Diploma in Oenology Thesis

This is the fourth of a series of papers written by Students of Roseworthy Agricultural College, South Australia.
They are selected from a number of papers submitted and are considered to be most valuable contributions to investigations of the wine industry.
The series will appear exclusively in this Journal, and the publication will extend over several months.

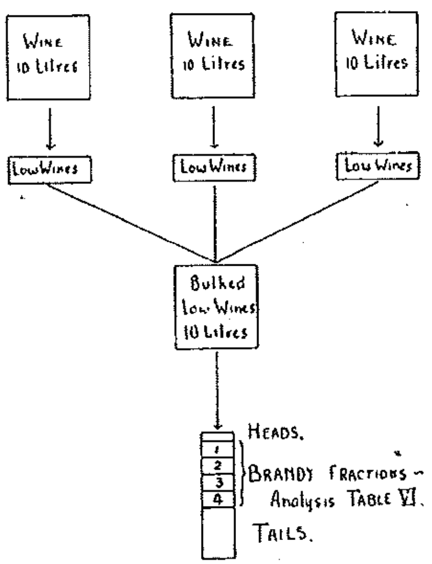
The Influence of Distillation Methods on Brandy Composition

By W. O. Graham, R.D.Oen.

(Continued from April Issue)

Section II.—A Comparison of the Composition of the Brandy Fractions as Obtained by Separation of Heads and Tails According to French Methods with those Obtained by Australian Methods.

The plan of the experimental work is again shown diagrammatically. The same wine was used as in the previous Section (I.), but diluted to a lower strength and left for three weeks to allow the constituents to attain equilibrium.



Flow Diagram, showing the Plan of the Distillations of Section II.

Three distillations of the wine were made, and the low wines were then bulked and redistilled, the distillate being divided into heads, heart and tail fractions according to French procedure as given by Elliott (4). To enable any changes that might occur in the heart or brandy to be followed, it was separated as four successive fractions which were analysed separately.

A comparison of the data given by Elliott and the experimental procedure and results is given in Table V., and from this it may be seen how closely the actual results compare with Elliott's figures, proving that the experimental procedure followed very closely along the lines indicated in the literature.

The results of the analyses of the four fractions into which the brandy or heart was divided are given in Table VI.

Table VI.—Analysis of the Four Brandy Fractions—French Method.

No.	Strength % P.S.	Time to Distil. Minutes.	Esters.	Aldehydes.	Volatile Acids.
1st . .	129.4	80	250	35.2	17.6
2nd . .	121.2	91	42.9	10.9	19.3
3rd . .	106.0	115	46.1	4.0	29.8
4th . .	71.2	150	89.6	5.1	81.8

Note.—Average strength of fractions 1, 2, 3 and 4 is 106.9% P.S.

Average strength of fractions 1, 2 and 3 only is 118.8% P.S.

According to Elliott fractions 1-4 are included in the brandy, but, when this is done, the strength is only 6.9 O.P. instead of 18.6 O.P. (the strength quoted by him). However, by transferring the 4th fraction to tails, the strength

Table V.—French and Australian Methods Compared.

Particulars.	French Method. (Elliott's Data)	Experimental Method. (Actual procedure and results)
Strength of wine	8% A.A. by weight = 17.31% P.S.	17.26% P.S.
Amount of wine distilled	3 charges of 1,000 litres	3 charges of 10 litres (10,000 ml)
Amount of low wines collected from each distillation	300-350 litres	3.33 litres (3,330 ml)
Strength of low wines	20-24% A.A. by weight = 46.90% P.S. (average)	45.6% P.S.
Amount of low wines distilled	1,000 litres	10 litres (10,000 ml)
Amount of heads	3-5 litres	.04 litres (40 ml)
Brandy fraction	360-380 litres	3.7 litres (3,700 ml)
Strength	60% A.A. by weight = 118.6% P.S.	118.8% P.S.
Time to distil spirit fraction	10-11 hrs.	7¼ hrs.
Tails	200-225 litres	2.125 litres (2,125 ml)
Strength of tails	16-20% A.A. by weight = 38.55% P.S. (average)	37.8% P.S.

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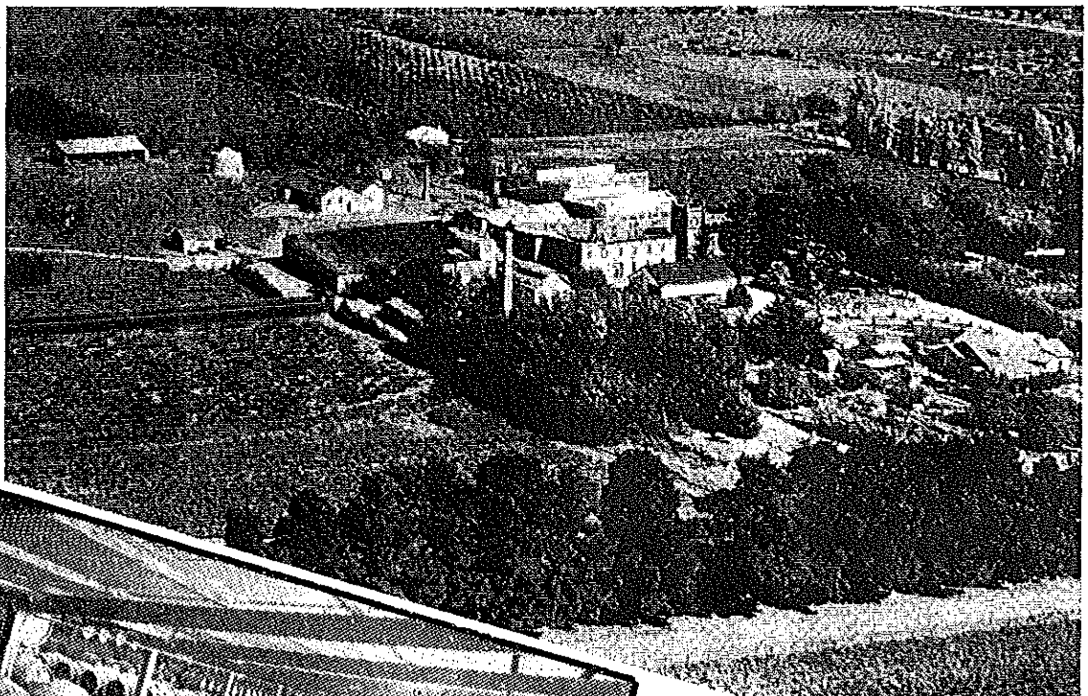

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of both the brandy and tail fractions agree almost exactly with his figures (see Table V.). Fraction 4 has therefore been included in the tails. This correction of Elliott's figures is undoubtedly justified, since other authorities, including Rocques (3) and Ravaz (7) state that the brandy is collected down to very nearly 50 per cent. by volume (13.5 U.P.), whereas, if fraction 4 were included, it would be very much below this strength.

Discussion:

The distribution of the secondary constituents may now be considered in detail.

1. **Esters.**—The average ester content of the fractions 1 to 3 inclusive (by French methods) is 113, which is altogether higher than the figure (viz., 37) obtained from the same wine by Australian methods (Section I.), and also of that (viz., 42.7) of the commercial Australian brandies shown in Table I. It does agree, however, with the ester content of genuine Cognacs for which the average figure, given in Allen's Organic Chemistry (8), is 120, and is in fair agreement with figures generally quoted in French literature.

Hence it is quite clear that the esters are concentrated in the early fractions and the exclusion of these explains the low ester content of Australian in comparison with French brandies.

2. **Aldehydes.**—The average for fractions 1-3 is 16.7, which is slightly lower than that for commercial brandies shown in Table I. The average figure by Australian methods is much lower, being about 5.5, while the figure for better quality brandies is just over 20, and that for Cognac, according to French literature, varies appreciably, but averages about 25.

3. **Volatile Acids.**—The figure is fairly typical of commercial brandies, the average of fractions 1-3 being 22.2, which is slightly higher than the figure by Australian methods. Gerard and Cuniasse (5) gave an average of 19 for three young genuine Cognacs.

General Observations and Conclusions.

Distillation and separation according to French methods gives a brandy of relatively high ester content, and, as regards other constituents determined, of composition much nearer to Cognac than the average Australian brandy. A similar result might be obtained by modifying the Australian methods to separate a smaller heads fraction and the proportion, as will be seen from Table IV., will depend upon the rate of distillation. The aldehyde content of the brandy fraction would be increased as well.

By altering the rate of distillation, other constituents, especially volatile acids, are affected. By separating a smaller fraction of heads, the volatile acidity will be greatly increased in a rapid, but only slightly in a slow distillation, and the slower the distillation the more of the heads will have to be included to give the required ester content.

The ester content of the best quality Australian brandies analysed was comparatively high (90-100) v. Table I., while the average figure for the true commercial types was relatively low (about 40). As mentioned above, published results of the analysis of French brandies show their ester content to vary widely, averaging around 100, but often considerably exceeding this figure. The average for young French brandies given by Flanzy (9) is 188.

In view of this, as well as the information gained from this section it is evident that the Australian distiller aims at producing (or, rather produces, according to his own ideas of brandy-making) a more neutral brandy, that is, one containing less secondary constituents, than do French distillers. This is necessary if the brandy is to be sold young, as less neutral brandies will probably require a longer maturation. The most important point of all, of course, is the type of wine used for the distillations. Soil, climate and variety are all important, but from one wine several types and qualities of brandy can be made.

In the Cognac region the wine is usually left on the lees, which are, as a rule, included in the distillation charge, and, together with the open-fired pot-stills, are said to contribute largely to the characteristic Cognac flavour. Such a procedure under local conditions might produce an undesirable "earthy characteristic" in the brandy, but if it were successful, a little of this type might greatly improve the quality of trade lines. Such full-flavoured types as Cognacs may lend themselves better to contain a larger amount of secondary constituents, but it seems reasonable to suppose that with any average quality brandy, those containing a reasonable proportion of secondary constituents will improve more during ageing than will the more neutral types.

Section III.—Other Factors Affecting Ester Content.

A. Volatile Acidity.

A sample of dry wine was divided into 4 portions. The volatile acidity was raised in two of them, and all were refluxed and distilled, the ester content of the resulting distillate being determined. Refluxing hastens esterification and therefore should have a similar effect on ester development to storage for a considerable period. The results are given in Table VII.

Table VII.—Effect of Volatile Acidity on Ester Content.

Flask No.	Volatile Acidity of Wine, g/l acetic acid.	Time of Refluxing (hours).	Ester Content as grms. ethyl acetate/100,000 parts absolute alcohol.
A	0.52	1	70.9
B	1.69	1	83.4
C	0.52	2½	71.4
D	1.69	2½	82.8

Discussion:

There is only a slight increase in ester content in spite of an increase in the volatile acidity by 300 per cent. Thus it has only a small influence in comparison with other factors as the method adopted for the separation of the heads and tails from this brandy fraction.

B. Changes in Ester Content During Storage.

The fractions obtained from the distillations by "high speed" (Table IV.) were stored in glass stoppered bottles and again analysed for esters about 3 months after the original analyses were made. The results are compared in Table VII.

Table VII., Change in Ester Content During Storage.

Fraction No.	After Distillation. Ester Content.	After Distillation. Vol. Acid Content.	After 3 Months Storage. Ester Content.	After 3 Months Storage. Change in Esters.
1	735	47.7	580	155 decrease
2	400	44.4	286	114 „
3	246	28.9	164	82 „
4	114	19.7	83.3	30.7 „
5	53.9	16.6	45.7	8.2 „
6	30.5	14.3	28.6	1.9 „
7	27.2	13.5	23.4	3.8 „
8	29.4	15.6	20.7	8.7 „
9	38.8	18.5	35.5	3.3 „
10	52.7	26.3	50.8	1.9 „
11	73.5	43.3	73.5	—

Discussion of Results:

There is a large decrease in head esters while practically none in the tail esters. This difference, although possibly partly due to the chemical nature of the esters themselves, is probably due mainly to the greater proportion of acid in the later fractions, because the esters revert to alcohol and acid forming an equilibrium mixture.

There is a very marked decrease in the ester content of those fractions high in esters, while in those whose ester content is relatively low the change is insignificant. According to these figures, a freshly-distilled brandy with an ester content much above 100 parts is liable to a loss of esters on storage, and the decrease may be as high as 30 per cent. Thus many brandies such as Cognacs having an ester content of about 100 or greater, may have had a very much higher level of esters when newly-distilled. This decrease in esters is contrary to the statements of many authorities, viz., that esters increase during ageing. Rocques, however, states that "in determining esters in brandy of different ages one does not observe that the proportion increases. In certain cases one finds less esters in older brandies than in young ones." It is evident that an increase (at least with brandies of high ester content) is not to be expected. It therefore seems reasonable to suppose that many French brandies are much higher in esters when newly distilled than is shown by the published analyses of brandy.

Summary.

I.—A number of samples of commercial brandy have been analysed and the results show considerable variations in the amounts of secondary constituents present. Compared with French brandies generally, the proportion especially with esters, is much smaller.

II.—The course of distillation has been studied and results show that:—

(1) The esters concentrate mainly in the first fractions, the decrease from these to the middle fractions being very marked.

(2) Aldehydes concentrate in first fractions but not to such a marked degree.

(3) With volatile acids there is no marked separation, but this is influenced by the rate of distillation.

There is a definite relationship between the composition of certain fractions of the distillate and the composition of commercial brandies. Australian methods of distillation eliminate the greater part of the esters by separating a large head fraction, and this elimination is assisted by not including heads from the previous charge. The heads fraction contains from 60-80 per cent. of the total esters, and its inclusion in the succeeding charges would greatly increase the ester content of the brandy distilled.

III.—The effect of the rate of distillation on the distribution of secondary constituents has been studied, and the results show that the rate of distillation has an important effect on the distribution of secondary constituents especially esters and volatile acids. The chief features are:—

(a) With a fast rate of distillation the decrease in alcoholic strength of the first fractions is small, with a fairly rapid decrease in later fractions. With a slow rate of distillation the strength falls gradually in increasing amounts from start to finish.

(b) Esters are concentrated in the heads—the proportion of heads taken governs the ester content of brandy to a marked extent. With a slow rate of distillation the concentration of esters in the early fractions is less marked, while the middle fractions are not quite so low in esters as in a fast distillation.

(c) The rate of distillation has no marked effect on the distribution of aldehydes.

(d) The rate of distillation has a very marked effect on the distribution of volatile acids. By rapid distillation the earlier fractions are high in volatile acids, while by a slow distillation there is a tendency to cocentration in the tails, and such concentration probably assists in ester formation during the distillation.

IV.—A distillation, modified to agree in certain particulars with French methods, was conducted and showed that:—

(a) The French methods of distillation differ greatly from the usual Australian methods, and it is mainly to this fact that the differences in composition of French and Australian brandies may be ascribed.

(b) By French methods the composition of the spirit is very much higher in esters, while the aldehyde content is relatively low. Similar results would be obtained in Australian distilleries by a suitable modification of distilling operations, but whether this would improve the quality of Australian commercial brandies can only be discovered by trial.

V.—It was also shown that:—

(a) The volatile acidity of the original wine, at least as regards ethyl acetate, has a negligible influence on the ester content.

(b) The ester content changes during storage. In spirits high in esters this change consists of a reduction, and it may be considerable. The statement that esters increase during maturation is, therefore, not always correct.

Acknowledgements.

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