THE EFFECT OF pH ON BRANDY COMPOSITION.

by

H.T. DAVOREN.
Roseworthy Agricultural College.

February, 1955.

INTRODUCTION.

Since the recent decrease in excise brandy production will probably increase within the next few years and though Australian brandies are of reasonably high quality, there is still room for improvement.

Different techniques and procedures may cause variations in the brandy product, but the composition of the initial base wine is one of the most important contributing factors.

French Cognacs have a much higher ester level than Australian brandies, and this is supposedly due to the high acid content of the French base wines. As the climatic conditions in our brandy producing areas do not lead to high acid wines as in France, we can only rely on reduction of pH, after fermentation, if we wish to increase the ester content of our brandies.

The object of this paper is to find what effect the pH of the base wine has on the spirit produced, especially as regards ester production. Some importing countries require a certain minimum ester level and some Australian brandies have found it hard to come up to this requirement.

Two other factors which determine the composition of a brandy are the type of still and the method of distillation.

It is generally accepted (1) that only good quality brandy can be made with a pot still; 90% of French brandy is made with pot stills.

In the method of distillation the main considerations are:-

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

These factors have been dealt with previously in other projects so, for the purposes of this paper the whole spirit run was taken for analyses i.e. all the fractions were bulked together, so as to find the effect of pH on the spirit as a whole.

LITERATURE REVIEW.

Very little work has been done on the subject in question, and about the only references available for a literature review are in previous projects.

Jamieson (2) states that wines low in total acids and high in pH will give less aroma and have a more undesirable aroma, if distilled at the same proof, than those brandies made from wines high in total acid and low in pH. The subsequent wine made from grapes with the desirable features will be thin and very acid with no special qualities.

In France the three chief varities used for brandy making are (3) :-

1. St. Emillion.
2. Folle blanc.
3. Semillon (Riesling Hunter River). X Colombard.

In Australia, a number of varieties are used (3) :-

1. Sultana.
2. Doradillo.
3. White Hermitage.
4. Pedro.
5. Mataro etc.

The main bulk of Australian brandies are produced from Sultana and Doradillo grown in the Murray River irrigation settlements.

Whilst lacking the delicate perfume of cognac, the brandy produced is clean and palatable.

Joslyn and Amerine (4) state that the base wines made in France from the varieties mentioned above give a moderate alcohol content and an above average total acidity. They also state that low acid wines are considered undesirable, particularly for use in pot stills.

It is a known fact that wines made from Doradillo and Sultana are low in acid, so it may be worth while to investigate the possibilities of introducing into Australia some of the varities that have proved so successful in France. It must be remembered however that though these varieties produce brandies of high quality in France they might not do so in Australia.

Australian brandies approaching French style could probably be produced in dry wine areas, such as the Hunter River, but this would be uneconomical as there is a ready market for these wines. However the dry wine areas produce wines very similar, as regards acidity etc., to the French base wines, though they probably have more character. If they were distilled in the same fashion as the French brandies there is no reason why the quality could not be the same.

I've heard that after World War 1 a firm was formed at Allandale, in the Hunter district, which made good French style brandies from local wines but, unfortunately, didn't last for long.

In order to bring the acid content of Australian base wines to a level favouring maximum ester production it is advantageous to make acid additions to the wine, so bringing about an alteration in pH.

Both Tummel (5) and Walters (6) investigated the effect of increased acidity on ester production.

Tummel states that the best way to reduce the pH is by means of sulphuric acid. He found that the spirit produced from wine in which the pH had been reduced by sulphuric gave a slightly higher ester content than that made from wine in which the p H had been reduced to the same level by tartaric acid, as well as the fact that sulphuric acid is more economical to buy than tartaric.

The effect of sulphuric acid on the copper of the still was also investigated by Tummel and he found that relatively no reaction takes place, and that wine treated with sulphuric causes less damage to the copper than that to which tartaric acid has been added.

Walters (6) found that increased acidity (lower pH) gave a decrease in aldehydes in the brandy fraction, but his results with esters were rather conflicting.

EXPERIMENTAL.

APPARATUS AND MATERIAL.

1. The Still.

A 2 - gallon, copper pot-still, fitted with a brandy column and brandy-ball. Still connected to a metal tubular condenser which differs from most condensers found in still houses in that the cooling water, not the vapours, goes through the tubes. This type is much easier to clean, as a brush may be pushed straight through the tube when the top is removed. Heat was applied by means of an electrical hot-plate, with a heat regulator.

2. Hydrometers.

There was no spirit safe supplied with the still so a means had to be devised for taking strength readings on the spirit as it left the condenser.

A number of glass bubbles were made which just floated in spirit of varying strengths, ranging from 40° O.P. to 100° U.P. (water).

The bubbles were placed in a separating funnel which was clamped under the spirit take-off from the condenser, and the spirit level in the funnel was kept constant by means of the tap.

3. Wine.

A dry white wine made from Riesling 1954 Vintage with a pH of 3.22.

METHODS OF ANALYSIS.

Alcohol - Sykes glass hydrometers.

Acids - Direct titration (Phenolphthalein) expressed as parts acetic acid per 100,000 parts Absolute Alcohol.

Esters - A.O.A.C. Method (7), modified by standing for 12 hours with $^{N}/_{10}$ NaOH instead of refluxing.

Expressed as parts of ethyl acetate per 100,000 parts A.A.

Aldehydes - Jaulmes and Espezel (8)

Expressed as parts acetaldehyde per 100,000 parts A.A.

PROCEDURE.

In order to obtain a wide variation in pH in the base wine, six gallons were prepared for each of the following pH's:- 2.5, 3.0, 3.5, 4.0, 4.5. The pH of the original wine was raised or lowered by means of calcium carbonate and sulphuric acid respectively.

In each case the rates of addition were determined by trial before the bulk was treated.

After the calcium carbonate was added it was well stirred in and the calcium tartrate formed was allowed to precipitate overnight. The clear wine was then drawn off and checked for the correct pH before being stored in readiness for distillation.

The pH's had to be checked again just prior to distilling as those of the portions to which carbonate had been added tended to drift. Any alterations were then corrected.

Before any project wine was put through the still, other wine of a similar type was distilled in order to study the still's behaviour. There was a pronounced tendancy for frothing when the heat regulator was turned much above the minimum setting needed to keep the wine boiling and turbid liquid came over through the condenser into the spirit receiver.

Various methods were tried to prevent this frothing, none of which were entirely successful.

Small quantities of soap chips were added to the wine and glass beads were placed in the pot before distilling, but frothing still occurred when the heat regulator was turned up much over the minimum possible for boiling. The spirit also had a strong soapy flavour and a cloudy appearance.

When distilling the project wines the beads were used in the pot and the regulator was turned on to the setting as determined above. The flow of water around the brandy ball was kept as constant as possible.

Frothing still occurred and turbid liquid came over into the receiving flagons during about half the distillations. However, as the whole of the spirit run was collected, these particular samples were diluted with water and distilled again.

By distilling all the spirit it is hoped to find the direct effect of pH on the spirit composition instead of just on the brandy, heads, tails, or whatever the case might be.

Though it hadn't originally been intended to distill any of the samples twice it will be interesting to see the effect of this double distillation.

Three samples of two gallons each were distilled at each pH and all the distillates were brought to the constant strength of 30^{o} U.P. before analyses.

Duplicates of each sample were analysed and the results all expressed as parts per 100,000 **A.A.** are as follows:-

TABLE OF ANALYSES 1.

pH	No.	Esters		Aldehydes		Acids.	
4.5	1	60.1	59.7	66.5	66.3	119.8	123.1
	a2	38.5	37.7	56.2	56.8	48.2	47.6
	3	56.8	57.3	72.4	72.7	115.5	117.8
4.0	1	68.5	67.8	71.7	72.0	155.4	154.6
	d2	50.9	51.4	76.2	76.2	68.8	68.2
	3	67.3	66.9	74.3	74.4	151.7	150.4
3.5	d1	53.8	53.6	113.8	113.3	91.5	93.2
	d2	54.1	53.9	110.5	111.9	95.5	94.2
	3	73.6	73.8	128.7	127.2	138.8	140.7
3.0	d1	70.6	72.4	163.1	161.1	114.8	116.5
	2	87.3	87.7	149.4	149.4	141.5	143.1
	d3	68.4	69.1	139.1	138.9	113.8	112.1
2.5	d1	74.1	69.3	214.5	217.9	99.8	100.5
	2	90.3	91.2	185.2	185.4	144.1	144.1
	3	91.0	89.7	227.8	228.0	143.1	141.5

Those samples marked thus "d" are those which received double distillation.

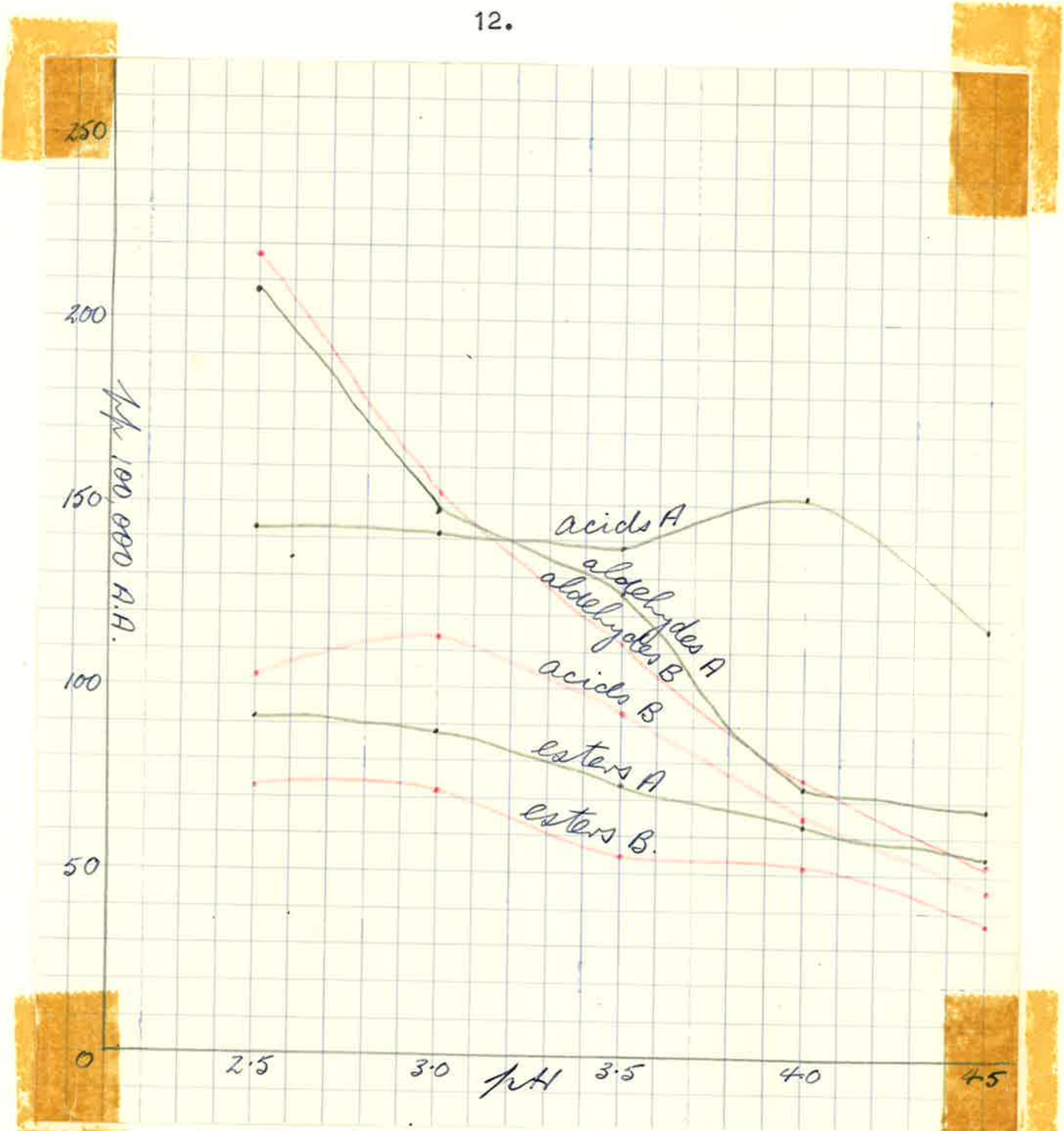
For the purposes of discussing the results found on previous page it was considered easier to take the single and double distilled samples separately as the difference between the two sets of results is quite considerable.

The results for each were averaged and graphs were drawn from the average results as found in **TABLE II.** A = Single distillation.

B = Double distillation.

TABLE 11

pH	Esters		Aldehydes		Acids.	
pH	A	B	A	B	A	B
4.5	58.5	38.1	69.5	56.5	119.0	47.9
4.0	67.6	51.1	73.1	76.2	153.0	68.5
3.5	73.7	53.8	127.9	112.3	139.7	93.6
3.0	87.5	70.1	149.2	150.5	142.3	114.3
2.5	90.5	71.7	206.6	216.2	143.2	100.1



SUMMARY OF RESULTS.

Esters: Both ester curves decrease slightly as the pH increases, whilst the decrease in each case between pH 2.5 and 3.0 is practically negligible. It appears therefore that reducing the pH of the wine to 2.5 doesn't cause any further ester production than does reducing it to pH 3.0.

The curves are very similar so there is a constant decrease in ester production over the range after second distillation.

Aldehydes: The aldehyde curves are also very similar except for small discrepancies at pH 3.5 and 4.5 which are probably due to experimental error or variations in the distillations. The curves are near enough together to be called the same so single or double distillation doesn't make any difference to the amount of aldehyde produced. The increase in aldehyde from the higher to the lower pH is considerable, but if the heads portions were removed, as is usual in commercial distillations, most of the aldehyde would be in these fractions.

Acids: The two acid curves are not at all similar, as the A curve reaches its peak at pH 4.0 and the B curve at pH 3.0. From the results obtained it seems that with doubly distilled brandy spirit the maximum acid production occurs at pH 3.0 and that double distillation reduces the acidity.

CONCLUSIONS:

1. Increased pH of base wine does give an increase in ester formation, with the maximum pH for such increase being about pH 3.0, but this might vary if only the brandy fraction of the run is taken.

2. The lower the pH of the base wine the more aldehyde is formed, which would probably necessitate the running of more spirit into the "heads" fraction when distilling low pH wines.

3. The results for the acid formation are too erratic to draw any worthwhile conclusions. It should be a fact that the lower the pH the more acid formed but this doesn't seem to be the case, in A curve and in B the curve reaches a peak at pH 3.0 but falls away again.

ACKNOWLEDGEMENTS.

Acknowledgement is made to Mr. R.H. Kuchel B. Sc. (HONS). R.D.OEN, Mr. J.G. Chappell B. Sc., and Mr. A.F. Twartz B. Sc. DIP. ED. for advice and assistance throughout the experiment.

BIBLIOGRAPHY.

1. Graham, W.O.
"A Comparison of the Composition of Successive Fractions obtained during Distillation and their relation to the Composition of Commercial Brandies."
R.A.C. Prpject. 1939. 3.

2. Jamieson, W.R.
"Factors affecting the Composition of French Style Brandies."
R.A.C. Project. 1950. 7.

3. R.A.C. Distillation notes. 5.

4. Joslyn, M.A. and Amerine, M.A.
"The Commercial Production of Brandies."
Univ. of California Bulletin. 652. 1941. 30, 69.

5. Tummel, P. Le H.
"Acidity modifies Brandy Composition."
R.A.C. Project. 1948. 5, 7, 15.

6. Walters, J.R.
"The Effect of Tartaric Content of Wine on the Composition of Distillates."
R.A.C. Project. 1947. 7.

7. Methods of Analyses.
A.O.A.C. Ed. V11., 1950. 130.

8. Jaulmes, P. and Espezel, P.
"Analyst 1935." 703.

9. Osborn, G.H. and Mott, O.E.
"The Analyst." Vol. 77, 1952. 260-262.

APPENDIX.

Acetals:

It was also intended to do a test for acetals on the spirit samples, but the only method found, - that in Amerine and Joslyn (3) - didn't give any details about the absorbing solution used, and though quite a bit of literature containing spirit analyses was studied no other references to acetal tests were found.

Higher Alcohols:

A modification of the British Government Lab. method was found in the 1952 edition of the Analyst (9) which showed promise of being suitable.

However higher alcohol free, 50% alcohol for making the standard solutions was unable to be obtained. The broken down commercial absolute alcohol first used as a blank was found to contain more higher alcohols than the standards.

It was then attempted to remove the higher alcohols from the absolute alcohol by means of carbon tetrachloride s aturation with Sodium Chloride as described in A.O.A.C. (7), but the blank again contained higher alcohols. As varying amounts of this alcohol are used when making the standard solutions, a set figure could not be subtracted in order to find the transmittance of the standard alone.

Though the transmittance of the samples themselves could have been measured only a rough comparison could have been made, but would have proved too inaccurate for this particular work.
