Lost Spirits

DISTILLED SPIRITS

- SCIENCE - INNOVATION - ART -

Trace Carboxylic Acid & Ester Origin in Mature Spirits

Part 1 of mapping the chemical composition of mature rum

Introduction

Oak matured distilled spirits are one of the least well-understood consumer products in the world. While other chemically complex products, such as beer, wine, and cheese have received millions of person hours of study as well as tens of millions of dollars in research funding, distilled spirits have received comparably little attention.

As a consequence of beer and wine research, distilled spirits fermentation is fairly well understood. Due to its importance to industrial chemistry, distillation is very well understood. Oak maturation, by contrast, is not well understood. Much of the information printed on the topic also contains gross factual errors and flawed assumptions. Perhaps even less well understood is the potentially important interactions of chemicals formed during the fermentation with compounds extracted from the oak. The most comprehensive study on the topic was published in the Journal of the American Chemical Society in 1908 by C. A. Crampton and L. M. Tolman. Unfortunately Crampton and Tolman lacked modern tools such as gas chromatography and mass spectroscopy making their work very incomplete.

As a new distillery, we desired to gain engineering control over the entire production process including maturation. The first step on this journey was to attempt to understand the chemistry so that we might discover novel ways to control it - beyond the simple 85 degree heated warehouse described by Crampton and Tolman.

The chemical compositions and variations found in aged spirits have proven highly complex and thus the work has been broken into parts. In this first part, I intend to break down the observations made studying the volatile range carboxylic esters in aged rums.

Background

Carboxylic esters are the compounds responsible for fruit flavors found in nature. They have long been observed to form during the oak maturation of distilled spirits are are thus of great interest to us as spirits makers. Carboxylic esters are formed when an alcohol chemically bonds to a carboxylic acid.

Several natural organisms make carboxylic esters, including brewers yeast, flowering plants, and fruit trees. Industrially they are manufactured by combining alcohols and carboxylic acids in the presence of strong acid catalysts. Carboxylic acids are necessary to form carboxylic esters. These acids are made by several natural organisms as well including yeast and bacteria that may colonize fermentations (both intentionally and unintentionally). Carboxylic acids (especially acetic) are also known to be thermal decomposition by-products of wood. While it is well known that esters form during oak maturation, what is not known is the degree to which precursor carboxylic acids originate from the charring/toasting of the barrel vs from bacteria and yeast in the fermentation and which ones originate where.

This investigation deals primarily with carboxylic esters and their precursor carboxylic acids. In order to study them in more detail 5 commercially available rum samples were subjected to direct inject mass spectroscopy and compared. The instrument also picked up peaks of some relevant aldehydes with similar volatility values.

The chromatograms have been arranged in pairs to better show key observations on a case by case basis.

NOTE: Traditionally ethyl acetate has been the most extensively monitored carboxylic ester, as it is the easiest to detect due to concentration. It almost certainly originates in the oak, because it is known to increase with every year that a spirit ages without stopping. However, ethyl acetate has a very high aroma detection threshold and thus has less impact on flavor than other trace carboxylic esters we are interested in studying in this paper. We also have an occupational interest in identifying ways to boost trace carboxylic ester production (fruity flavors), as opposed to ethyl acetate (solvent aromas).

Isoamyl Acetate
Aroma: Sweet banana, fruity, with a ripe estry
Human detection threshold: 2ppb

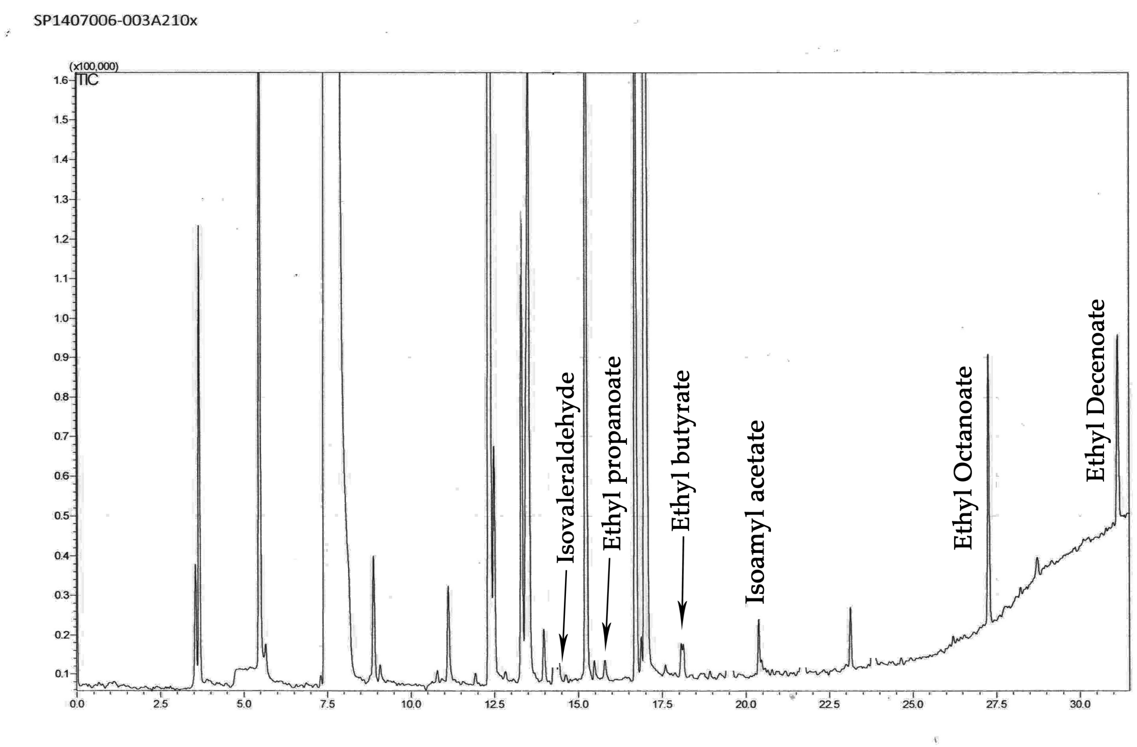
Ethyl Octanoate
Aroma: Waxy, sweet, pineapple, fruity, with creamy dairy
Human detection threshold: 15ppb

Ethyl Butyrate
Aroma: Fruity, Juicy Fruit, pineapple, cognac
Human detection threshold: 1ppb

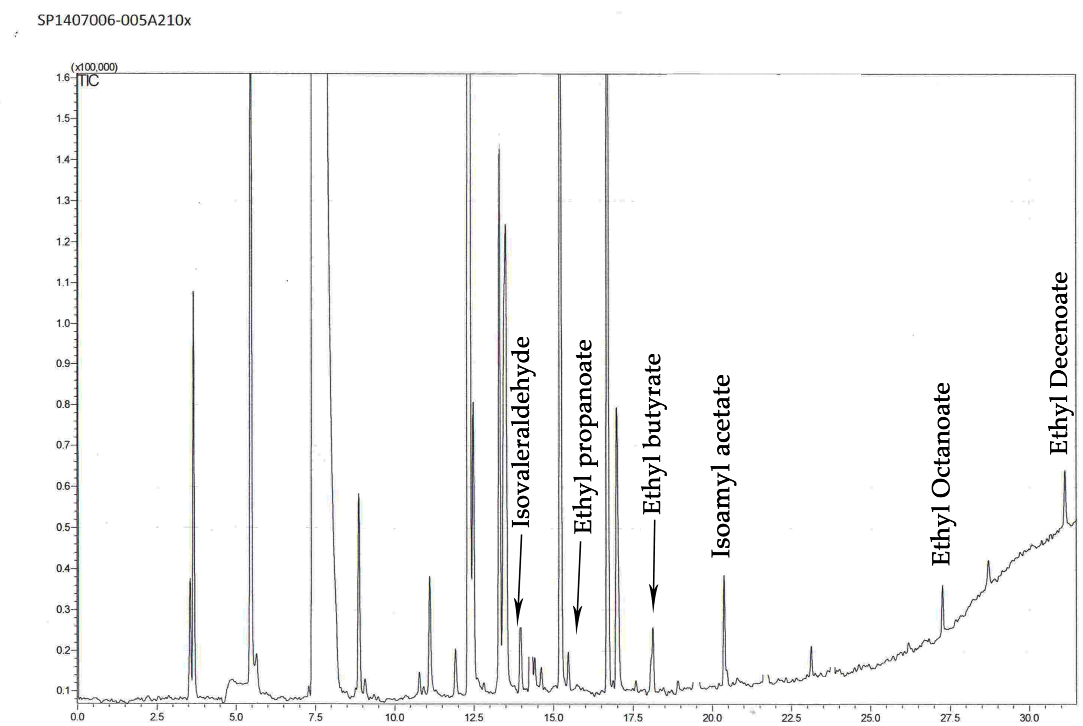
Isovaleraldehyde
Aroma: Chocolate, peach, fatty
Human detection threshold: 1ppb

Ethyl propanoate
Aroma: Sweet fruity rum, Juicy Fruit, grape, pineapple
Human detection threshold: 10ppb

Ethyl Hexanoate
Aroma: Sweet fruity pineapple, waxy green banana
Human detection threshold: 1ppb



7 year aged column still rum



8 year (circa) aged column still rum

The above two VOC chromatograms compare and contrast two ex-bourbon barrel aged, column distilled rums from two different distilleries in the Caribbean. Though in general the two have similar fingerprints, the subtle differences in these two compositions is strikingly large when the extreme pungency (low human detection threshold) of the labeled compounds are taken into account. The 7 year old rum on the left has nearly 3x the concentration of ethyl octanoate (pineapple aroma) as compared to the 8 year sample on the right. However, the 8 year sample on the right compensates with 2x-4x the concentrations of Isovaleraldehyde (chocolate, peach), ethyl propanoate (fruity rum), ethyl butyrate (pineapple), and Isoamyl acetate (ripe bananas). Interestingly the rum on the right is held in higher regard critically.

The fact that the aging and distillation of these two products was so similar appears to suggest that the key difference originates in the fermentation (likely yeast strain choice). However, more comparisons will be necessary to conclude anything. It is possible that a variation in charing of the wood could have provided the difference, or perhaps a subtle difference in distillation protocol. The warehouse climates are assumed to be highly similar so that was likely not a factor. Also idiosyncratic barrels could be ruled out as both products are blends of hundreds of casks.

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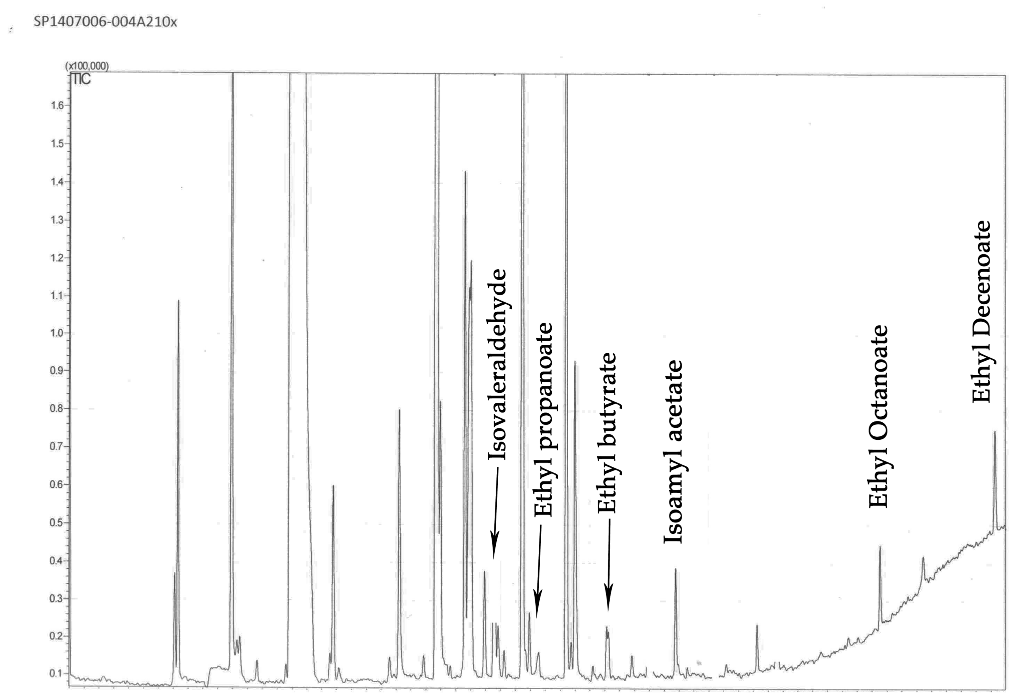
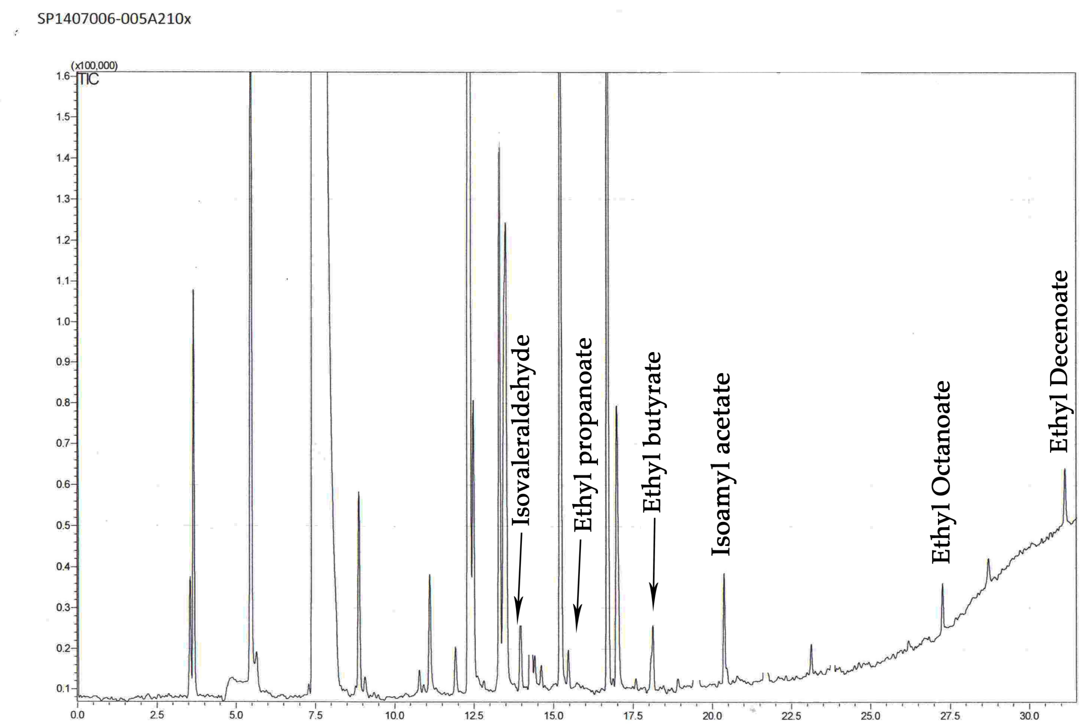


15 year aged column still rum



8 year (circa) aged column still rum

The above two VOC chromatograms compare and contrast two ex-bourbon barrel aged, column distilled rums from two different distilleries in the Caribbean. Again in general they have similar overall fingerprints, the subtle differences in these two compositions appear to be within the tolerances shown in the prior comparison. If anything the 8 year on the right is more similar to the 15 year sample show here than it was to the 7 year shown previously despite the fact that the rum on the left is almost twice the age of the rum on the right.

The fact that the fermentation and distillation of these two products was so similar yet the sample on the left is nearly twice the age of the product on the right, and is nearly identical in VOC fingerprint appears to suggest that by the 7-8th year of oak aging all of the volatile range carboxylic ester formation is complete. This would strongly suggest that the carboxylic acid precursors for these pungent trace esters originate entirely in the fermentation and are not derived from the oak. If the precursor acids were derived from the oak we would expect to see far higher peaks in the 15 year rum.

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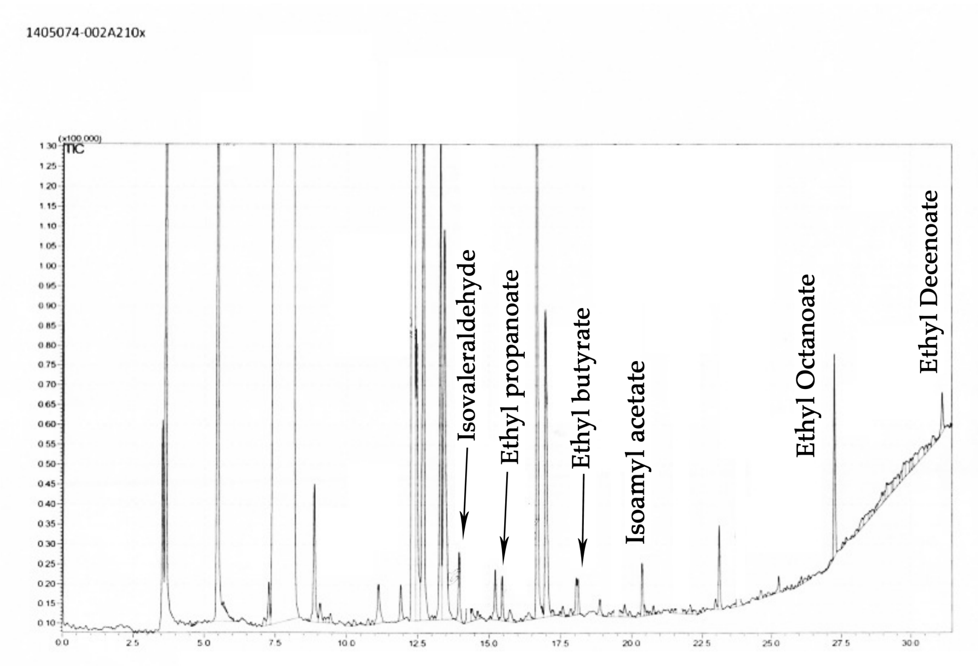
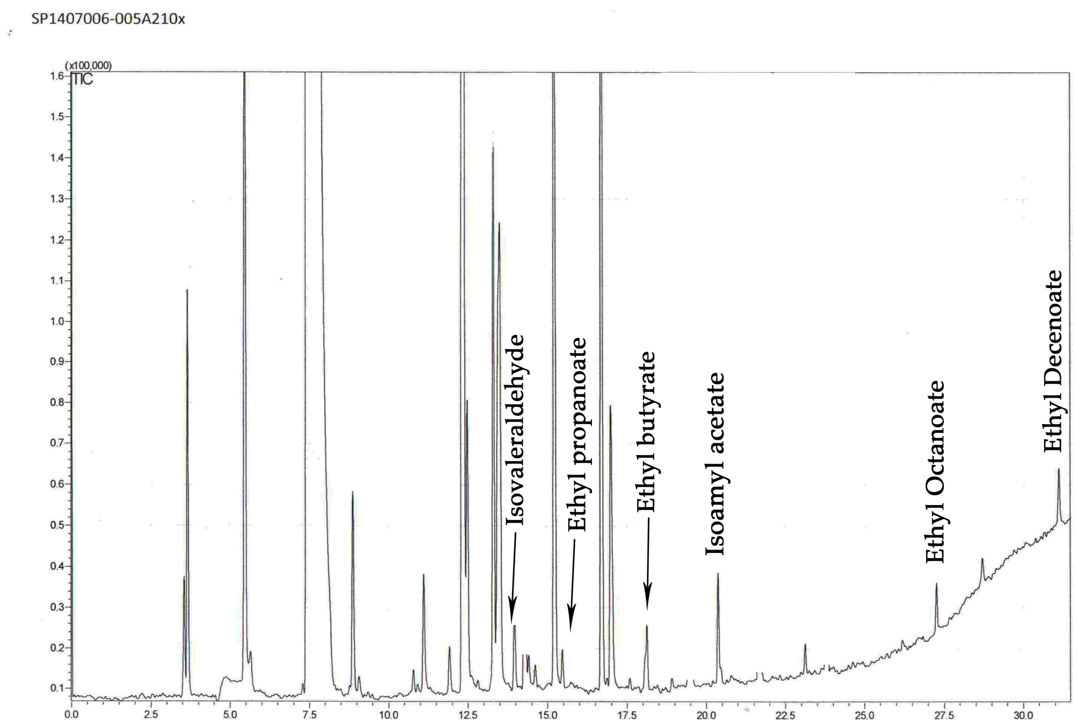


25 year aged column still rum



8 year (circa) aged column still rum

The above two VOC chromatograms compare and contrast two ex-bourbon barrel aged, column distilled rums from two different distilleries in the Caribbean. Again in general they have similar overall fingerprints, the subtle differences in these two compositions appear to be within the tolerances shown in the prior comparisons. However, this time we are comparing a 25 year aged rum to the 8 year old rum and again we see very little change.

The fact that the fermentation and distillation of these two products was so similar yet the sample on the left is over 3x the age of the sample on the right appears to further confirm the suspicion that the carboxylic ester formation is complete by 7-8 years of aging. It also appears to soundly confirm that the trace carboxylic ester profile of a mature rum are essentially predetermined prior to aging. Though it may take as many as 7 years to complete the process - further aging cannot form additional trace carboxylic esters beyond the level of precursors available from in the white spirit.

Note: The scale on the chromatogram on the left is slightly different from the one on the right. It has been sized to provide an approximate apples to apples comparison of peak heights.

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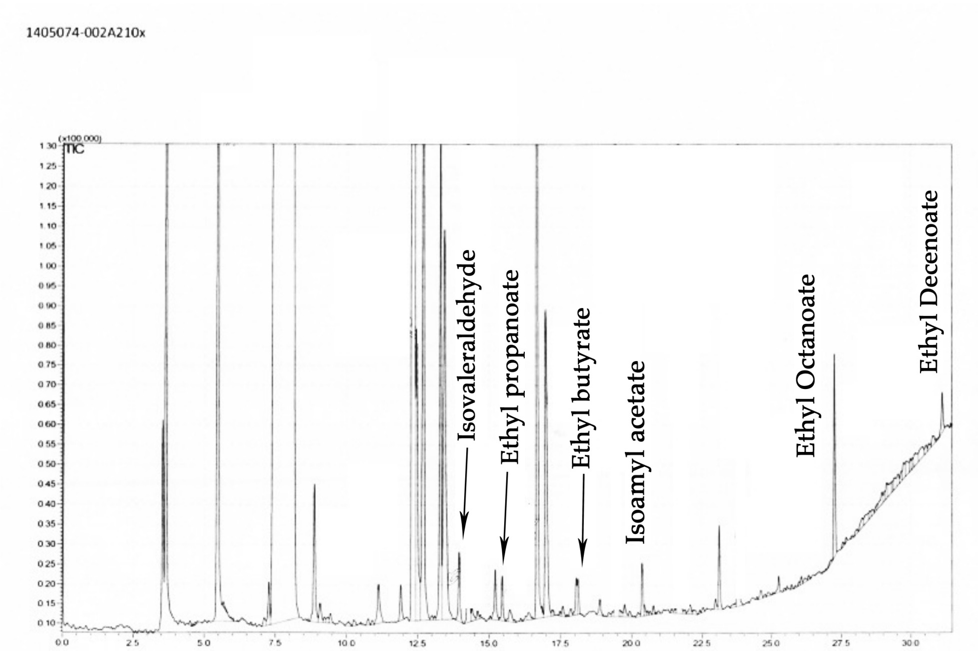
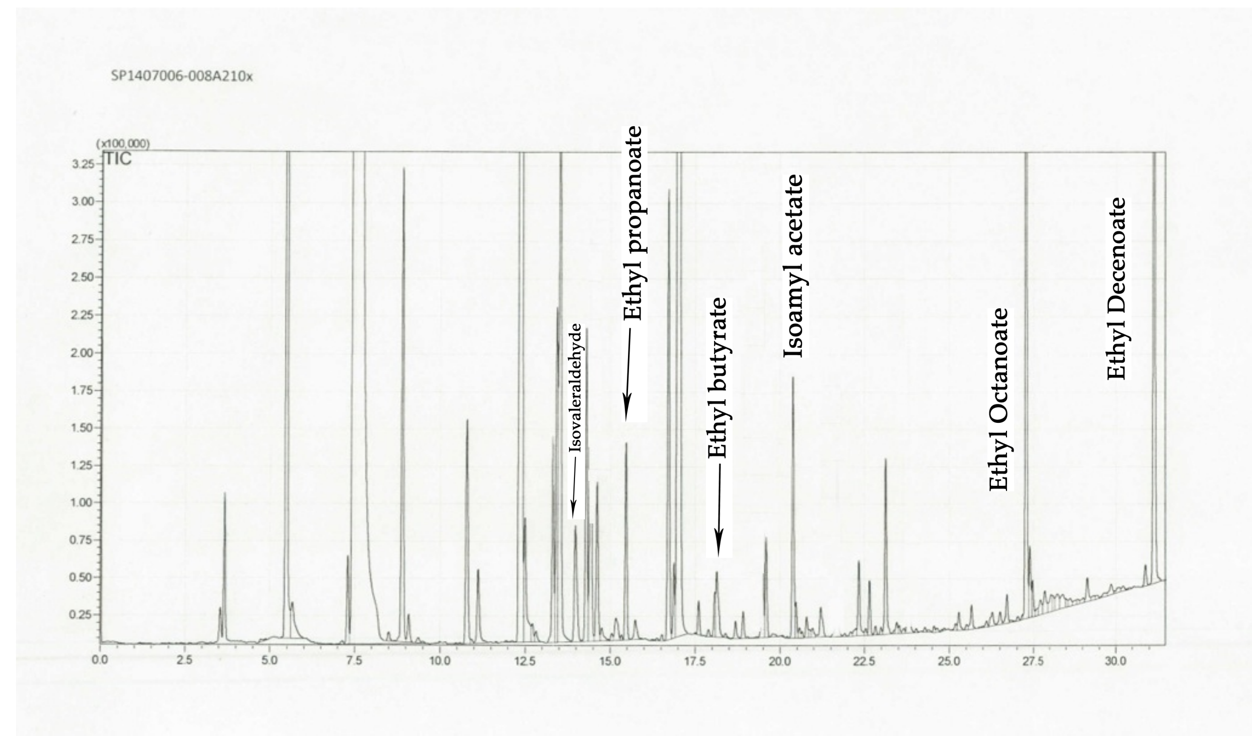


25 year aged column still rum



33 year aged pot still rum

Given the prior observations comparing and contrasting various column distilled rums a final comparison was made against a 33 year aged pot distilled rum. As was expected the pot distilled rum showed significantly higher peaks for every target ester owing to the fact that the pot still provides much less efficient separation and allows far more of the chemical composition of the fermentation to pass into the final spirit. This observation appears to confirm that the trace ester density is not only predetermined prior to the spirit entering the cask but that the distillation cuts and level of rectification has a massive effect on the final character of the aged spirit. Given the conventional wisdom that aging can “fix” certain off notes in spirits, this is not surprising as many off notes are in fact carboxylic acids that have not yet been esterified during the aging process.

NOTE: The 33 year pot distilled rum is shown “zoomed out” by a factor of almost 3x. Every target ester out preformed the column still. The most striking effects are shown in the Isoamyl acetate with a peak height over 7x higher in the pot still rum. The ethyl propanoate peak is 5x higher in the pot still rum and the ethyl octanoate peak is off the chart.

Conclusion

Trace carboxylic esters (excluding ethyl acetate) in mature distilled spirits are responsible for the fruit flavors often seen in desirable products. While it is true that the spirit must be aged in oak to increase ester density and convert off notes from carboxylic acids to desirable esters, it was found that their peak concentration is limited by precursor carboxylic acids generated in the fermentation.

It was further observed that pot stills are far better at capturing precursor acids from the fermentation than column stills. However, I would expect column stills designed for lower rectification as is common in Armagnac or Martinique produce to results more closely related to those shown for the pot still rum.

To achieve Lost Spirits's goals of making the most heavy, robust, rich rum possible, it is apparent that a pot still is ideal. The observations also show that special attention must be paid to the bacteria and yeast strain choices in fermentation. Fermentations could be engineered to generate higher concentrations of favorable precursors. This optimized fermentation coupled with a pot distillation could then generate white spirits more suited to gain substantial flavor density through esterification during the aging process.

Of course esterification of trace carboxylic acids (excluding ethyl acetate) is only one component of the aging process. Oak extractives and phenolic compound reactions must be addressed with the same vigor to gain a full picture of the maturation process. The ethyl acetate formation must also be studied in the context of these observations as acetic acid extraction from the oak is likely influencing the equilibrium of the aging spirit (as a buffer solution) in an important way.