Lost Spirits

DISTILLED SPIRITS

- SCIENCE - INNOVATION - ART -

Comparing and Contrasting Semi-Volatile Fingerprinting of Mature and Immature Heavy Pot Still Rum

Part 2 of mapping the chemical composition of mature rum

Summary & Background

Summary:
In part 1, *Trace Carboxylic Acid & Ester Origin in Mature Spirits,* we looked in detail at the volatile range compounds and how they change as a spirit matures. We learned that the VOC range aroma compounds (primarily fruity esters) mature concentration appears to be predetermined prior to barreling. We also learned that low rectification products (generally pot distilled) exhibited far more ester precursors and thus the ability to age longer and to a greater aroma and flavor density than the more common high rectification rums.

In this follow up document, we looked at the semi-volatile organics (SVOCs) to see how they change during maturation. The SVOC range includes the majority of maturation compounds including phenolic aldehydes extracted from the oak, medium chained carboxylic esters, complex esters, phenylated esters, higher alcohols, furanic aldehydes, etc.

A SVOC analyses was carried out using gas chromatography - mass spectroscopy (GCMS) with the goal of fingerprinting mature rum. Many rums were sampled organoleptically to choose products for use as benchmarks of maturity. Two samples were selected from the available products. A 31 year old heavy pot still rum and a 33 year old heavy pot still rum. Both products met our target criteria of maturity - in terms of flavor density, smoothness (perception of alcohol burn), and complexity. Unfortunately, only the 33 year old product was analyzed due to difficulty obtaining a second sample of the 31 year old product.

Background:
Carboxylic esters like ethyl butyrate and ethyl octanoate are 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. While the majority of them were explored in the VOC paper (part 1), two additional esters, ethyl decanoate, and ethyl dodecanoate proved very important in the SVOC range.

Phenolic aldehydes like sinapaldehyde and vanillin are byproducts of the thermal decomposition of lignin in oak. They are responsible for a host of flavors in mature spirits ranging from smoky to vanilla pipe tobacco and wintergreen. As expected they played a major role in the maturation of spirits. While phenolic aldehydes were expected, the extreme importance of sinapaldehyde in particular was unexpected.

(1) Acetyl
Aroma: Waxy, sweet, pineapple, fruity, with creamy dairy
Human detection threshold: 15ppb

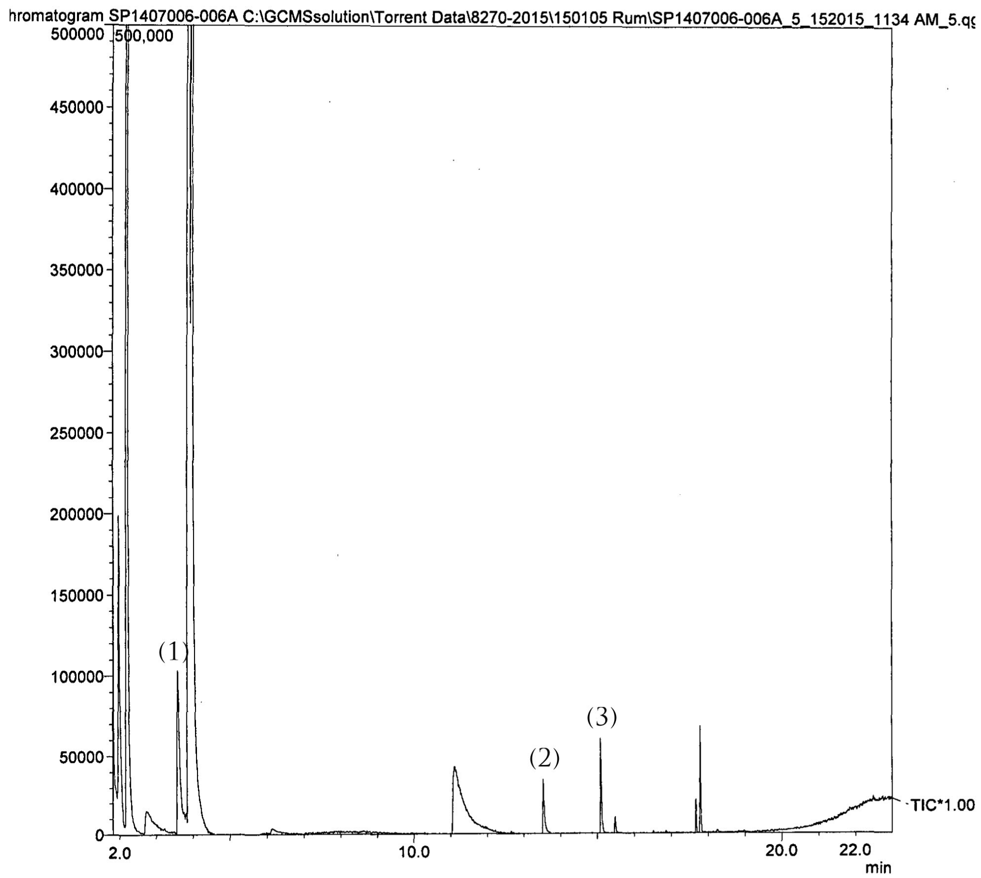
(2) Ethyl Decanoate
Aroma: Sweet, waxy, fruity, apple
Human detection threshold: 510ppb

(3) Ethyl Dodecanoate
Aroma: Oily, fatty, floral with fatty fruity taste
Human detection threshold: 2000ppb

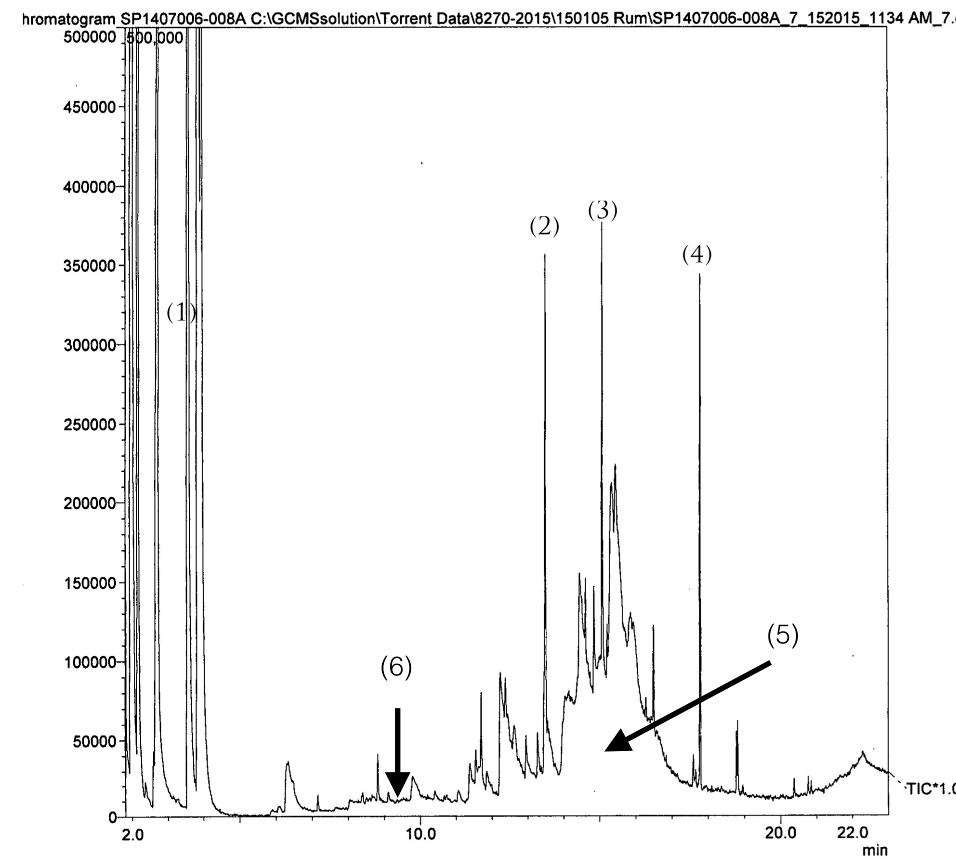
(4) Sinapaldehyde
Aroma: Sweet, woody, tobacco
Human detection threshold: UNKNOWN

(5) Primary Sucrose (table sugar)
Likely caramelized sugar added prior to barreling, Obscures data.

(6) White noise
A complex mix of low concentration compounds including phenylated esters, complex esters, phenols and furanic aldehydes. Much of the white noise is obscured by the added sucrose.



Un-aged heavy pot still rum



Surrogate

33 year aged heavy pot still rum

The above two SVOC chromatograms compare and contrast two heavy pot still rums. The sample on the left is freshly distilled heavy pot still rum (from Lost Spirits Distillery in California). The sample on the right is a Caribbean heavy pot still rum aged for 33 years in an oak barrel.

The overall signature of mature rum was clearly visible in the comparisons and was dominated by four distinct characteristics. The mature rum exhibited a significant increase in the esters ethyl decanoate and ethyl dodecanoate. Both of these esters were present in the freshly distilled rum but in much lower concentrations than those found in mature rum. The mature rum also exhibited a high concentration of sinapaldehyde and acetal which appear to be oak derived. Perhaps most importantly the mature sample exhibited a large complex mass of “white noise” along the bottom of the chromatogram. This “white noise” represents hundreds of different compounds formed during aging or extracted from the oak. However, the concentrations of the compounds are low and the volatility values are so similar that they merge together into one large unidentifiable mass.

NOTE: The 33 year old sample appears to have been aged with added sugar in the rum.
The large mass in the center is primarily sucrose (table sugar) which could not have been extracted from the barrel.
Unfortunately, the sugar obscures some of the data.

Conclusion

While the volatile esters (seen in the VOC range) in mature distilled spirits are responsible for the fruit flavors in desirable products, it is the semi-volatile range compounds that provide much of the character, flavor, finish, and wood derived aromas in a mature spirit. As a distillery seeking to produce high quality products, a semi-volatile fingerprint was needed to establish a gold standard for quality. Without it, it is not possible to objectively determine when a product has attained maturity or if it is developing the correct signature of a mature spirit in process.

Unfortunately, the available chromatogram libraries did not contain semi-volatile fingerprints for aged rums. They only contained fingerprints for malt whisky. This project identified the chemical signature of a mature heavy pot still rum providing the missing baseline data to assess maturity. In the future this method could be used to compare and uncover counterfeits (immature spirits laced with coloring and flavoring additives) by comparing them to legitimately mature rum. It could also be used to compare subtle differences in products aged with different types of woods or to assess alternative methods and compare them against the signature of a legitimately mature spirit.

The addition of caramelized sucrose to the rum was disappointing. While it may be argued that it is part of the style of these rums, it would have been beneficial to see the chromatogram without the data obscured by the added sugar. While we can compare this chromatogram to whisky chromatograms, in order to gain an idea of what it would look like without the sugar, we cannot obtain a perfect image that way. We must continue to look for a mature rum that does not contain the added sugar in order to gain an perfect unobscured image of maturity. However, this example does provide the majority of the data needed, especially for the compounds with high peak values.