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THE ANALYTICAL IDENTIFICATION OF RUM

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SUMMARY

Analytical data have been collected on more than 600 spirits, resulting in a synoptic key from which an unknown spirit may be identified. The data comprise contents of higher alcohols, methanol and ethyl acetate, which can be obtained from a single gas chromatographic injection. Four criteria suffice to distinguish rums from virtually all other spirits, and it can be shown that these criteria are in fact related to the known method of production of rum.

In many countries, rum is subject to control by fiscal, consumer protection or state alcohol authorities, and for these purposes some definition is necessary. The usual features of such definitions are restrictions on the raw materials used and a specification of the minimum content of congeners (volatile compounds other than ethanol), while in some countries congener contents may be used to distinguish different types of rum. In the United Kingdom, rum is subject to a different rate of customs duty from other distilled spirits, but there is no legal definition of rum and no sub-division into types. The generally accepted definition is that it must be produced by fermentation and distillation from sugar cane products in a sugar cane growing area, and it is further understood that it must have the organoleptic characteristics normally associated with rum.

In the event of any dispute concerning the authenticity of rum, the authorities in Britain may possess documentary evidence of the country of origin of the product, but this rarely gives any indication of the method of manufacture. Any confirmation that can be provided by analysis may therefore be valuable. For this purpose, the analytical requirement is for a profile of all the secondary constituents present, rather than an overall total as is the case in many other countries. Other tasks of a revenue protection laboratory are to distinguish spirits which have been produced by illicit stills, and to identify stolen spirits, particularly where the theft is of undutied goods from a bonded warehouse. In each of these cases, detailed analysis of the secondary constituents may enable a positive identification of the sample to be made.

The traditional chemical methods for determining total higher alcohols, total esters, total aldehydes, etc, are of limited value in building up characteristic profiles of spirits, and only the detailed analyses provided by gas-liquid chromatography are suitable for this purpose. Other determinations, such as volatile acidity and extract (non-volatile matter), may also be diagnostic.

Gas chromatographic examination of fractions obtained from rum by solvent extraction and chemical separation has revealed the presence of more than 200 volatile constituents (Liebich, Koenig and Bayer, 1970). However, for fingerprinting purposes, a simple technique was required, based only on the major constituents which could readily be determined by direct injection. A data file has therefore been built up using results for methanol, *n*-propanol, 2-methylpropanol (*iso*-butanol), butan-2-ol, 2-methylbutanol (active amyl alcohol), 3-methylbutanol (*iso*-amyl alcohol) and ethyl acetate. Data on more than 600 spirits of all kinds have been accumulated in this file, and use of a computer enables ratios of individual compounds also to be stored.

EXPERIMENTAL

Samples

Most samples were obtained by retail purchase or were submitted to our laboratory by H. M. Customs and Excise for determination of spirit strength for duty purposes. Samples described as illicit were seized in connection with prosecutions for illicit distillation, and a few high-strength samples were obtained from warehouses prior to bottling. The descriptions of the spirits entered in the data file were taken from the bottle labels or accompanying Customs documents – only in the case of certain samples from distilleries was it possible to verify the source personally.

Gas chromatography

The ethanol content of each sample was adjusted to approximately 40 p. 100 v/v ; a 5 ml aliquot was then mixed with 0.5 ml internal standard (5 g/l *n*-pentanol in 40 p. 100 v/v aqueous ethanol). Two µl portions of the mixture were injected into the gas chromatograph.

Column and conditions : 10 ft (3.05 m) × 1.8 mm i.d. stainless steel column packed with 8p. 100 polyethylene glycol 200 on celite 100-120 mesh ; flame ionisation detectors ; injector temperature 160°C, column 60°C, detector 230°C, nitrogen carrier gas flow adjusted to give retention time for *n*-pentanol of about 45 minutes.

Order of elution of peaks and typical response factors : ethyl acetate 0.19, methanol 0.89, butan-2 ol 0.35, *n*-propanol 0.36, 2-methylpropanol 0.36, 2-methylbutanol 0.67, 3-methylbutanol 0.67, *n*-pentanol 1.00. Contents of individual compounds calculated from peak heights, expressed as g/100 l based on ethanol content.

RESULTS AND DISCUSSION

Table 1 shows the range of figures (expressed as g/100 l ethanol) obtained for each individual congener for the principal types of unsweetened and unflavoured spirits. Brandies and whiskies have each been sub-divided according to type or

TABLE I

Ranges of congener contents (g/100 l)

	N° of samples	Methanol	Ethyl acetate	*n*-propanol	Butan-2-ol	2-methyl-propanol	2-methyl-butanol	3-methyl-butanol
Brandy (Armagnac and Cognac)	104	24-110	26-180	24-93	0-14	45-105	32-71	73-290
Brandy (Marc and Grappa)	18	60-2 900	54-500	32-88	0-370	39-110	30-71	97-240
Brandy (other)	116	23-510	0-470	2-79	0-120	0-160	1-65	2-240
Brandy (overall)	238	23-2 900	0-500	2-93	0-370	0-160	1-71	2-290
Fruit brandies	57	42-2 100	25-510	8-2 400	0-340	5-320	2-80	8-310
Whisky (Scotch blends)	49	9-30	20-70	31-65	—	46-92	12-34	27-85
Whisky (Scotch malt)	39	4-11	25-84	28-64	0-4	42-170	31-73	125-225
Whisky (Bourbon)	15	12-32	44-180	11-42	—	35-125	35-120	75-350
Whisky (overall)	138	2-45	9-180	1-98	0-4	7-170	0-120	0-350
Vodka	15	3-83	1-26	0-4	—	0-6	0-5	0-17
Rum (congeners < 280) (1)	47	0-20	4-120	5-105	0-10	0-71	0-26	0-125
Rum (congeners > 280) (1)	28	4-23	37-1 200	40-1 300	0-350	8-103	5-61	17-290
Rum (overall)	75	0-23	4-1 200	5-1 300	0-350	0-103	0-61	0-290
Illicit spirits	35	0-5	17-82	8-45	0-5	36-250	11-112	70-540

(1) Total congeners (g/100 l) for this purpose taken as higher alcohols plus ethyl acetate.

origin, while the rums have been separated into two groups containing more or less than 280 g/100 l congeners.

From these figures it can be seen that :

(1) even the lightest rums contain more *n*-propanol than any of the vodkas;

(2) the methanol content of all the rums is lower than that of any brandy or fruit brandy ;

(3) nearly all whiskies and all vodkas are distinguished by the absence of any measurable amount of butan-2-ol.

The latter is only a negative feature, since this compound is also absent from the majority of rums and brandies. The figures in table 1 are thus insufficient on their own to distinguish with certainty rums from whiskies or from illicit spirits, and also (although it is not the concern of this symposium) brandies from fruit brandies or from whiskies. To assist in this further separation, the ratios of certain congener contents have been calculated and are shown in table 2.

The ranges for these ratios still overlap to some extent, but it can be seen that :

(1) the ratio ethyl acetate/methanol is frequently much higher for rums and illicit spirits than for other spirits ;

(2) the ratio *n*-propanol/2-methylpropanol is generally higher for rums than for whiskies and illicit spirits ; and

(3) the ratio 2-methylbutanol/3-methylbutanol is often lower for rums than for whiskies.

The ratio of the combined amyl alcohols to 2-methylpropanol was used by SINGER (1966) to distinguish brandies from whiskies, but with the greater number of results now available it is clear that this distinction is only valid for restricted classes of spirits, e.g. in distinguishing Cognacs from blended Scotch whiskies, and this ratio is of no value in identifying rums.

For the purpose of identifying any unknown sample solely by analytical data, a lengthy synoptic key has been produced, but this can be greatly simplified if the object is *only to distinguish rum from other spirits*. Virtually all rums were found to possess the following characteristics :

Methanol content	< 23 g/100 l ethanol
Ratio *n*-propanol/2-methylpropanol	> 0.7
Ratio 2-methylbutanol/3-methylbutanol ..	< 0.38
Ratio ethyl acetate/methanol	> 1.8

Samples in which any of these constituents were not detectable were automatically excluded, and for this reason two white rums, together with two imitation rums, all the vodkas and several grain whiskies were rejected. These two white rums contained no amyl alcohols and might well be unacceptable as rums according to the definitions used in some european countries. In contrast, 10 of the 500 samples not described as rum also possessed all four of these characteristics given for rum. Three of these were illicit spirits, probably produced from sugar or treacle, three were oriental spirits of unknown origin and four were Scotch malt whiskies. The latter have quite pronounced flavours and are unlikely in practice to be confused with rums. This combination of four criteria is thus capable of separating rums from all other spirits with a success rate of about 98 p. 100.

TABLE 2

Ratios of congener contents

	Nº of samples	ethyl acetate / methanol	2-methylbutanol / 3-methylbutanol	*n*-propanol / 2-methylpropanol	2 + 3-methylbutanol / 2-methylpropanol
Brandy (Armagnac and Cognac)	104	0.2-3.1	0.20-0.55	0.34-1.07	1.2-4.5
Brandy (Marc and Grappa)	18	0.07-1.7	0.23-0.35	0.44-1.32	2.3-4.3
Brandy (other)	116	0-2.8	0.03-2.0	0.05-4.0	0.2-6.5
Brandy (overall)	238	0-3.1	0.03-2.0	0.05-4.0	0.2-6.5
Fruit brandies	57	0.04-4.2	0.14-0.40	0.32-77	0.7-5.9
Whisky (Scotch blends)	49	1.0-6.5	0.34-0.46	0.46-1.2	0.5-1.5
Whisky (Scotch malt)	42	3.1-15	0.29-0.56	0.23-1.0	1.3-2.9
Whisky (Bourbon)	15	2.4-7.4	0.27-0.57	0.12-0.52	2.9-4.6
Whisky (overall)	138	0.4-17	0.27-0.57	0.12-2.2	0.5-4.6
Vodka	15	0.07-3.1	—	—	—
Rum (congeners < 280) (1)	47	0.5-31	0.15-0.45	0.7-6.7	0-5.8
Rum (congeners > 280) (1)	28	2.6-167	0.14-0.33	0.9-42	1.9-7.2
Rum (overall)	75	0.5-167	0.14-0.45	0.7-42	0-7.2
Illicit spirits	35	7-194	0.15-0.41	0.08-0.9	0.9-6.5

(1) See footnote in table 1.

Since some of the figures used are critical, it should be pointed out that they may be to some extent dependent on the column conditions used. The system chosen was intended primarily to give the best separation of the higher alcohols, and it is not necessarily the ideal column for methanol or ethyl acetate. It is possible that slightly lower methanol results may be obtained with other column materials, while the ethyl acetate peak is known to be subject to interference from any diethylacetal present. This does not prevent the result from being used in an empirical classification scheme, and any disadvantage is outweighed by the convenience of obtaining all the results from a single injection. The effect of the column on the ratio of the two amyl alcohols will be considered later.

Before considering the significance of these four criteria, it is instructive to see which of them exclude which other classes of spirits. In the first place, all vodkas and some grain whiskies are eliminated by the absence of amyl alcohols. The limit on methanol excludes all brandies and fruit brandies, and indeed virtually all other spirits except whiskies and the illicit spirits. The ratio of *n*-propanol to 2-methylpropanol eliminates most of the illicit spirits, all the U. S., Canadian, Japanese, Dutch and Irish whiskies and about two-thirds of the Scotch whiskies. The remainder are then excluded by the ratio of the amyl alcohols. The fourth criterion, the ratio of ethyl acetate to methanol, is thus not essential but is included as an additional filter to ensure the elimination of Scotch grain whiskies. The latter are used mainly for blending and only one brand is known to be commercially available in bottle, so relatively few samples were included in this survey. Many of these contained no amyl alcohols, but where these alcohols are present it is possible that the ratio could fall below 0.38, leading to their inclusion with the rums unless the ethyl acetate/methanol ratio is also considered.

The separation scheme so far described was developed quite empirically from the results of examining nearly 600 spirit samples. However, its value in distinguishing different spirits would be enhanced if it could be demonstrated that the criteria used were attributable to the materials used or the method of production of the various spirits. The congeners in a distilled spirit may depend upon the raw materials used, the conditions of fermentation and the distillation technique, and all three of these factors are important in the case of rum.

The first and most significant characteristic of rums is the very low content of methanol. This is shared with vodkas (and also gins), the illicit spirits, which in Britain are mostly obtained from fermented sugar or treacle solutions, and the Scotch whiskies. On the other hand, very high methanol contents are found in the fruit brandies and the marc and brandies other than Cognac and Armagnac. REINHARD (1969), commenting on the derivation of methanol in brandy from breakdown of pectin, has correlated the higher values in marc brandies with the presence of pectolytic enzymes in grape skins, and a similar explanation is probably valid for the fruit brandies. Conversely, the low methanol content of other spirits may be ascribed to the absence of pectin in grain and sugar products.

The methanol content of a spirit is not significantly affected by rectification, but in the case of the higher alcohols the overall content and the proportions of individual alcohols are very much dependent on the technique of distillation. An exception to this statement is butan-2-ol, which occurs in appreciable amounts in some rums and brandies but is virtually absent in many others. REINHARD (1969)

observed a correlation with the methanol content in brandies and fruit brandies, and this is confirmed in general terms by the present work : butan-2-ol was found in nearly all fruit brandies, marc brandies and, to a smaller extent, the lesser French brandies, but was not measurable in Armagnacs, Cognacs and brandies from Spain, Cyprus, Greece and Australia. These results, together with the absence of this alcohol from grain spirits, suggest a derivation from some ingredients of fruit skins, but this explanation is clearly not applicable to rums. Some 20 p. 100 of the rum samples, particularly those from Jamaica, contained butan-2-ol, but none of these had exceptional methanol contents. A possible explanation is provided by HIEKE (1972), who ascribed a high butan-2-ol content in wines to spoilage by bacterial or mould fermentation, and it is significant that those Jamaica rums which contain more than 100 g/100 l p.A. of butan-2-ol also contain exceptional amounts of *n*-propanol.

Turning to the primary alcohols, the quantity and proportions of fusel alcohols in fermented liquors are known to be affected by the strain of yeast used (ENGAN, 1974), while in distilled spirits the distillation technique is also a major influence. These alcohols may be formed in various ways, but a major contribution is generally attributed to the Ehrlich pathway from α-amino acids :

$$\underset{\displaystyle NH_2}{R.CH.COOH} \longrightarrow R.CO.COOH \longrightarrow R.CHO \longrightarrow R.CH_2OH$$

Thus a proportion of the 2-methylpropanol and 2- and 3-methylbutanols is formed from valine, leucine and isoleucine. Formation of *n*-propanol by the Ehrlich pathway is less certain, since the amino-acid precursor would be α-aminobutyric acid, which is not normally present in yeast fermentation systems. GUYMON, INGRAHAM and CROWELL (1961) have attributed the formation of *n*-propanol in the fermentation of glucose to an Ehrlich-type pathway starting from α-ketobutyric acid, an intermediate in the synthesis of isoleucine, which itself gives rise to 2-methylbutanol. The values for the ratio *n*-propanol/2-methylpropanol show that rums in general contain proportionately more propanol than all other spirits except some fruit brandies. If this additional propanol were derived from α-ketobutyric acid, one might expect it to be associated with an increased 2-methylbutanol content, but in fact the ratio of 2- to 3-methylbutanol in rums is comparable to that for Cognacs and distinctly lower than the value for whiskies, so some other explanation is necessary.

Exceptionally high figures for the *n*-propanol/2-methylpropanol ratio (*i.e.* 10 or more compared with typical values of 2 for other rums and about 0.5 for most brandies and whiskies) are found in some heavy Jamaica rums, most of which also contain high levels of butan-2-ol and ethyl acetate. It is probably safe to attribute these to bacterial fermentation, but this cannot be true for the majority of rums. Coupled with the low methanol content, the high propanol figure is one of the most characteristic analytical features of rum from all parts of the world, and must therefore be associated with its starting materials. It is significant that the illicit spirits produced in Britain from refined sugar or refinery syrups do not show this feature, so it seems reasonable to attribute it to a constituent of cane juice or molasses which is removed during the manufacture of sugar. One of the major amino acids in molasses is the dicarboxylic acid glutamic acid, either in the free state or as its amide glutamide. BÖTTGER and STEINMETZER (1960) have shown that in beet molasses some of the glutamic acid is decarboxylated by means of an enzyme to give γ-amino-butyric acid, which is also a known constituent of cane molasses. There is also evidence (RODRIGUEZ, 1968) for the presence of α-aminobutyric acid in cane molasses and this has been shown to be formed from glutamic acid in sunlight, particularly in the presence of sucrose (PERTI, BAHADUR and PATHAK, 1961). A possible mechanism for the formation of *n*-propanol in rum fermentation would thus be the Ehrlich pathway from α-aminobutyric acid and ultimately from glutamic acid. Some support for this comes from the observation by MAUREL, SANSOULET and GIFFARD (1965) that *n*-propanol is more predominant in rums made from molasses than in those from cane juice.

The other higher alcohol ratio used in the classification scheme is that of the two amyl alcohols, 2- and 3-methylbutanol. This measurement depends on the use of a GLC system which gives complete resolution of these peaks and data in the literature is therefore limited. DRAWERT, HEIMANN and TSANTALIS (1967) comment on different relative proportions of these alcohols between Cognacs and German brandies, and much greater differences are apparent in this work, but the actual results all show higher ratios of 2-methylbutanol/3-methylbutanol than those of the German workers. Correlation with the results of MARTIN and CARESS (1971) is also difficult and the differences are presumably due to varying degrees of resolution on the different column systems used. By the technique used on this work, nearly all rums and brandies give a ratio below 0.35 while most whiskies are above this figure. The only other spirits giving a consistently high ratio are Dutch genevas, so this appears to be a characteristic of grain spirits. The final ratio characteristic of rum is that of ethyl acetate to methanol. Ethyl acetate is present in all potable spirits and is one of the predominant aroma constituents. The ethyl acetate content increases during maturation of the spirit at a rate dependent on the amount of acetic acid present (SCHOENEMAN, DYER and EARL, 1971). The relatively high ratio (generally between 3 and 20) in most rums is in fact due more to the low methanol content than to a high value for ethyl acetate, but in certain Jamaica rums the ester content is much greater, so that the ratio may increase to over 100. The conditions of fermentation of these rums permit the development of acetic acid and thus of ethyl acetate, and the pot still distillation technique does little to remove these constituents. The illicit spirits also tend to have a high ethyl acetate/methanol ratio, which again is probably due to the acidity of the wash.

CONCLUSIONS

The scheme we have outlined has shown itself capable of distinguishing rums as a class from all other spirituous beverages available in Britain. The constituents on which the scheme is based are not peculiar to rum and are consequently not those mainly responsible for the characteristic flavour and aroma associated with rum. Nevertheless, the relative proportions of these constituents can be related to the raw material or the method of production of rum and their use as diagnostic features can thus be justified. Detailed comparison with individual results may allow an unknown sample to be identified as a particular type of rum and even, in favourable circumstances, as a particular commercial brand.

RÉSUMÉ

IDENTIFICATION ANALYTIQUE DU RHUM

Des résultats analytiques ont été réunis sur plus de 600 eaux-de-vie, donnant une clé synoptique à partir de laquelle une eau-de-vie inconnue peut être identifiée.

Les résultats comprennent les taux d'alcools supérieurs, de méthanol et d'acétate d'éthyle, qui peuvent être obtenus à partir d'une seule injection en chromatographie en phase gazeuse.

Quatre critères suffisent pour distinguer les rhums des autres alcools ; ces critères sont en fait liés à la méthode connue de production du rhum.

RESUMEN

IDENTIFICATION ANALITICA DEL RON

Han sido reunidos los resultados analíticos respecto a más de 600 aguardientes, que constituyen una llave sinóptica a partir de la cual puede ser identificado un aguardiente.

Los resultados integrán los contenidos de alcoholes superiores, de metanol y de acetato de etilo, que pueden ser obtenidos a partir de una inyección única en cromatografía de fase gaseosa.

Cuatro criterios bastan para distinguir los rones de los demás alcoholes. Estos criterios se encuentran vinculados, en realidad, al método conocido de producción de ron.

RIASSUNTO

IDENTIFICAZIONE ANALITICA DEL RUM

Più di 600 acquaviti sono state sottoposte ad analisi. I risultati hanno permesso di stabilire una tabella sinottica che permette di identificare un'acquavite sconosciuta.

In questi risultati sono inclusi i tassi d'alcooli superiori, di metanolo e di acetato d'etile che passono essere ottenuti a partire da una sola iniezione in gas-cromatografia.

Quattro criteri bastano per distinguere i rums dagli altri alcooli ; questi criteri sono infatti legati al noto metodo di produzione del rum.

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