

## The Classification of Whiskies by Reference to their *Iso*-Pentanol/*Iso*-Butanol Ratio

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Published data giving the *iso*-butanol and *iso*-pentanol contents of various whiskies are collated and reviewed. The ratio between these components is derived and found to be sufficiently characteristic of the type of whisky to provide a means of identification.

Complaints concerning spirituous liquor which the Public Analyst has to investigate are usually concerned with strength. Occasionally a more discerning consumer complains about the type or brand of spirits supplied. The present investigation was initiated by an allegation that an "inferior American rye" had been served at a bar in answer to a request for a well-known brand of Scotch whisky.

The major constituents of the so-called "impurities" in spirits have been well established, but only to the extent that it is possible broadly to distinguish whisky, brandy, rum, etc. Since the advent of gas chromatography a more detailed examination of the congeners in spirits has become possible and from published work it would appear that the composition of the fusel oil is clearly the most fruitful line to pursue in the present case.

### Experimental

Practical details have been discussed by Singer<sup>1</sup> and by the Research Committee on the Analysis of Potable Spirits.<sup>2</sup>

The analyses made in this laboratory, on which Table V is based, were by gas chromatography using a 5 ft  $\times$   $\frac{1}{4}$  in o.d. glass column having a stationary phase consisting of 100/200 celite coated with 10 per cent. PEG 400. The column was operated isothermally at 90°C using a flame ionisation detector and nitrogen as carrier gas at a flow rate of about 20 ml/min. These conditions provided sufficient resolution to separate *iso*-butanol and *iso*-pentanol, which showed retention times of approximately 7 and 14 minutes respectively. The isomeric *iso*-pentanols were not resolved.

Before injection, the samples were adjusted, if necessary, to 40 per cent. v/v ethanol. To 10 ml of the adjusted sample was added 1 ml of a solution of *n*-pentanol as internal standard. This solution consisted of 5 g of pure *n*-pentanol made up to 1 litre with 40 per cent. v/v aqueous ethanol. The response was compared with appropriate standards made up in 40 per cent. v/v aqueous ethanol containing the same amount of internal standard as in the sample.

## Results

Singer<sup>1</sup> reports a number of typical analyses of spirits and draws attention to the significance of the ratios between the higher alcohols and the consistency with which the ratios are reproduced in spirits of the same type. He reports only a limited number of whiskies other than Scotch, however, and there is insufficient evidence to show whether a distinction on this basis is possible. Singer's results for whisky are summarised in Table I. More extensive data

TABLE I  
DATA REPORTED BY SINGER

| Type            | Number of samples |      | <i>Iso</i> -butanol<br>as parts per 10 <sup>5</sup> of absolute<br>alcohol in the sample | <i>Iso</i> -pentanol | Ratio<br><i>iso</i> -pentanol,<br><i>iso</i> -butanol<br>all samples |
|-----------------|-------------------|------|------------------------------------------------------------------------------------------|----------------------|----------------------------------------------------------------------|
| Scotch Blend    | 11                | Max. | 100                                                                                      | 94                   | 1.36                                                                 |
|                 |                   | Min. | 61                                                                                       | 74                   | 0.74                                                                 |
|                 |                   | Mean | 83.5                                                                                     | 80.1                 | 0.98                                                                 |
| Scotch All-malt | 9                 | Max. | 138                                                                                      | 220                  | 1.99                                                                 |
|                 |                   | Min. | 88                                                                                       | 164                  | 1.58                                                                 |
|                 |                   | Mean | 116                                                                                      | 206                  | 1.80                                                                 |
| Scotch Grain    | 5                 | Max. | 126                                                                                      | 19                   | 0.19                                                                 |
|                 |                   | Min. | 49                                                                                       | 4.3                  | 0.06                                                                 |
|                 |                   | Mean | 85                                                                                       | 9.2                  | 0.11                                                                 |
| U.S. Bourbon    | 3                 |      | 140                                                                                      | 505                  | 3.61                                                                 |
|                 |                   |      | 135                                                                                      | 475                  | 3.52                                                                 |
|                 |                   |      | 155                                                                                      | 406                  | 2.62                                                                 |
| Canadian        | 1                 |      | 22                                                                                       | 88                   | 4.0                                                                  |

are reported by Schoeneman *et al.* for American cistern room (immature) whiskies<sup>3</sup> (Table II), for mature bourbon<sup>4</sup> (Table III) and for Scotch whisky<sup>5</sup> (Table IV). In the first of these three papers, the ratios between the *mean* figures for *iso*-pentanol and *iso*-butanol are derived for bourbon, rye and corn

TABLE II  
CISTERN ROOM WHISKIES (SCHOENEMAN *ET AL.*)

| Type         | Number of samples |      | <i>Iso</i> -butanol<br>as parts per 10 <sup>5</sup> of absolute<br>alcohol in the sample | <i>Iso</i> -pentanol | Ratio<br><i>iso</i> -pentanol,<br><i>iso</i> -butanol<br>all samples |
|--------------|-------------------|------|------------------------------------------------------------------------------------------|----------------------|----------------------------------------------------------------------|
| Bourbon Mash | 82                | Max. | 129.6                                                                                    | 454.6                | 7.33                                                                 |
|              |                   | Min. | 40.8                                                                                     | 194.2                | 2.31                                                                 |
|              |                   | Mean | 73.0                                                                                     | 310.5                | 4.40                                                                 |
| Corn Mash    | 16                | Max. | 137.6                                                                                    | 418.0                | 6.37                                                                 |
|              |                   | Min. | 42.0                                                                                     | 223.6                | 2.66                                                                 |
|              |                   | Mean | 75.6                                                                                     | 302.4                | 4.31                                                                 |
| Rye Mash     | 10                | Max. | 239.4                                                                                    | 389.2                | 3.23                                                                 |
|              |                   | Min. | 106.8                                                                                    | 255.0                | 1.57                                                                 |
|              |                   | Mean | 150.4                                                                                    | 314.8                | 2.19                                                                 |

TABLE III  
BOURBON WHISKY (SCHOENEMAN *ET AL.*)

| Age     | Number of samples | <i>Iso</i> -butanol                                        |       | <i>Iso</i> -pentanol | Ratio                                                       |
|---------|-------------------|------------------------------------------------------------|-------|----------------------|-------------------------------------------------------------|
|         |                   | as parts per 10 <sup>5</sup> of absolute alcohol in sample |       |                      | <i>iso</i> -pentanol,<br><i>iso</i> -butanol<br>all samples |
| 2 Years | 44                | Max.                                                       | 147.2 | 407.8                | 6.72                                                        |
|         |                   | Min.                                                       | 45.8  | 259.6                | 2.42                                                        |
|         |                   | Mean                                                       | 79.3  | 317.4                | 4.22                                                        |
| 4 Years | 41                | Max.                                                       | 150.8 | 446                  | 6.75                                                        |
|         |                   | Min.                                                       | 42.6  | 218.4                | 2.41                                                        |
|         |                   | Mean                                                       | 84.1  | 326.9                | 4.24                                                        |
| 6 Years | 39                | Max.                                                       | 171.8 | 467.2                | 6.26                                                        |
|         |                   | Min.                                                       | 41.4  | 245                  | 2.39                                                        |
|         |                   | Mean                                                       | 91.6  | 350.2                | 4.14                                                        |
| 8 Years | 34                | Max.                                                       | 198.2 | 505.8                | 6.57                                                        |
|         |                   | Min.                                                       | 47.2  | 251.2                | 2.54                                                        |
|         |                   | Mean                                                       | 102.4 | 373.6                | 4.03                                                        |

liquors, but the ratios for individual samples are not reported in any of Schoeneman's papers. These can easily be calculated, however, from the reported data and the results are summarised in Table II, III and IV. In compiling these tables, a few of Schoeneman's individual results have been eliminated on statistical grounds as "outliers". These amount to four samples in Table II

TABLE IV  
SCOTCH WHISKY (SCHOENEMAN *ET AL.*)

| Type     | Number of samples | <i>Iso</i> -butanol                                            |       | <i>Iso</i> -pentanol | Ratio                                                        |
|----------|-------------------|----------------------------------------------------------------|-------|----------------------|--------------------------------------------------------------|
|          |                   | as parts per 10 <sup>5</sup> of absolute alcohol in the sample |       |                      | <i>iso</i> -pentanol,<br><i>iso</i> -butanol,<br>all samples |
| Blended  | 34                | Max.                                                           | 104.6 | 133.2                | 1.42                                                         |
|          |                   | Min.                                                           | 54.2  | 48.6                 | 0.73                                                         |
|          |                   | Mean                                                           | 74.4  | 76.0                 | 1.04                                                         |
| All-malt | 17                | Max.                                                           | 172.4 | 268.6                | 2.49                                                         |
|          |                   | Min.                                                           | 81.8  | 175.8                | 1.51                                                         |
|          |                   | Mean                                                           | 112.4 | 214.8                | 1.95                                                         |
| Grain    | 7                 | Max.                                                           | 96.8  | 30.4                 | 0.70                                                         |
|          |                   | Min.                                                           | 20.4  | 0                    | 0                                                            |
|          |                   | Mean                                                           | 44    | 10.6                 | 0.27                                                         |

and four samples in Table III. Standard deviations are not reported, since the distributions are sufficiently skew to make them misleading, the ranges quoted giving a more useful guide. The analytical results, originally expressed as grams per 100 litres at 100° American Proof, have been calculated to parts per 10<sup>5</sup> of absolute ethanol. Similar results have been obtained in the author's laboratory and are shown in Table V.

TABLE V  
RESULTS OBTAINED BY THE AUTHOR

| Type                  | <i>Iso</i> -butanol<br>as parts per 10 <sup>3</sup> of absolute<br>alcohol in the sample | <i>Iso</i> -pentanol | Ratio<br>$\frac{\text{iso-pentanol}}{\text{iso-butanol}}$<br>all samples |
|-----------------------|------------------------------------------------------------------------------------------|----------------------|--------------------------------------------------------------------------|
| Blended Scotch        | 72                                                                                       | 74                   | 1.03                                                                     |
|                       | 73                                                                                       | 83                   | 1.14                                                                     |
|                       | 70                                                                                       | 98                   | 1.40                                                                     |
|                       | 63                                                                                       | 70                   | 1.11                                                                     |
|                       | 70                                                                                       | 61                   | 0.87                                                                     |
|                       | 68                                                                                       | 93                   | 1.37                                                                     |
|                       | 55                                                                                       | 74                   | 1.35                                                                     |
|                       | 105                                                                                      | 118                  | 1.12                                                                     |
| All Malt Scotch       | 104                                                                                      | 228                  | 2.19                                                                     |
| Immature Scotch Malt  | 84                                                                                       | 210                  | 2.50                                                                     |
| Immature Scotch Grain | 22                                                                                       | Nil                  | —                                                                        |
| Bourbon               | 100                                                                                      | 360                  | 3.60                                                                     |
| Bourbon               | 65                                                                                       | 332                  | 5.11                                                                     |
| American Rye          | 235                                                                                      | 500                  | 2.13                                                                     |
| Canadian Rye          | 10                                                                                       | 28                   | 2.80                                                                     |
| Canadian              | 33                                                                                       | 83                   | 2.52                                                                     |

### Discussion

The results from all the sources show the same pattern and indicate the essential differences between the different types of whisky. Schoeneman<sup>4</sup> states that there appears to be a slight increase in the fusel oil content of bourbon whisky on ageing. The mean figures in Table VI show this and also indicate a slight downward trend in the *iso*-pentanol/*iso*-butanol ratio. No figures are available for mature corn and rye whisky and the figures for the cistern room liquors must be interpreted with the effect of ageing in mind. However, the general picture is that both bourbon and corn whisky show a higher content of fusel oil than Scotch whiskies and the ratio of *iso*-pentanol to *iso*-butanol

TABLE VI  
SUMMARY OF MEAN RESULTS (SCHOENEMAN *ET AL.*)

| Type            | Number of<br>samples | <i>Iso</i> -butanol<br>as part per 10 <sup>3</sup> of absolute<br>alcohol in the sample | <i>Iso</i> -pentanol | Ratio<br>$\frac{\text{iso-pentanol}}{\text{iso-butanol}}$<br>all samples |
|-----------------|----------------------|-----------------------------------------------------------------------------------------|----------------------|--------------------------------------------------------------------------|
| Bourbon Mash    | 82                   | 73                                                                                      | 310.5                | 4.40                                                                     |
| Corn Mash       | 16                   | 75.6                                                                                    | 302.4                | 4.31                                                                     |
| Rye Mash        | 10                   | 150.4                                                                                   | 314.8                | 2.19                                                                     |
| Bourbon 2 Years | 44                   | 79.3                                                                                    | 317.4                | 4.22                                                                     |
| Bourbon 4 Years | 41                   | 84.1                                                                                    | 326.9                | 4.24                                                                     |
| Bourbon 6 Years | 39                   | 91.6                                                                                    | 350.2                | 4.14                                                                     |
| Bourbon 8 Years | 34                   | 102.4                                                                                   | 373.6                | 4.03                                                                     |
| Scotch Blend*   | 53                   | 75.9                                                                                    | 77.7                 | 1.05                                                                     |
| Scotch Malt*    | 27                   | 113.3                                                                                   | 212.4                | 1.91                                                                     |
| Scotch Grain*   | 12                   | 61.1                                                                                    | 10.0                 | 0.20                                                                     |

\* Including results from Singer<sup>1</sup> and the author.

TABLE VII  
COMPARISON OF UNKNOWN SAMPLES WITH THOSE OF KNOWN ORIGIN

|                      | <i>Iso</i> -butanol                                               | <i>Iso</i> -pentanol | Ratio<br><i>iso</i> -pentanol,<br><i>iso</i> -butanol<br>all samples |
|----------------------|-------------------------------------------------------------------|----------------------|----------------------------------------------------------------------|
|                      | as parts per 10 <sup>5</sup> of absolute<br>alcohol in the sample |                      |                                                                      |
| Sample 1             | 65                                                                | 340                  | 5.23                                                                 |
| Branded Scotch Blend | 70                                                                | 98                   | 1.4                                                                  |
| Straight Bourbon     | 65                                                                | 332                  | 5.11                                                                 |
| Sample 2             | 105                                                               | 118                  | 1.12                                                                 |
| Canadian             | 33                                                                | 85                   | 2.43                                                                 |

is also higher. Rye whisky is closer to Scotch all-malt whisky, but the Scotch malts, blends and grain whiskies all show significantly different figures, particularly in the ratio between the two alcohols.

The application of these results is illustrated in Table VII, where sample 1 is that which initiated this investigation. This was sold in answer to a request for a branded Scotch whisky blend, the figures for an authentic sample of which are also shown. There is clearly a substantial difference between the *iso*-pentanol figures for these two samples, which is conveniently reflected in the ratio *iso*-pentanol to *iso*-butanol. The figures for the suspect whisky appear to indicate a bourbon, not "inferior rye" as was alleged. Detective work finally identified a certain brand of straight bourbon giving the figures shown in the table.

In the case of sample 2, a brand of Canadian whisky was demanded, but the figures show that a Scotch blend was supplied. The genuine Canadian whisky showed a lower total content of the two alcohols, but a higher ratio.

#### References

1. Singer, D. D., *Analyst*, 1966, **91**, 127.
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4. Schoeneman, R. L., Dyer, R. H., and Earl, E. M., *Ibid.*, 1971, **54**, 1247.
5. Schoeneman, R. L., and Dyer, R. H., *Ibid.*, 1973, **56**, 1.

