico Reserva straight rum, "DR20" is 1:2 dilution of Diplomatico Reserva with water to achieve 20% ABV, "DR40" is 1:2 dilution of Diplomatico Reserva with 40% ethanol to achieve 40% ABV. * "A" is aroma, "ABM" is aroma-by-mouth, "AT" is aftertaste, "MF" is mouthfeel, "Ta" is taste.

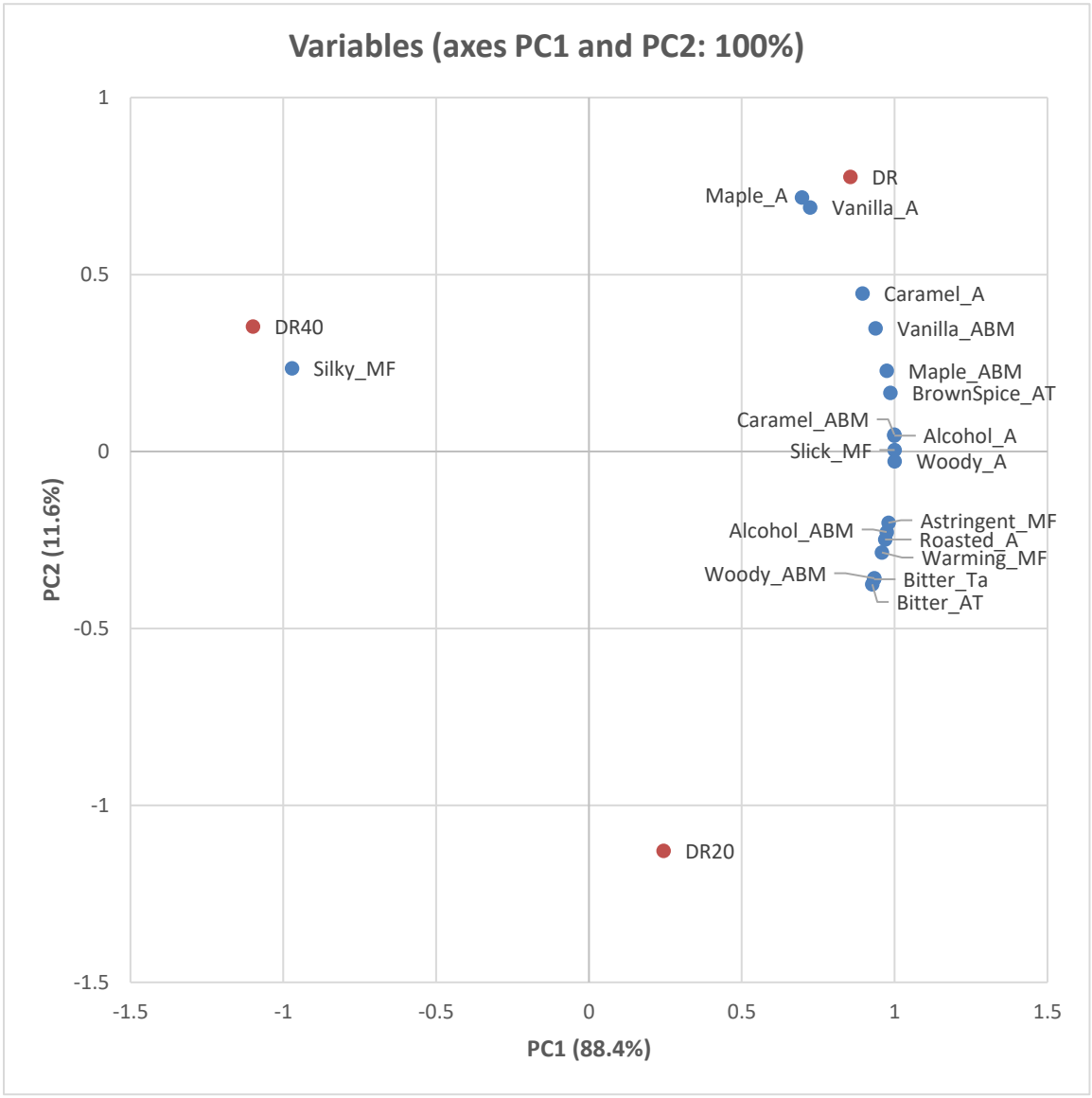


Figure 7.2 Principal component analysis biplot of significant attributes present on principal component 1 (PC1) and 2 (PC2) by the correlation matrix of mean significant attribute intensity rating across all three Diplomatico Reserva 12 year dilution samples

Table 7.4 Pearson correlation coefficients for significant attributes for DR12 dilution series samples

Attributes	Alcohol A	Caramel A	Maple A	Vanilla A	Roasted A	Woody A	Astringent MF	Silky MF	Slick MF	Warming MF
Alcohol_A	**1.000**									
Caramel_A	0.914	**1.000**								
Maple_A	0.728	0.944	**1.000**							
Vanilla_A	0.754	0.956	0.999*	**1.000**						
Roasted_A	0.956	0.756	0.496	0.530	**1.000**					
Woody_A	0.997*	0.882	0.676	0.705	0.975	**1.000**				
Astringent_MF	0.970	0.786	0.537	0.570	0.999*	0.985	**1.000**			
Silky_MF	-0.960	-0.765	-0.508	-0.541	-1.000**	-0.978	-0.999*	**1.000**		
Slick_MF	0.999*	0.897	0.699	0.727	0.968	1.000*	0.979	-0.971	**1.000**	
Warming_MF	0.945	0.730	0.462	0.497	0.999*	0.966	0.996*	-0.999*	0.957	**1.000**
Bitter_Ta	0.915	0.673	0.390	0.426	0.993	0.942	0.986	-0.991	0.931	0.997
Bitter_AT	0.909	0.662	0.376	0.412	0.991	0.937	0.984	-0.989	0.925	0.995
BrownSpice_AT	0.993	0.956	0.806	0.828	0.914	0.981	0.932	-0.919	0.987	0.898
Alcohol_ABM	0.963	0.770	0.515	0.548	1.000*	0.980	1.000*	-1.000**	0.973	0.998*
Caramel_ABM	1.000**	0.915	0.730	0.756	0.956	0.997	0.969	-0.960	0.999*	0.944
Maple_ABM	0.983	0.973	0.842	0.862	0.886	0.967	0.908	-0.893	0.975	0.868
Vanilla_ABM	0.952	0.994	0.903	0.919	0.821	0.928	0.848	-0.829	0.939	0.799
Woody_ABM	0.917	0.675	0.393	0.429	0.993	0.943	0.987	-0.992	0.932	0.997*

Table 7.4 (cont.) Pearson correlation coefficients for significant attributes for DR12 dilution series samples

Attributes	Bitter T	Bitter AT	BrownSpice AT	Alcohol ABM	Caramel ABM	Maple ABM	Vanilla ABM	Woody ABM
Alcohol_A								
Caramel_A								
Maple_A								
Vanilla_A								
Roasted_A								
Woody_A								
Astringent_MF								
Silky_MF								
Slick_MF								
Warming_MF								
Bitter_Ta	**1**							
Bitter_AT	1.000**	**1**						
BrownSpice_AT	0.85969	0.85177	**1**					
Alcohol_ABM	0.99025	0.988	0.92246	**1**				
Caramel_ABM	0.91416	0.90784	0.99296	0.96171	**1**			
Maple_ABM	0.82546	0.81672	0.998*	0.89604	0.98341	1		
Vanilla_ABM	0.7486	0.73836	0.98224	0.83365	0.9531	0.99219	**1**	
Woody_ABM	1.000**	1.000*	0.86116	0.99065	0.91532	0.82708	0.7505	**1**

*, **, *** stand for significance at $p<0.05$, $p<0.01$, and $p<0.001$ respectively.

Table 7.5 Analysis of variance (ANOVA) F-ratios for sensory attributes rated for dilutions of Ron Abuelo 7 year rum[+]

Modality	Attribute	Dilution	Panelist	Rep	DxP[†]	DxR[†]	RxP[†]	Adjusted Sample F
Aroma	Alcohol	40.85***	8.71***	0.23	2.03	1.22	2.37	
	Caramel	5.94*	11.54***	0.81	1.20	0.15	1.08	
	Maple	3.66	8.94***	1.06	0.94	0.67	2.30	
	Vanilla	5.36*	8.96***	2.64	1.37	1.48	1.10	
	Dark Fruit	3.98*	12.04***	0.16	1.48	0.66	0.80	
	Roasted	2.38	4.15*	0.52	1.42	0.51	1.68	
	Toasted	0.72	15.38***	5.56***	4.18**	1.17	1.58	0.17
	Woody	0.18	9.18***	4.61***	1.94	0.08	1.89	
Mouthfeel	Astringent	15.17***	15.17***	0.24	1.56	0.47	2.18	
	Silky	10.09***	6.85***	1.04	3.19***	2.01	1.18	3.17
	Slick	20.36***	7.36***	0.51	2.96*	4.44*	2.68	6.87**
	Warming	59.21***	11.57***	0.06	1.17	1.20	3.02***	
Taste	Bitter	49.87***	13.75***	0.08	0.78	0.84	6.62***	
	Sweet	3.60	7.58***	6.62*	3.26*	1.00	4.73**	1.11
Aftertaste	Bitter	29.14***	11.98***	2.28	1.11	0.77	2.30	
	Brown Spice	11.79**	5.91**	2.51	1.53	0.01	1.25	
	Vanilla	5.62*	11.8***	0.34	1.80	0.26	1.28	
	Plastic	4.34*	12.72***	6.42*	2.23	3.26	3.38*	
Aroma-by-mouth	Alcohol	47.80***	7.54***	2.29	0.57	1.37	0.66	
	Caramel	16.90***	9.47***	0.01	2.08	1.50	0.37	
	Maple	26.65***	17.89***	1.18	3.41*	0.68	3.72*	7.81**
	Vanilla	23.49***	33.16***	1.20	2.58*	0.93	1.57	9.10**
	Woody	1.56	13.48***	0.38	1.77	0.43	0.78	

[+]F-rations are shown as a source of variation. *, **, *** stand for significance at $p<0.05$, $p<0.01$, and $p<0.001$ respectively.
†D x P, R x P, and D x R represent the interaction between dilution samples and panelists, replications and panelists, and dilution samples and replications, respectively.

Table 7.6 Mean intensity rating for significant aroma, mouthfeel, taste, aftertaste and aroma-by-mouth attributes of the Ron Abuelo 7 year rum dilution series†

Modality	Attribute	RA*	RA20	RA40
Aroma	Alcohol	9.63^{A}	7.94^{B}	4.88^{C}
	Caramel	8.13^{A}	7.31^{A}	5.81^{B}
	Vanilla	8.44^{A}	$7.50^{A,B}$	6.19^{B}
	Dark Fruit	7.13^{A}	5.13^{B}	5.50^{B}
Mouthfeel	Astringent	10.25^{A}	8.81^{B}	4.75^{C}
	Slick	6.63^{A}	5.75^{A}	3.13^{B}
	Warming	9.63^{A}	9.06^{A}	3.63^{B}
Taste	Bitter	9.06^{A}	8.38^{A}	4.13^{B}
Aftertaste	Bitter	10.25^{A}	9.06^{A}	6.00^{B}
	Brown Spice	7.56^{A}	7.13^{A}	5.63^{B}
	Vanilla	7.06^{A}	$6.25^{A,B}$	5.31^{B}
	Plastic	4.94^{A}	$4.50^{A,B}$	3.44^{B}
Aroma-by-mouth	Alcohol	10.81^{A}	9.38^{A}	3.94^{B}
	Caramel	8.44^{A}	7.06^{B}	5.06^{C}
	Maple	8.06^{A}	7.19^{B}	5.38^{C}
	Vanilla	8.63^{A}	7.19^{B}	5.75^{C}

†Superscripts of the same letter within an attribute indicate no significant difference by Fisher's Least Significant Difference (LSD) test at $\alpha=0.05$. *"RA" is Ron Abuelo 7 year straight rum, "RA20" is 1:2 dilution of Ron Abuelo 7 year with water to achieve 20% ABV, "RA40" is 1:2 dilution of Ron Abuelo 7 year with 40% ethanol to achieve 40% ABV.

Figure 7.3 Spider plot of mean significant attribute intensities the Ron Abuelo 7 year rum dilution series†*

†"RA" is Ron Abuelo 7 year straight rum, "RA20" is 1:2 dilution of Ron Abuelo 7 year with water to achieve 20% ABV, "RA40" is 1:2 dilution of Ron Abuelo 7 year with 40% ethanol to achieve 40% ABV. * "A" is aroma, "ABM" is aroma-by-mouth, "AT" is aftertaste, "MF" is mouthfeel, "Ta" is taste.

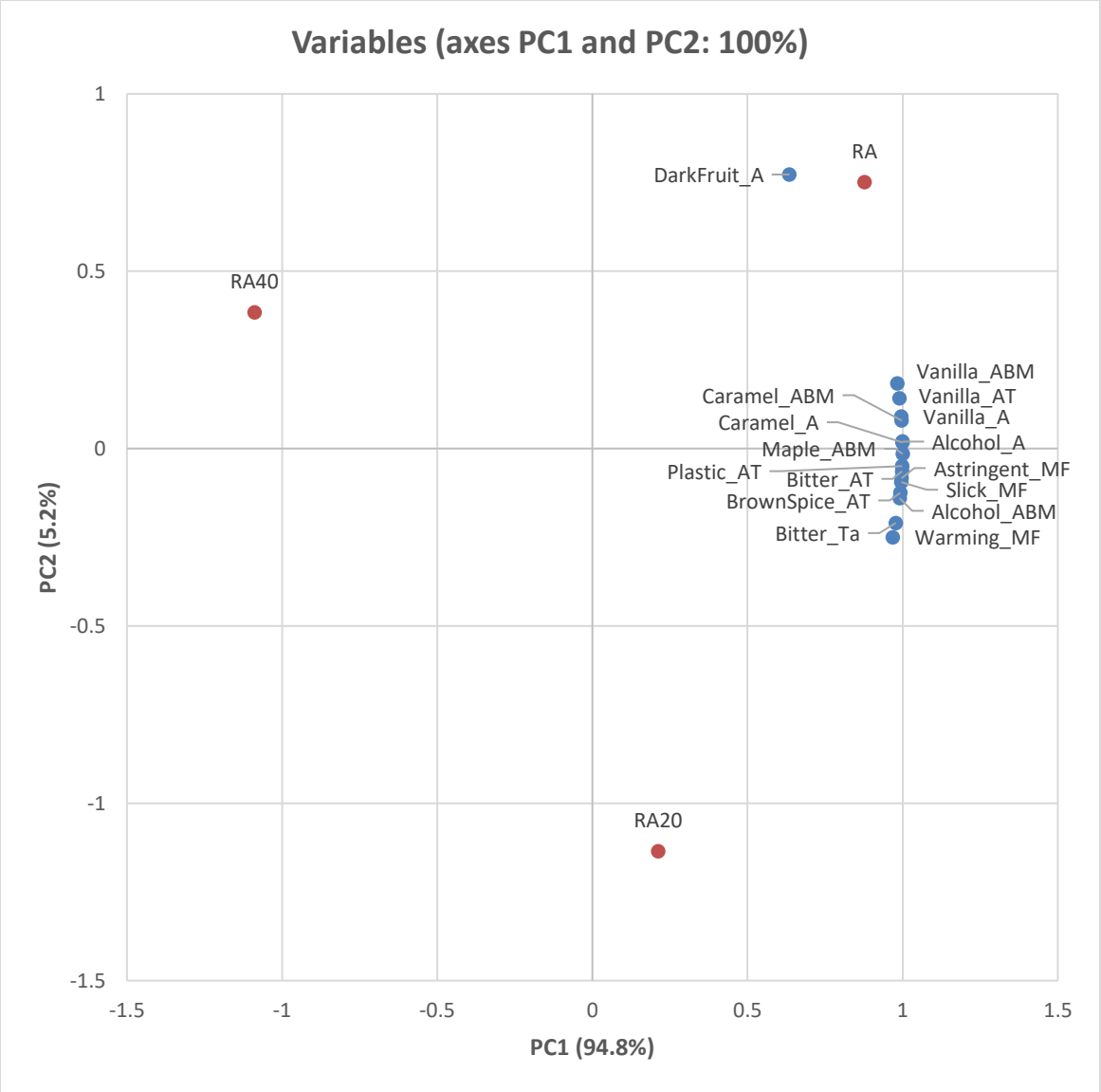


Figure 7.4 Principal component analysis biplot of significant attributes present on principal component 1 (PC1) and 2 (PC2) by the correlation matrix of mean significant attribute intensity rating across all three Ron Abuelo 7 year dilution samples

Table 7.7 Pearson correlation coefficients for significant attributes for RA7 dilution series samples

Attributes	Alcohol A	Caramel A	Vanilla A	DarkFruit A	Astringent MF	Slick MF	Warming MF	Bitter T	Bitter AT	BrownSpice AT
Alcohol_A	**1.000**									
Caramel_A	1.000**	**1.000**								
Vanilla_A	0.998*	0.997*	**1.000**							
DarkFruit_A	0.650	0.648	0.702	**1.000**						
Astringent_MF	0.995	0.995	0.985	0.568	**1.000**					
Slick_MF	0.993	0.994	0.983	0.559	1.000**	**1.000**				
Warming_MF	0.963	0.964	0.942	0.421	0.986	0.988	**1.000**			
Bitter_Ta	0.973	0.974	0.955	0.459	0.992	0.993	0.999*	**1.000**		
Bitter_AT	0.996	0.997	0.988	0.584	1.000*	1.000	0.982	0.989	**1.000**	
BrownSpice_AT	0.990	0.990	0.977	0.533	0.999*	1.000*	0.992	0.996	0.998*	**1.000**
Vanilla_AT	0.993	0.992	0.999*	0.738	0.975	0.972	0.923	0.938	0.979	0.965
Plastic_AT	0.998*	0.998*	0.990	0.596	0.999*	0.999*	0.979	0.987	1.000**	0.997*
Alcohol_ABM	0.987	0.988	0.974	0.520	0.998*	0.999*	0.994	0.997*	0.997*	1.000**
Caramel_ABM	0.998*	0.998*	1.000**	0.694	0.987	0.985	0.945	0.958	0.990	0.979
Maple_ABM	0.999*	0.999*	0.994	0.623	0.998*	0.997	0.972	0.981	0.999*	0.994
Vanilla_ABM	0.986	0.986	0.996	0.766	0.964	0.961	0.906	0.923	0.969	0.952

Table 7.7 (cont.) Pearson correlation coefficients for significant attributes for RA7 dilution series samples

Attributes	Vanilla AT	Plastic AT	Alcohol ABM	Caramel ABM	Maple ABM	Vanilla ABM
Alcohol_A						
Caramel_A						
Vanilla_A						
DarkFruit_A						
Astringent_MF						
Slick_MF						
Warming_MF						
Bitter_Ta						
Bitter_AT						
BrownSpice_AT						
Vanilla_AT	**1.000**					
Plastic_AT	0.982	**1.000**				
Alcohol_ABM	0.960	0.996	**1.000**			
Caramel_ABM	0.998*	0.992	0.976	**1.000**		
Maple_ABM	0.988	0.999*	0.992	0.996	**1.000**	
Vanilla_ABM	0.999*	0.973	0.948	0.994	0.980	**1.000**

*, **, *** stand for significance at $p<0.05$, $p<0.01$, and $p<0.001$ respectively

7.6 References

Athès, V., Pena-Lillo, M., Bernard, C., Perez-Correa, R., & Souchon, I. (2004). Comparison of Experimental Methods for Measuring Infinite Dilution Volatilities of Aroma Compounds in Water/Ethanol Mixtures. *Journal of Agricultural and Food Chemistry*, *52*, 2021–2027.

Aznar, M., Tsachaki, M., Linforth, R. S. T., Ferreira, V., & Taylor, A. J. (2004). Headspace analysis of volatile organic compounds from ethanolic systems by direct APCI-MS. *International Journal of Mass Spectrometry*, *239*, 17–25. http://doi.org/10.1016/j.ijms.2004.09.001

Boothroyd, E. L., Linforth, R. S. T., & Cook, D. J. (2012). Effects of Ethanol and Long-Chain Ethyl Ester Concentrations on Volatile Partitioning in a Whisky Model System. *Journal of Agricultural and Food Chemistry*, *60*, 9959–9966. http://doi.org/10.1021/jf3022892

Cipiciani, A., Onori, G., & Savelli, G. (1988). Structural Properties of Water-Ethanol Mixtures: A Correlation with the Formation of Micellar Aggregates. *Chemical Physics Letters*, *143*(5), 505–509.

Conner, J. M., Birkmyre, L., Paterson, A., & Piggott, J. R. (1998). Headspace Concentrations of Ethyl Esters at Different Alcoholic Strengths. *Journal of the Science of Food and Agriculture*, *77*, 121–126.

D'Angelo, M., Onori, G., & Santucci, A. (1994a). Self-Association Behaviour of Alcohols in Diluted Aqueous Solutions. *Il Nuovo Cimento D*, *16*(9), 1499–1514. http://doi.org/10.1007/BF02462035

D'Angelo, M., Onori, G., & Santucci, A. (1994b). Self-Association of Monohydric Alcohols in Water: Compressibility and Infrared Absorption Measurements. *The Journal of Chemical Physics*, *100*(4), 3107–3113. http://doi.org/10.1063/1.466452

Demiglio, P., & Pickering, G. J. (2008). The influence of ethanol and pH on the taste and mouthfeel sensations elicited by red wine. *Journal of Food, Agriculture and Environment*, *6*(3–4), 143–150.

Escalona-Buendia, H., Piggott, J. R., Conner, J. M., & Paterson, A. (1998). Effect of ethanol strength on the release of higher alcohols and aldehydes in model solutions. *Developments in Food Science*, *40*(C), 615–620.

Escudero, A., Campo, E., Fariña, L., Cacho, J., & Ferreira, V. (2007). Analytical Characterization of the Aroma of Five Premium Red Wines. Insights into the Role of Odor Families and the Concept of Fruitiness of Wines. *Journal of Agricultural and Food Chemistry*, *55*, 4501–4510. http://doi.org/10.1021/jf0636418

Fontoin, H., Saucier, C., Teissedre, P. L., & Glories, Y. (2008). Effect of pH, ethanol and acidity on astringency and bitterness of grape seed tannin oligomers in model wine solution. *Food Quality and Preference*, *19*(3), 286–291. http://doi.org/10.1016/j.foodqual.2007.08.004

Franks, F., & Ives, D. J. G. (1966). The Structural Properties of Alcohol-Water Mixtures. *Quarterly Reviews*, 1–44.

Goldner, M. C., Zamora, M. C., Di Leo Lira, P., Gianninoto, H., & Bandoni, A. (2009). Effect of Ethanol Level in the Perception of Aroma Attributes and the Detection of Volatile Compounds in Red Wine. *Journal of Sensory Studies*, *24*(2), 243–257. http://doi.org/10.1111/j.1745-459X.2009.00208.x

Guth, H. (1998). Comparison of Different White Wine Varieties in Odor Profiles by Instrumental Analysis and Sensory Studies. *ACS Symposium Series*, *714*, 39–52. Retrieved from http://www.scopus.com/inward/record.url?eid=2-s2.0-0347804788&partnerID=40&md5=d77c8f8f9d686ec570e3e57b7c623e13

Jolliffe, I. (2014). Principal component analysis. In *Wiley StatsRef: Statistics Reference Online* (pp. 1–5).

Jones, P. R., Gawel, R., Francis, I. L., & Waters, E. J. (2008). The influence of interactions between major white wine components on the aroma, flavour and texture of model white wine. *Food Quality and Preference*, *19*(6), 596–607. http://doi.org/10.1016/j.foodqual.2008.03.005

King, E. S., Dunn, R. L., & Heymann, H. (2013). The influence of alcohol on the sensory perception of red wines. *Food Quality and Preference*, *28*(1), 235–243. http://doi.org/10.1016/j.foodqual.2012.08.013

Lawless, H. T., & Heymann, H. (1999a). Data Relationships and Multivariate Applications. In *Sensory Evaluation of Food: Principles and Practices* (pp. 585–601). New York: SPRINGER SCIENCE+BUSINESS MEDIA, LLC.

Lawless, H. T., & Heymann, H. (1999b). Descriptive analysis. In *Sensory Evaluation of Food: Principles and Practices* (pp. 227–257). New York: SPRINGER SCIENCE+BUSINESS MEDIA, LLC. http://doi.org/10.1007/978-1-4419-6488-5

Le Berre, E., Atanasova, B., Langlois, D., Etiévant, P., & Thomas-Danguin, T. (2007). Impact of ethanol on the perception of wine odorant mixtures. *Food Quality and Preference*, *18*(6), 901–908. http://doi.org/10.1016/j.foodqual.2007.02.004

Marangoni, C. (1865). *On the expansion of a drop of liquid floating on the surface of another liquid*. University of Pavia, Pavia, Italy.

Meilgaard, M., Civille, G. V., & Carr, B. T. (2007). The Spectrum Descriptive Analysis Method. In *Sensory Evaluation Techniques* (Fourth Edi, pp. 189–254). Boca Raton, FL: CRC Press/Taylor & Francis.

Munoz, A. M., & Civille, G. (1992). The Spectrum Descriptive Analysis Method. In R. C. Hootman (Ed.), *Manual on Descriptive Analysis Testing for Sensory Evaluation* (pp. 22–34). Baltimore, MD: American Society for Testing and Materials.

Nolden, A. A., & Hayes, J. E. (2015). Perceptual Qualities of Ethanol Depend on Concentration, and Variation in These Percepts Associates with Drinking Frequency. *Chemosensory Perception*, *8*(3), 149–157. http://doi.org/10.1007/s12078-015-9196-5

Nurgel, C., & Pickering, G. (2006). Modeling of sweet, bitter and irritant sensations and their interactions elicited by model ice wines. *Journal of Sensory Studies*, *21*, 505–519.

Onori, G., & Santucci, A. (1996). Dynamical and structural properties of water/alcohol mixtures. *Journal of Molecular Liquids*, *69*, 161–181.

Parke, S. A., & Birch, G. G. (1999). Solution Properties of Ethanol in Water. *Food Chemistry*, *67*, 241–246.

Petrillo, C., Onori, G., & Sacchetti, F. (1989). Hydration structure of ethanol water solution at low alcohol concentration. *Molecular Physics*, *67*(3), 697–705. http://doi.org/10.1080/00268978900101381

Rayleigh, Lord. (1916). LIX. On convection currents in a horizontal layer of fluid, when the higher

temperature is on the under side. *Philosophical Magazine*, *32*(192), 529–546. http://doi.org/10.1080/14786441608635602

Smith, G. D., & Roskrow, D. (2012). *Whiskeyopus*. New York: DK Publishing.

Stone, H. (1992). Quantitative Descriptive Analysis. In R. C. Hootman (Ed.), *Manual on Descriptive Analysis Testing for Sensory Evaluation* (pp. 15–21). Baltimore, MD: American Society for Testing and Materials.

Stone, H., & Sidel, J. L. (1993). Descriptive Analysis. In S. L. Taylor (Ed.), *Sensory Evaluation Practices* (2nd ed., pp. 202–242). San Diego: Academic Press Inc.

Stone, H., Sidel, J. L., Oliver, S., Woolsey, A., & Singleton, R. (1974). Sensory Evaluation by Quantitative Descriptive Analysis. *Food Technology*, *8*(1), 24–32. http://doi.org/10.1002/9780470385036.ch1f

Taylor, A. J., Tsachaki, M., Lopez, R., Morris, C., Ferreira, V., & Wolf, B. (2010). Odorant Release from Alcoholic Beverages. *ACS Symposium Series*, *1036*, 161–175. http://doi.org/10.1021/bk-2010-1036.ch012

Tsachaki, M., Aznar, M., Linforth, R. S. T., & Taylor, A. J. (2006). Dynamics of flavour release from ethanolic solutions. *Developments in Food Science*, *43*, 441–444. http://doi.org/10.1016/S0167-4501(06)80104-4

Tsachaki, M., Gady, A.-L., Kalopesas, M., Linforth, R. S. T., Athès, V., Marin, M., & Taylor, A. J. (2008). Effect of Ethanol, Temperature, and Gas Flow Rate on Volatile Release from Aqueous Solutions under Dynamic Headspace Dilution Conditions. *Journal of Agricultural and Food Chemistry*, *56*, 5308–5315. http://doi.org/10.1021/jf800225y

Tsachaki, M., Linforth, R. S. T., & Taylor, A. J. (2005). Dynamic Headspace Analysis of the Release of Volatile Organic Compounds from Ethanolic Systems by Direct APCI-MS. *Journal of Agricultural and Food Chemistry*, *53*, 8328–8333. http://doi.org/10.1021/jf051202n

Tsachaki, M., Linforth, R. S. T., & Taylor, A. J. (2009). Aroma Release from Wines under Dynamic Conditions. *Journal of Agricultural and Food Chemistry*, *57*(15), 6976–6981. http://doi.org/10.1021/jf901174y

Wakisaka, A., Komatsu, S., & Usui, Y. (2001). Solute-solvent and solvent-solvent interactions evaluated through clusters isolated from solutions: Preferential solvation in water-alcohol mixtures. *Journal of Molecular Liquids*, *90*, 175–184. http://doi.org/10.1016/S0167-7322(01)00120-9

Williams, A. A. (1972). Flavour Effects of Ethanol in Alcoholic Beverages. *The Flavour Industry*, *3*(12), 604–607.

Zamora, M. C., Goldner, M. C., & Galmarini, M. V. (2006). Sourness - Sweetness Interactions in Different Media: White Wine, Ethanol and Water. *Journal of Sensory Studies*, *21*, 601–611. http://doi.org/10.1111/j.1745-459X.2006.00085.x

Chapter 8: Summary, Conclusions, and Future Research

Rum is one of the most diverse distilled spirits on the market. The breadth of variation within the rum category makes it difficult to ascertain the key odor-active compounds that define rum flavor. The goal of this study was to gain a better understanding of rum flavor through analytical and sensory evaluation of mixing and premium aged rums. The central hypothesis of this study was that premium aged rums, while produced using a variety of methods, still have a defining set of aroma characteristics caused by a unique combination of flavor compounds that set these rums apart from those of lower quality, or so-called mixing rums, and that ethanol concentration plays an important role in the perception of overall rum flavor.

Identification of the odor-active compounds in the nine rums by gas chromatography-olfactometry (GCO) and GC-mass spectrometry (GC-MS) analysis yielded 59 odor-active regions containing 64 odor-active compounds. Aroma extract dilution analysis (AEDA) provided a ranking of the potency of odorants. Acetal (melon), 2-/3-methyl-1-butanol (chocolate), β-damascenone (applesauce), 2-phenethyl alcohol (roses), *cis*-whiskey lactone/4-methylguaiacol (sweet, coconut-like), eugenol (spicy, clove), sotolon (curry, maple-like), syringol (smoky, spicy), (*E*)-isoeugenol (floral, cloves), vanillin (vanilla, sweet-like), ethyl vanillate (vanilla, sweet aromatic), and syringaldehyde (vanilla) were the most potent odorants across all rums. Comparison of mixing and premium rums indicated that they contained many of the same compounds, but generally present at lower potency in mixing rums. Premium rums contained additions compounds that were not detected in the mixing rums. Fourteen unknown odor-active regions were identified by GCO. Future research should focus on identification of these unknowns, particularly unknown 59 (Wax RI-2951, campfire) as it was identified in all nine rums and may contribute to the smoky and woody perception of rums.

Thirty-four of the compounds identified by GCO and AEDA were quantitated by stable isotope dilution analysis. Quantitation results revealed the same compounds to be present in all rums samples with the exception of 4-ethylguaiacol and eugenol in BW and ethyl vanillin which was only detected in DR12 and DX. The mixing rums, BW and BG, and DX were found to have the lowest concentrations of all compounds quantitated in the rums. Concentrations were converted to odor activity values (OAVs) to gain a better understanding of the importance of the compounds to the

overall aroma of the rum. Twenty-six compounds were found to have OAVs >1 in at least one rum. Fifteen compounds had OAVs >1 in all nine samples including 2-methylpropanal, acetal, 3-methylbutanal, 2-methylbutanal, ethyl 2-methylpropanoate, ethyl butanoate, ethyl 2-methylbutanoate, ethyl 3-methylbutanoate, 3-methyl-1-butanol, 2-methyl-1-butanol, ethyl hexanoate, β-damascenone, guaiacol, *cis*-whiskey lactone, and vanillin. Several low potency odorants identified by GCO were not quantitated due to time limitations. Quantitation of these compounds should be the focus of future studies, particularly 1-octen-3-one, ethyl cyclohexanecarboxylate, methional, (*Z*)-2-nonenal, 3-methylbutyric acid, 4-propylguaiacol, and sotolon.

A run flavor lexicon wax created to characterize the sensory differences among rum products. Web-based materials were used to gather the terms for the lexicon to minimize the time and cost and allow for the inclusion of a greater number of rums. This was the first lexicon developed using this methodology. The final lexicon consisted of 147 terms sorted into 22 categories

Descriptive sensory analysis was then conducted to verify the rum flavor lexicon and quantitate the sensory differences between nine rums previously evaluated by analytical measures. Thirty-three of the thirty-eight terms used to evaluate the rums were found on the flavor wheel, validating that the lexicon contained terms relevant to the sensory evaluation of rums. The additional five terms generated during the panel demonstrate that the lexicon will need to be updated over time, which is typical of other lexicons that have been developed for beer, wine, and coffee.

Twenty-three sensory attributes were found to be significantly different among the rums. Two rums, DX and DR12, were found to be significantly different from the other seven rums, having higher intensity ratings for brown sugar, caramel, vanilla and chocolate aroma, caramel, maple and vanilla aroma-by-mouth, and caramel aftertaste. Sensory profiles of the other seven rums were very similar to each other. Lack of differences observed between the other seven rums is likely a result of panelists not using the entire scale, improper scoring of references, as well as sensory fatigue. Additionally, several terms characterized different but similar attributes in rums such as caramel, vanilla, and maple aroma that followed similar intensity ratings among rum samples. Future studies on rum should focus on the evaluation of fewer attributes that characterize the largest differences among rums. Terms that evaluate similar attributes should be reduced, allowing panelists to better focus on the other sensory changes among rums. Additionally, panelists may be able to better

identify the difference among the rums if they were evaluated at 20% ABV rather than 40% ABV to reduce ethanol pungency and sensory fatigue.

Descriptive sensory evaluation was also conducted to gain insight into the effect of ethanol on flavor perception. Two rums, RA7 and DR12, were evaluated at three different dilution levels: straight rum, 1:2 dilution with water, and a 1:2 dilution with 40%ABV. Dilutions of rum with water, while hypothesized to alter the flavor profile of rum, yielded similar profiles to straight rum, except with slightly lower attribute intensity ratings. However, dilution with 40% ethanol did significantly change the profile of rum and also had the lowest intensity rating in the dilution series for most attributes. This study validates the typical practice in the whiskey and rum industry of diluting samples to 20-23% for blending and evaluation. Further sensory studies are needed to further explore the effects of ethanol concentration on sensory perceptions. This study only focused on two levels of ethanol, 20% ABV and 40%ABV, where the concentrations of the aroma compounds were cut in half in both dilutions relative to the straight rum. Creation of an accurate rum model system would allow researchers to account for sensory changes caused by dilution of both ethanol and the aroma constituents, as models could also be constructed that where two samples had the same concentration of compounds and only differed in ethanol concentration rather than evaluation the dilution of an actual rum as in the present study. Corresponding analytical studies following the same samples should be included as well, primarily focusing on the release of compounds into the headspace under dynamic conditions. Additional ethanol concentrations should be evaluated in the future as well.

Finally, chemometric analysis was conducted to correlate the sensory and analytical data using principal component analysis. Correlations between sensory evaluations, quantitation and OAV data explained the most variation between rums, accounting for 68.6 % and 65.5% respectively. Results indicate the changes in vanilla, caramel, maple and chocolate aromas are driven by vanillin and ethyl vanillin. Additionally, roasted aroma is defined by an absence of compounds rather than increases in concentration of any particular compounds. Overall, the correlations between sensory and quantitative data did not identify as many correlations as originally thought. The lack of significant correlations may be due to the minimal aroma differences perceived among the seven rums not high in the sweet aroma sensory attributes. A more in-depth sensory analysis focusing on the difference among rums other than sweet aroma attributes may aid in the identification of more analytical and sensory relationships. Additionally, only nine rums were evaluated which is much lower than the

total number of variables used for the correlation. The inclusion of a greater variety and number of rums may provide deeper insights.

In conclusion, the main differences between mixing and premium rums is the concentrations of compounds, with mixing rums having lower concentrations of all compounds. This is reflected in the similar aroma profiles obtained for the mixing and premium rums through descriptive analysis. Rums that contained added ethyl vanillin, DR12 and DX, had higher perceptions of sweet-like aroma and aroma-by-mouth attributes. Differences in concentration and ratios of compounds relative to each other seem to be the driving forces behind the difference in flavor perception among rums.

Future research is needed to characterize the compounds responsible for the distinct "rummy" perception of rums. Rum contains many of the same compounds as other distilled spirits such as whiskey, and a more in-depth analysis of rums high in "rummy" perception is needed. The creation of an accurate rum model system would aid in the evaluation of both the effects of ethanol on flavor perception and the importance of the identified compounds to overall rum flavor, specifically what compounds characterize "rummy" flavor.

Finally, we are still only analyzed a relatively small subset of rums. The increased number of samples compared to previous studies has allowed greater insight into the compounds that are significant aroma contributors across all rums. However, compounds that may be present only in the lower dilutions in these samples may be more important to other brands of rum. A broader study of all types of rums is needed. A preliminary sensory evaluation and sorting exercise of a larger variety of rum samples using techniques such as Napping to identify similar types of rums could be employed. Selection of one rum from each category could then be subject to sensory and analytical evaluation to provide greater insight into the differences among rums across the class.

Appendix A: Standard curves

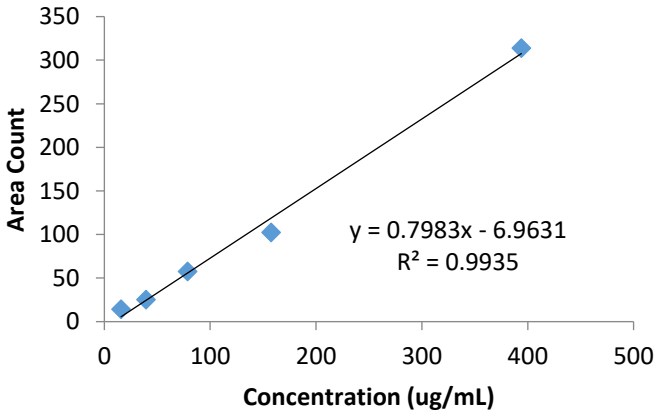
Response Factor of acetaldehyde

Standard:	acetaldehyde
CAS:	75-07-0
Mfg/Reference:	Sigma-Aldrich, St. Louis, MO
No.:	627
% Purity (by GC-FID):	99.9%

Standard Curve

acetaldehyde (density g/mL)	0.788
retention time (min)	2.12

	Concentration ug/mL	Area
2uL 1:100 dilution 40ABV	15.76	14.3
5uL 1:100 dilution 40ABV	39.4	25.2
10uL 1:100 dilution 40ABV	78.8	57.3
2uL 1:10 dilution 40ABV	157.6	102.1
5uL 1:10 dilution 40ABV	394	313.6



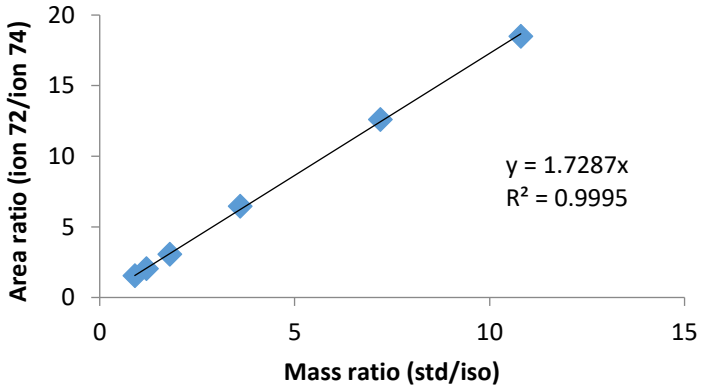
slope	Rf
0.7983	1.253

Response Factor of d_2-2-methylpropanal

	Isotope	Unlabeled
Standard:	d_2-2-methylpropanal	2-methylpropanal
CAS:	N/A	78-84-2
Mfg/Reference:	synthesized	Aldrich, Milwaukee, WI
No.:	ISO-159	858
% Purity (by GC-FID):	N/A	99.3%

Standard Curve

selected ion mass ratio	unlabeled 72	labeled 74	area ratio
10.8	358925	19428	18.5
7.2	242780	19324	12.6
3.6	127238	19701	6.46
1.8	138396	45065	3.07
1.2	124167	60586	2.05



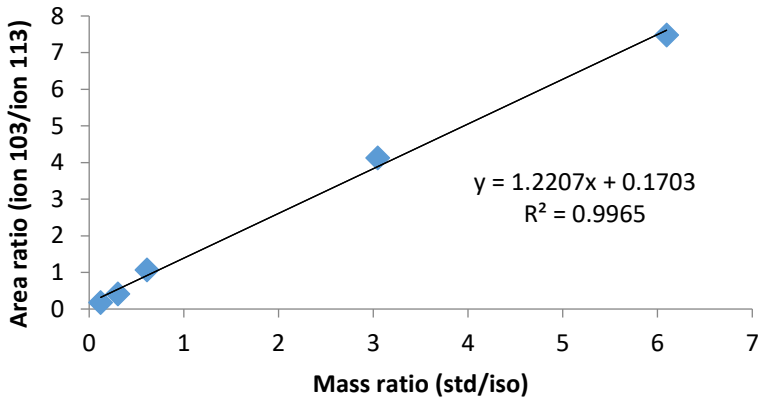
slope	Rf
1.7287	0.579

Response Factor of d_{10}-acetal

	Isotope	Unlabeled
Standard:	d_{10}-acetal	acetal
CAS:	N/A	105-57-7
Mfg/Reference:	synthesized	Acros Organics, NJ
No.:	N/A	9
% Purity (by GC-FID):	N/A	98.88%

Standard Curve

selected ion mass ratio	unlabeled 103	labeled 113	area ratio
0.122	73612	412802	0.178
0.305	147584	358468	0.412
0.609	115742	108059	1.071
3.047	1450470	351010	4.132
6.095	3759819	502441	7.483



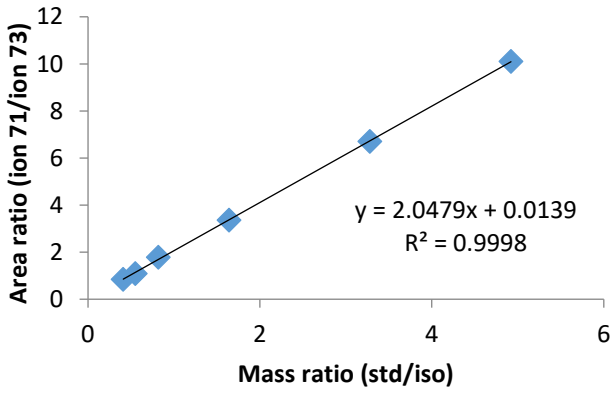
slope	Rf
1.2207	0.518

Response Factor of d_2-3-methylbutanal

	Isotope	Unlabeled
Standard:	d_2-3-methylbutanal	3-methylbutanal
CAS:	N/A	590-86-3
Mfg/Reference:	synthesized	Sigma-Aldrich, St. Louis, MO
No.:	N/A	859
% Purity (by GC-FID):	N/A	91.4%

Standard Curve

selected ion mass ratio	unlabeled 71	labeled 73	area ratio
4.920	8014	80562	10.100
3.280	7920	53170	6.710
1.640	10195	34214	3.360
0.820	23412	41725	1.780
0.550	30803	33474	1.090



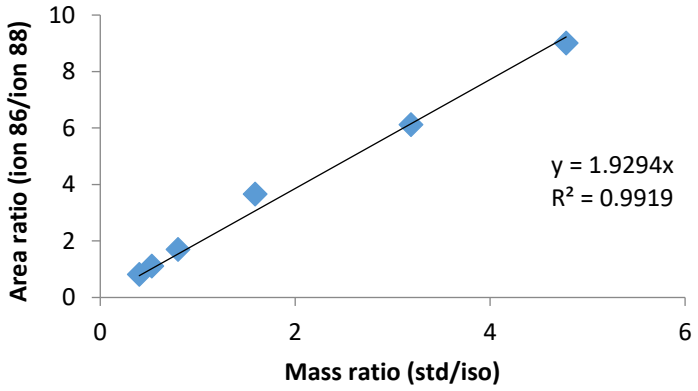
slope	Rf
2.0479	0.488

Response Factor of d_2-2-methylbutanal

	Isotope	Unlabeled
Standard:	d_2-2-methylbutanal	2-methylbutanal
CAS:	N/A	96-17-3
Mfg/Reference:	synthesized	Bedoukian, Danbury, CT
No.; Catalog#; Batch#/Lot#:	N/A	1163
% Purity (by GC-FID):	N/A	99.1%

Standard Curve

selected ion mass ratio	unlabeled 86	labeled 88	area ratio
4.78	34323	3811	9.01
3.19	21287	3481	6.12
1.59	15324	4190	3.66
0.8	16128	9473	1.7
0.53	13548	12181	1.11



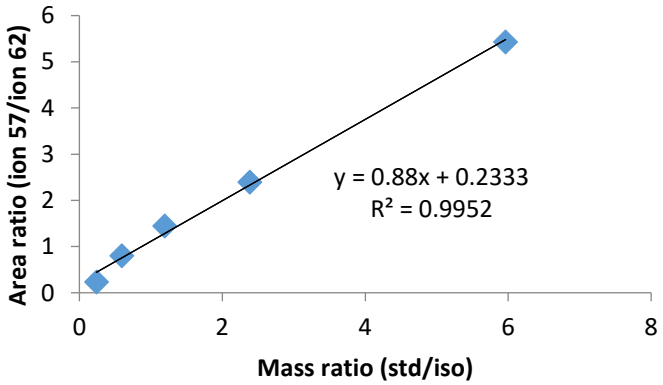
slope	Rf
1.9294	0.518

Response Factor of d_5-ethyl propanoate

	Isotope	Unlabeled
Standard:	d_5-ethyl propanoate	ethyl propanoate
CAS:	N/A	105-37-3
Mfg/Reference:	CDN	Aldrich, Milwaukee, WI
No.; Catalog#; Batch#/Lot#:	N/A	293
% Purity (by GC-FID):	N/A	99.5%

Standard Curve

selected ion mass ratio	unlabeled 57	labeled 62	area ratio
5.963	6114367	1126476	5.428
2.385	2054324	858676	2.392
1.193	1138318	786559	1.447
0.596	580622	726698	0.799
0.239	208686	907427	0.230



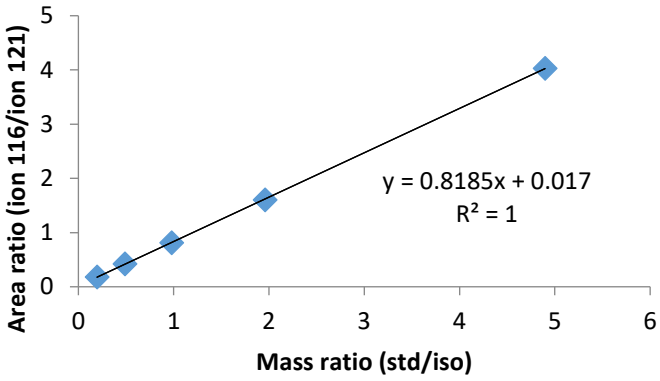
slope	Rf
0.880	1.136

Response Factor of d_5-ethyl 2-methylpropanote

	Isotope	Unlabeled
Standard:	d_5-ethyl 2-methylpropanoate	ethyl 2-methylpropanoate
CAS:	N/A	97-62-1
Mfg/Reference:	synthesized	Sigma-Aldrich, St. Louis, MO
No.:	ISO-81	341
% Purity (by GC-FID):	N/A	98.8%

Standard Curve

selected ion mass ratio	unlabeled 116	labeled 121	area ratio
4.896	103646	25720	4.030
1.959	28906	17989	1.607
0.979	20050	24695	0.812
0.490	11352	26637	0.426
0.196	4145	22665	0.183



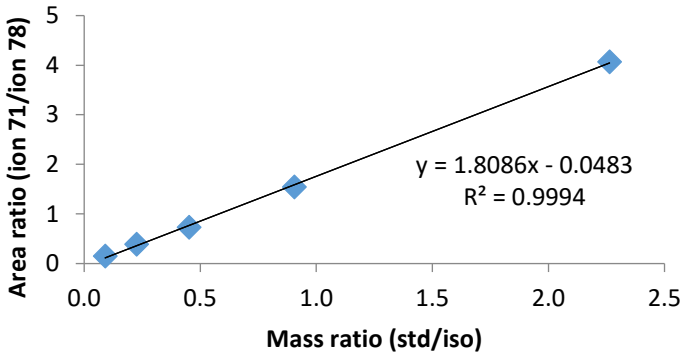
slope	Rf
0.8185	1.220

Response Factor of *d*$_7$-ethyl butyrate

	Isotope	Unlabeled
Standard:	*d*$_7$-ethyl butyrate	ethyl butyrate
CAS:	N/A	105-54-4
Mfg/Reference:	CDN	Sigma-Aldrich, St. Louis, MO
No.:	ISO-17	283
% Purity (by GC-FID):	N/A	92.7%

Standard Curve

selected ion mass ratio	unlabeled 71	labeled 78	area ratio
2.263	1634048	401807	4.067
0.905	532332	344723	1.544
0.453	297583	407924	0.730
0.226	159134	411304	0.387
0.091	55615	363203	0.153



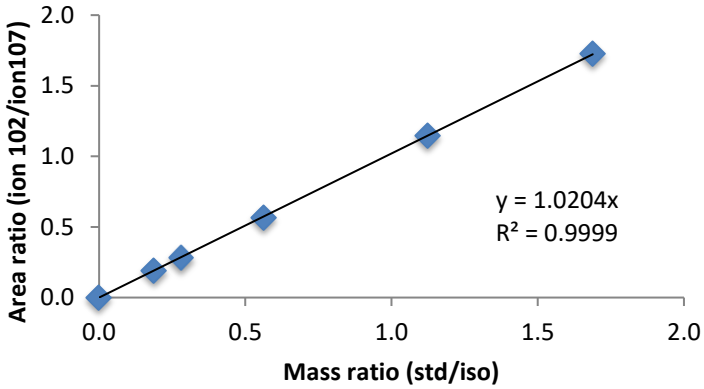
slope	Rf
1.8086	0.553

Response Factor of d_5-ethyl 2-methylbutanoate

	Isotope	Unlabeled
Standard:	d_2-ethyl 2-methylbutanoate	ethyl 2-methylbutanoate
CAS:	N/A	7452-79-1
Mfg/Reference:	synthesized	Sigma-Aldrich, St. Louis, MO
No.:	N/A	623
% Purity (by GC-FID):	N/A	N/A

Standard Curve

selected ion mass ratio	unlabeled 102	labeled 107	area ratio
1.688	8111874	4700583	1.726
1.125	5125493	4461740	1.149
0.563	2445898	4306635	0.568
0.281	3052775	10920483	0.280
0.188	2946222	15657814	0.188



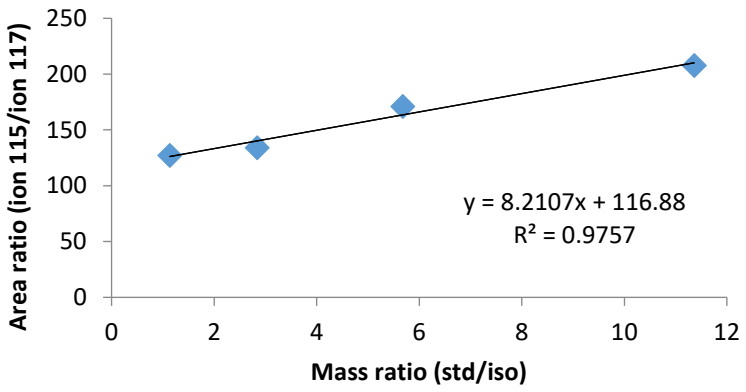
slope	Rf
1.0204	0.980

Response Factor of d_5-ethyl 3-methylbutanoate

	Isotope	Unlabeled
Standard:	d_5-ethyl 3-methybutanoate	ethyl 3-methybutanoate
CAS:	N/A	108-64-4
Mfg/Reference:	synthesized	Aldrich, Milwaukee, WI
No.:	ISO-74	324
% Purity (by GC-FID):	N/A	87.4%

Standard Curve

selected ion mass ratio	unlabeled 115	labeled 117	area ratio
11.361	3350867	16124	207.819
5.681	1822182	10650	171.097
2.840	1043567	7783	134.083
1.136	545127	4289	127.099



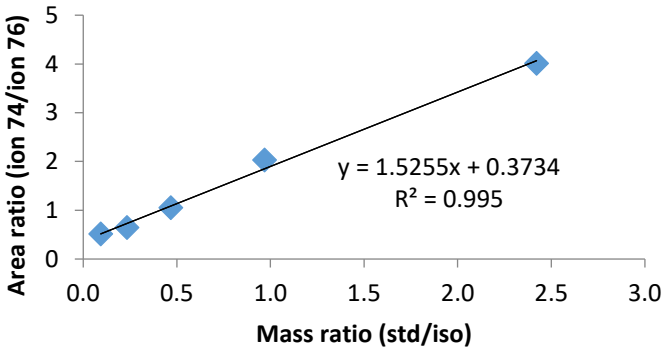
slope	Rf
8.2107	0.122

Response Factor of d_2-isobutanol

	Isotope	Unlabeled
Standard:	d_2-isobutanol	isobutanol
CAS:	N/A	78-83-1
Mfg/Reference:	synthesized	Fisher, Fair Lawn, NJ
No.:	ISO-79	196
% Purity (by GC-FID):	N/A	99.3%

Standard Curve

selected ion mass ratio	unlabeled 74	labeled 76	area ratio
2.421	1387358	345867	4.011
0.968	687684	339327	2.027
0.468	432091	410322	1.053
0.234	197861	305494	0.648
0.094	159254	310886	0.512



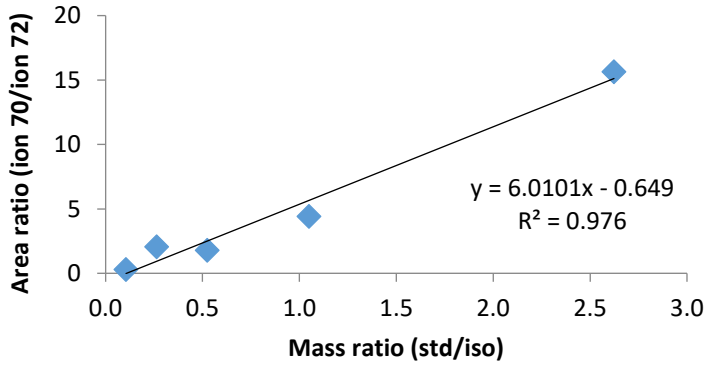
slope	Rf
1.5255	0.656

Response Factor of d_2-isoamyl acetate

	Isotope	Unlabeled
Standard:	d_2-isoamyl acetate	isoamyl acetate
CAS:	N/A	123-92-2
Mfg/Reference:	synthesized	Aldrich, Milwaukee, WI
No.:	ISO-83	74
% Purity (by GC-FID):	N/A	90.3%

Standard Curve

selected ion mass ratio	unlabeled 70	labeled 72	area ratio
0.105	104728	349266	0.300
0.262	772117	375522	2.056
0.525	1145880	642027	1.785
1.049	1866231	422745	4.415
2.623	1773329	113440	15.632



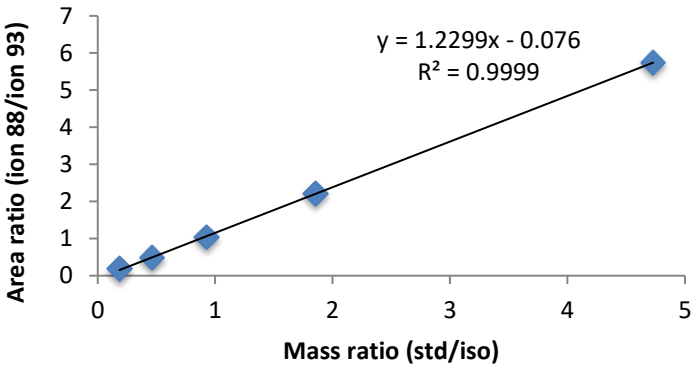
slope	Rf
6.0101	0.166

Response Factor of d_5-ethyl pentanoate

	Isotope	Unlabeled
Standard:	d_5-ethyl pentanoate	ethyl pentanoate
CAS:	N/A	539-82-2
Mfg/Reference:	synthesized	Sigma-Aldrich, St. Louis, MO
No.:	N/A	296
% Purity (by GC-FID):	N/A	99.9

Standard Curve

selected ion mass ratio	unlabeled 88	labeled 93	area ratio
4.728	1622578	282564	5.742
1.857	1412594	637979	2.214
0.929	1285894	1241451	1.036
0.464	648668	1336336	0.485
0.186	256265	1399108	0.183



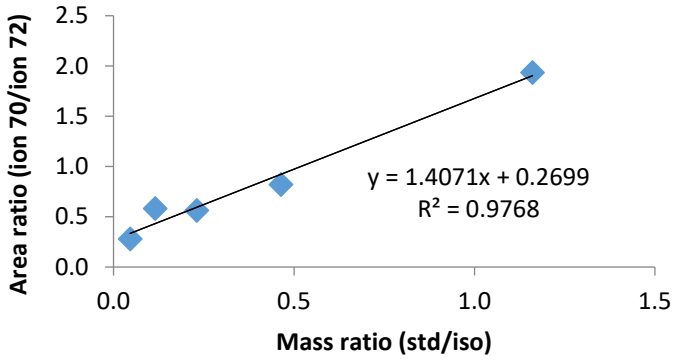
slope	Rf
1.2309	0.812

Response Factor of d_2-3-methyl-1-butanol

	Isotope	Unlabeled
Standard:	d_2-3-methyl-1-butanol	3-methyl-1-butanol
CAS:	N/A	123-51-3
Mfg/Reference:	synthesized	Sigma-Aldrich, St. Louis, MO
No.:	ISO-148	1058
% Purity (by GC-FID):	N/A	78.1%

Standard Curve

selected ion mass ratio	unlabeled 70	labeled 72	area ratio
1.161	11679784	6029549	1.937
0.464	5297421	6442510	0.822
0.231	3335765	5899612	0.565
0.116	3250796	5559691	0.585
0.046	1551266	5537305	0.280



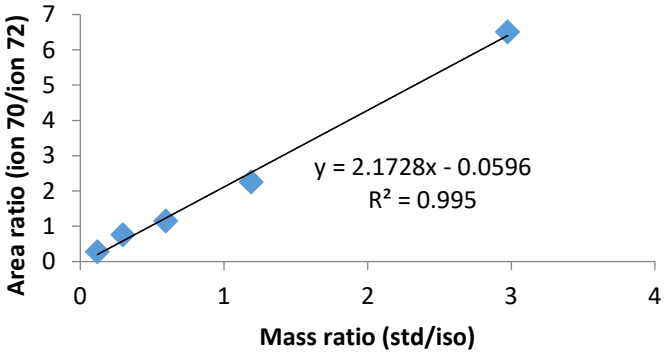
slope	Rf
1.4071	0.711

Response Factor of d_2-2-methyl-1-butanol

	Isotope	Unlabeled
Standard:	d_2-2-methyl-1-butanol	2-methyl-1-butanol
CAS:	N/A	137-32-6
Mfg/Reference:	synthesized	Sigma-Aldrich, St. Louis, MO
No.:	N/A	590
% Purity (by GC-FID):	N/A	95.8%

Standard Curve

selected ion mass ratio	unlabeled 70	labeled 72	area ratio
2.975	8199139	1259561	6.510
1.190	3848920	1707206	2.255
0.595	1899249	1654228	1.148
0.297	937157	1241201	0.755
0.119	444565	1578854	0.282



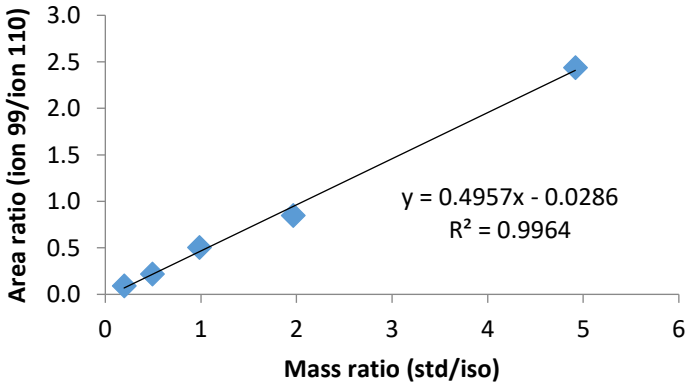
slope	Rf
2.1728	0.478

Response Factor of d_{11}-ethyl hexanoate

	Isotope	Unlabeled
Standard:	d_{11}-ethyl hexanotate	ethyl hexanoate
CAS:	N/A	123-66-0
Mfg/Reference:	CDN	Aldrich, Milwaukee, WI
No.:	ISO-21	287
% Purity (by GC-FID):	N/A	99.3%

Standard Curve

selected ion mass ratio	unlabeled 99	labeled 110	area ratio
0.197	146350	1622266	0.090
0.492	228891	1046768	0.219
0.983	645393	1282753	0.503
1.967	659733	778491	0.847
4.917	949068	389313	2.438



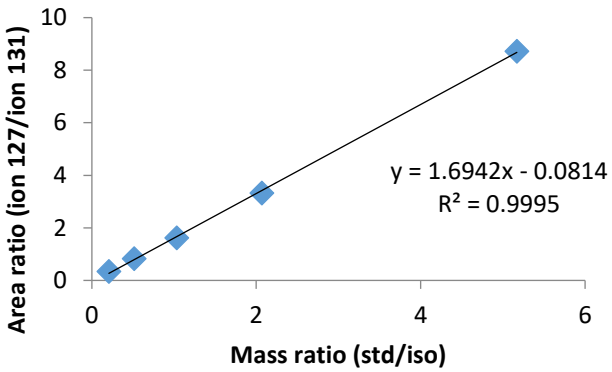
slope	Rf
0.4957	2.018

Response Factor of d_4-ethyl octanoate

	Isotope	Unlabeled
Standard:	d_2-ethyl 2-methyl propanoate	ethyl 2-methyl propanoate
CAS:	N/A	106-32-1
Mfg/Reference:	synthesized	Aldrich, Milwaukee, WI
No.:	ISO-22	288
% Purity (by GC-FID):	N/A	98.4%

Standard Curve

selected ion mass ratio	unlabeled 127	labeled 131	area ratio
5.170	4110447	471356	8.720
2.068	1947214	585986	3.323
1.034	966212	597518	1.617
0.517	447574	539078	0.830
0.207	214758	628811	0.342



slope	Rf
1.6942	0.580

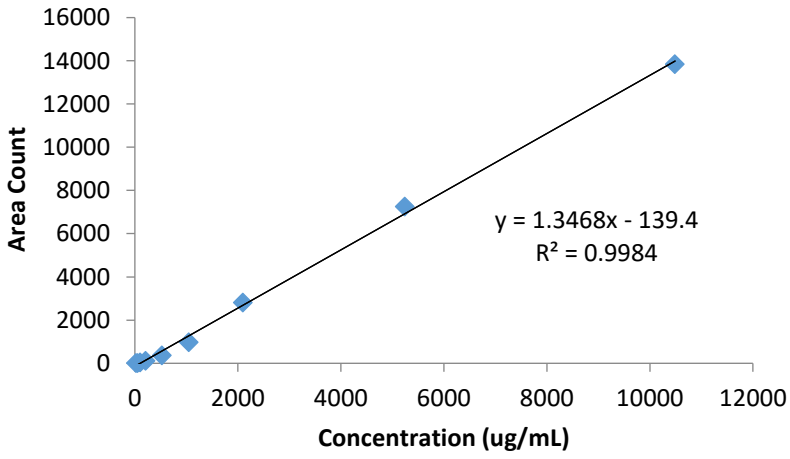
Response Factor of acetic acid

Standard:	acetic acid
CAS:	64-19-7
Mfg/Reference:	SAFC, St. Louis, MO
No.:	1099
% Purity (by GC-FID):	99.9%

Standard Curve

acetaldehyde (density g/mL)	1.049
retention time (min)	16.2

	Concentration (ug/mL)	Area
2uL 1:100 dilution 40ABV	20.98	6.9
5uL 1:100 dilution 40ABV	52.45	13.6
10uL 1:100 dilution 40ABV	104.9	41
2uL 1:10 dilution 40ABV	209.8	106.9
5uL 1:10 dilution 40ABV	524.5	371.4
10uL 1:10 dilution 40ABV	1049	968.1
2uL 40ABV	2098	2806.9
5uL 40ABV	5245	7247
10uL 40ABV	10490	13843.5



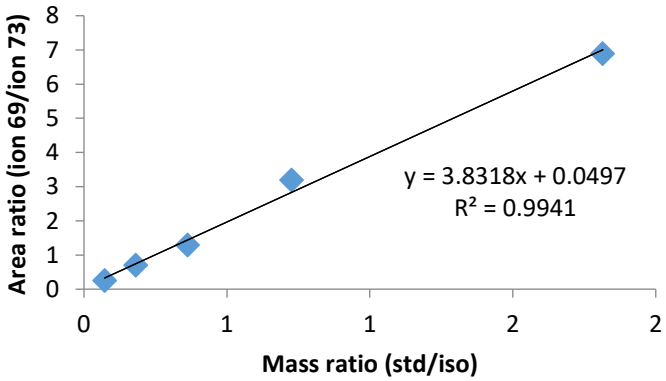
slope	Rf
1.3468	0.743

Response Factor of d_4-β-damascenone

	Isotope	Unlabeled
Standard:	d_4-β-damascenone	β-damascenone
CAS:	N/A	23696-85-7
Mfg/Reference:	synthesized	Firmenich, Switzerland
No.:	ISO-1085	1085
% Purity (by GC-FID):	N/A	89.3%

Standard Curve

selected ion mass ratio	unlabeled 69	labeled 73	area ratio
0.073	80790	313914	0.257
0.181	327220	464352	0.705
0.363	870785	672145	1.296
0.726	1270478	397271	3.198
1.815	412918	59906	6.893



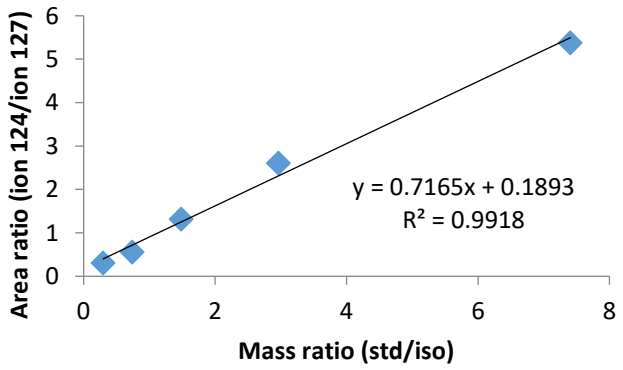
slope	Rf
3.8318	0.261

Response Factor of d_3-guaiacol

	Isotope	Unlabeled
Standard:	d_3-guaiacol	guaiacol
CAS:	N/A	90-05-1
Mfg/Reference:	CDN	Sigma-Aldrich, St. Louis, MO
No.:	ISO-9	617
% Purity (by GC-FID):	N/A	99.6%

Standard Curve

selected ion mass ratio	unlabeled 124	labeled 127	area ratio
0.296	43530	139601	0.312
0.741	68138	122602	0.556
1.481	448341	339782	1.319
2.962	819010	313879	2.609
7.406	713461	132557	5.382



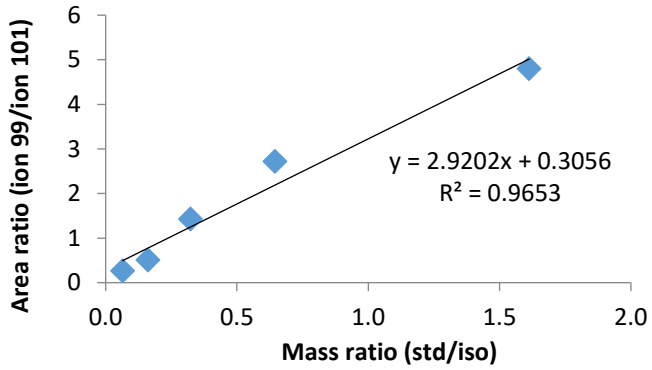
slope	Rf
0.7165	1.384

Response Factor of *d_2-trans*-whiskey lactone

	Isotope	Unlabeled
Standard:	*d_2-trans*-whiskey lactone	*trans*-whiskey lactone
CAS:	N/A	39212-23-2
Mfg/Reference:	synthesized	Sigma-Aldrich, St. Louis, MO
No.:	ISO-130	666
% Purity (by GC-FID):	N/A	51.5%

Standard Curve

selected ion mass ratio	unlabeled 99	labeled 101	area ratio
0.064	77609	290225	0.267
0.161	206812	408854	0.506
0.322	438316	307494	1.425
0.645	1335543	490995	2.720
1.612	684362	142503	4.802



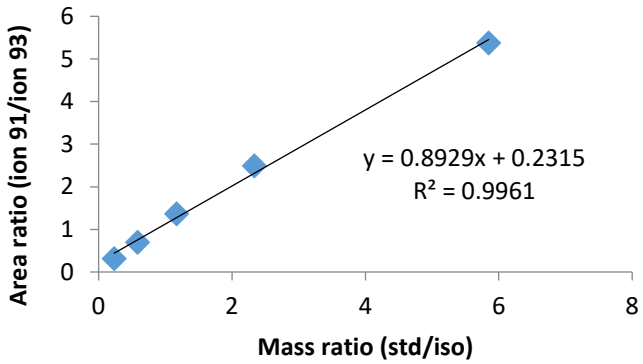
slope	Rf
2.9202	0.342

Response Factor of $^{13}C_2$-2-phenethyl alcohol

	Isotope	Unlabeled
Standard:	$^{13}C_2$-2-phenethyl alcohol	2-phenethyl alcohol
CAS:	N/A	60-12-8
Mfg/Reference:	synthesized	Sigma-Aldrich, St. Louis, MO
No.:	ISO-33	377
% Purity (by GC-FID):	N/A	98.7%

Standard Curve

selected ion mass ratio	unlabeled 91	labeled 93	area ratio
5.848	17041004	3169702	5.376
2.339	7863291	3153643	2.493
1.170	3874655	2832114	1.368
0.585	1891567	2724069	0.694
0.234	864877	2784859	0.311



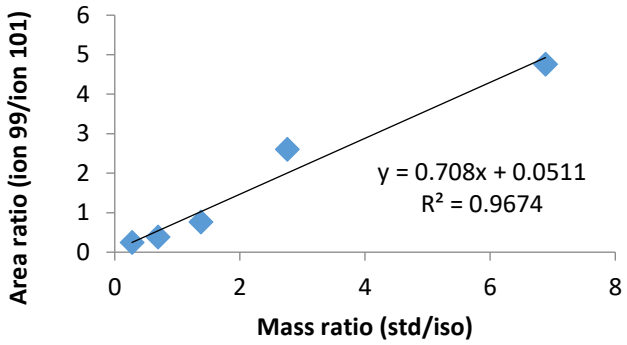
slope	Rf
0.8929	1.177

Response Factor of *d*$_2$-*cis*-whiskey lactone

	Isotope	Unlabeled
Standard:	*d*$_2$-*trans*-whiskey lactone	*trans*-whiskey lactone
CAS:	N/A	39212-23-2
Mfg/Reference:	synthesized	Sigma-Aldrich, St. Louis, MO
No.:	ISO-130	666
% Purity (by GC-FID):	N/A	46.5%

Standard Curve

selected ion mass ratio	unlabeled 99	labeled 101	area ratio
0.221	53757	219739	0.245
0.552	118047	312803	0.377
1.104	218836	288048	0.760
2.209	924270	355450	2.600
5.522	554684	116630	4.756



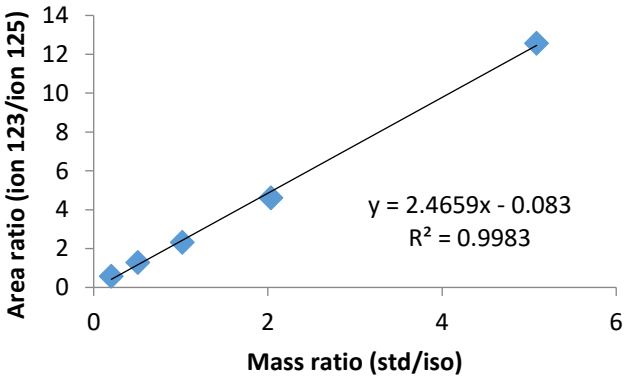
slope	Rf
0.7080	1.366

Response Factor of d_3-4-methylguaiacol

	Isotope	Unlabeled
Standard:	d_3-4-methylguaiacol	4-methylguaiacol
CAS:	N/A	93-51-6
Mfg/Reference:	synthesized	SAFC, St. Louis, MO
No.:	ISO-117	644
% Purity (by GC-FID):	N/A	100%

Standard Curve

selected ion mass ratio	unlabeled 123	labeled 125	area ratio
5.086	6896091	548017	12.584
2.034	8727925	1887058	4.625
1.017	6783094	2918659	2.324
0.509	4625970	3572590	1.295
0.203	2191429	3778477	0.580



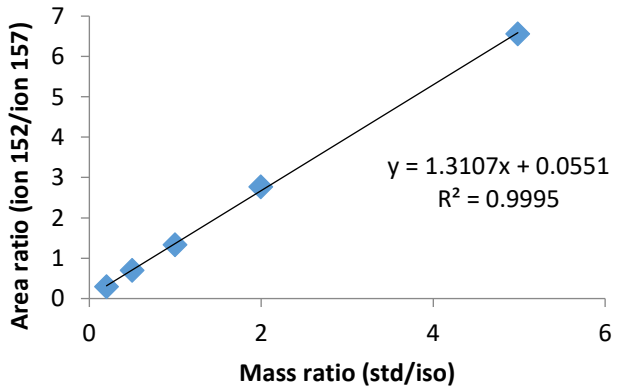
slope	Rf
2.4659	0.393

Response Factor of d_5-4-ethylguaiacol

	Isotope	Unlabeled
Standard:	d_2-4-ethylguaiacol	4-ethylguaiacol
CAS:	N/A	2785-899
Mfg/Reference:	synthesized	SAFC, St. Louis, MO
No.:	ISO-71	618
% Purity (by GC-FID):	N/A	98.1%

Standard Curve

selected ion mass ratio	unlabeled 152	labeled 157	area ratio
4.985	4992823	761451	6.557
1.994	6701591	2422162	2.767
0.997	4874989	3654887	1.334
0.498	3394426	4863630	0.698
0.199	1372047	4761892	0.288



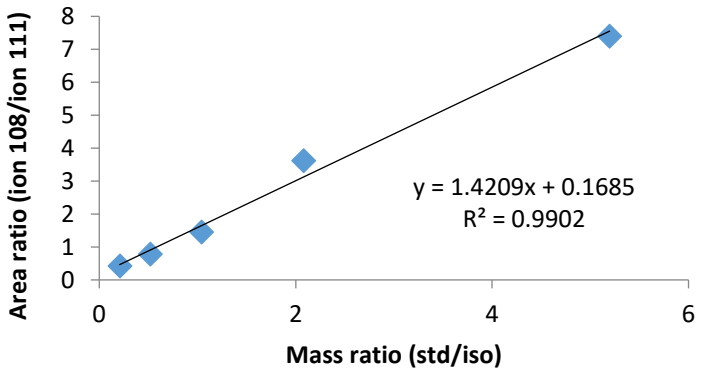
slope	Rf
1.3107	0.763

Response Factor of d_3-*p*-cresol

	Isotope	Unlabeled
Standard:	d_3-*p*-cresol	d_3-*p*-cresol
CAS:	N/A	106-44-5
Mfg/Reference:	CDN	Aldrich, Milwaukee, WI
No.:	ISO-5	425
% Purity (by GC-FID):	N/A	98.5%

Standard Curve

selected ion mass ratio	unlabeled 108	labeled 111	area ratio
5.196	1307609	176601	7.404
2.078	1719412	474785	3.621
1.039	1249138	861544	1.450
0.520	801677	1019327	0.786
0.208	496526	1162991	0.427



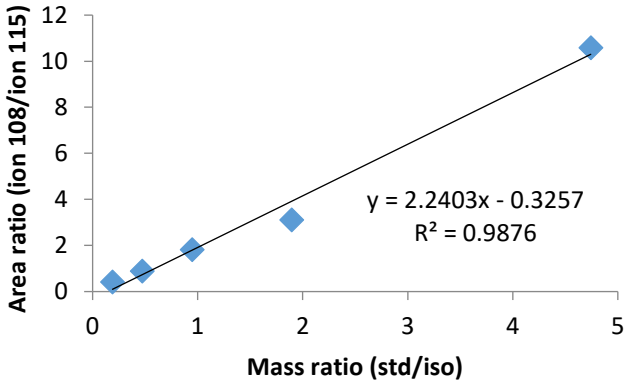
slope	Rf
1..4209	0.704

Response Factor of d_8-*m*-cresol

	Isotope	Unlabeled
Standard:	d_8-*m*-cresol	*m*-cresol
CAS:	N/A	108-39-4
Mfg/Reference:	Aldrich	SAFC, St. Louis, MO
No.:	ISO-4	539
% Purity (by GC-FID):	N/A	93.8%

Standard Curve

selected ion mass ratio	unlabeled 108	labeled 115	area ratio
4.742	21686876	2048880	10.585
1.897	29764034	9542716	3.119
0.948	20467879	11170228	1.832
0.474	14279977	15836671	0.902
0.190	6288968	14966468	0.420



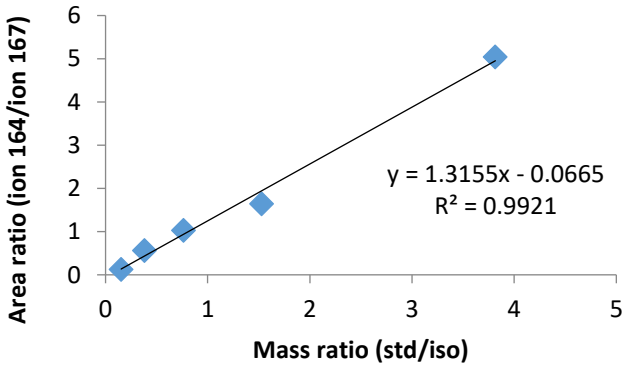
slope	Rf
2.2403	0.446

Response Factor of d_3-eugenol

	Isotope	Unlabeled
Standard:	d_3-eugenol	eugenol
CAS:	N/A	97-53-0
Mfg/Reference:	synthesized	Aldrich, Milwaukee, WI
No.:	ISO-36	640
% Purity (by GC-FID):	N/A	98.1%

Standard Curve

selected ion mass ratio	unlabeled 164	labeled 167	area ratio
0.168	6794	55013	0.123
0.419	23642	41945	0.564
0.838	96818	94054	1.029
1.675	123948	75390	1.644
4.188	114206	22653	5.042



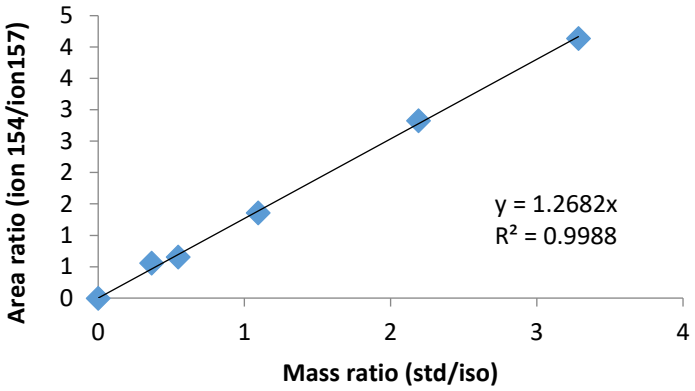
slope	Rf
1.3155	0.760

Response Factor of d_3-syringol

	Isotope	Unlabeled
Standard:	d_2-ethyl 2-methyl propanoate	ethyl 2-methyl propanoate
CAS:	N/A	91-10-1
Mfg/Reference:	synthesized	Sigma-Aldrich, St. Louis, MO
No.:	ISO-60	611
% Purity (by GC-FID):	N/A	N/A

Standard Curve

selected ion mass ratio	unlabeled 154	labeled 157	area ratio
3.284	3381619	817384	4.137
2.190	2090506	739854	2.826
1.095	608543	446841	1.362
0.547	1009339	1534358	0.658
0.365	711995	1272803	0.559



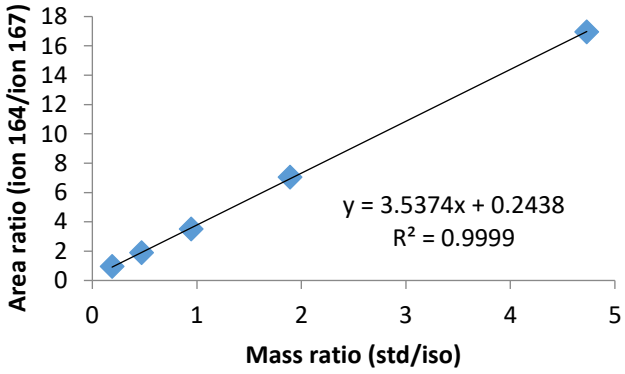
slope	Rf
1.2682	0.789

Response Factor of d_3-(*E*)-isoeugenol

	Isotope	Unlabeled
Standard:	d_2-(*E*)-isoeugenol	(*E*)-isoeugenol
CAS:	N/A	97-54-1
Mfg/Reference:	synthesized	Sigma-Aldrich, St. Louis, MO
No.:	ISO-43	183
% Purity (by GC-FID):	N/A	92.5%

Standard Curve

selected ion mass ratio	unlabeled 164	labeled 167	area ratio
4.731	1502212	88599	16.955
1.892	1190469	169018	7.043
0.946	1091538	311041	3.509
0.473	871157	462533	1.883
0.189	259738	274291	0.947



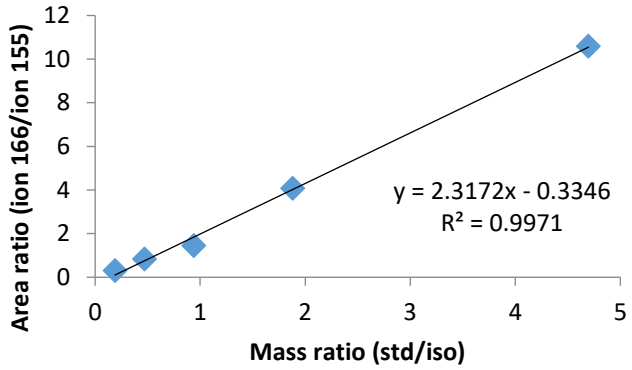
slope	Rf
3.5374	0.283

Response Factor of ethyl vanillin

	Isotope	Unlabeled
Standard:	d_3-vanillin	ethyl vanillin
CAS:	N/A	121-32-4
Mfg/Reference:	synthesized	Sigma-Aldrich, St. Louis, MO
No.:	ISO-32	475
% Purity (by GC-FID):	N/A	99.9%

Standard Curve

selected ion mass ratio	unlabeled 166	labeled 155	area ratio
4.695	5561105	525516	10.582
1.878	6728710	1650289	4.077
0.939	3234969	2226836	1.453
0.470	2588756	3095085	0.836
0.188	994895	3218473	0.309



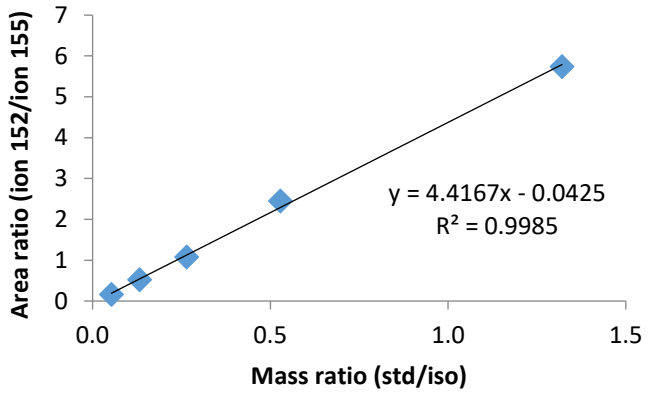
slope	Rf
2.3172	0.416

Response Factor of d_3-vanillin

	Isotope	Unlabeled
Standard:	d_3-vanillin	vanillin
CAS:	N/A	121-33-5
Mfg/Reference:	synthesized	SAFC, St. Louis, MO
No.:	ISO-32	70
% Purity (by GC-FID):	N/A	84.1%

Standard Curve

selected ion mass ratio	unlabeled 152	labeled 155	area ratio
0.053	90007	581323	0.155
0.132	256913	498072	0.516
0.264	986398	914371	1.079
0.528	409299	167430	2.445
1.320	430856	75062	5.740



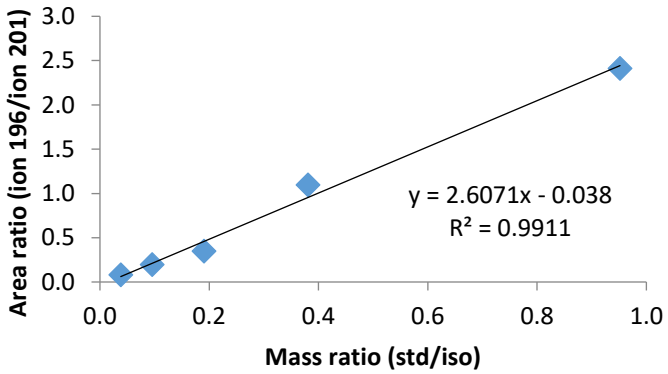
slope	Rf
4.4167	0.229

Response Factor of d_5-ethyl vanillate

	Isotope	Unlabeled
Standard:	d_3-ethyl vanillate	ethyl vanillate
CAS:	N/A	617-05-0
Mfg/Reference:	synthesized	Alfa Aeasar, Lancaster, UK
No.:	ISO-73	1123
% Purity (by GC-FID):	N/A	99.9%

Standard Curve

selected ion mass ratio	unlabeled 196	labeled 201	area ratio
0.038	30912	387496	0.080
0.095	45802	234305	0.195
0.190	155963	448551	0.348
0.381	263567	240807	1.095
0.952	183540	76150	2.410



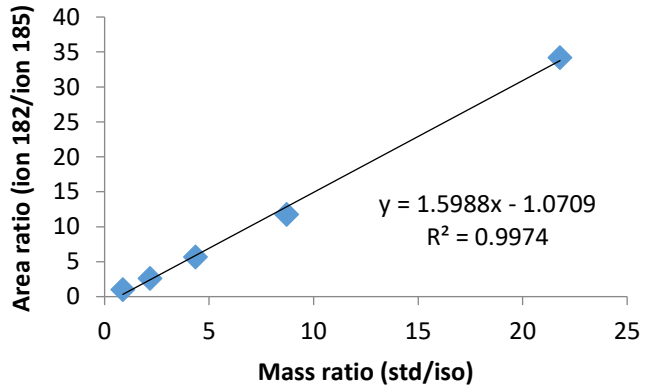
slope	Rf
2.6071	0.380

Response Factor of d_3-syringaldehyde

	Isotope	Unlabeled
Standard:	d_3-syringaldehyde	syringaldehyde
CAS:	N/A	134-96-3
Mfg/Reference:	synthesized	SAFC, St. Louis, MO
No.:	ISO-78	1065
% Purity (by GC-FID):	N/A	99.9%

Standard Curve

selected ion mass ratio	unlabeled 182	labeled 185	area ratio
21.789	8081107	236287	34.200
8.716	3621510	307692	11.770
4.358	1835874	323291	5.679
2.179	821049	315918	2.599
0.872	364613	359941	1.013



slope	Rf
1.5988	0.603

Appendix B: IRB approval letter for threshold determination in alcoholic matrices

IRB EXEMPT APPROVAL

RPI Name: Keith Cadwallader
Project Title: Difference Testing of Alcoholic Beverages
IRB #: 17508
Approval Date: February 14, 2017

Thank you for submitting the completed IRB application form and related materials. Your application was reviewed by the UIUC Office for the Protection of Research Subjects (OPRS). OPRS has determined that the research activities described in this application meet the criteria for exemption at 45CFR46.101(b)(2). This message serves to supply OPRS approval for your IRB application.

Please contact OPRS if you plan to modify your project (change procedures, populations, consent letters, etc.). Otherwise you may conduct the human subjects research as approved for a period of five years. Exempt protocols will be closed and archived at the time of expiration. Researchers will be required to contact our office if the study will continue beyond five years.

Copies of the attached, date-stamped consent form(s) are to be used when obtaining informed consent.

We appreciate your conscientious adherence to the requirements of human subjects research. If you have any questions about the IRB process, or if you need assistance at any time, please feel free to contact me at OPRS, or visit our website at http://oprs.research.illinois.edu

Sincerely,

Rebecca Miller, MSW
Human Subjects Research Specialist, Office for the Protection of Research Subjects

Appendix C: Determination of odor thresholds in a 40% ABV ethanolic matrix

Determination of odor threshold of isoeugenol

Odor threshold: Isoeugenol added to a blank 40% ABV matrix
Procedure: ASTM Practice E679
Presentation: three Teflon plastic sniff bottles (two identical controls and one bottle containing the added compound). Weakest concentrations were presented first
Number of scale steps: seven –each panelist observed each sample twice
Dilution factor per step: three
Temperature: samples were at room temperature (21°C)
Panelist selection: lab members experienced with sensory evaluation
Type of threshold: detection
Best-estimate threshold:

BET = 1860 µg/L
Log_{10}BET= 3.27
Log standard deviation= 0.35

Panelist	Concentration of isoeugenol in sample (µg/L)							Individual Threshold	Log10 of individual thresholds
	3.059	**9.177**	**27.53**	**82.59**	**247.8**	**743.3**	**2230**		
A-1	0	1	1	0	0	0	0	3862	3.59
B-1	1	0	1	0	0	0	1	1287	3.11
C-1	0	0	0	0	0	0	1	1287	3.11
D-1	0	1	1	0	0	0	1	1287	3.11
E-1	1	0	1	0	0	0	0	3862	3.59
F-1	0	1	0	0	0	0	1	1287	3.11
G-1	1	0	1	0	0	0	1	1287	3.11
H-1	0	1	1	0	0	1	1	429	2.63
A-2	0	1	1	1	0	0	0	3862	3.59
B-2	0	0	0	0	0	1	1	429	2.63
C-2	0	0	1	0	1	0	0	3862	3.59
D-2	0	0	1	0	0	0	0	3862	3.59
E-2	0	0	1	0	1	0	0	3862	3.59
F-2	0	0	1	0	0	0	0	3862	3.59
G-2	0	0	1	0	0	0	1	1287	3.11
								Σlog 10	49.03
								Σlog 10/ replications	3.27
								Group BET Threshold (µg/L)	1860
								Standard Deviation (of Log_{10} Values)	0.35

Determination of odor threshold of ethyl vanillate

Odor threshold: ethyl vanillate added to a blank 40% ABV matrix
Procedure: ASTM Practice E679
Presentation: three Teflon plastic sniff bottles (two identical controls and one bottle containing the added compound). Weakest concentrations were presented first
Number of scale steps: seven –each panelist observed each sample twice
Dilution factor per step: three
Temperature: samples were at room temperature (21°C)
Panelist selection: lab members experienced with sensory evaluation
Type of threshold: detection
Best-estimate threshold:

BET = 769000 μg/L
Log_{10}BET= 5.90
Log standard deviation= 1.26

	Concentration of ethyl vanillate in sample (ug/L)								
Panelist	**13660**	**40979**	**122938**	**368815**	**1106444**	**3319333**	**9958000**	Individual Threshold	Log10 of individual thresholds
A-1	1	0	1	0	1	1	1	638806	5.81
B-1	0	1	0	1	1	1	1	212935	5.33
C-1	1	1	1	1	1	1	1	7886	3.90
D-1	1	1	0	0	1	0	1	5749254	6.76
E-1	1	1	1	1	1	1	1	7886	3.90
F-1	0	0	0	0	0	0	1	5749254	6.76
G-1	1	1	1	1	0	1	1	1916418	6.28
H-1	0	0	0	0	0	0	1	5749254	6.76
I-1	0	0	0	0	0	1	1	1916418	6.28
J-1	0	1	1	1	1	1	1	23659	4.37
A-2	0	1	1	1	1	0	1	5749254	6.76
B-2	1	1	1	1	0	1	0	17247762	7.24
C-2	1	1	1	0	1	1	1	638806	5.81
D-2	1	1	1	1	1	0	0	17247762	7.24
E-2	0	1	1	1	1	1	1	23659	4.37
F-2	0	0	1	0	0	0	0	17247762	7.24
G-2	1	0	1	1	1	1	1	70978	4.85
H-2	1	0	1	0	0	1	0	17247762	7.24
I-2	1	1	1	0	0	0	0	17247762	7.24
J-2	1	1	1	1	1	1	1	7886	3.90
								Σlog 10	118.02
								Σlog 10/replications	5.90
								Group BET Threshold	796000
								Standard Deviation	1.26

Determination of odor threshold of syringaldehyde

Odor threshold: syringaldehyde added to a blank 40% ABV matrix
Procedure: ASTM Practice E679
Presentation: three Teflon plastic sniff bottles (two identical controls and one bottle containing the added compound). Weakest concentrations were presented first
Number of scale steps: seven –each panelist observed each sample twice
Dilution factor per step: three
Temperature: samples were at room temperature (21°C)
Panelist selection: lab members experienced with sensory evaluation
Type of threshold: detection
Best-estimate threshold:

BET = 6490000 µg/L
Log_{10}BET= 6.81
Log standard deviation= 0.75

	Concentration of syringaldehyde in sample (ug/L)								
Panelist	**26700**	**80099**	**240296**	**720889**	**2162667**	**6488000**	**19464000**	Individual Threshold	Log10 of individual thresholds
A-1	0	1	0	1	0	1	1	3745849	6.57
B-1	0	0	0	0	1	1	1	1248616	6.10
C-1	1	1	0	0	1	1	1	1248616	6.10
D-1	0	0	0	0	1	0	0	33712637	7.53
E-1	0	0	0	1	1	0	0	33712637	7.53
F-1	0	1	1	0	1	0	0	33712637	7.53
G-1	0	1	1	0	0	0	0	33712637	7.53
H-1	0	1	1	0	0	0	0	33712637	7.53
I-1	0	0	0	1	1	1	1	416205	5.62
A-2	0	1	0	0	0	0	1	11237546	7.05
B-2	0	0	0	1	1	1	1	416205	5.62
C-2	1	0	0	0	0	0	1	11237546	7.05
D-2	0	1	0	1	0	0	0	33712637	7.53
E-2	1	0	1	0	1	1	1	1248616	6.10
F-2	1	0	0	0	0	1	0	33712637	7.53
G-2	1	1	0	0	0	0	0	33712637	7.53
H-2	0	1	0	0	1	1	1	1248616	6.10
I-2	0	0	0	0	1	1	1	1248616	6.10
								Σlog 10	122.62
								Σlog 10/replications	6.81
								Group BET Threshold	6490000
								Standard Deviation	0.75

Appendix D: IRB approval letter for descriptive analysis panels

UNIVERSITY OF ILLINOIS
AT URBANA-CHAMPAIGN

Office of the Vice Chancellor for Research

Office for the Protection of Research Subjects
528 East Green Street
Suite 203
Champaign, IL 61820

June 16, 2016

Keith Cadwallader
Department of Food Science & Human Nutrition
102 Agriculatural Bioprocess Lab
1302 West Pennsylvania Avenue
Urbana, IL 61801

RE: *Descriptive Analysis of Distilled Spirits and Model Systems*
IRB Protocol Number: 16854

Dear Dr. Cadwallader:

Your response to required modifications for the project entitled *Descriptive Analysis of Distilled Spirits and Model Systems* has satisfactorily addressed the concerns of the University of Illinois at Urbana-Champaign Institutional Review Board (IRB) and you are now free to proceed with the human subjects protocol. The UIUC IRB approved the protocol as described in your IRB-1 application with stipulated changes, as part of their monthly review. Certification of approval is available upon request. The expiration date for this protocol, IRB number 16854, is 06/14/2017. The risk designation applied to your project is *no more than minimal risk.*

Copies of the attached date-stamped consent form(s) must be used in obtaining informed consent. If there is a need to revise or alter the consent form(s), please submit the revised form(s) for IRB review, approval, and date-stamping prior to use.

Under applicable regulations, no changes to procedures involving human subjects may be made without prior IRB review and approval. The regulations also require that you promptly notify the IRB of any problems involving human subjects, including unanticipated side effects, adverse reactions, and any injuries or complications that arise during the project.

If you have any questions about the IRB process, or if you need assistance at any time, please feel free to contact me at the OPRS office, or visit our website at https://www.oprs.research.illinois.edu.

Sincerely,

Dustin Yocum, MA, CIP
Human Subjects Research Specialist, Office for the Protection of Research Subjects

Attachment(s): Written informed consent document

c: Chelsea Ickes

Appendix E: Rum DA panel recruitment questionnaire

Rum Descriptive Analysis Panel

Please answer all the questions below.

Q1
Please enter your first name

Q2
Please enter your last name

Q3
Please enter your e-mail address

Q4
Do you have any food or beverage allergies?

- Yes
- No

Q5
If yes, please list your allergy/sensitivity

Q6
Are you 21 years old or older?

- Yes
- No

Q7
Do you enjoy drinking distilled spirits?

- Yes
- No

Q8
If yes, how do you prefer them

- Neat
- With water
- On the rocks

- With a mixer
- Other
-

Q9
How often do you drink distilled spirits?

- Everyday
- 4-6 Times a Week
- 2-3 Times a Week
- Once a Week
- 2-3 Times a Month
- Once a Month
- Once every couple months
- Once a year
- Only on special occasions
- Never

Q10
What types of distilled spirits do you typically drink? (Select all that apply)

- Brandy
- Bourbon
- Cognac
- Gin
- Rum
- Scotch
- Tequilla
- Vodka
- Whiskey
- Other
-
- None

Q11
Do you smoke?

- Yes
- No

Q12
Are you pregnant or breastfeeding?

- Yes
- No

Q13
Are you a native English speaker?

- Yes
- No

Q14
Have you ever suffered a chronic disease related to alcohol consumption?

- Yes
- No

Q15
Please check **ALL** times that you are available every day between _____ and _____.

- 10am - 11am
- 11am - 12pm
- 12pm - 1pm
- 1pm - 2pm
- 2pm - 3pm
- 3pm - 4pm
- 4pm - 5pm
- 4:30pm - 5:30pm
- 5pm - 6pm

Appendix F: Rum DA panel prescreening ballot

PRESCREENING TEST

Basic Tastes

Instructions:

1. Taste each solution in the order presented below.
2. For each solution identify which of the basic tastes (sweet, sour, salty, bitter) is being presented. You can also answer non if no taste is perceived.

568 _____

425 _____

328 _____

741 _____

195 _____

Aroma Identification

Instructions:

1. Smell the samples in the order presented below.
2. To smell the sample, remove the lid from the cup and then take short shallow sniffs.
3. Next check if you perceive an odor, and then identify what the odor is (ie/grape).
4. For each solution identify which of the basic tastes (sweet, sour, salty, bitter) is being presented. You can also answer non if no taste is perceived.

	Odor Perceived	Describe Odor
625	☐ Yes ☐ No	_____
539	☐ Yes ☐ No	_____
842	☐ Yes ☐ No	_____
654	☐ Yes ☐ No	_____
197	☐ Yes ☐ No	_____

Appendix G: Rum DA panel informed consent form

INFORMED CONSENT FORM FOR SENSORY EVALUATION PANELISTS

"Descriptive Analysis Panel of Rum and Rum Model Systems"

You are invited to participate in a study involving sensory evaluation of rum. The goal of this research is to determine the sensory characteristics of premium aged rums as well as the effect of ethanol on the sensory perception of rums. Several types of rum and rum models will be evaluated in this study to determine the sensory similarities and differences of various premium rums. The products will be evaluated using a sensory Descriptive Analysis panel. You will be presented with rum samples and asked to generate terms, definitions and references to describe sensory attributes. Panelists will work together to define the significant attributes and corresponding references. Once determined, the significant attributes will be rated individually based on the references. This research will allow the investigators to gain a better understanding of the sensory attributes associated with premium aged rums.

To participate in this study, you must first complete a sensory screening process involving the identification of odors and basic taste solutions. Based on the results of this sensory screening you may not qualify to participate in this study. Screening and testing for this study will be conducted in Agricultural Bioprocess Laboratory (ABL) Room 201 and Bevier Hall Room 376. We anticipate that the research will consist of 5 hours of testing sessions per week for 8-weeks for a total of 38 hours of testing. Each day testing will last approximately 1 hour, either a one hour session or two 30 minute session. The total number of sessions required for each panelist is 52 (24 one hour sessions and 28 thirty minute sessions), and you will be compensated monetarily for your participation in the amount of $99 upon completion of the study. Participation in this study is voluntary and you are free to withdraw from the study at any time for any reason and it will have no effect on your grades at, status at, or future relations with the University of Illinois. The experimenter(s) also reserve the right to terminate the participation of an individual subject at any time. You will be terminated if you miss sessions, are consistently late, cannot follow directions or become intoxicated after evaluating samples. In the event you withdraw from, or are terminated from the study by the experimenter you will be compensated at a rate of $2.50 per hour of testing completed.

A complete list of the rums will be available for review after testing has concluded. Information about the references will be available throughout the panel. If you have any food or beverage allergies you should not participate in this research. All foods and ingredients have been designated as safe for food use by their respective manufacturers and are commonly found in commercially available foods.

During this study there are slight physical risks associated with alcohol consumption. These risks will be minimized since all rum samples tasted will be expectorated. In addition you will be asked to eat something one hour before coming to panel. Even if some rum is swallowed during tasting, the total amount of alcohol you receive at each session will be similar to that of a 12 oz beer and should not be enough to intoxicate you. Additionally, you should not drive yourself to or from the testing sessions. You must be over 21 years of age to participate. Anyone who has a chronic disease related to alcohol consumption or is pregnant or breastfeeding should not participate in this study. The University of Illinois does not provide medical or hospitalization insurance coverage for participants in this research study nor will the University of Illinois provide compensation for any injury sustained as a result of participation in this research study, except as required by law.

Your participation in this study will be kept confidential, but not always. In general, we will not tell anyone any information about you. When this research is discussed or published, no one will know that you were in the study. However, laws and university rules might require us to tell certain people about you. For example, your records from this research may be seen or copied by the following people or groups: Representatives of the

university committee and office that reviews and approves research studies, the Institutional Review Board (IRB) and Office for Protection of Research Subjects; other representatives of the state and university responsible for ethical, regulatory, or financial oversight of research; federal government regulatory agencies such as the Office of Human Research Protections in the Department of Health and Human Services. Any publications or presentations of the results of the research will only include information about group performance. Data gathered from the entire project will be summarized in the aggregate, excluding references to any individual responses. Photos of the panelists participating in this research may be taken and used in oral presentations, in order to give information about the experiment procedure. Names of panelists will not be associated with the photos. Panelists may opt for not having their photographs taken and this option is included on the consent form. The aggregated results of our analysis will be for journal articles and conference presentations. Again, your input is very important to us and any information we receive from you will be kept secure and confidential.

You are encouraged to ask any questions about this study whether before, during, or after your participation. However, specific questions about the samples that could influence the outcome of the study will be deferred to the end of the experiment. Questions can be addressed to Dr. Keith Cadwallader (217-333-5803, cadwlldr@illinois.edu) or Chelsea Ickes (443-845-1404, homes2@illinois.edu). If you have any questions about your rights as a participant in this study or any concerns or complaints, please contact the University of Illinois Office for the Protection of Research Subjects (OPRS) at 217-333-2670 or via email at irb@illinois.edu.

I understand the above information and voluntarily consent to participate in the study described above.

I have been offered a copy of this consent form.	☐ Yes	☐ No
I am 21 years of age or older.	☐ Yes	☐ No
I agree to have photographs taken of me while participating in this research.	☐ Yes	☐ No
I am not pregnant or breastfeeding .	☐ Yes	☐ No
I do not take any medication.	☐ Yes	☐ No
I do not have any chronic diseases related to alcohol consumption.	☐ Yes	☐ No
I do not smoke.	☐ Yes	☐ No

Signature Date

Print Name

Appendix H: Sample term generation sheet for descriptive analysis panels

Term Generation Day 1

Sample :XXX

	Terms	Definitions	References
Aroma			
Aroma-by-mouth			
Texture/ Mouthfeel			
Taste			
Aftertaste			

Appendix I: Product information for attributes for rum descriptive analysis panel

Modality	Attribute	Product Name	Brand	Manufacturer	Location
Aroma	alcohol	Ethanol 190 Proof, USP Grade	Decon Laboratories, Inc.	Decon Labs, Inc.	King of Prussia, PA
	almond	roasted almonds, unsalted	True Goodness by Meijer	Meijer Distribution Inc	Grand Rapids, MI
	brown spice	Ground nutmeg	McCormick	McCormick & Co., Inc.	Hunt Valley, MD
	brown sugar	Dark Brown Sugar	Meijer	Meijer Distribution Inc	Grand Rapids, MI
	butter	Sweet Cream Butter Unsalted	Meijer	Meijer Distribution Inc	Grand Rapids, MI
	caramel	Smucker's Sundae Syrup Caramel	Smucker's	The J.M. Smucker Company	Orrville, OH
	cherry	Cherry Pie Filling	Meijer	Meijer Distribution Inc	Grand Rapids, MI
	chocolate	Unsweetened Baking Chocolate Bar	Baker's	Kraft Foods Group, Inc.	Northfield, IL
	citrus	lime	Susie		
	coconut	Toasted Flake Coconut	Coral Bay	Marx Brothers, Inc.	Birmingham AL
	dried fruit	Sunsweet Amazin Pruntes Pitted	Sunsweet	Sunsweet Growers Inc.	Yuba City, CA
	maple	Maple Extract	McCormick	McCormick & Co., Inc.	Hunt Valley, MD
	phenolic	Plastic Bandages	Meijer	Meijer Distribution Inc	Grand Rapids, MI
	roasted	Brown Malt	Thomas Fawcett & Sons Ltd.	The Country Malt Group	Castleford, West Yorkshire
	smokey	Hardwood Smoked Bacon	John Morrell	John Morrell & Co	Cincinnati, OH
	vanilla	All Natural Pure Vanilla Extract	McCormick	McCormick & Co., Inc.	Hunt Valley, MD
	walnut	raw chopped walnuts	True Goodness by Meijer	Meijer Distribution Inc	Grand Rapids, MI
	woody	Oak wood chips	LD Carlson Company	LD Carlson Company	Kent, OH
Mouthfeel	astringent	Lipton Pure Green Tea	Lipton	Unilever	Englewood Cliffs, NJ
	slick	Vegetable Glycerin	Heritage Store	Heritage Store	Virginia Beach, VA
	warming	Ethanol 190 Proof, USP Grade	Decon Laboratories, Inc.	Decon Labs, Inc.	King of Prussia, PA

Appendix I (cont.): Product information for attributes for rum descriptive analysis panel

Modality	Attribute	Product Name	Brand	Manufacturer	Location
Taste	bitter	Caffeine	Fisher Scientific	Fisher Scientific	Fair Lawn, NJ
Aftertaste	bitter	Caffeine	Fisher Scientific	Fisher Scientific	Fair Lawn, NJ
	brown spice	Ground nutmeg	McCormick	McCormick & Co., Inc.	Hunt Valley, MD
	caramel	Smucker's Sundae Syrup Caramel	Smucker's	The J.M. Smucker Company	Orrville, OH
	cherry	Cherry Pie Filling	Meijer	Meijer Distribution Inc	Grand Rapids, MI
	coffee	Eight O'clock French Roast Coffee	Eight O'clock	Eight O'clock Coffee Company	Montcale, NJ
Aroma By Mouth	alcohol	Ethanol 190 Proof, USP Grade	Decon Laboratories, Inc.	Decon Labs, Inc.	King of Prussia, PA
	brown spice	Ground nutmeg	McCormick	McCormick & Co., Inc.	Hunt Valley, MD
	caramel	Smucker's Sundae Syrup Caramel	Smucker's	The J.M. Smucker Company	Orrville, OH
	cherry	Cherry Pie Filling	Meijer	Meijer Distribution Inc	Grand Rapids, MI
	coconut	Toasted Flake Coconut	Coral Bay	Marx Brothers, Inc.	Birmingham AL
	maple	Maple Extract	McCormick	McCormick & Co., Inc.	Hunt Valley, MD
	roasted	Brown Malt	Thomas Fawcett & Sons Ltd.	The Country Malt Group	Castleford, West Yorkshire
	smokey	Liquid Smoke - Hickory	Wright's	B&G Foods, Inc.	Parsippany, NJ
	vanilla	All Natural Pure Vanilla Extract	McCormick	McCormick & Co., Inc.	Hunt Valley, MD
	walnut	raw chopped walnuts	True Goodness by Meijer	Meijer Distribution Inc	Grand Rapids, MI
	woody	Oak wood chips	LD Carlson Company	LD Carlson Company	Kent, OH

Appendix J: Eigenvalues for factor loading using covariance matrix

Factor	Eigenvalue	Proportion	Cumulative
1	71.5924322	0.8836	0.8836
2	2.9243101	0.0361	0.9197
3	2.0241442	0.025	0.9447
4	1.6381673	0.0202	0.9649
5	1.5601022	0.0193	0.9842
6	0.7638361	0.0094	0.9936
7	0.3044791	0.0038	0.9973
8	0.2158511	0.0027	1

Appendix K: Principle component analysis factor correlations of significant attributes on principal component 1 (PC1) and 2 (PC2) for all nine rum samples in covariance matrix

Modality	Attribute	PC1	PC2
Aroma	Brown Sugar	0.97	0.01
	Caramel	0.97	-0.22
	Maple	0.93	-0.15
	Vanilla	0.99	-0.06
	Alcohol	-0.95	0.08
	Citrus	-0.81	-0.36
	Coconut	0.82	0.25
	Roasted	0.41	-0.01
	Smoky	-0.61	0.31
	Phenolic	-0.94	0.18
	Chocolate	0.97	-0.15
Mouthfeel	Warming	-0.84	0.02
	Slick	0.59	0.75
Taste	Bitter	-0.88	0.05
Aftertaste	Brown Spice	0.85	0.17
	Caramel	0.99	0.07
Aroma-by-mouth	Caramel	0.97	0.15
	Maple	0.99	0.03
	Vanilla	0.96	0.26
	Coconut	0.85	0.26

Appendix L: Product information for attributes for ethanol dilution descriptive analysis panel

Modality	Attribute	Product Name	Brand	Manufacturer	Location
Aroma	alcohol	Ethanol 190 Proof, USP Grade	Decon Laboratories, Inc.	Decon Labs, Inc.	King of Prussia, PA
	caramel	Smucker's Sundae Syrup Caramel	Smucker's	The J.M. Smucker Company	Orrville, OH
	maple	Maple Extract	McCormick	McCormick & Co., Inc.	Hunt Valley, MD
	vanilla	All Natural Pure Vanilla Extract	McCormick	McCormick & Co., Inc.	Hunt Valley, MD
	dark fruit	Sunsweet Amazin Prunes Pitted	Sunsweet	Sunsweet Growers Inc.	Yuba City, CA
	roasted	Brown Malt	Thomas Fawcett & Sons Ltd.	The Country Malt Group	Castleford, West Yorkshire
	toasted	Jet-Puffed Marshmallows	Jet Puffed - Kraft	Kraft Foods Group,	Northfield, IL
	woody	Oak wood chips	LD Carlson Company		Kent, OH
Mouthfeel	astringent	Lipton Pure Green Tea	Lipton	Unilever	Englewood Cliffs, NJ
	silky	Almond milk - Reduced Sugar, Vanilla	Silk	Whitewave Foods	Broomfield, CO
	slick	Vegetable Glycerin	Heritage Store	Heritage Store	Virginia Beach, VA
	warming	Ethanol 190 Proof, USP Grade	Decon Laboratories, Inc.	Decon Labs, Inc.	King of Prussia, PA
Taste	bitter	Caffeine	Fisher Scientific	Fisher Scientific	Fair Lawn, NJ
	sweet	C&H Pure Cane Sugar	C&H	Domino Foods, Inc	Yonkers, NY
Aroma By Mouth	alcohol	Ethanol 190 Proof, USP Grade	Decon Laboratories, Inc.	Decon Labs, Inc.	King of Prussia, PA
	caramel	Smucker's Sundae Syrup Caramel	Smucker's	The J.M. Smucker Company	Orrville, OH
	maple	Maple Extract	McCormick	McCormick & Co., Inc.	Hunt Valley, MD
	vanilla	All Natural Pure Vanilla Extract	McCormick	McCormick & Co., Inc.	Hunt Valley, MD
	woody	Oak wood chips	LD Carlson Company		Kent, OH

Appendix L (cont.): Product information for attributes for ethanol dilution descriptive analysis panel

Modality	Attribute	Product Name	Brand	Manufacturer	Location
Aftertaste	bitter	Caffeine	Fisher Scientific	Fisher Scientific	Fair Lawn, NJ
	brown spice	Ground nutmeg	McCormick	McCormick & Co., Inc.	Hunt Valley, MD
	vanilla	All Natural Pure Vanilla Extract	McCormick	McCormick & Co., Inc.	Hunt Valley, MD
	woody	Oak wood chips	LD Carlson Company		Kent, OH
	plastic	Magnetic Vinyl Shower Curtain Liner	Maytex	Maytex Mills, Inc	China

Appendix M: Principle component analysis factor correlations of significant attributes on principal component 1 (PC1) and 2 (PC2) for DR12 dilution samples in covariance matrix

Modality	Attribute	PC1	PC2
Aroma	Alcohol	0.98158	0.19104
	Caramel	0.81937	0.57327
	Maple	0.58324	0.8123
	Vanilla	0.61463	0.78882
	Roasted	0.99461	-0.10367
	Woody	0.99281	0.11971
Mouthfeel	Astringent	0.99847	-0.05531
	Silky	-0.99597	0.08973
	Slick	0.98852	0.15108
	Warming	0.98994	-0.14151
Taste	Bitter	0.97549	-0.22004
Aftertaste	Bitter	0.97201	-0.23495
	Brown Spice	0.95102	0.30913
Aroma-by-mouth	Alcohol	0.99663	-0.08202
	Caramel	0.98095	0.19427
	Maple	0.92943	0.36899
	Vanilla	0.87614	0.48205
	Woody	0.97612	-0.21724

Appendix N: Principle component analysis factor correlations of significant attributes on principal component 1 (PC1) and 2 (PC2) for RA7 dilution samples in covariance matrix

Modality	Attribute	PC1	PC2
Aroma	Alcohol	0.99353	0.1136
	Caramel	0.99382	0.11099
	Vanilla	0.98308	0.18316
	Dark Fruit	0.55935	0.82893
Mouthfeel	Astringent	0.99995	0.01046
	Slick	1	-0.00066
	Warming	0.98745	-0.15792
Taste	Bitter	0.99315	-0.11687
Aftertaste	Bitter	0.99955	0.03008
	Brown Spice	0.99952	-0.03092
	Vanilla	0.97228	0.23381
	Plastic	0.99901	0.04458
Aroma-by-mouth	Alcohol	0.99893	-0.04617
	Caramel	0.98501	0.17248
	Maple	0.99688	0.07897
	Vanilla	0.96137	0.27525

Appendix O: Detailed day-by-day procedural description of rum descriptive analysis panel

Day 1: Introductory session and term generation for rum samples

After granting informed consent (Appendix G), the panel facilitator introduced themselves and their role in the panel. Panelists then introduced themselves to each other. The panel facilitator gave a short presentation that introduced basic sensory science principles and DA methodology. The panelists were then presented with four of the twelve rums (Bacardi Gold, El Dorado 12 year, Ron Abuelo 7 year, and Model 2). Panelists were instructed to evaluate the first sample and develop terms for the different modalities (aroma, aroma-by-mouth, taste, texture/mouthfeel, and aftertaste), they were presented with a term generation worksheet (Appendix H) to aid in the development of terms. The panelists discussed their findings briefly and then were instructed to evaluate the remaining three samples. The panelists evaluated all four rums and were asked to generate attributes for all modalities. Panelists were also encouraged to identify corresponding definitions and references matching these attributes. During discussion, panelists mentioned all terms, definitions and references that had been generated. Through discussion, the panelists compiled an extensive list of possible attributes and corresponding references to be investigated the following day.

While rating, panelists were asked to determine and effective rinsing protocol. Rinses such as water (warm (40°C) and room (23°C)), crackers (saltine (Great Value Unsalted Tops Saltine Crackers, Wal-Mart Stores, Inc., Bentonville, AR) and water (Carter's Water Crackers)) and bread (SaraLee Honey Wheat Bread, Bimbo Bakeries USA, Inc., Horsham, PA) were made available. Panelists were given the opportunity to suggest any other rinses they would like to evaluate.

The panel was then dismissed and panelists were instructed to return at the same time the following day. Once the session concluded, the panel facilitator compiled the final list of terms, attributes and references, including any that may have been written on a panelist's term generation sheet, but not brought up during panel discussion due to time restraints. The initial list consisted of 38 terms and 35 references. The panel facilitator then purchased the references the panel had identified from local stores.

Day 2: Term generation and reference refinement for rums

After signing in, panelists were presented will all of the references they had requested during term generation on day 1. Panelists determined if these references correctly represented the attribute detected in the rums in terms of both quality and concentration. After examining all of the references, panelists were presented with 4 new rum samples (Bacardi White, Appleton Estate 12 Year, Dictador XO, and Model 3) to continue term generation and reference refinement. After panelists had a chance to evaluate all of the rum samples, panelists discussed their findings and put forth new terms and references. Panelists reached consensus on terms and references that needed to be added, modified or eliminated for the next session. Panelists also selected their

rinse protocol, choosing bread, warm and then room temperature water. Panelists were then dismissed and the facilitator compiled the observations from the session in preparation for the next day.

Day 3: Term generation and reference refinement for rums

After signing in, panelists were presented with the references that they kept from day 2 and as well as the new references they generated the previous day. Panelists were asked to evaluate the references and then evaluate the four rum samples (Appleton Estate V/X, Diplomatico Reserva 12 year, Ron Zacapa and Model 1). At the end, panelists were brought back together to discuss if the new references fit in terms of quality and intensity and were given an opportunity to propose any new terms as well. Panelists reached consensus on terms and references that needed to be added, modified or eliminated for the next session. Panelists were then dismissed and the facilitator compiled the observations from the session in preparation for the next day.

Day 4: Term generation and reference refinement for rums

After signing in, panelists were presented with the references that they kept from day 3 and the new references that they generated the previous day. At the beginning of the session, panelists were introduced to the rum aroma wheel. The wheel was presented to help aid in the generation of terms to describe the rum samples. Panelists were asked to evaluate the references and then evaluate the four rum samples (Appleton Estate V/X, Appleton Estate 12 year, Ron Abuelo 7 year, and Model 1) using the wheel to help aid in term generation. At the end, panelists were brought back together to discuss if the new references fit in terms of quality and intensity and were given an opportunity to propose any new terms as well. Panelists reached consensus on terms and references that needed to be added, modified or eliminated for the next session. Panelists were then dismissed and the facilitator compiled the observations from the session in preparation for the next day.

Day 5: Term generation and reference refinement for rums

After signing in, panelists were presented with the references that they kept from day 4 and the new references that they generated the previous day. Panelists were again provided with the flavor wheel and encouraged to use the wheel to aid in the evaluation of the samples. Panelists were asked to evaluate the references and then evaluate the four rum samples (Bacardi Gold, El Dorado 12 year, Dictador XO Insolent, and Model 2) using the wheel to help aid in term generation. After evaluating the samples, group discussion focused of going through the samples together and making sure everyone was able to pull out the same attributes in each sample. Panelists aided each other in helping to pull out those terms in the samples by checking the references and going back and evaluating the samples. Panelists also discussed terms that need to be added, modified or eliminated for the next session. Panelists were then dismissed and the facilitator compiled the observations from the session in preparation for the next day.

Day 6: Reference refinement for rums

After signing in panelists were presented with the references they had generated in previous sessions as well as the new references they had asked for on day 5. After evaluating the references the panelists were asked to evaluate the samples (Bacardi White, Diplomatico Reserva 12 Year, Ron Zacapa, Model 3). Then panelists were asked to refine the list of terms, definitions and references to a semi-final list for which to start scaling with. Panelists were asked to clarify terms and definitions that had not been made clear during previous panel sessions. Panelists were also asked to clarify which modality they detected many of the aroma and aroma-by-mouth attributes as they had been used fluidly between the two during term generation. Panelists were informed that scaling would start the next day. The panel facilitator asked if it would be easier for panelists if the terms were grouped into larger categories to aid in identifying and ranking those terms during scaling and testing. The panelists agreed that would be helpful and the list was adjusted for the next day. The facilitator then dismissed the panel and compiled the observations from the session to prepare for the next day. The final list of generated terms (table X) consisted of 28 aroma, 25 aroma-by-mouth, 4 mouthfeel, 1 taste, and 5 aftertaste attributes, for a total of 63 initial attributes that were identified in the rum samples.

Day 7: Introduction to scaling method and scaling of aroma attributes

After signing in, the panelists were also informed that a subset of the samples, the models, were being removed from the study due to the fact that they were clearly distinguishable from the rums they were models of. Continued evaluation of the samples at this point in time would be futile until further modifications to the model system could be made.

The panelists were then introduced to the concept of scaling. Panelists were instructed on the use of a 15 point categorical scale with 0 being no perception of an attribute and 15 being the strongest intensity of that attribute in the rum samples. Panelists were then trained how to rate the references. Panelists were instructed to select the sample with the highest intensity of that attribute and assigning it a score of 15 and then rate the reference and other two according to where they fell along that 15 point scale. Panelist then used the three rum samples (Appleton Estate V/X, Diplomatico Reserva 12 Year, and Dictador XO Insolent) to score the references for the 35 aroma terms the panel had generated. Due to the number of samples and references that the panelists had to rate, there was no time for group discussion and panelists were dismissed once they finished rating the references. After the panel, the reference and sample scores were calculated and any reference that received a score of 15 or greater was adjusted to be re-rated the following day.

Day 8: Scaling of aroma attributes

After signing in, the same or modified references (where necessary) were presented to the panelists for continued rating and scoring. Panelists were also presented with reference scores for the unmodified

references and their individual and group score from the previous session to aid in training. Panelists were then presented with three rum samples (Bacardi Gold, Appleton Estate 12 year, and Ron Abuelo 7 year) and asked to rate the aroma references that had been adjusted from the previous day. Panelists were encouraged to try different evaluation protocols, such as letting the sample air for 3 seconds before evaluating, if the reference intensity was to strong when the sample was opened and evaluated immediately. Panelists were asked to make note if a different evaluation procedure brought the reference intensity on scale. Panelists were also asked to practice scoring the rums for the attributes with established reference ratings, using the reference rating as the anchor to score the rum samples, if they had time. After the panel, the reference and sample scores were calculated and any reference that received a score of 15 or greater was adjusted to be re-rated the following day.

Day 9: Scaling of aroma atrributes

After signing in, the same or modified references (where necessary) were presented to the panelists for continued rating and scoring. Panelists were also presented with reference scores for the unmodified references and their individual and group score from the previous session to aid in training. The panelists were presented with three samples (Bacardi White, El Dorado 12 year, and Ron Zacapa) and asked to score the references that had been adjusted from the previous day. Due to the intensity of some of the references in comparison to the rum samples, two evaluation protocols were developed. The first protocol was to remove the lid of the reference and immediately evaluate the aroma intensity using bunny sniffs. The second protocol was to remove, the lid, let the sample air for three seconds and then evaluate the aroma intensity. Panelists were free to provide feedback as to how references, definition or evaluation procedures may need to be adjusted. The facilitator then dismissed the panel and compiled the reference and samples score to provide feedback to the panelists the following day.

Day 10: Scaling Mouthfeel and Taste attributes

After signing in, the panelists were presented with all of the references for the mouthfeel and taste modalities for reference scoring. Panelists were asked to score the samples in the same way they had scored the aroma attributes. Panelists were reminded that all references needed to be evaluated in the mouth. Panelists were then presented with three rum samples (Bacardi Gold, Appleton Estate 12 year, and Dictador XO Insolent) and asked to rate the 10 mouthfeel, taste, and aftertaste references the panel had generated during term generation. Panelists were also asked to practice scoring the rums for the attributes with established reference ratings, using the reference rating as the anchor to score the rum samples. Panelists were free to suggest any terms, definitions or references that needed to be modified or eliminated. Panelists chose to remove tingling from the mouthfeel terms. The facilitator then dismissed the panel. After the panel, the reference and sample scores were calculated and any reference that received a score of 15 or greater was adjusted to be re-rated.

Day 11: Scaling aroma-by-mouth attributes

After signing in, panelists were presented with all of the aroma-by-mouth attributes for reference scoring. Panelists were asked to score the samples in the same way they had scored the previous attributes. Panelists were reminded of the importance of evaluating all of the reference in the mouth, as well as the importance of rinse protocol. Panelists were then presented with three rum samples (Bacardi White, Diplomatico Reverva 12 year, and Ron Abuelo 7 year) and asked to rate the 23 aroma-by-mouth attributes the panel had generated during term generation. Panelists were free to suggest any terms, definitions or references that needed to be modified or eliminated. Panelists chose to remove citrus, green apple, butterscotch, and cucumber from the aroma-by-mouth attributes. The facilitator then dismissed the panel. After the panel, the reference and sample scores were calculated and any reference that received a score of 15 or greater was adjusted to be re-rated the following day.

Day 12: Scaling

After signing in, panelists were presented with the same or modified references (where necessary) continued rating and scoring. Panelists were provided with their individual scores along with the scores of the other panelists and group average in order to aid in training. Panelists were then provided with a paper ballot similar to the one they use during booth testing, both in terms of modality presentation order, grouping of terms, and attribute and reference information. Panelists were instructed to rate the three samples (Appleton Estate V/X, El Dorado 12 year, and Ron Zacapa), one at a time, using the reference scores that had been generated during the scaling sessions the previous days. Panelists were asked to re-score any references that had been modified from previous days and indicate their score on the references sheet. The facilitator dismissed the panelist's once they had finished rating their rums and informed them that they would receive the same samples the following day to be able to discuss their ratings and work towards a better group consensus. The facilitator then compiled the sample scores to provide feedback and aid in training the following day.

Day 13: Scaling

After signing in, panelists were presented with their references and the same samples from the previous day (Appleton Estate V/X, El Dorado 12 year, and Ron Zacapa). Panelists were also provided with their scores as well as the scores of the other panelists and the group average to aid in guiding them to rate the samples in a more uniform way. Panelists were encouraged to rerate the samples using the references as anchors. Panelists then discussed their rating and provided feedback as to any terms, definitions or references that needed to be modified or eliminated. During the group discussion, panelists elected to form protocols for the evaluation of each modality as follows: aroma – removed the cover and let air for three seconds without fanning the sample, then place your nose in the middle of the glass and evaluate the aroma, aroma-by-mouth, place the sample in your mouth and hold for 5 seconds and then evaluate the aroma-by-mouth attributes,

mouthfeel and taste – place the samples in your mouth and then hold for 3 seconds and evaluate the attributes, aftertaste, place the samples in your mouth, hold for three seconds and expectorate and they evaluate once the burning sensation has dissipated. Panelists also chose to eliminate raisin, green and vegetal aroma terms. The facilitator then dismissed the panel and compiled the sample scores to provide feedback and aid in training the following day.

Day 14: Scaling

After signing in, panelists were provided with their references and scores from the previous day. Panelists then evaluated one sample (Diplomatico Reserva 12 year), as the previous day they had indicated being able to focus on and discuss one sample would be most beneficial to aiding in reaching group consensus in rating the rums. During discussion, panelists focused on attributes they had the most difficulty with including baking spices, alcohol, and woody terms. Panelists elected to consolidate dried apricots and prunes into one term, dried fruit. Panelists also eliminated the terms toffee, and liquorice, as well as removed coffee from aroma and aroma-by-mouth. The facilitator then dismissed the panel and compiled the sample scores to provide feedback and aid in training the following day.

Day 15: Individual practice booth testing

Panelists attended two 30 minutes booth testing sessions in order to become familiar with the individual testing and Compusense software (session 1: Bacardi White and Appleton Estate 12 year, session 2: Dictador XO Insolent and Bacardi Gold). When panelists arrived at the session, they were presented with a tray of references, their rinses, and a table which detailed each term and its corresponding definition, reference and intensity rating. Panelists were also provided with their scores from the previous day. Panelists were encouraged to review their tray of references to refresh themselves as to the intensity and rating of the references for each attribute. Panelists were allowed to review their references for as long as they wanted. After reviewing all of the references, panelists moved to the booths to individually rate the samples.

Testing took place in individual booths, with positive airflow and temperature set to 68°F. All samples were presented in black double old-fashion glasses (Threshold, Target, USA) labeled with random three digit codes and evaluated under red lighting. The samples in each set were presented to the panelists in random order. The ballot was presented to panelists using Compusense seven as the interface in the booth and Compusense five to launch the test (Need Product Information). When panelists entered the booth they were instructed to enter their panelist code, and then indicated to the session facilitator that they were ready for the test by turning on their light. Panelists reviewed both samples at the same time and were told to check the sample codes before proceeding with the test. Panelists were cued with instructions for each modality, and the test had built in timers so that the sampling procedures were consistent between all panelists. Panelists strictly followed the tasting protocols they developed (described in day 13). Panelists were given a 0 - 15 point

categorical scale with which to rate the samples, with 0 being no perception of the attribute and 15 being the greatest intensity of the attribute in the rum samples. Panelists were provided with the attribute, definition, reference and reference score for each term. After evaluating the first samples, panelists were given a 2 minute break where they were instructed to follow the rinse procedure to cleanse their pallet before the next sample. After rating the second sample panelists indicated to the facilitator that they were done.

Panelists then came back a second time during the day, at least 30 minutes after finishing the first session to evaluate a second sample set. Panelists were asked to review any references that they felt gave them trouble but were told they did not have to review every attribute. The second sample was also evaluated in the booths. After all panelists had finished the data was exported and evaluated in Microsoft excel.

Day 16: Scaling

After signing in, panelists were presented with their references and samples (Appleton Estate 12 year and Dictador XO Insolent). Panelists were also provided with their scores as well as the scores of the other panelists and the group average from the previous day to aid in guiding them to rate the samples in a more uniform way. Panelists were asked to rate the samples using the references as anchors on the scale. The facilitator then compiled all of the ratings in order to provide feedback and aid in group discussion. Panelists decided to eliminate the cucumber aroma and brown sugar aroma-by-mouth terms. The facilitator then dismissed the panel and compiled the sample scores to provide feedback and aid in training the following day.

Day 17: Scaling

After signing in, panelists were presented with their references, scores from the previous day and samples (Bacardi White, Diplomatico Reserva 12 year, Appleton Estate V/X, and Ron Zacapa). The four samples selected were chosen to give the broadest spectrum possible in sample variations for panelists to practice with. Panelists were only presented with the 15 references that they had the most difficulty rating consistently. Panelists were again reminded that at least one of the samples should receive a 15 for each attribute when sampling. All of the scores were then tabulated and terms that had standard deviations of 3 or greater were discussed. The facilitator encouraged panelists to finalize all terms, definition, reference scores and evaluation protocols. During the discussion, panelists elected to eliminate clove, malty, and cola from aroma and aroma-by-mouth terms, cooling from aroma, and to change the nutmeg term to brown spice. The facilitator then dismissed the panel and compiled final list of all sample modalities, terms, definition and intensities in Table 6.1 for the rum samples. The final list consisted of 19 aroma, 12 aroma-by-mouth, 3 mouthfeel, 1 taste, and 5 aftertaste terms.

Day 18: Scaling

On the final day of scaling, panelists were provided with their finalized list of terms and reference and their scores from the previous day to aid in training to score more consistently as a group. Panelists were instructed on booth protocol and reminded of the specific sample evaluation procedures that they had set for each modality. Panelists were then given one last opportunity to change any of the sampling protocols or the order in which the modalities or attributes were presented on the ballot. Panelists then reviewed their references and practiced rating one sample (El Dorado 12 year). Panelist discussed terms they were struggling with rating consistently. The panelists were then dismissed and the panel facilitator compiled the observations from the session in preparation for booth testing the next day.

Day 19: Individual booth testing of rum sample sets 1 and 2

Panelists attended two 30 minutes booth testing sessions, at least 30 minutes apart, to rate the attributes they had identified in the rums according to the selected references (session 1: Bacardi Gold and Dictador XO Insolent, session2: Appleton Estate V/X and Ron Zacapa). When panelists arrived at the session, they were presented with a tray of references, their rinses, and a table which detailed each term and its corresponding definition, reference and intensity rating. Panelists were encouraged to review their tray of references to refresh themselves as to the intensity and rating of the references for each attribute. Panelists were allowed to review their references for as long as they wanted. After reviewing all of the references, panelists moved to the booths to individually rate the samples. Testing took place in individual booths, with positive airflow and temperature set to 70°F. All samples were presented in black double old-fashion glasses (Threshold, Target) labeled with random three digit codes and evaluated under red lighting. The samples in each set were presented to the panelists in random order. The ballot was presented to panelists using Compusense seven as the interface in the booth and Compusense five to launch the test.

When panelists entered the booth they were instructed to enter their panelist code, and then indicated to the session facilitator that they were ready for the test by turning on their light. Panelists received both samples at the same time and were told to check the sample codes before proceeding with the test. Panelists were cued with instructions for each modality, and strictly followed the evaluation protocols they had developed for each modality as outlined in day 15. Panelists were allowed to re-evaluate the sample provided that they follow the rinse protocol between tastings. Panelists were given a 0-15 point categorical scale with which to rate the samples, with 0 being no perception of the attribute and 15 being the greatest intensity of the attribute in the rum samples. Panelists were provided with the attribute, definition, reference and reference score for each term. After evaluating the first samples, panelists were given a 2 minute break where they were instructed to follow the rinse procedure to cleanse their pallet before the next sample. After rating the second sample panelists indicated to the facilitator that they were had concluded the test.

Panelists then came back a second time during the day, at least 30 minutes after finishing the first session to evaluate a second sample set. Panelists were asked to review any references that they felt gave them trouble but were told they did not have to review every attribute. The second sample was also evaluated in the booths.

Day 20: Individual booth testing of rum sample sets 3 and 4

Panelists again attended two 30 minute sessions and the procedure was the same as outlined for day 19 (session 3: Ron Abuelo 7 year and El Dorado 12 Year, session 4: Bacardi White and Diplomatico Reserva 12 year).

Day 21: Individual booth testing of rum sample sets 5 and 6

Panelists again attended two 30 minute sessions and the procedure was the same as outlined for day 19 (session 5: Bacardi Gold and Appleton Estate 12 Year, session 6: Diplomatico Reserva 12 year and Ron Abuelo 7 year).

Day 22: Individual booth testing of rum sample sets 7 and 8

Panelists again attended two 30 minute sessions and the procedure was the same as outlined for day 19 (session 7: Appleton Estate V/X and Dictador XO Insolent, session 8: El Dorado 12 Year and Appleton Estate 12 year).

Day 23: Individual booth testing of rum sample set 9

Panelists attended only one 30 minute session and the procedure was the same as outlined for day 19 (session 9: Bacardi White and Ron Zacapa). Throughout the five days of booth testing, rums were assigned to the test sessions randomly, making sure that all 9 rums were presented one time before the second set of evaluated took place. All rums were evaluated in duplicate.

Appendix P: Detailed day-by-day procedural explanation of ethanol dilution descriptive analysis panel

Day 1: Introductory session and term generation for rum samples

After signing in, the facilitator gave a short presentation introducing the panelists to the purpose of the second DA panel and a review of basic DA procedures and protocols. Panelists were informed that samples would be presented in sets of three, with the same three samples always appearing together, samples sets consisted of the same rum at different dillutions. The importance of following the rinse protocol was highly stressed as differences between samples would be smaller than the first panel. The rinse protocol was the same as the previous panel, bread, warm water and room temperature water, with the panelist expectorating all of the rinses and samples. Panelists were then presented with three samples, all dilutions of Ron Abuelo 7 year (straight rum, 1:2 dilution with 40% ethanol, 1:2 dilution with water). Panelists were instructed to evaluate all three samples and develop terms for the different modalities (aroma, aroma-by-mouth, taste, mouthfeel, and aftertaste) along with corresponding definitions and references. They were presented with a term generation worksheet (Appendix H) to aid in the development of terms. During discussion, panelists mentioned all terms, definitions and references that had been generated. Through discussion, the panelists compiled an extensive list of possible attributes and corresponding references to be investigated the following day. The panel was then dismissed and the panel facilitator compiled the final list of terms, definitions and references. The initial list consisted of 55 terms and 39 references. The panel facilitator then purchased the references the panel had identified from local stores.

Day 2: Term generation and reference refinement

After signing in, the panelists were presented will all of the references they had requested during term generation on day 24. Panelists determined if these references correctly represented the attribute detected in the rums in terms of both quality and concentration. After examining all of the references, panelists were presented with a different dilution series, this time the Diplomatico Reserva 12 year rum (straight rum, 1:2 dilution with 40% ethanol, 1:2 dilution with water), to continue term generation and reference refinement. After panelists had a chance to evaluate all of the rum samples, panelists discussed their findings and put forth new terms and references. Panelists reached consensus on terms and references that needed to be added, modified or eliminated for the next session. Panelists were then dismissed and the facilitator compiled the observations from the session in preparation for the next day.

Day 3: Term generation and reference refinement

After signing in, the panelists were presented will all of the references they had kept from the previous day and the new references generated on day 25. Panelists determined if these references correctly represented the attribute detected in the rums in terms of both quality and concentration. After examining all of the

references, panelists were presented with the Ron Abuelo 7 year dilution series to continue term generation and reference refinement. After panelists had a chance to evaluate all of the rum samples, panelists discussed their findings and put forth new terms and references. Panelists had stated that they were having a difficult time generating at silky mouthfeel reference. The facilitator provided the panel with several potential references to aid in reference selection, including 2% ,whole, almond and coconut milks. Panelists identified almond milk as having the same silky mouthfeel as found in the rums. Panelists reached consensus on terms and references that needed to be added, modified or eliminated for the next session. As a group, the panelists and facilitator discussed which attributes were identified in each rum sample. Panelists were then dismissed and the facilitator compiled the observations from the session in preparation for the next day.

Day 4: Reference refinement

After signing in, the panelists were presented will the references from the previous day, modified if necessary. Panelists determined if these references correctly represented the attribute detected in the rums in terms of both quality and concentration. After examining all of the references, panelists were presented with the Diplomatico Reserva 12 year rum dilution series to continue term generation and reference refinement. Panelists reached consensus on terms and references that needed to be added, modified or eliminated for the next session. As a group, the panelists and facilitator discussed which attributes were identified in each rum sample. Panelists were then dismissed and the facilitator compiled the observations from the session in preparation for scaling the next day.

Day 5: Scaling of aroma, taste and mouthfeel attributes

After signing in, panelists were presented with the references they had identified during term generation and were presented with the Diplomatico Reserva 12 year dilution set. Panelists were reminded of the reference rating procedure, as presented on day 7. Paneilsts were asked to select the sample with the highest intensity of that attribute and rate it a 15 and then rate the reference and other two samples accordingly. Panelists rated the intensity of the aroma, mouthfeel and taste attributes. Panelists then discussed which references needed to be modified for the next day. The facilitator then dismissed the panel and then compiled the reference and samples score to provide feedback to the panelists the following day. Any reference that received a score of 15 was modified to be presented to the panelists again the next day.

Day 6: Scaling of aroma-by-mouth and aftertaste attributes

After signing in, panelists were presented with the references they had identified during term generation and were presented with the Ron Abuelo year dilution set. Panelists were reminded of the reference rating procedure, as presented on day 7. Panelists rated the intensity of the aroma-by-mouth, and aftertaste attributes, as well as any attributes that had scored about a 15 the previous day. Panelists discussed which

references needed to be modified for the following day. The facilitator then dismissed the panel and then compiled the reference and samples score to provide feedback to the panelists the following day. Any reference that received a score of 15 was modified to be presented to the panelists again the next day.

Day 7: Scaling

After signing in, panelists were presented with the modified references as well as the Ron Abuelo 7 year dilution set. Panelists were asked to review their references and then score the references that had been modified from the previous day. Panelists then scored the three rums for each attribute in order as they would in the booth, using their reference as an anchor point for the scale. Panelists then discussed terms they were struggling with and worked towards rating those terms uniformly. The panel eliminated terms that were difficult to identify or didn't change between samples in either rum set. The facilitator then dismissed the panel and then compiled the reference and samples score to provide feedback to the panelists the following day.

Day 8: Scaling

After signing in, panelists were presented with the references and their scores from the precious day to aid in panel training. Panelists were also presented with the Diplomatico Reserva 12 year dilution set. Panelists were asked to rate the samples using the references as anchors on the scale. The facilitator and panel then discussed terms the group was struggling with. Panelists decided to eliminate the grassy aroma and floral aroma-by-mouth terms. The facilitator then dismissed the panel and compiled the sample scores to provide feedback and aid in training the following day.

Day 9: Scaling

After signing in, panelists were presented with the references and their scores from the precious day to aid in panel training. Panelists were also presented with the Ron Abuelo 7 year dilution set. Panelists were asked to rate the samples using the references as anchors on the scale. The facilitator and panel then discussed terms the group was struggling with, and panelists were free to adjust or remove any terms. The facilitator then dismissed the panel and compiled the sample scores to provide feedback and aid in training the following day.

Day 10: Scaling

After signing in, panelists were presented with the references and their scores from the precious day to aid in panel training. Panelists were again presented with the Ron Abuelo 7 year dilution set to aid in training and allow panelists to evaluate their repeatability when scoring the samples. Panelists were asked to rate the samples using the references as anchors on the scale. Once the panelists had finished rating the samples the facilitator disclosed which samples corresponded to each other from the previous day. The facilitator and

panel then discussed terms the group was struggling with, and panelists were free to adjust or remove any terms. The facilitator then dismissed the panel and compiled the sample scores to provide feedback and aid in training the following day.

Day 11: Booth Practice

Panelists attended one booth practice session, to evaluate the Diplomatico Reserva dilution set. When panelists arrived, the reviewed their references and then proceeded to the booth for testing. Booth testing conditions were the same as for the first session with the panelists receiving three samples per set and only rating one sample set for booth practice.

Day 12: Scaling Final Day

After signing in, panelists were presented with their scores from the previous day booth testing in order to aid in training. Panelists were also presented with their references and the Diplomatico Reserva 12 year dilution set, the same set they evaluated in booth testing in order to better work towards group consistency and work on precision. Panelists rated the samples for the different modalities using the references as anchors for the scale. After consolidating the rating for the day, panelists discussed the samples and compared their results to their scores from the previous day. Panelists finalized the list of terms, definitions, references and reference scores. The finalized list consisted of 24 total attributes: 8 aroma , 5 aroma-by-mouth, 2 taste, 4 mouthfeel and 5 aftertaste attributes. The facilitator then dismissed the panel and compiled the data to prepare for booth testing.

Day 13: Booth Testing

When panelists entered, they were presented with their finalized reference list. After reviewing the references, panelists proceeded to the booth. Booth testing conditions were the same as in the first study, except this time panelists were presented with a dilution sample set consisting of three rums, instead of the two rums like before. Panelists evaluated both the Ron Abuelo and Diplomatico Reserva sample sets. Sample presentation within the dilution set was randomized as well as which dilution set the panelists received first. Panelists evaluated bo Panelists evaluated two sample sets, with a minimum of a thirty minute break between the end of one evaluation session and the beginning of the next.

Day 14: Booth Testing

Panelists arrived for booth testing, which proceeded in the same fashion as presented above in day 36.

Day 15: Wrap-up and panelist payment

When panelists arrived, they were compensated for their participation in the study. Once all panelists had been paid, the facilitator presented a short PowerPoint revealing to the panelists the brands of rums they had been evaluating for the past 8 weeks. Panelists were allowed to ask any question they had about the samples or DA panel procedures. Panelists were then dismissed.

Appendix Q: Permission statements

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