A COMPARISON OF THE COMPOSITION OF SUCCESSIVE FRACTIONS OBTAINED DURING DISTILLATION AND THEIR RELATION TO THE COMPOSITION OF COMMERCIAL BRANDIES.

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S Y N O P S I S:

The composition of commercial brandies varies within wide limits, and there appears to be no definite relationship between the composition of a brandy and its quality.

There is a gradual change in the composition of the successive fractions obtained by the distillation of low wines in a pot still similar to those used in Australian Wineries and distilleries for the production of brandy spirit. Some fractions are of higher alcoholic strength and contain more secondary constituents as ester, aldehydes and volatile acids than others. Certain fractions of the distillate are unsuitable for the making of brandy, and it is upon the manner of separation of the "spirit" fraction from the remainder of the distillate that the composition of the brandy spirit will depend. Part of this paper is devoted to the study of the relation between the composition of these fractions and their relation to the composition of commercial brandies.

Various modifications in the operation of the still and in the separation of the "spirit" running are adopted commercially in Australia, but there are no recognised standards for the distiller to work upon. The rate of distillation is of prime importance, and a section of this paper is devoted to the study of it and its effects on the distribution of impurities in the fractions of the distillate.

Some of the finest quality brandy in the worls is made in France withsmall pot- stills. The French methods differ from the usual methods adopted here in the manner of separation of the spirit from the "heads" and"tails", as well as in the type of wine distilled. The "heads" ~~&&&&Tails", a~~ fraction is relatively small, and the composition of the spirit is affected as a realt. A distillation on French principles was conducted, and a comparison drawn between the composition of the spirit obtained and that obtained by local methods.

Much importance has benn attached to the ester content by some countries importing Australian brandy, and methods of in-

creasing the amount of esters have been attempted by some distillers even as far as allowing the wine to become slightly "pricked" to raise its volatile acidity before distillation. The volatile acidity of a wine was thought to have considerable influence on its ester development, and experiments were carried out to verify this. The ester content of a brandy is subject also to changes during storage, and changes during storage in ester content of freshly-distilled spirit were studied.

The investigations may therefore be divided into five sections :-

(i) A comparison and study of the composition of commercial brandies.

(ii) A comparison of the composition of successive fractions obtained during distillation.

(iii) The effect of the rate of distillation on the distribution of secondary constituents amongst the fractions of the distillate.

(iv) A comparison of the composition of the spirit fraction as obtained by separation of the "heads" and "tails" on French methods with that obtained on local method

(v) Other factors affecting the ester content of a brandy as the volatile acidity of the wine from which it is distilled and changes in ester content duting storage.

A. INTRODUCTION.

(a) Commercial and Practical Aspects.

The importance of the export trade to the Australian wine industry is well recognised. The overseas market is however already saturated, and the present crisis will tend to make wine-makers look for other avenues as brandy-making to relieve the situation.

The production of brandy has been increasing rapidly during the last few years, and it will probably conti to do so while markets can be found for it. Speaking generally the quality of Australian brandy is only average, and any efforts to improve it will help in t expansion of overseas markets.

By systematising distillation methods, and perhaps by separation of the distillate into fractions and blending composition may be able to be standardised, and analytical methods for judging quality might the become significant.

At the present time there appears neither any relation between quality and composition, nor any methods of securing a spirit of desired composition (at least with a pot still) and it was for these reasons mainly that this subject was undertaken for investigation.

Another consideration of practical importance is the fact that certain importing countries require a brandy containing not less than 60 grms. of ester as ethyl acetate per 100,000 parts of absolute alcohol. This is doubtful proof of the maturity or quality of a brandy, as some high quality brandies have been found to contain less than this amount of ester.

(b) Present Knowledge of the Subject and a General Review of the Literature.

The study of the distillation of brandy spirit and its relation to the composition of commercial brandies has had very little attention, and literature pertaining to the subject is limited.

For the sake of convenience the factors determining the composition of a brandy are dealt with in 4 sections, and the composition of brandy is then dealt with in general.

FACTORS DETERMINING THE COMPOSITION OF THE BRANDY.

I. Raw Produce:

It is generally considered that grapes suitable for brandy material should be high in acid 8-10 grms HT/1 preferably, and of low baume 9-12^{0} Be, and that attention should be paid during and after fermentation to keep the temperatures low and to rack off the gross less early. It is safe to say that the wine should be distilled as soon after vintage as possible. These points are mentioned only briefly as they do not concern this paper.

II. Type of Still.

It is generally accepted that only good quality brandy can be made with a pot still; 90% of French brandy is made with pot stills. A pot still (Symmonds 8) ensures the retention in the distillate of the large bulk of the impurities, which give the brandy its character and flavour. In poor quality wines, especially if they have been allowed to become "pricked", the proportion of acids, esters and other substances whichare likely to be distilled, is high. For such wines a continuous or patent still is used to give a hgiher degree of rectification as may be required to eliminate the unwanted flavour and odour due to these impurities.

By usinga patent still, separation into fractions cannot be accomplished, and the desired composition cannot be obtained by blending.

III. <u>Method of Distillation.</u>

Upon this more than anything else does the composition of the spirit depend.

There are 4 main considerations :-

1. The strength at which the spirit is distilled.
2. The speed of distillation.
3. The distribution of impurities in the fractions of the distillate.
4. The separation of the "heads" and "tails".

A. <u>The strength at which the spirit is distilled.</u>

Vizetell - (1) says that the nearer brandies are distilled to their drinkable degree, the more perfect are their vinous flavour and aroma, and the more distinguishable their taste and smell.

The original strength of the wine will determine the strength of the distillate. This, however, may be altered by diluting the wine to give a distillate of lower strengt French brandies are distilled at about 20 O.P. Elliot (2) While brandies are distilled at a much higher strength usually between 30° and 40° O.P. By distilling at a lower strength the B.PT. of the vapours will be higher and the amount of impurities present in the distilate will be greater. Distillation at a low strength may be quite satisfactory for clean sound wines, but those unsound or of poor quality should be distilled at a higher strength to eliminate undesirable impurities and off-flavours.

B. Rate of Distillation.

Young (3) slow and regular distillation will give a more selective separation of impurities. Different rates of distillation will give different distribution of impurities in the distillate. Elliot (2) In brandy-making in France the distillation of the spirit fraction which amounts to 80-85 gallons for a still holding about 220 gallons, occupies from 10 to 11 hours, while the whole distillation occupies from 16 to 18 hours. This is a very slow rate of distillation. Schidrowitz (4) By vigorous distillation certain impurities as furfural may be formed.

C. The distribution of impurities in the fractions of the Distillate.

It is well-known fact that in distillation, those substances with a higher vapour pressure (i.e. lower B boiling point) will tend to distil over first. Consequently the more volatile substances as aldehydes will accumulate in the foreshots to a greater extent, and the slower the disdillation the more marked should this separation be - Young (3) Young (3) The distribution of the impurities is, however also affected by their relative mixibility with the alcohol-water mixture. The rectifying action of the neck of the still will cause differences in the distribution also, and the longer the neck the greater will be the degree of rectification and the more marked should be the separation of the various constituents.

G. Buttner and A. Miermeister (5) studied the course of distillation and found that acelaldehyde distils early, furfuraldehyde at the middle of the run, while esters and higher alcohols distil more or less regularly and no appreciable partition is effected.

Acetaldehyde B.Pt. 21°C. would naturally be a foreshot impurity, while it might be expected that esters (ethyl acetate B.Pt. 77.15°C most prominent) would distil over at about the same rate as ethyl alcohol (B.Pt. 78.4°C).

Higher alcohols whose boilings point range from nearly that of ethyl alcohol to about 140°C might be expected to be present in nearly all fractions, but should tend to accumulate in the later ones. Furfural B.Pt.136°C should tend to concentrate in the "tail" fractions.

L. W. Cornell and R.E. Montanna (6) showed that acetic acid (principle volatile acid in wine) distilled more or less regularly from start to finish.

D. The separation of the "heads" and "Tails" - is an important factor in determining the final composition of the product.

It is a common practice in Australia in the distillation of brandy spirit to run the still on "heads" for a considerable time. By doing this a large proportion of the more volatile impurities are removed and the spirit obtained will be more neutral.

The distilation of wine for brandy in France is conducted on very different lines - Elliot (2). A very small proportion of foreshots is separated, and the composition of the spirit fraction will be affected as a result.

Where poor quality wine or wine obtained from marc is distilled, continuous stills are used to give a higher degree of rectification and thus aid in separating the greater bulk of the impurities. The product from such stills is, however, of lowqaulity.

It may be concluded then that the composition of the distillate will alter with the method of separation; this composition will vary considerably and is dependant upon the judgement of the distiller.

The results of analysis of 49 Australian brandies obtained from a reliable source show that groups of samples of apparently the same origin contain similar quantities of secondary constituents. This further shows that the method off distillation has a very important bearing on the composition of the distillate, and that with systematised distillation methods, standards of composition to give the best quality product should be able to be laid down.

IV. Changes in Composition during Storage.

The composition of brandy is subject to change, both physical and chemical, during storage. Allen (4).
The chief physical changes which it undergoes are a slight increase~~s~~ in alcoholic strength (about 1%) and in total acidity. Resins, gums and tannins are extracted from the wood, and are in part responsible for the improvement and mellowing of the spirit.
The chief chemical changes (14) consist of an increased aldehyde, acid, (both fixed and volatile) and ester content, the latter being formed by the esterification of the alcohols and acids present, this change being subject to an equilibrium constant which is only obtained after long periods at ordinary temperatures, and occurs when two thirds of the equilibrium mixture is esterified.
Whatever the modifications in composition of the brandy occurring during maturation, there must be in the newly distilled spirit some optimum amount of impurities which will give a final product of highest quality for the type of wine from which it was distilled.

THE COMPOSITION OF BRANDY OR BRANDY SPIRIT IN GENERAL.

A considerably amount of work has been done on the "judgement" of spirits. Most authors state that spirits cannot be judged on results of analyses alone, but by combining analyses with tasting. Hehner (7) Analyst - 1905 - says that the quality of brandy cannot be judged by the amount of impurities present, and also that esters fluctuate as widely as other impurities. He says that too much importance is attached to the ester content.
Quoting Hessler and Booth 1883, he says that the nose and palate of a brandy are better reagents for quality and purity than re

are chemical means. This was also recommended by Fresenius 1890, Sell 1892, Bersch 1895, and Koenig 1904. (Analyst 1905) (7). Hehner says that, taking all circumstances into consideration, it follows that the amount of impurities (Coefficient of impurities) is largely an accidental quantity, applicable under proper restrictions, to products made in the same way from approximately uniform crude products, but not appàicable to all brandies alike, not useful for fixing a standard.

Dr. Schidrowitz (7) did not agree that it was an impossible matter to practically substantiate the genuine character of a spirit. He said that of the analysis done, the samples did not represent those coming from the still-head. There was practical conditions under which samples might be taken so as to enable it to be shown within what limits the different qualities are types of brandy did vary.

It is evident that there is no definite relationship between the quality of a mature brandy and its composition, but there is possibl some relationship between the composition of a newly-distilled s spirit and its potential quality.

SUMMARY OF GENERAL REVIEW OF LITERATURE AND PRESENT KNOWLEDGE.

The composition of a brandy spirit is determined by the type of raw produce, the type of still used and the method of distillation.

In the methods of distillation the chief considerations are the strength at which the spirit is distilled, the speed of distillation, the distribution of impurities in the fractions of the distillate and the separation of the "heads" and "tails" from the sp spirit fraction.

French brandies are usually considered of high quality, and French methods of distillation differ considerably from the Australian methods.

The composition of the brandy is modified by changes occurring during storage.

The composition of commercial brandies varies considerably, and there appears to be no relationship between composition and quality, but there may be some methods of estimating the potential quality of a newly distilled spirit by analytical methods.

B. EXPERIMENTAL.

MATERIALS USED.

1. **Brandy Samples used for the Analysis.**

12 Samples (including a cognac) of various ages were collected from various wineries and distilleries throughout the State. Full particulars of manufacture including variety of grapes used, type of still, and type of storage as well as age and strength were supplied with each sample.

2. **The Still.**

A one-gallon copper still of the pot type. The source of heating was an electrical hot-plate having an adjustable heat-regulator. The still was connected to a metal tubular condenser.

3. **Wine Used.**

A dry white wine made from Sultana. Vintage 1938. Alcoholic strength 21.1% P.S. Volatile acidity 1.2 grms. acetic acid litre.

METHODS OF ANALYSIS.

See Appendix.

PLAN OF EXPERIMENTAL WORK.

This was divided into 5 sections as follows:-

Section I. A Comparison and study of the results of analysis of commercial brandies.

II. Comparison of the composition of successive fractions obtained during distillation.
(Note: A comparison drawing between I and II).

III. The effect of the rate of distillation on the distribution of impurities (secondary constituents) amongst the fractions of the distillate.

IV. A comparison of the composition of the "spirit" fraction as obtained by separation of the "heads" and "tails" on French methods with that obtained on local methods.

V. Other Factors affecting the Ester Content of a Brandy.
(a) The relationship between the volatile acidity of a wine and the ester content of the spirit distilled from it.

(b) Changes in Ester Content during storage.

A COMPARISON AND STUDY OF THE ANALYSIS OF COMMERCIAL BRANDIES.

The Samples were analysed for esters, aldehydes, volatile and total acids. For methods of analysis v. Appendix.

Also examined by nose and palate to discover any relationship between composition and quality.

RESULTS OF ANALYSIS :

SAMPLE	AGE (yrs)	STRENGTH % P.S.	ESTERS as Grms.Ethyl acetate/ 100,000 parts Abs. Alc.	ALDEHYDES as Grms.Acet aldehyde/ 100,000 parts Abs. Alc.	VOL.ACIDS as G.acetic acid/ 100,000 parts Abs. Alc.	TOTAL ACIDS as grs.acetic acid/ 100,000 parts Abs. Alc.
1	1	35.6 O.P.	37.4	7.5	9.0	9.1
2	3	34.3 O.P.	30.5	9.8	34.6	41.9
3	5	32.5 O.P.	47.5	33.4	25.2	37.7
4	1	27.7 O.P.	45.0	5.2	15.1	15.2
5	5	23.5 U.P.	58.5	22.0	64.0	102.9
6	2	10.0 O.P.	34.5	79.2	36.0	218
7	7	17.0 U.P.	74.0	15.0	61.7	97.3
8	20av	17.5 U.P.	94.0	20.4	79.2	127
9	1	4.2 O.P.	22.0	13.7	19.2	32.3
10	4	5.5 O.P.	38.0	18.0	44.8	66.1
11	3	33.0 U.P.	163.0	26.4	110.6	175
12 Cognac	-	21.9 U.P.	90.0	24.7	74.1	117

DISCUSSION OF RESULTS OF ANALYSIS AND TASTING.

There is a very wide variation in composition and this variation is to some extent proportional to age.

Esters increase due to the esterification of acids and alcohols, the latter being oxidised to aldehyde, which also increases with age. Volatile acids also increase due to the further oxidation of the aldehydes to acids. Total acids increase due to substances extracted from the wood, as well as to the increased volatile acidity. There were very marked differences on nose and palate, Nos 8 and 12 being by far the best quality brandies. It is significant t that both have a high quantity of impurities, and that the various constituents occur in approximately the same proportions. However, both are old brandies and their composition cannot very well be compared with that of the young brandies.

The composition of the young brandies and brandy spirits shows a noticeably low quantity of impurities.

Apart from Nos. 8 and 12 most outstanding samples were Nos 9 and 10, both of which were a very neutral spirit as might be expected by the small amounts of impurities present. On the other hand, No 11 very high in impurities, was a very poor quality brandy, and its high volatile acidity might even suggest that the wine from which it was distilled was slightly unsound. Samples 1, 2 and 3. low in impurities were of poor quality and definitely lacked "character".

Definite conclusions cannot be drawn, but it is evident that the quality of a brandy cannot be gauged from its composition. The composition of a brandy made in the same way from the same raw produce may possibly determine its quality, but brandies made from dissimilar raw produce apparently have different optimum amounts of secondary constituents. Another significant point is that those samples having a comparatively high volatile acidity also have a high ester content, while the aldehyde content appears to have no relation. This may be due to methods of distillation but is more probably related to the esterification of acids and alcohols. Increased concentration of acid will give increased ester content.

Section II.

A Comparison of the Composition of Successive Fractions obtained during Distillation.

Materials used - V. P. 10.

Wine used - V. P. 10.

9 distillations of the wine with hot-plate running on HIGH were made, the distillate being collected until all of the alcohol had distilled over.

Amount of each charge = 10,230 mls.

Amount of each distillate collected = 3,890 mls.

Total amount of disstillate (low wines) collected = 3,890 X 9=35,010mls

The distillates were bulked, and then divided into 3 charges of 11, 200 mls. each. The remainder was analysed for aldehydes, esters and volatile acids.

Each charge of 11,200 mls. was distilled separately, and each distillate was divided into 11 fractions of 400 mls. each, and one large fraction of "tails".

Corresponding fractions from Distillations I and III were bulked making in all 11 fractions of tails. The time for each fraction to distil was recorded.

Both series of fractions were analysed for aldehydes, esters I and volume acids after determining the alcoholic strength.

For methods of analysis see Appendix.

RESULTS. v. SECTION III. For the sake of convenience results of SECTIONS II and III and the conclusions drawn from them are grouped in SECTION III.

Section III.

The Effect of the Speed of Distillation on the Distribution of the Secondary Constituents in the Fractions of the Distillate.

The same materials and wine used as in SECTION II.
The hot-plate was run on LOW to give a slower distillation rate.
The still was lagged to give a suitable distillate flow for the amount of heat applied.
6 distillations of wine were made in the same manner as before.
The time for the completion of distillation was noted.
The distillates were bulked, and two charges as before were separated, the remainder being analysed as in previous section.
The charges were distilled separately, each distillater being divided into 11 fractions and "tails" as before. Time for each fraction to distill was recorded.
The fractions were analysed and volatile acids and alcohol as in previous section.

RESULTS FROM SECTION II AND III.

DISTILLATION OF THE WINE.

PARTICULARS.	HIGH SPEED.	LOW SPEED.
Duration of distillation	2 hrs. 25 mins.	13 hrs. 35 mins
Strength of the distillate (LOW WINES).	43.5% P.S.	48.3% P.S.
Analysis of the low wines		
(1) Esters as grms. ethyl acetate/100,000 parts abs. alc.	182	191
(2) Aldehydes as grms. acetaldehyde/100,000 parts abs. alc.	26.3	27.4
(3) Volatile Acids as grms. acetic acid/100,000 parts abs. alc.	27.0	19.2

DISTILLATION OF THE LOW WINES.
HIGH SPEED.

DISTILLATIONS I AND III (bulked).

FRACTION NO.	STR. % P.S.	TIME to distil. mins.	ESTERS as grms. ethylacetate/ 100,000 parts abs. alc.	ALDEHYDES as grms. acetaldehyde/ 100,000 parts abs. alc.	VOL.ACIDS as grms.acetic acid/100,000 parts abs.alc.
1	36.0.O.P.	8	735	57.6	47.7
2	36.8 "	8	400	44.5	44.4
3	35.9 "	8	246	31.0	28.9
4	34.4 "	9	114	19.5	19.7
5	33.1 "	9(	53.9	11.7	16.6
6	30.0 "	9	30.5	6.7	14.3
7	26.5 "	8	27.2	6.1	13.5
8	22.3 "	9	29.4	2.1	15.6
9	16.1 "	10	38.8	2.6	18.5
10	6 "	11½	52.7	1.9	26.3
11	7.3U.P.	13	73.5	3.3	43.3
Tails	69.2U.P.	126	123	10.3	28.8

DISTILLATION NO. II.

FRACTION NO.	STG. %P.S.	Time to distil. in Mins.	ESTERS as grms.ethyl acetate/ 100,000 parts abs.alc.	ALDEHYDES as grms.acet-aldehyde/ 100,000 parts abs. alc.	VOL. ACIDSas grms.acetic acid/100,000 parts abs.a
1	36.1 O.P.	8	746	61.2	60.5
2	36.6 "	8	406	46.1	49.6
3.	35.6 "	8	249	31.2	36.1
4.	34.4 "	9	115	20.4	22.3
5.	33.2 "	9	56.9	11.7	17.8

This table continued overleaf.

DISTILLATION NO. II (continued).

FRACTION NO.	STG. % P.S.	Time to distil in Mins.	ESTERS as grms.ethyl acetate/ 100,000 parts abs. alc.	ALDEHYDES as grms.acetaldehyde/ 100,000 parts abs. alc.	VOL.ACIDS as grms.acetic acid/100,000 parts abs. alc.
6	30.4 O.P.	9	32.7	6.80	14.9
7	27.1 "	8	27.8	3.98	13.8
8	22.8 "	9	31.0	2.57	16.0
9	16.9 "	11	38.2	2.19	17.8
10	7.7 "	12	51.5	2.91	23.9
11	6.8 U.P.	13	77.3	3.34	41.0
TAILS	68.8 "	136	120	7.39	28.2

LOW SPEED.

DISTILLATION NO. I.

FRACTION NO.	STG. % P.S.	Time to distil Mins.	ESTERS as grms.ethyl acetate/ 100,000 parts abs. alc.	ALDEHYDES as grms.acetaldehyde.100,000 parts abs. alc.	VOL. ACIDS as grms.acetic acid/100,000 parts abs. alc.
1	35.1 O.P.	38	559	64.0	14.0
2	33.8 "	44	282	41.7	18.4
3	31.7 "	41	136	25.9	16.4
4	29.5 "	38	68.4	15.8	14.7
5	26.7 "	42	46.1	8.89	12.7
6	23.4 "	49	36.9	5.90	12.4
7	18.5 %	55	39.9	4.39	15.1
8	11.6 "	60	46.9	3.84	19.0
9	2.9 "	54	58.1	4.44	27.1
10	9.9 U.P.	61	74.6	5.60	41.4
11	26.9 "	68	102	7.79	68.7
TAILS	77.5 "	10 hrs.	271	21.9	43.3

DISTILLATION NO. II.

FRACTION NO.	STG. % P.S.	Time to distil Mins.	ESTERS as grms.ethyl acetate/ 100,000 parts abs. alc.	ALDEHYDES as grms.acetaldehyde/100,000 parts abs. alc.	VOLACIDS as grms.acetic acid/100,000 parts abs. alc.
1	33.1O.P.	37	535	65.1	14.4
2	32.9	33	276	41.7	18.8
3	31.5	36	131	25.6	17.0
4	29.1	36	65.7	15.8	14.8
5	26.1	39	40.6	9.05	14.1
6	22.1	39	31.7	6.48	15.6
7	17.4	42	35.0	3.98	16.9
8	10.0	47	42.9	4.02	21.1
9	[illegible]	49	57.0	4.20	29.6
10	18.9	54	75.0	5.92	45.2
11	29.7	60	105	7.74	73.8
TAILS	82.0	6 hrs. 40m.	339	22.0	51.8

DISCUSSION OF RESULTS FROM SECTIONS I AND II.

The alcoholic strength of the low wines by high and low speed distillations show a difference of 4.8% P.S. This is inexplicable as the same amount of distillate was collected each time, and the strength of the distillate at the end of each distillation was 100 U.P. The ester content of the distillate obtained by low speed distillation is significantly higher than that of the distillate obtained by high speed. This may be caused by a loss of esters due to incomplete condensation when distilling rapidly, or to the formation of more esters during the longer distillation.

The difference between the aldehyde contents is not significant.

The lower volatile acidity of the low wines by slow distillation is explained in a later paragraph.

The distillation of the Spirit Fractions.

The rate of distillation The results show that the difference in the duration of distillation by high and low speeds is very considerable being in the ratio of at least 1 : 5, so that any difference in the distribution of impurities due to varying the rate of distillation should be shown by the results.

Graphs have been drawn showing the distribution of alcohol, esters, aldehydes and vol. acids in the fractions of the distillate, and the effects of the rate of distillation of their distribution.

Each constituent is dealt with separately hereunder:

(1) Alcohol. By rapid distillation the strength of the distillate remains fairly constant for the first part of the distillation but after the 5th fraction the strength drops gradually in increasing amounts. When distilling slowly the strength falls gradually from beginning to end in increasimg amounts. Thus when distilling slowly the temperature in the still will increase gradually, and impurities will distil over more uniformily, and their separation should be more marked. The lower strength of the fractions by the slow distillations is probably due to the difference in strengths of the low wines.

(2) Esters. By rapid distillation there is a sharp decrease in esters from the first to the fifth fractions, but from the 5th to the 10th fractions the change is not appreciable.

According to Australian methods of separating the "heads" and "tails" fractions, 1 to 3 and possibly 4 would be separated as "heads" while fractions 10 and 11, owing to their low strength, would most probably be included in the "tails". This leaves fractions 5 to 9 (inclusive) as representing the spirit fraction. The average ester content would then be about 37, which is not high enough to satisfy the customs authorities of certain importing countries. On consulting the results of analysis of commercial brandies it is noted that the average ester content of the samples (excluding the samples 8,11 and 12, none of which are really typical commercial brandies in Australia) is 39, which agrees remarkably well with the above figure. The above method of separation is probably a fair indication of Australian method

The rate of distillation has considerable influence on the distribution of the esters throughout the distillate. When distilling slowly the ester content of the first fractions is not so high, and the decrease is not so sharp. The value for the middle fractions is not so low, and consequently the ester content of the spirit as obtained by the aforesaid method of separation will be higher. The actual value is 46 as compared with 37 obtained by rapid distillation.

In both rates of distillation there is a gradual increase of esters after the 6th and 7th fraction, and consequently by leaving this middle portion of the distillate out of the spirit fraction, the ester content of the latter would be increased. However, this is not practicable, and probably the best spirit is obtained from this portion of the distillate.

As the boiling points of ethyl alcohol and ethyl acetate (principle ester in spirit) are very close to one another (78.4° and 77.15°) respectively, it would be thought that these constituents would distil over at approximately equal rates, and the big difference in the manner of distillation of these two constituents is difficult to explain.

(3) ALDEHYDE. As with esters there is a sharp decrease in aldehyde content in the first few fractions of the distillate. There is only a slight fall from the 5th to the 9th fractions, when the aldehydes begin to increase again. However, aldehydes are not as important constituents as esters in brandy, and their elimination receives more attention. It may be seen from the graph that any attempt to eliminate aldehydes will have a considerably greater effect in eliminating esters.

Slow distillation results in a more gradual elimination of aldehydes, and by separating the "heads" and "tails" according to above methods, will give a slighly higher aldehyde content than rapid distillation.

(4) Volatile Acids. Greatest differences due to varying the speed of distillation are noted in the distribution of the volatile acids.

By rapid distillation the first few fractions are comparatively high in volatile acids, there being a sharp decrease from the first to the fourth fraction, when variations become relatively small. The amount gradually decreases up to the seventh fraction when a slight increse in each fraction becomes noticeable. Marked increses are noticeable towards the end of the distillate.

By slow distillation the first fractions show only small amounts of vol. acids. There is a significant rise from the first to ~~th~~ the second fractions while variations from then on are small, except for the latter part of the distillate when a marked increa occurs. The value for the tails for the slow distillation is very much greater than that for the rapid distillation, and it m be concluded that by slowing down the rate of distillation the volatile acids will tend more so to concentrate in the tail fractions. This explains the difference in the volatile acid values of the low wines.

By distilling slowly less of the volatile acids are driven off. It might be expected that the volatile acids would accumulate in the latter fractions since the boiling point of acetic acid (116°C) is much greater than that of ethyl alcohol.

Section IV.

A Comparison of the Composition of the Spirit Fraction as Obtained by Separation of the "heads" and "Tails" according to French Methods with that obtained by Local Methods.

The same wine was used as in the previous distillations, but dituled to a lower strength, and left for 3 weeks to allow the constituents to regain their equilibrium.

Three distillations of wine were made, and the low wines bulked and re-distilled, the distillate being divided into heads, spirit and tails fractions, according to French methods as given by Elliott (2). The spirit fraction was separated into 4 minor fractions, which were analysed for esters, aldehydes and volatile acids as well as alcoholic strength.

PARTICULARS	FRENCH METHOD	EXPERIMENTAL METHO[D]
Strength of wine	8% A.A. by wt.=17.31%P.S.	17.26% P.S.
Amount of wine distilled	3 charges of 1000 litres	3 charges of 10 litres (= 10,000mls.)
Amount of low wines collected	300-350 litres from each distillation	3.33 litres for each distillation
Strength of low wines	20-24% A.A by wt. =46.90% P.S. (average)	45.6% P.S.
Amount of low wines distilled	1,000 litres	10 litres (=10,000mls.
Amount of "heads"	3 - 5 litres	.04 litres (=40mls.)
Spirit fraction	360-380 litres	3.7 litres (=3,700 ml
(Strength)	60% A.A. by wt. = 118.6% P.S.	106.9% P.S.
Time to distil spirit fraction	10 - 11 hours	7½ hours.
"Tails"	200-225 litres	2.125 litres (=2.125m
Strength of "tails"	16-20% A.A. by wt. (=38.55% P.S. (average)	12% P.S.

RESULTS -

Analysis and period of Distillation of Spirit Fractions (1925 mls each).

FRACTION NO.	STRENGTH % P.S.	TIME TO DISTIL MINS.	ESTER as grms.ethyl acetate/ 100,000 parts A. A.	ALDEHYDES as grms.acetaldehyde.100,000 parts A. A.	VOL.ACIDS as grms.acetic acid/100,000 parts A. A.
1	29.4 O.P.	80	250	35.2	17.6
2	21.2 "	91	42.9	10.9	19.3
3	6.0 "	115	46.1	4.03	29.8
4	28.8 U.P.	150	89.6	5.07	81.1

NOTE. - Average strength of Fractions 1 - 4=6.9 O.P.

" " " " 1 - 3=18.8 O.P.

DISCUSSION OF RESULTS OF ANALYSIS.

There appears to be some discrepancy in the figures given by Elliott (2). The strength of the low wines are practically the same, but the strength of the spirit fraction, which should, according to his figures be about 18 O.P. is only 6.9 O.P. The strength of the "tails" is about 12% P.S. while the figure given is about 39 % P.S. By excluding the fourth fraction from the spirit running, the average strength of the latter becomes 18.8 O.P. while the strength of the tails is raised to about 39% P.S. It appears therefore, that the figure for the spirit-fraction is at fault, and by transferring the last quarter of the spirit-running to the "tail" fraction, both the strengths of the spirit and tail fractions would be rectified according to his figures. Moreover, the strength of fraction 4 is rather too low to be included in a spirit-running. Therefore, fraction 4 is to be considered as part of the tails in the analysis. The secondary constituents are dealt with hereunder.-

(1) Esters. - The average ester content of the fractions (1-3) is 113 which is considerably higher than the figure obtained by Australian methods (v. SECTION III), and also that of commercial Australian brandies (v. SECTION II).

(2) <u>Aldehyde.</u> On the other hand the figure for aldehyde is slightly lower than that for commercial brandies (v. SECTION II) the average (fractions 1-3) being 16.7 The average figure by Australian methods is even lower lower being about 5.5 while the figure for the better quality brandies is just over 20.

(3) <u>Volatile Acids</u> - The figure for volatile acids is fairly typical for commercial brandies, the average (fractions 1-3) being 22.2. In comparison with Australian methods this figure is slightly higher.

<u>GENERAL OBSERVATIONS AND CONCLUSIONS.</u>

The ester content of the best quality brandies analysed was significantly high (90-100) (v. SECTION I), while the aldehyde content was about 20.

It appears therefore, that by distillation and separation according to French methods, a relatively high ester content may be obtained without necessarily increasing the aldehyde content beyond the figure for commercial brandies.

By distillation according to Australian methods (v. SECTION III RESULTS) in order to obtain a high ester content more of the "heads" fraction must be included in the spirit-running, the proportion depending upon the rate of distillation. Aldehyde content of spirit, as well as esters, will be increased as a result. The slower the rate of distillation the more of the "heads" fraction will have to be included.

<u>N.B.</u> In considering the rate of distillation other constituents, as volatile acids and aldehydes are affected. Separation of less "head" fraction will greatly increase the volatile acidity in a rapid distillation, but only a slight increase will result in a slow distillation. The differences in increase of aldehyde depending on the rate of distillation will be insignificant.

Section V.

Other Factors Affecting the Ester Con-tent of a Brandy.

A. The Relationship Between the Volatile Acidity of a Wine and the Ester Content of the Spirit Distilled from it.

Wine Used - A dry white wine of fairly low volatile acidity.

8 litres of wine were divided into four 2 litre portions in large Florence flasks, A,B,C, and D.

Acetic acid was added to B and D to raise the volatile acidity about 300%.

Volatile acidity of the wine in each flask was determined.

The wine in all flasks was then boiled under reflux for varying periods.

NOTE - This heating should have similar affect on ester-development as storing the wine for 12 months in the presence of the added acid.

After heating the flasks were cooled, and a fractionating head and condenser fitted to each flask.

Exactly 250mls. were distilled into a flask from each one, any loss of alcohol vapours being prevented by means of attaching a mercury trap.

Ester determinations were made on the 4 distillates.

RESULTS -

FLASK NO.	VOLATILE ACIDITY. grms./1 acetic acid	TIME OF REFLUXING. (hours)	ESTER CONTENT as grms. ethyl acetate/ 100,000 parts abs. alc.
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 OF RESULTS AND CONCLUSIONS.

From a commercial point a view a dry wine having a volatile acidity of 1.69 grms/l. acetic acid would be considered most probably "pricked".

There is a signigicant increase in ester content due to increasing the volatile acidity of the wine, the increase being about 10 gms. ester as ethyl acetate/100,000 parts of abs. alc. for a three-fold increase acid, the time of refluxing having very little influence. Allowing a wine to become "pricked" to increase the ester content of the spirit to conform to regulations should be unnecessary, and, on the basis of this experiment, is unlikely to give any useful increases, besides being undesirably in that good brandy, accorking to literature, can only be made from sound wine.

The volatile acidity of a wine has only a small influence on the ester content of the spirit distilled from it in comparison with other factors as the separation of the "heads" and "tails" from the spirit fraction.

B. Changes in Ester Content During Storage.

The fractions from distillations Nos.1 and III (bulked) by "high speed" (v. SECTION III) were re-analysed for esters about 3 months after the original analyses were made.

RESULTS.

FRACTION NO.	ORIGINAL ESTER CONTENT in grms.ethyl acetate/100,000 parts abs. alc.	VOL.ACID CONTENT in grms.acetic acid/100,000 parts abs. alc.	ESTERCONTENT in grms. ethyl acetate/100,000 parts abs. alc. after 3 months.	CHANGE IN EST in grs.ethyl acetate/100,0 parts abs. al
1	735	47.7	580	155 decrea
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 and Conclusions.

There is a very marked decrease in esters in those fractions high in ester, while in those whose ester content is relatively low, the change is insignificant. A freshly-distilled brandy spirit with an ester content above 100 is liable to a loss of esters on storage, and the decrease may be as high as 30%.
This decrease may be due to evaporation losses, but is more probably due to a reversion of esters to alcohols and acids to form the equilibrium constant.

$$\frac{\text{Molecules of ester} \times \text{Molecules of water.}}{\text{Molecules of alcohol} \times \text{Molecules of acid.}}$$

which occurs when 2/3rds of the equilibrium mixture is esterfied.

SUMMARY.

1. A number of samples of commercial brandy have been analysed and the results show considerably variations in the amounts of secondary constituents present.

The course of distillation has been studied and results show that (1) there is a gradual change, very marked in the earlier fractions, in the composition of successive fractions.

(2) there is a definite relationship between the composition of certain fractions of the distillate and the composition of commercial brandies.

III. The effect of the rate of distillation on the distribution of secondary constituents has been determined, and the results show that -

(1) The rate of distillation has an important effect on the distribution of secondary constituents especially volatile acids and esters, and 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 distillation rate the strength falls gradually in increasing amounts from start to finish.

b. The separation of esters is less marked by distilling slowly.

c. The rate of distillation has no marked affect on the distribution of the aldehydes.

d. But has a very marked affect on the distribution of volatile acids.
By rapid distillation the earlier fractions are high in volatile acids, which by slow distillation there is a tendency to concentration in the "tail" fractions.

IV. A distillation was conducted on French methods and results show that -

(1) The French methods of distillation differs greatly from the usual Australian methods.

(2) The composition of the spirit is high in esters while the aldehyde content is relatively low.

V. Two factors affecting the ester content of commercial brandy were stutied, and results show that -

(a) The volatile acidity of the original wine has only a slight influence on the ester content.

(b) The ester content is liably to change during storage and in spirits very high in esters this change may be considerably.

The general conclusions drawn are that -

1. The composition of a brandy spirit is determined mainly by the manner of separation of the "heads" and "tails" from the spirit fraction.
2. The rate of distillation has a less important influence on the composition.
3. The manner of distillation of French brandies is mainly responsible for their high ester content, and similar results should be able to be obtained in Australian distilleries by modifying distilling operations.
4. The coeficeient of impurities im different brandies will vary due to munerous causes, but the manner of distillation will have most influence on this quantity, and their is probably dome optimum amount of impurities for a brandy made from similar raw produce and by the same methods of distillation which will give it a high potential quality.

A C K N O W L E D G E M E N T S.

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A P P E N D I X.

Modification of Ester Determination by A.O.A.C. Method. (8).

For the determination of esters, the method given in the A.O.A.C. was followed, with one modification, viz. the time of refluxing. The A.O.A.C. advises 1 hour as the time of refluxing. Hossack (9) mentions that a shorter time of refluxing (viz. 10 minutes) is sufficient.

Ester determinations were made on two samples of spirit of fairly high ester content, the refluxing being carried out for varying times, viz. 60, 30 and 15 minutes.

SAMPLE	TIME OF REFLUXING.	MLS. N/10 NAOH USED.	ESTER CONTENT as grms. ethylacetate/100,000 parts of absolute alcohol.
1	60mins.	29.40	517.4
	60 "	29.52	519.5
	30 "	29.46	518.5
	30 "	29.45	518.3
	15 "	29.42	517.3
	15 "	29.48	518.9
2	60 "	12.82	225.6
	60 "	12.77	224.8
	15 "	12.80	225.3
	15 "	12.84	226.0

From these results it is evident that 15 minutes refluxing is quite sufficient, and gives just as reliable results as refluxing for 1 hour. The small differences above are within the limits of experimental error.

The Determination of Aldehydes in Spirit.

Owing to the inconsistent results obtained by the A.O.A.C. method (10) method of determination outlined in the Analyst 1935 ( ) and also outlined by Joslin and Comar (12) was chosen. This method gave consistent results, and was used with one modification viz. The colour of the iodine was used as an end-point as this gave a more delicate end point than starch whose action is affected by the alcohol present (13).

Other Methods of Analysis.

Alcohol - determined by Sikes glass hydrometers directly in the spirit.

<u>Volatile Acids</u> -

(a) for brandies the determination was the same as for wines. The Official Method of the A.O.A.C. using a Settler tube and phenolphthalein as indicator was used.

(b) for the fresh distillate direct titration with N/10 NaOH using phenolphthalein as indicator. (All of the acid present is volatile).

<u>Total Acid.</u> - by the Official Method of the A.O.A.C. using phenolphthalein as indicator.

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