THE EFFECT OF CERTAIN DISTILLATION PROCEDURES ON THE BRANDY COMPOSITION.

by

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INTRODUCTION.

During the last decade or so brandy-making has definitely established itself in conjunction with the wine industry, and the output of this spirit has been increasing yearly.

However, although much of the brandy distilled under Australian conditions is of a reasonably high standard, it differs in type and does not attain to the quality of French brandies made in the Cognac area. Experiments by Graham (12) Angove (13) have been carried out recently in an endeavour to establish the cause of these differences, by modifying the distilling procedures; and a certain amount of success has been attained, especially regarding:

(a) Rate of distillation.

(b) The practice of distilling the wine in conjunction with it lees, and

(c) The returning of the "heads" and 'Tails' of the brandy-run to the next wine charge.

In Australia and elsewhere, stills have been modified and distillation methods varied in an endeavour to produce a superior spirit, and it is true that satisfactory results have been obtained, but little is known of the chemical effect these varied conditions have on the composition of the distillate.

The object of this paper is to see:

1. What effect reflux, as governed by the length of the column has on the resultant brandy fractions, and comparing with reflux obtained bythe use of the brandy ball; and to establish:

II. A recheck on the run-back of heads and tails to the next wine charge, as it is still in doubt whether the final brandy is cleaner and or a longer cut in the brandy-run is obtained under this method.

LITERATURE REVIEW.

1. 'REFLUX'

The reputation of the brandies of the Cognac and Armagnac districts depend on their bouquet, therefore, it is desirable to avoid high rectification and consequent removal of those secondary constituents upon which the flavour depends.

The extent and careful control of distillation are undoubtedly vital factors in the determination of the composition and quality of brandy, and it is found that if only the early fractions which contain the aldehydes and more volatile acids are eliminated, the resulting product is very agreeable and agrees favourably with analytical standards. However, the latter fractions, containing the higher alcohols and furfural can be greatly improved by the use of dephlegmators, as the excess of higher alcohols, furfural, acetic acid &c., though only in small proportions, have a pronounced adverse effect on odour and flavour. It is, therefore, seen that a certain degree of rectification is necessary to prevent an excess of these substances occurring in the distillate.

We read from literature, Elliott (5) that the stills in the Cognac area are, on the whole, simple pot-stills; small in capacity (50-150 galls) and are usually jacketed by brickwork, with only a small bulbous head exposed, and generally furnace heated. However, in the neighbouring districts where the quality of the distillation material is slightly inferior, stills of many designs are used to obtain an improved spirit, and illustrations of various designs are given by Nettleton (2) Elliott (5).

A still constructed by Pontifex and Wood similar to the brandy-ball effect, where the whole column up to the bend is cooled by water overflowing from the top tray to one immediately below, and so on down the column -- the cooler water therefore being at the top, this being only one of the many types of stills used. Others as given by Nettleton(2), having an extended column of 24-30 feet from the bend to the worm; some with a slightly upward incline, others horizontal--these being 4,000 gallon capacity stills.

Mathews (9) illustrates yet another modification of the still-neck, producing a similar effect as the brandy-ball; consisting of a cooling coil inside the neck of the still.

II '<u>RUN-BACK</u>'

It is the practice widely adopted in France of introducing all or some of the feints of the brandy charge into the next wine or brouillis charge; and according to Rene et Jean Lafeu (16) all heads and tails are run-back to the next wine charge, whereas others state that only part of the feints are returned; some to the brouillis charge, some to the next wine charge, while proportions may be discarded altogether.

Emerson (8) also states that under general French methods, it requires three charges of wine to obtain sufficient brouillis for one brandy-charge, of which approximately 5%, according to nature and quality of the wine, is separated as 'heads' which is later mixed with another brouillis. The brandy is cut out to 'tails' at 50-55 per cent A.A., leaving the brandy with a strength of 66-70 per cent A.A. The tails are sometimes separated into two portions; the first fraction down to 20 per cent A.A. returned to the next brouillis, while the second fraction from 20 per cent to 0 per cent is returned to the next wine charge.

Throughout Australian distilleries no doubt similar practices in treating the feints are adopted, and from observations made in some distilleries, small portions of the heads and tails are discarded altogether, playing no further part in either the brouillis or wine charge, that is, where any feints are utilised at all.

Recently important data was obtained by Angove (13) concerning the effect run-back had on the fractions but unfortunately time prevented observations being made in full.

EXPERIMENTAL.

APPARATUS AND MATERIAL.

1. **The Still.**

A 2-gallon, copper pot-still, fitted with an 18" column and brandy-ball. Still connected to a metal tubular condenser. An adjustable arm of 27" for lengthening column.

Heat applied by an electrical hot-plate, with heat regulator.

2. **Hydrometers:**

Specific gravity hydrometers covering spirit ranges 70°O.P. to 100° U.P.

3. **WINE:**

Dry white wine made from White Hermitage 1940 Vintage including its second lees.

Alcohol	20% P.S.	11.4% A.A.
Total Acidity		7.57 grams/litre $H_2\bar{T}$
Volatile Acidity		.56 grms/litre $H\bar{A}$
Esters		370 parts/100000 A.A.

Methods of Analysis:

Alcohol ---Sykes Glass Hydrometers . % by volume.

Acids--- Direct Titration (Phenolphthalein) parts of acetic acid per 100000 parts absolute alcohol.

Esters--- A.O.A.C. (14) expressed as parts ethyl acetate per 100000 parts A.A.

Aldehydes---Jaulmes & Espezel (11), but using ½ quantity reagents, parts acetaldehyde per 100000 parts A.A.

Secondary Alcohols--- Gerard & Cuniasse (15) but using Caustic in place of metaphenylenediamine, parts iso-butyl alcohol per 100000 parts A.A.

Furfural--- A.O.A.C. (14) parts per 100000 parts per A.A.

Part I 'Reflux" as obtained by lengthening the column and use of brandy ball.

Plan of Experiment.

A study of the resultant brandy fractions after:--

(a) Lengthening the column, by raising the arm in an upward slope to the condenser.

(b) using a cool brandy-ball, without lengthening column.

(c) Comparisons of the above made against fractions obtained without the use of either (a) or (b)

Each distillation carried out as below:-

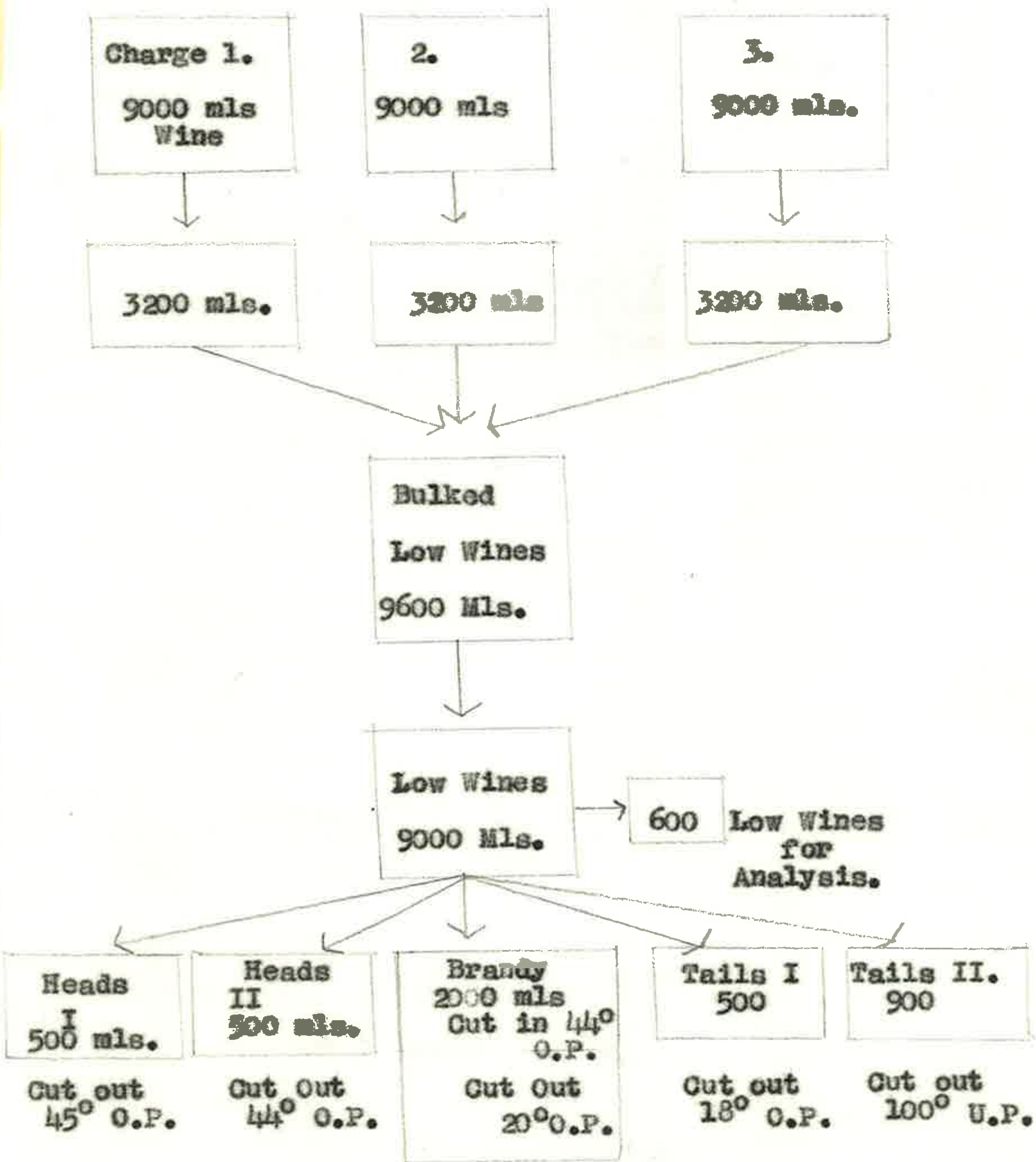

FIGURE I.

Owing to the fact that many designs of stills have been made incorporating reflux, it is obvious that reflux should produce a more neutral spirit and therefore the composition of the spirit be considerably influenced due to this partial rectification. By referring to the following TableI, it will be seen just what effect the above methods has on the chemical composition of the distillate.

TableI. Composition of Fractions.

(a) Lengthened column: (b) brandy Ball;

(c) Straight distillation.

Fraction	Alcohol			Acids			Esters			Aldehydes			Sec. Alcohols			Furfural		
	A.	B.	C.	a.	b.	c.	a.	b.	c.	a.	b.	c.	a.	b.	c.	a.	b.	c.
Low Wines	30.7	31.7	31.8	90	85	170	166	155	227	37	41	36	13	60	50	.5	.9	.4
Heads I	73.9	68.0	68.3	16	29	112	340	398	531	31	30	34	430	520	520	-	-	-
Heads II	84.4	81.8	78.3	7	8	52	85	70	220	29	22	25	140	220	230	.4	.6	.8
Brandy	81.3	78.4	76.4	9	8	18	32	19	62	24	25	26	50	70	70	.5	.7	1.0
Tails I	58.0	62.0	61.2	32	23	31	142	86	108	32	28	21	20	50	20	2.1	3.6	1.8
TailsII	7.0	16.4	19.7	210	144	188	709	585	428	83	70	31	-	-	-	3.4	7.6	2.4

Firstly, in dealing with the Low-wines received under these methods, the Table shows a definite decrease in the acid and ester content, both by the Lengthened column and brandy-ball whereas the other constituents remain more or less constant, except perhaps a decrease in secondary alcohols obtained by means of the lengthened column.

Therefore, from the low-wines produced similar effect would be expected to occur in the same constituents in the brandy-fractions, and such is the case.

To discuss the constituents separately:

ALCOHOL. As would be expected a greater degree of rectification is obtained with the aid of (a) Lengthened column and (b) brandy ball in the heads and brandy fraction, leaving less spirit in the tals.

However, (a) is responsible for a much higher strength spirit in heads and brandy than that produced by (b), which is slightly higher than the ordinary straight distillation.

Results of Brandy Fraction:

(a)	(b)	(c)
81.3% A.A.	78.4%	76.4%

which shows only an increase of 2.0% with the use of the brandy-ball, as to an increase of 4.9% in the lengthened column. However, this added rectification and consequent higher strength of spirit is not altogether advantageous to quality, as it becomes more neutral, leaving more flavouring and essential aromatic substances in the pot, as shown by Table I.

ACIDS: A decrease is noticed in all fractions down to brandy, increasing slightly in Tails I and then rapidly increasing to Tails II. The lengthened column and brandy-ball affording a marked rectification over the straight distillation in the early fractions but to very little degree in the tails. Small amounts occurring in heads and brandy with greater amounts in tails, this being reasonable as the boiling point of Acetic Acid is approx. 116°C, and thus would be expected to be more of a tail product.

ESTERS. As ethyl acetate has a boiling point approaching that of ethyl alcohol it would be expected that the esters would distil over in more or less constant proportions, but is found not to do so, distillation probably upsetting the ester balance. In practice, however, this constituent is generally considered to be a head and tail product, and by the table the esters tend to concentrate in 1st. heads and 2nd tails with decreasing amounts in towards the brandy fraction.

A considerable decrease is noticed in heads of the lengthened column and to a lesser extent in the brandy ball methods, this is counterbalanced by the fact that under these reflux methods more are pushed into the tails than under the straight distillation. The heart of the run, or brandy, also has a decreased ester content with the use of lengthened column and more so by the use of the brandy ball.

ALDEHYDES. These in all distillations are only small and remain fairly constant in all fractions.
Table shows them to be more a tail than a head product, but decrease slightly to distil over constantly throughout second heads, brandy and first tails, increasing again as alcohol content falls.

SECONDARY ALCOHOLS. Concentrate in first heads and decrease throughout fractions with an absence altogether in second tails, more being left behind in the pot in (a) than either of the other two methods. The brandy ball appears to make no difference whatsoever in this constituent throughout the fractions.

FURFURAL. Being a product produced in the pot, furfural does not appear in the distillate until 2nd, heads, where it is present only in trace amounts, and showing no definite increase until tails. This is to be expected as the boiling point of furfural is approximately 136°C and should tend to accumulate in the tail fractions.

Organoleptic Examination.

All samples of the brandy fractions were considered neutral to the nose and palate as regards suitable brandy material, but this is not surprising as a large proportion of foreshots were extracted to be divided into 1st and 2nd heads to enable a study of analyses to be obtained throughout the fractions.

The material produced by the lengthened column was considered to be more neutral than either that produced with the aid of the brandy ball or straight distillation, the sample from the brandy ball method more so than that of the straight distillation. This correlates to the table more or less but the only constituent in a lesser degree than that of the brandy-ball run is the secondary alcohols, yet has a higher ester level, which appears to indicate that the higher alcohols have a very marked effect on the bouquet, more so than esters.

Discussion of Results:

The operation of the brandy-ball in this instance was conducted at a temperature of 33-35°C. which meant a fair stream of water passing through all the time; this temperature being much lower than most brandy-balls operated under Australian conditions, in which case the brandy-ball being most often hot.

Also the brandy-ball used is large, built out of proportion to the still in use, as compared with modern pot-stills, so as to produce maximum effect on the distillate.

As the results obtained show that more effect is attained by lengthening the column, a longer cut in the brandy run would be possible. Whereas to produce the same result with the aid of the brandy-ball, it must be kept very cool, necessitating a faster flow of water and this questions the economy of the plant. Therefore it appears that the use of a hot brandy-ball is very limited, yet on the other hand it is obvious that the degree of coolness in the brandy-ball must have its limitations, as too much reflux would stop distillation under normal heating operations.

PART II. Recheck on 'run back' of heads and tails to the next wine charge.

Plan of Experiment.

Analyses made of the low wines and brandy fractions of four separate brandy charges, three of the charges derived from wine containing the heads and tails of the previous brandy charge.

Step (a) Three 9 litre charges wine distilled to procure 9.6 litres low wines.

Low wines distilled to Heads—brandy—tails.

(b) Three 9 litre charges wine plus feints from (1) to 9.6 litres low wines.

Low wines distilled to heads—brandy—tails.

(c) Three 9 litre charges wine plus feints from (2) to 9.6 litres low wines.

Low wines distilled to heads—brandy—tails.

(d) Three 9 litre charges wine plus feints from (3) to 9.6 litres low wines.

Low wines distilled to heads—brandy—tails.

Each brandy charge divided into 5 fractions, i.e. 2 heads, brandy and 2 tails, and each fraction collected in the same manner as previous plan (see Figure I).

In each case the feints (heads and tails) obtained from the previous brandy-run were broken down to the wine strength before adding to the next wine charge. This was to obtain uniformity throughout, as it is evident that without breaking down the alcohol content would increase due to the addition of feints each time, therefore, by so doing results obtained are made more or less comparable.

TABLE II.

Effect of 'run back' on composition of subsequent fractions.
b, c and d representing progressive runbacks.

FRACTION	ALCOHOL				ACIDS.				ESTERS				ALDEHYDES				SEC. ALCOHOLS				FURFURAL.			
	a.	b.	c.	d.	a.	b.	c.	d.	a.	b.	c.	d.	a.	b.	c.	d.	a.	b.	c.	d.	a.	b.	c.	d.
Low Wines	31.8	31.6	31.7	31.7	170	91	89	94	227	239	247	254	36	30	20	19	50	60	63	66	.4	.4	.4	.4
Heads I	68.3	60.8	63.9	63.1	112	45	27	28	531	570	578	602	34	31	16	22	520	400	420	460	-	-	-	-
Heads II	78.3	79.8	80.8	80.1	52	25	14	11	220	225	214	217	25	19	16	18	230	220	225	200	.8	.5	.2	.2
Brandy	76.4	76.4	76.9	76.3	18	12	10	11	62	64	66	67	26	18	20	22	70	60	70	50	1.0	.9	.6	.9
Tails I	61.2	60.6	61.1	59.2	31	21	23	26	108	110	126	128	21	24	21	29	20	10	23	13	1.8	1.4	1.2	1.5
Tails II	19.7	19.0	19.3	18.6	188	123	127	135	428	454	488	539	31	39	32	40	-	-	-	-	2.4	2.0	1.0	1.3

From Table II it will be seen that, as regards the low-wines, the main constituent affected by 'run-back' is the acids, where there is considerable decrease obtained from the first run-back (b), but with progressive distillations of run-backs (c) and (d) no further appreciable change is noticed. Therefore, it appears that with the use of the feints an equilibrium is established in this constituent which distils over unchanged throughout progressive distillations.

As for the other constituents, the esters appear to gradually increase throughout subsequent distillations, while aldehydes decrease slightly. Secondary alcohols and Furfural, however, have undergone little or no change whatever with the use of the feints.

Effect produced on the Brandy-fractions.

Alcohol: All strengths are comparatively uniform, as was anticipated as all feints were diluted to wine strength before mixing with the wine itself.

Acids. Definitely a head and tail product, and the effect of run-back is to produce cleaner fractions, and as is the case, with the low wines, the 1st run back (b) markedly reduces acid content, but from then on (c) and (d) no appreciable change noticed throughout corresponding fractions.

Esters: Here it is interesting to note that although the low wines gradually increase in ester content, produced by the effect of run-back, this increase is not uniformly distributed among the brandy fractions, but in each case more are pushed into 1st. heads and 2nd tails, leaving the fractions 2nd heads, brandy and 1st tails uniform within themselves.

The course taken by the esters is to concentrate in heads and tails with decreasing amounts in towards brandy.

ALDEHYDES. As is the case with the low wines there is a slight cleansing effect on the fractions down to brandy, the tail fractions gradually accumulating extra aldehyde content. This constituent appears to have distilled over fairly constantly throughout all fractions, as even the brandy fractions contain only slightly less amounts than both heads and tails.

SECONDARY ALCOHOLS: Little difference is noticed throughout except a slight decrease in 1st. heads with the use of run-back. Definitely a head product, decreasing to tails with an absence in final tails.

FURFURAL: Present in small quantities, and run-back seems to reduce amount present, but only in trace amounts.

Organoleptic Examination:

This was conducted on all four brandy fractions, with the object to ascertain any differences on nose and palate among the subsequent distillations. On studying Table II it will be noticed that the brandy in all four distillations shows very little, if any, difference among themselves in all constituents; yet when tasted, an improved difference was acclaimed to those samples produced by inteducing run-back (i.e. b, c, and d.) over the sample produced by the ordinary straight distillation, (a). To the palate, however, (b), (c) and (d) did not improve progressively but remained on a par with one another.

Therefore, with the aid of run-back a difference is obtained which cannot be shown by a measurement of the constituents present, and it appears to be little doubt that this difference is a beneficial one. This difference took the form of a more balanced character.

All samples were considered clean, able to take water well, promising material although slightly neutral.

DISCUSSION.

As regards the practice of utilising the feints in the manufacture of brandy, it seems to be a well established fact in France that they play an important role as to quality. However, according to several writers, Emerson (8), Rent et Jean Lafeu, Nettleton (2), no hard and fast rule is adopted, even in the Cognac and Armagnac Areas, as to how they should be utilised; the methods varying widely.

Results obtained in the above experiment also show that the feints play an important part. It does not necessarily mean that by introducing the dirty or undesirable fractions of a brandy-run to the following brandy charge a corresponding dirtier spirit will result; but on the contrary, it cleanses all fractions of their respective constituents except perhaps esters which tend to increase gradually—this being an advantage to Australian brandies as they are generally low in ester content, as compared with French standards. Consequently, by utilising the feints it is evident that a longer run on brandy could be obtained than otherwise.

This now leads us to an interesting feature of what the result would be on obtaining a longer brandy run; in this case introducing 2nd heads and 1st tails to the brandy fraction, and comparing the results with analyses made on a typical first class French Brandy, Wiley (1). This is outlined in Table II and Table IV.

TABLE III.

Showing composition of brandies from Table II (S) as compared with the same brandies after addition of 2nd heads and first tails (x).

Brandy	Alcohol		Acids		Esters		Aldehydes		Sec.Alcohols		Furfura.	
	S	X	S	X	S	X	S	X	S	X	S	X
(a)	76.4	74.2	18	26	62	93	26	25	70	89	1.0	1.1
(b) 1st run back	76.4	74.3	12	16	64	98	18	19	60	78	.9	.9
(c) 2nd " "	76.9	74.9	10	13	66	101	20	20	70	86	.6	.6
(d) 3rd " "	76.3	74.1	11	13	67	102	22	23	50	66	.9	.9

Results are self explanatory, acids, esters, and Secondary Alcohols have definitely increased, particularly the ester content, while no change has occurred in the aldehyde and furfural content. Alcohol content has decreased and the strengths obtained above are on the borderline of the 30°O.P. limitation for the two year restriction on fortifying spirit. This would easily be made safe by introducing a little less 1st tails in this instance. However, we are not dealing with fortifying spirit but quality brandy, so strengths are of no paramount importance.

In Table IV it is shown how the composition of the above brandies after addition of end heads and 1st tails compared with analyses made on a typical first class French brandy, viz. Grande fine champagne as extracted from Wiley (1).

TABLE IV Showing French method of distillation((d) X Table III) as compared with composition of genuine French Brandy.

Brandy	Alcohol	Acids	Esters	Aldehydes	Sec.Alcohols	Furfural
(d)X Table III	74.1	13	102	23	66	.9
Grande fine Champagne	69.3	36	160	9	124	2.1

Table shows that the total constituents other than alcohol are (d) X 205 and Grande fine champagne 331. Therefore to produce a closer ratio still more heads rather than tails are necessary in the brandy-run.

S U M M A R Y.

Concerning the above experiments, duplicates were performed of both sections with similar results, therefore as far as the experimental still and material used are concerned, the results may be taken as authentic, but it must be realised that with commercial stills and different materials, results may or may not vary.

1. The brandy-ball must be kept reasonably cool to obtain any marked affect on the brandy compositions, whereas by lengthening the column cleansing effect is produced more easily— longer cut in the brandy possible.

2. The utilisation of feints play an important role in the cleansing of the distillate, obviating a longer brandy run. Also enhances to quality of the resultant brandy.

3. As far as chemical composition is concerned it is not difficult to produce a French style brandy using Australian apparatus and wine, and with further experience we may be able to determine the relationship between chemical composition and quality.

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APPENDIX.

WINE USED. In the foregoing experiments, White Hermitage of South Australia, although not extensively grown in Australian Vineyards, was chosen, as it is a wine to the nearest approach to that made in France for Cognac manufacture that was available; having most of the characteristics that is present in Cognac material, i.e. thin in body, acid and not itself very palatable, and from white grapes grown on a calcareous soil.
Wiley (1)

This wine was fermented in hogsheads without addition of $S.O_2$ being made, and finally distilled in conjunction with its "second" lees.

ESTERS. As the ester content of the brandy is the most discussed Sec. Constituent as to quality, it is found that Australian brandies all fall below French quality lines in this constituent. However, it must be remembered that the acid content of Australian materials is much lower than that of French wines made for Cognac, due to climate and time of picking mainly; therefore with less acid to interact with the alcohols, the ester formation is lower.

Hence, theoretically, it appears that the ester content could be raised by the addition of acid to the distillation material to a desired level; and an interesting experiment could be carried out along such lines to determine if beneficial to Australian brandies.

SECONDARY ALCOHOLS.

Experiments made by Angove (13) were conducted with the reagent meta Phenylenediamine, which gave fairly constant results; however, Caustic was substituted and by increasing the amount from 2 grams metaphenylenadiamine to 6 grams Caustic the same results were obtained at a considerable reduction in cost.

DISTILLATION.

With this still 9 litre charges were used in all cases, as it was found that when using greater amounts of turbid liquid (wine and lees) the first portion of the distillate was apt to rush and be very dirty, upsetting analyses. This was overcome by using a lesser amount of material in the pot. Nettleton (2) stresses the point that French stills are never filled to capacity, only partly filled say half to two-thirds total capacity.