

A New Approach to the Identification of Flavour Compounds in Rum

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The volatile flavour compounds in rum have been identified by analysing distillery oil which is a waste product from a continuous alcohol still which distills the same ferment as that used to produce rum.

Research on the flavour compounds of all alcoholic beverages has forged ahead in the last ten years with the use of gas chromatography and other even more sophisticated analytical methods such as mass spectrometry. However, the research laboratories of few alcoholic beverage companies can afford a mass spectrometer to perform basic research which is so vital to formulating completely new beverages.

Analysing the flavour compounds in rum or any other spirit is simplified by the fact that the raw spirit contains no non-volatile fraction as do wine and beer, and the compounds are more concentrated. Even so, the number of flavour compounds in rum is immense — Liebich(1) has identified over 300 in a Jamaican Rum. As many have been found in whisky and brandy by Kahn(2) and Schaefer(3).

Rum distilleries use gas chromatography to analyse quantitatively six compounds of highest concentration. These are the heads: acetaldehyde, acetal and ethyl acetate and the fusel oil: n-propanol, isobutanol and isoamyl alcohol. Brandy and whisky distilleries analyse the same compounds, although fusel oil could include n-butanol or isoamyl acetate. There is no doubt that the quantitative analysis of these few compounds will tell one the strength of flavour of a spirit, e.g. heavy bodied rums contain up to 1,500 ppm of isoamyl alcohol and light bodied rums can contain as little as 50 ppm of isoamyl alcohol or even none. One can also determine the method of industrial distillation from this simple analysis.

Concentration of Flavour Compounds

To concentrate the many other flavour compounds the rum is extracted with pentane-ether. All organic compounds other than most of the ethanol are extracted into the pentane-ether, which in turn can be distilled off, leaving a concentrate of flavour compounds. A litre of rum will produce about 1 ml of concentrate, thus giving a concentration increase of 1000 times. This concentrate contains hundreds of compounds in addition to ethanol (40 per cent) and fusel oil (55 per cent), and it is therefore difficult to separate out individual compounds.

Even so, the flavour compounds are concentrated to such an extent that a gas chromatogram of this concentrate reveals numerous peaks and many can be tentatively identified by comparing their retention time (time for a compound to be eluted from the instrument) with the retention times of known pure compounds, the assumption being made that

those with identical retention times are the same compound. However, we found that identification of flavour compounds by retention time only was most inconclusive. It is possible to improve the identification by treating the extract so as to remove certain classes of compounds e.g. the extract can be hydrolysed to remove esters. The extract is then reinjected into the gas chromatograph and one can note the peaks that have been removed from the chromatogram. This method of analysis still does not allow for the identification of individual compounds. Only two really acceptable methods of identification exist.

The first is to concentrate and fractionate the extract as much as possible, then inject microlitre quantities of each fraction into a combined gas chromatograph-mass spectrometer (gc-ms). The mixture is separated into individual compounds by the gas chromatograph and these compounds are in turn fragmented in the mass spectrometer and identified by their fragmentation patterns. The second method is to extract vast quantities of spirit; possibly several hundred litres, to obtain enough concentrate for individual compounds to be separated out by vacuum fractional distillation and identified by conventional means.

As we possessed only a gas chromatograph, the latter method was chosen. However, after extracting 10 litres of O.P. rum, only 30 ml of concentrate had been produced, containing mainly ethanol and fusel oil. It was obvious that too much rum would have to be destroyed to obtain a reasonable quantity of extract. The process was uneconomical and wasteful.

The New Approach

To positively identify the individual flavour compounds, at least 1 ml of each was required. Examination of the process in commercial use in the Bundaberg distillery suggested that the problem could be solved by utilising a by-product of industrial alcohol production known as 'distillery oil,' which, on theoretical grounds, should contain the flavour compounds present in rum.

Description of Distillery Operations

In the Bundaberg distillery, the same fermented wash from the fermentation of molasses is used for the distillation of both rum and industrial alcohol and it is evident that those compounds which are present in the rum but not in the industrial alcohol must be removed in one of the other streams leaving the alcohol still. A flow diagram is produced in Fig. 1.

A. Processes Common to Rum and Alcohol Production

The molasses is fermented by the yeast *S. cerevisiae*. After about thirty hours, the fermented wash is pumped to a holding tank

from which it is fed continuously into two separate wash columns. Fractional distillation in the wash columns separates the fermented wash into vapour containing 50 per cent alcohol and aqueous waste (dunder) which runs to drain from the bottom of the wash column.

From this stage the two processes differ.

B. Production of Rum

The vapour from the wash column is condensed and stored. The condensate is called low wine. Batches of low wine are placed in a pot still. The first minutes of condensate are called 'fore-shots' and are discarded. During the next few hours, rum is collected. The water remaining in the pot is discarded. Because of azeotropic distillation in the pot, it was assumed that volatile compounds with considerably higher boiling points than that of isoamyl alcohol would appear in the rum. This was confirmed by chromatography of a pentane-ether extract which revealed many peaks after isoamyl alcohol.

C. Production of Industrial Alcohol

Industrial alcohol is produced by continuous distillation. Instead of condensing vapours from the wash column, they are fed into the middle of a rectifying column which contains about 50 plates. Fractional distillation occurs and alcohol is removed at the top through a series of condensers. The aqueous fraction is discharged at the bottom. Because of the vapour-liquid equilibrium relationships between alcohol, water and distillery oil, the latter collects near the middle of the still.

This oil is removed by tapping off the vapour from a number of middle plates and condensing it. The condensate is mixed with water and the oil floated to the top and removed. The alcohol-water mixture is returned to the rectifying column.

A distribution profile of distillery oil in the rectifying column was obtained by placing taps above every third plate and taking gallon samples.

The fractions were analysed on the gas chromatograph for their ethyl acetate and fusel oil content and the results are given in Table 1. The fractions contained many other compounds besides those mentioned in Table 1.

Table 1 — Distribution Profile of Compounds in Rectifying Column

Plate*	Ethyl Acetate ppm	N-Propanol ppm	Isobutanol ppm	Isoamyl Alcohol ppm	Fusel Oil Total ppm
1	75	8	10	8	26
4	65	8	10	8	26
7	50	8	20	10	38
10	12	25	50	20	45
13	2	300	450	70	820
16	—	1200	1400	700	3300
19	—	1400	1800	1800	5000
22	—	8400	12800	30800	52000
25	—	400	2000	15600	18000
28	—	800	800	12400	14000
31	—	150	80	2200	24300
34	—	250	150	3200	3600

Lower plates were not sampled.

*Plates are numbered from the top of the still.

Comparing Gas Chromatograms of Distillery Oil and Pentane-Ether Extracts of Rum

The gas chromatograms of mature rum extract, raw rum extract and distillery oil are very similar, the main difference being in

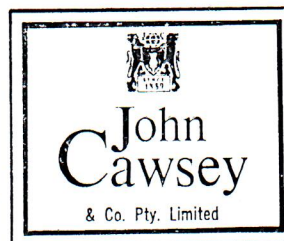


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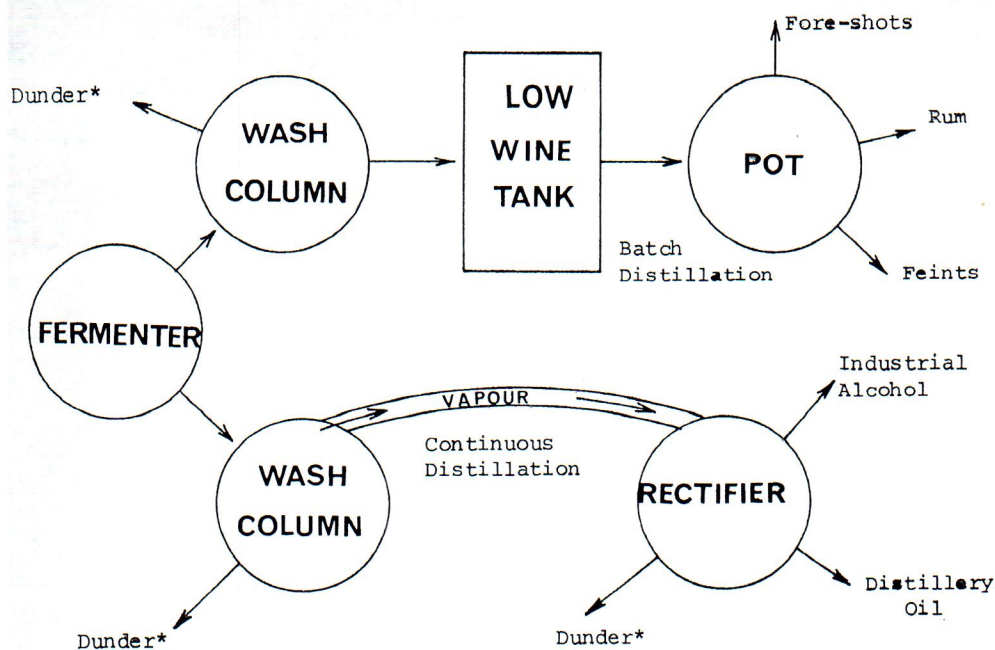


Fig.1. Flow sheet of distillery

* Dunder is the aqueous residue from the stills.

concentration of various peaks. Chemical as well as gas chromatographic comparisons were made where necessary between corresponding peaks in the distillery oil and the pentane-ether extracts to prove that they were identical.

It is evident from these results that distillery oil contains all the flavour compounds which are present in raw rum, as expected from the consideration of the distillery operations.

Separation of Distillery Oil into 'Fusel Oil' and 'Rum Oil'

The distillery oil was concentrated by distilling 5 litres of it at atmospheric pressure. The residue from the distillation consisted of oil alone, while the more volatile materials were distilled off in two fractions. The ethanol was distilled off and discarded. The next fraction contained the water as an oil-water azeotrope. The oil was separated, dried and added to the water-free residue in the pot.

This oil was distilled in the same apparatus and separated into two fractions. The larger fraction, collected up to 132 deg. C, contained the higher alcohols up to isoamyl alcohol and was defined as fusel oil. The residue (100 ml) in the pot contained compounds with higher boiling points than 132 deg. C and was called 'rum' oil.

Analysis of Distillery Oil

The higher alcohols in the fusel oil were n-propanol, isobutanol, n-butanol and isoamyl and active amyl alcohols. A number of esters including isoamyl acetate were also identified. The 'rum' oil contained all of the less volatile flavour compounds in rum. It has been analysed in considerable detail with remarkable success. Many compounds have been isolated pure. They include methyl salicylate, 1-octen-3-ol, 2 heptanol, ethyl decanoate and

1,1,6-trimethyl-1,2-dihydronaphthalene, which Liebich identified in Jamaican Rum using a gc-ms. (We hope to publish full chemical details in a chemical journal).

The fact that compounds that until now have only been identified in rum by gc-ms, have actually been isolated from the distillery oil, shows the great worth of this method of attack. One is still faced with identifying some other compounds in mature rum which, for instance, contains non-volatile compounds extracted from the wood, but our work shows that volatile compounds change only in concentration during maturation and therefore all of the results for raw rum can be applied to a mature rum.

Conclusion

The analysis of the numerous less concentrated but very important, flavour compounds in rum became feasible once distillery oil was analysed and the results applied to rum. It was necessary to extract only a few litres of rum to obtain concentrates for comparison. Many flavour compounds were positively identified, including some that had never before been identified in rum.

No doubt some brandy distillers also produce industrial alcohol or potable spirit, and must therefore produce distillery oil. Even if a distillery does not produce industrial alcohol or potable spirit, it more than likely uses a fractionating still during the distillation of its product and it should be possible to tap off some of the distillery oil from the appropriate portion of the still.

Research so far has shown that the same compounds occur in the heads and fusel oil fractions of all spirits and this leads one to believe that the 'rum' oil portion is where the characteristic flavours of a rum lie, making the analysis of 'rum' oil by way of distillery oil exceptionally important, both to the understanding of flavour and the formulation of a new product.

Acknowledgements

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