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B R A N D Y M A K I N G.

Two types of spirit can be produced from the juice of the grape by distillation viz., beverage brandy or fortifying. Essentially the difference is in the method of distillation although other factors contribute to the decision as to whether brandy or fortifying spirit is to be manufactured. Generally, pressings, leachings and wines from grapes unsuitable for brandy production are distilled at high proof (160 - 190% pf.) and is used for fortifying sweet wine and brandy is distilled at 135 - 140% pf. from the wine of selected grapes. The Australian Pure Food Regulations specify that brandy must be the distillate from fresh fermented grapes.

"Proof" is an old English term for the strength of spirits and 100% pf. contains 57.1% by volume of alcohol at 60° F. In the U.S.A. - 100% pf. spirit contains 50% by volume of alcohol therefore Absolute alcohol is 200% pf.

The problems of producing high quality, commercial, beverage brandies are many, particularly if it is desired to produce a brandy similar in type to the renowned cognacs of France. Some of these problems are bound up with the economics of production as the manufacture of cognac entails the use of equipment that is too slow and cumbersome for Australian methods of production. Many of these problems have been studied at Roseworthy Agricultural College from the angle of producing brandies more closely resembling cognac and it is the purpose of this project to include a re-survey of the work accomplished.

Although Australians, in general, have come to regard a comparatively neutral brandy as a desirable feature, this is not the case overseas, where the full bodied brandy with plenty of character, mellowed by maturity, is accepted as the criterion. If we are to develop and expand our export markets we will have to modify our distillation procedure and methods of manufacture to comply with this existing demand. South Africa, our sister dominion, and rival on the overseas market with wines and brandies, is making strenuous efforts to capture this market. The Govt. Brandy Board which has to pass all wines before distillation has lately declared itself in favour of a Cognac type brandy for South Africa. This will mean the exclusion of the two most prolific bearers of grapes, from the varieties specified as being suitable for distillation for the production of beverage brandies.

In the eusuing controversy Professor C. J. Theron and Dr. C. J. G. Neehaus of the Shellenbosh-Elsenburg College of Agriculture in supporting the Govt. Brandy Board's as to the necessity for conforming to this demand concisely summed up the situation thus.

(a) There is a great demand for certain types of South Africa brandies overseas and these resemble Cognacs. South Africa is in need of this demand and should foster it.

(b) Cognac type of brandy derives most benefit from maturation and the future of the South African wine industry lies in the production of well matured brandies. (4)

PRODUCTION OF COGNAC.

Cognac is the standard in assessing the quality of any brandy produced from grapes from any part of the world and therefore a resume of its manufacture is given so that the essential differences between methods of production can be discussed.

The term Cognac is jealously safeguarded in France to protect the name and reputation of a particular type of brandy. It is legally recognised and the name can only be applied to brandies produced within a limited area. This region is known as the Charentawhich is divided into four main areas, Grande Champagne, Petit Champagne, Borderies and Premier Bois. The whole area lies to the north of Bordeaux. (A district to the south of Bordeaux also produces a very fine brandy, Armagnac, which is similar to Cognac, in many respects.)

The soil in the Charente district where the best quality Cognacs are produced is very shallow, about 15 inches in depth and below the soil is a calcareous subsoil. The prices paid for wines for distillation varies and this correlates to the composition of the soil on which the grapes were grown.

Those that receive a higher price are grown on the more calcareous soils. (1)

The winter is severe in comparison with Australian conditions but not as rigorous as many parts of France. Fainfall is high (47.6 inches per annum) and this falls frequently in small amounts. (2)

A French decree (May 16th 1936) limits the varieties which may be grown in the Charente for Cognac and these are Saint Emilion, Colombard, Folle blanche, Blanc romay, Montellis White Sauvignon and Jurnac blanc. (13).. The first three varieties are the main ones and the Folle blanc which is considered the best for Cognac often attains 1.2% acid and only 7-8% alcohol by volume. Saint Emilion generally 7-9% alcohol by volume and Colombard 8-11%. (3)

In some years, during the harvesting period, many of the grapes are damaged by rain and mould and such damaged bunches are scrupulously rejected. The grapes are crushed on the day they are picked and the juice separated from the skins immediately. Fermentation on the free run juice is carried out in small, closed containers (up to 500 gals capacity).

No $S.O._2$ is used during fermentation as it is found that any wine fermented in the presence of considerable quantities of $S.O._2$ will contain a considerable quantity of aldehydes, even though the wine itself may have only negligible $S.O._2$ content at the time of distillation. This is due to the formation of an aldehyde bi sulphite complex. The quantities of $S.O._2$ used to prevent distillation wines from becoming diseased will always result in too much aldehyde production. (4)

Fermentation is carried out at low temperatures and the 'silent' fermentation takes about 3-4 weeks, the wine then containing about 8% alcohol by volume and up to 12 gms/litre of acid as tartaric. (13)

When the wine has fermented out dry it is left on lees but distilled as soon as possible to reduce risk of wine spoilage. Wines left too long on gross lees develop a typical stale lees flavour which may be imparted to the spirit. If the wine is racked from its lees the quality of the brandy suffers as distillation of wines with large numbers of yeast cells is one of the essentials for imparting the Cognac character. (4) Just before charging the still wine and lees are agitated to give a uniform suspension.

Distillation is carried out in simple brandy pot stills of 50-250 gals. capacity and are generally direct heated, instead of steam heated. The procedure is not in any way standardised and distillation practices arepassed on from father to son. The distiller is called upon to show great judgement in the selection of wines for Cognac; and in deciding when to take off 'head' and 'tails' from the wines made from the different varieties and grown in different areas. As the pot stills are direct fired great care must be taken in controlling the heat of the fire to avoid scorching of the contents.

The wine is fed into the cold still, the fire lit and distillation carried out at a very slow rate. It is an essential that the pot be never any more than 75% filled with wine. When one fourth to one third of the original volume has come over the distillation of the wine is stopped. This first distillation is known as the 'bråullis' and the strength of the low wine (bråullis) is about 30 - 40% alcohol by volume. It contains a considerable amount of aldehydes and higher alcohols. To minimise risk of spoilage the whole of the distillation wine for the season is sometimes put through as low wines before commencing the redistilling. The best brandy, however, is obtained by redistilling immediately and where there is only a single still in operation this is done when three charges of low wines have been collected, and the joint distillate is then redistilled. (4)

This second distillation is carried out much more carefully than when distilling the 'brouillis' and the 'heads' or 'foreshots' are received separately. The taking off of 'heads' and 'tails' is considered the most important phase of the distillers work and is carried out organoleptically. These heads are mixed with the next brouillis. The brandy begins to run at 80 - 85% alcohol by volume and collected until it falls to approximately 50% alcohol by volume and the average strength of the brandy collected is 66 - 70% alcohol by volume. (2)

The distillation is continued until the alcoholometre shows zero and this is kept separate and is known as the 'tail' fraction and contains 20 - 24% alcohol by volume. Sometimes the 'tails' are fractionated into a portion running from 50 - 20% alcohol by volume and this is mixed with the 'brouillis' and the portion running from 20 - 0% alcohol by volume is mixed with the distillation wine. About eight gallons of wine are used in the production of one gallon of Cognac.

Brandy distilled thus is totally unsuitable for immediate consumption while young, but has to mature for a number of years whereby its secondary constituents interact to remove the disagreeable, burning taste and to impart mellowness and palatability. This maturation can only take place where the wood of the container can contribute certain qualities to the brandy. Limonsin oak is used exclusively for Cognac and generally the young brandy is stored in new hogsheads for a year at low temperatures and then transferred to bigger wood and stored in warmer locations to undergo maturation. The period of maturation depends on various factors and may vary from 3 - 10 years. The best brandies require the longest periods of maturation and the blender when making up his blends selects those that will undergo further improvement for longer maturation and less full bodied brandies are blended earlier.

After blending they may undergo a further period of ageing in the wood before bottling.

Thus the problems involved in the production of Cognac type brandies involves consideration of

(1) the base wine

(2) type of still

(3) method of distillation

(4) maturation.

FACTORS AFFECTING THE COMPOSITION OF BRANDIES.

(1) The base wine.

(a) Variety of Grape.

The composition of the grape will have an effect on the wine and hence on the spirit produced during distillation. Climate and soil will modify the composition of the grape - cold climates prpducing grapes of higher acidities and lower sugar content than the corresponding grapes grown in hot climates. High acidity and low alcohol content are important features in the production of quality brandy.

The calcareous soils of the Charente are said to impart a delicate and characteristic bouquet to the Cognacs. The exact explanation of why these soils give the grapes their desirable characteristics is not known but in the wine the delicate bouquet may be due to a p H effect.

Coloured varieties are not suitable for brandy making and even when the juice is separated immediately from the skins undesirable characteristics are found in the spirit. Jocelyn and Amerine (1) suggest that red grapes contain larger amounts of the undesirable substances and if fermented on skins greater quantities of pigments and tannins are extracted. Possibly these substances are hydrolysed. The above workers also consider that the bloom of the grapes on hydrolysis yields a variety of fatty acids and other hydrocarbons and thus fermentation on skins of both red and white varieties will produce more of the hydrolytic products. More likely, as pointed out by Kuchel (12), contain a greater quantity of volatile constituents in the skin.

Varietal aromas have a great influence on the character of brandies and this is generally considered undesirable in better class brandies.

Grapes with a high sugar content are to be avoided for the production of quality brandy. Of two wines with the same percentage composition of volatile constituents, the wine with the lower alcohol content will yeild a brandy having a greater percentage of volatile constituents <u>if</u> both are distilled at the same proof. (1).

This may be due to the fact that the weaker the alcoholic solution the higher the temperature at which it boils and the more of the less volatile constituents pass over in the vapour. If the wine is of comparatively high alcoholic strength the higher boiling point substances remain behind in the pot. As pointed out earlier in the production of Cognac, the desirable alcoholic strength is about 8% by volume.

The grapes that are high in total acids are superior to those containing lesser amounts. They should be picked when mature - fully ripe or over ripe grapes do not give the same quality brandy. Wines low in total acids and high in p H 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 p H.

The subsequent wine made from grapes with the desirable features will be thin and very acid with no special qualities.

In Australia, the following varieties are used in the production of brandy. (13)

Sultana
Doradillo
Pedro Ximenes
Mataro
White Hermitage
Sherry (syn. Albillo)
Grenache
Madeira (21) (probably the Greengrape of the Cape (17),).

The main bulk of Australian brandies are produced from the Sultana and Doradillo grown in the irrigation settlements along the Murray river. Whilst lacking the delicate perfume and other congenerics of Cognac, the brandy produced is clean and palatable.

It may be worth while to investigate the possibilities of introducing some of the varieties that have proved so successful in France. These could be used for blending purposes as both the Doradillo and Sultana are low in acid. It must be borne in mind however that though these wines are eminent in the production of classical brandies it may not necessarily be the case when grown in Australia even if all other things were equal.

Amerine and Winkler (18) have found that in America, Saint Emilion (synonyms, Trebbiano in Italy and Ugni blanc in some parts of France and Algiers) lacked acid and the wine was easily oxidised and of no value. However Folle blanc under the same conditions was a wine of outstanding quality for brandy production. The French Colombard is another variety, which, under the name of Winkler and West's Prolific, is of the greatest value. It retains a high degree of acidity at full maturity even in the warmer regions. The wines have been distinct in aroma, fairly full and pleasing in flavour, tart and well balanced.

In South Africa, Saint Emilion and Colombard are grown with great success but Folle blanc has proved disappointing.

These and other sorts, would pay investigation under Australian conditions.

(b) MANUFACTURE OF THE WINE.

The nature of the fermentation and the substances obtained during fermentation are closely related and these factors will have an influence on the composition of the brandy.

The grapes are fermented "off skins" either by medium of a foredrainer or by fitting a false bottom for immediate drain off. It is imperative that no $S.O._2$ be added and should only be used as a last resource and then the wine should be distilled at high proof and not used in the production of beverage brandy. Mouldy grapes will impart their taint to the wine and thus to the spirit. Where $S.O._2$ is used the risk of mercaptan formation is very great and apart from the danger of these evil smelling compounds being produced, the aldehydes formed during fermentation are fixed in the wine by the sulphur and released during distillation increasing the aldehyde content of the spirit.

Wines fermented at high temperatures show less retention of the more desirable volatile products and in addition may give a taint to the spirit. (1) Under Australian conditions where the grapes arrive at the crusher hot and are fermented in large vats it is impossible to keep the temperatures down to a reasonable degree without the use of coolers, particularly if no $S.O._2$ is used.

In order to bring the acid content of the wine to a level favouring maximum ester production it is advantageous to make acid additions to the wine prior to distillation.

Both Le Tummel (2) and Walters (19) carried out investigational work on the effect of increased acidity on ester production. Their results were at variance.

Le Tummel found that by reducing the p H of the base wine the ester content is increased.

TABLE. 1.

EFFECT OF p H ON ESTER PRODUCTION.

	Raised pH with KOH to pH 4	pH Lowered to pH 3.5 with H_2T	pH Lowered to pH 3.5 with H_2SO_4	pH Lowered to pH 3 with H_2T	pH Lowered to pH 3 with H_2SO_4
ESTERS	96	116	123	122	132
ACIDS	128	68	67	70	69
ALDEHYDES	12	14	12	11	13
SEC. ALCOHOLS.	90	80	76	108	81

The use of Sulphuric Acid proved superior to Tartaric Acid in the production of esters.

It was also found that by putting through the distillation wine as a low wine and incorporating the 'heads' and 'tails' from the brandy run into the next low wine charge caused an increase in esters. This was particularly noticeable at pH 3.

Reducing the pH with Sulphuric acid was found to be more economical and at the required strength had no adverse affect on copper plate (2).

Walters (18) claims slightly lower aldehyde production in acid media and that ester production was not increased.

As $S.O._2$ must be kept out of distillation wines Shipster (20) carried out a comprehensive series of tests using sodium fluoride as an antiseptic and preservative. Its use as a preservative is well known and has given satisfactory results but there has been great uncertainty as to its value as an antiseptic during fermentation.

Before using the sodium fluoride, he found it was necessary to estimate the purity of the sample in order that the correct additions to the wine be given. The methods for determining insoluble and soluble impurities are given in his project.

A study of the tolerance of different strains of yeasts showed a variation in the inhibitory coefficient of the yeast and also that this inhibitory coefficient varied with the pH of the media. By the term 'inhibitory coefficient' is meant the dose of sodium fluoride necessary to retard fermentation for a definite length of time.

Some strains of yeasts took a longer time to habituate themselves to sodium fluoride than did others. The yeasts were considered sufficiently acclimatised when they commenced to ferment juice within 12 - 24 hours with a dose of 600 p.p.m., of sodium fluoride. Shipster found it impossible to habituate yeasts to much greater doses than 600 - 700 p.p.m. and in studying two different strains of yeast (Sacch. Ellipsoideus strains) the rate of fermentation varied between 26 - 38 days.

Using sodium fluoride as an antiseptic it was found that a dose of 100 - 150 p.p.m. could be safely added to the must without the inhibitory coefficient interfering with the fermentation.

A comparison of alcohol produced from material fermented with 400 p.p.m.

Na F (sodium fluoride) and without Na F showed that there were no differences either on the nose or on the palate between the corresponding fractions of the distillation.

The inhibitory effect of Na F on lactobacilli and acetobacter in wine was also studied. In media made suitable for the growth of lactobacilli it was found that for the particular strain of lactobacilli it was inhibited at 200 - 300 p.p.m. Na F. The retarding effect of Na F varied with the type of wine, pH, temperature, etc.

Acetobacter were inhibited at 100 - 150 p.p.m. NaF Mycoderma vini grown ?? on grapejuice.

Trials were conducted to ascertain the inhibitory coefficient of Na F. against the development of wild yeasts in the must. It was considered that a dose of Na F that would check spontaneous fermentation for 30 - 36 hours at 25° C. would give the inhibitory coefficient. This varied with the p H but with the must below p H 4., 150 p.p.m. Na F. may be taken as the inhibitory coefficient.

Conditions for growth were made very favourable for each organism and the inhibitory coefficient was estimated under these conditions thus leaving a margin of safety. When conditions for growth are adverse (for example, low p H) the ascertained dose of Na F. would undoubtedly prohibit growth (20).

FACTORS AFFECTING THE COMPOSITION OF BRANDY.

(2) TYPE OF STILL.

The reputation of the brandies of Charente and Armagnac depends upon their characteristic bouquet and character, therefore it is desirable to avoid high rectification leading to consequent removal of these secondary constituents upon which the flavour depends. (12).

It is not proposed in this project to consider the different types of still used in the production of brandy in Australia. Brandy is however, made in practically all of the common types of still from the simple pot still to the modern three stage continuous still. Comparison of brandies from the different stills are practically meaningless as the methods of distillation and wine types used are not known when the finished brandy is presented for analysis at the laboratory.

In order to complete the precis on the production of Cognac, the following is a description of the type of still employed.

The still consists of a closed copper vessel, bricked in so that a fire may be built under it, a gooseneck for partially condensing the vapours of high boiling point, a worm condenser for cooling the vapours and a preheater. It is important that the fire be well maintained without causing the contents of the pot to become scorched. The heat of the fire is regulated by a damper in the chimney and the rate of stoking the fire. Three hours before the first distillation is finished the preheater or chauffe vin is filled with wine and this helps to condense the alcoholic vapours from the still and at the same time absorb heat so that there is a saving in fuel when it is run into the pot. After each distillation the fire is damped down and the vinasse or spent wash run off. The body of the still is then filled from the chauffe vin and the operation repeated. (6). Direct fired pot stills are said to produce important flavouring constituents when the wine is distilled on lees. Small stills have been found to give better results than large ones and the sizes favoured in the Charente district are those with a capacity of 75 - 250 gals.

In regard to modifications in the design of stills, Kuchel (12) points out that the angle the vapour line makes with the column is an important consideration. If the angle is less than 90 degrees a "fatter" spirit is obtained than if the angle is greater than 90 degrees, thus allowing more condensate to return to the pot, or in othere words, providing a reflux.

Heath (22) in his project studied the effect of (a) a lengthened column (b) a brandy ball - in providing a reflux. The reflux provided by a lengthened column and a brandy ball and the resultant fractions were analysed and compared with that obtained from a straight distillation.

An analysis of the low wine obtained from the distillation showed a definite decrease in acid and ester content by both the lengthened column and the brandy ball; and the lengthened column showed a decrease in secondary alcohols. All other constituents remained more or less constant.

ANALYSIS OF LOW WINE FRACTION.

(A) Lengthened column (B) Brandy ball (C) Straight distillation.

ALCOHOL			ACIDS			ESTERS			ALDEHYDES			SEC. ALCOHOL			FURFURAL		
A	B	C	A	B	C	A	B	C	A	B	C	A	B	C	A	B	C
30.7	31.7	31.8	90	85	170	166	155	227	37	41	36	13	60	50	.5	.9	.4

The low wines were then redistilled and analysed. The distillate was collected in 5 fractions, Heads 1, Heads 2, Brandy, Tails 1 and Tails 2.
Each constituent is discussed separately.

ALCOHOL. Greater rectification was given by the lengthened column and brandy ball. Lengthened column gave a higher strength spirit than the brandy ball. This high strength spirit is not altogether advantageous to quality as it becomes more neutral leaving more flavouring and essential aromatic substances in the pot.

ALCOHOL Brandy fraction.

A.	B.	C.
81.3% A.A.	78.4%	76.4%

ACIDS. There was a greater decrease in acids in all fractions down to Brandy, a slight increase in Tails 1, and then a rapid increase in Tails 2.

The lengthened column and the brandy ball showed marked differences in the amount in the Brandy fraction compared with the straight distillation.

A C I D S.

	HEADS 1	HEADS 2	BRANDY	TAILS 1	TAILS 2
A	16	7	9	32	210
B	29	8	8	23	144
C	112	52	18	31	188

ESTERS - tend to concentrate in Heads 1 and Heads 2 with decreasing amounts in towards the brandy fraction. With lengthened column and brandy ball there is considerable decrease in esters. Under reflux esters tend to become more of a Tail product.

E S T E R S.

	HEADS 1	HEADS 2	BRANDY	TAILS 1	TAILS 2
A	340	85	32	142	709
B	398	70	19	86	585
C	531	220	62	108	428

ALDEHYDES. In all distillations are small and remained constant in all fractions. Heath showed them to be more of a tail product but they decrease slightly to distil ever constantly throughout Heads 2, Brandy and Tails 1, increasing again as alcohol content falls.

E S T E R S. aldehydes

	HEADS 1	HEADS 2	BRANDY	TAILS 1	TAILS 2
A	31	29	24	32	83
B	30	22	25	28	70
C	34	25	26	21	31

SECONDARY ALCOHOLS. Concentrate in Heads 1 and decrease throughout all fractions with an absence altogether in Tails 2 more being left behind in the foot in the lengthened column than in either of the other two methods. Brandy ball makes no difference to this constituent throughout all fractions.

SECONDARY ALCOHOLS.

	HEADS 1	HEADS 2	BRANDY	TAILS 1	TAILS 2
A	430	140	50	20	-
B	520	220	70	50	-
C	520	230	70	20	-

FURFURAL. Being a product produced within the pot, furfural does not appear in the distillate until Heads 2, where it is present only in traces and shows no definite increase until tails.

ORGANOLEPTIC EXAMINATION - The lengthened column produced the most neutral material and then the brandy ball. The brandy ball has a higher ester content but less secondary alcohols than the straight distillation and this appears to indicate that higher alcohols have a more marked effect on the bouquet than the esters.

Heath showed that by lengthening the column a longer run on the brandy fraction is possible. To produce the same result with a brandy ball it must be kept very cool thus necessitating a fast flow of water which may be uneconomical. Also too cold a brandy ball may provide too much reflux stopping distillation.

The temperature of the water in the brandy ball was maintained at 30 - 35° C. which is considerably lower than that obtained in actual practice in wineries.

FACTORS AFFECTING THE COMPOSITION OF BRANDIES.

(3) METHOD OF DISTILLATION.

In the production of Cognac this factor has the greatest effect of all in modifying the composition of the brandy.

The first distillation in the Charente district, (i.e. the production of the brouillis) takes eight hours, the still containing about 250 gals. In the redistillation of the brouillis, the heads (about 1% of the brouillis) and tails (1¼% of the brouillis) are added from a previous brandy run, (bonne chauffe) and again distilled slowly and this distillation takes about ten hours. As the brouillis represents only one third of the original volume, it is necessary to have three brouillis charges to fill the pot for the second distillation (6). The separation of heads and tails is the culmination of the distillers art and is done entirely by smell and palate.

As pointed out by Angove (7) French methods differ from those commonly used in Australia mainly in (a) the strength of wine, (b) use of lees, (c) rate of distillation, (d) procedure in separating heads and tails, (e) return of heads and tails to low wines or brouillis, (f) amount of reflux. Cognac is distilled with the minimum of reflux, the still having almost no column and generally the gooseneck is dispensed with (23).

In an intensive study of the influence of distillation methods, Graham (5), provided considerable data on the strength of wine, rate of distillation and the separation of heads and tails.

It was found that French brandies were distilled at a comparatively lower strength than Australian brandies 0 20. O.P. as compared to 35 - 40 O.P. - due mainly to a lower original wine strength and to differences in the methods of distillation and construction of stills.

The rate of distillation was much slower - a still of 220 gals capacity taking 16 - 18 hours for complete distillation as against the Australian method whereby 2,000 gals takes 30 - 40 hours.

Graham pointed out that slow distillation gives a more selective separation of the secondary constituents their distribution being governed by (a) their respective volatilities, (b) their respective miscibilities in water/alcohol mixtures of different strengths. Also that slow distillation accounts for the nature or composition of these secondary constituents as well as their amounts.

In the separation of heads, the French separate only a small fraction (about 5% of the brandy running) whereas in Australia a comparatively large head fraction is taken off (about 20% of the brandy running). The heads are always mixed with the next low wine charge in France and the tail fraction may be mixed with the distillation wine or fractionated and the richer alcohol fraction returned to the low wine charge and the poorer alcohol fraction to the distillation wine.

In an endeavour to find some relationship between composition and quality Graham analysed a number of commercial brandies and then made a study of the variations in the composition of brandies made under selected experimental conditions.

COMPOSITION OF AUSTRALIAN BRANDIES.

Results of analysis of commercial brandies showed a marked variation in composition and this variation was somewhat proportional to the age of the brandy.

The young brandies were found to be very low in esters and their total acidities was practically the same as their volatile acidities. There appears to be some relationship between volatile acidity and ester content, those samples having a relatively high volatile acidity are also high in esters.

Organoleptic impressions indicate that Samples Nos. 8 and 12, see table, were the best quality brandies and these have a large quantity of secondary constituents in about the same proportions but being old brandies their composition can not be a fair comparison with that of young brandies.

Definite conclusions can not be drawn but results indicate that Australian brandies are low in secondary constituents.

TABLE 2. COMPOSITION OF COMMERCIAL BRANDIES.

SAMPLE No.	AGE (years)	STRENGTH	ESTERS AS GRMS. ETHLY ACETATE 100,000 PARTS ABS.	ALDEHYDES AS GRMS Acetadehyde 100,000 Parts Abs.	VOLATILE ACIDS as GRMS Acetic Acid 100,000 Parts Abs.	TOTAL ACIDS as GRMS Acetic Acid 100,000 Parts Abs.
1	1	35.6 O.P.	37.4	7.5	9	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 O.P.	58.5	22.0	64.0	102.9
6	2	10.0 O.P.	34.5	79.2	36.0	218.0
7	7	17.0 O.P.	74.0	15.0	61.7	97.3
* 8	20 Av	17.5 O.P.	94.0	20.4	79.2	127.0
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 O.P.	163.0	26.4	110.6	175.0
* 12	(Cognac)	21.9 O.P.	90	24.7	74.1	117.0

Omitting Nos. 8,11, and 12 the average composition of Australian brandies may be regarded for the purposes of comparison, thus -

TABLE 3. AVERAGE COMPOSITION OF AUSTRALIAN BRANDIES.

(Expressed in p.p. 100,000 of Absolute Alcohol)

ESTERS	ALDEHYDES	VOLATILE ACIDS.
42.7	15.6	34.4

FACTORS AFFECTING COMPOSITION OF BRANDIES.

(3) METHOD OF DISTILLATION.

EFFECT OF RATE OF DISTILLATION ON THE COMPOSITION OF SUCCESSIVE FRACTIONS.

Graham studied the effect of high speed and low speed distillations on the composition of the low wines and on successive fractions of the brandy run.

RESULTS.

LOW WINES. The ester content was significantly higher by slow distillation probably due to the formation of esters during the longer boiling in the pot. Differences in aldehyde content were insignificant but decrease in volatile acids during slow distillation was appreciable.

TABLE 4. COMPOSITION OF LOW WINES.

	RAPID	SLOW
Duration of Distillation	2 hours 25 mins.	13 hours 35 mins.
Strength of Distillate	43.5% P.S.	48.3% P.S.
ESTERS p.p. 100,000 Abs.	182	191
ALDEHYDES "	26.3	27.4
VOLATILE ACIDS "	27.0	19.2

Each distillation charge amounted to 10 litres.

The low wines were then bulked and redistilled. Each constituent is dealt with separately hereunder.

ALCOHOL (see Table 5) When distilling slowly the strength fell gradually from beginning to end in increasing amounts. Distilling rapidly the strength remains fairly constant for the first part of the distillation but after the 5th fraction, the strength drops gradually in increasing amounts. The lower strength of the fractions by the slow distillations is due to the combined effects of the more efficient rectification by the still column and to the lower strength of the wines (as shown in Table 4).

TABLE 5. EFFECT OF RATE OF DISTILLATION ON COMPOSITION OF SUCCESSIVE FRACTIONS OF THE BRANDY DISTILLATE

	HIGH SPEED DISTILLATION.				LOW SPEED DISTILLATION.			
FRACTION NO	STRENGTH % PROOF	ESTERS	ALDEHYDES	VOLATILE ACIDS	STRENGTH % PROOF	ESTERS	ALDEHYDES	VOLATILE ACIDS.
1	136.0	735	57.6	47.7	135.1	559	64	14.0
2	136.8	400	44.5	44.4	133.8	282	41.7	18.4
3	135.9	246	31.0	28.9	131.7	136	25.9	16.4
4	134.4	114	19.5	19.7	129.5	68.4	15.8	14.7
5	131.1	53.9	11.7	16.6	126.7	46.1	8.9	12.7
6	130.0	30.5	6.7	14.3	123.4	36.9	5.9	12.4
7	126.5	27.2	6.1	13.5	118.5	39.9	4.4	15.1
8	122.3	29.4	2.1	15.6	111.6	46.9	3.8	19.0
9	116.1	38.8	2.6	18.5	102.9	58.1	4.4	27.1
10	106.0	52.7	1.9	26.3	90.1	74.6	5.6	41.4
11	93.7	73.5	3.3	43.3	73.1	102	7.8	68.7
TAILS	30.8	123	10.3	28.8	22.5	271	21.9	43.3

ESTERS. (Table 5).

Rapid distillation gave a sharp decrease down to the 5th fraction but little change from the 5th to the 10th fraction. Thefraction from 5 - 9 inclusive represents the brandy fraction and the ester content of this is only 37. Slow distillation gave an ester content of 47 for the brandy fraction. In practice, the French as well as distilling more slowly, separate a much smaller amount of heads from the brandy and thus it is to be expected that the French brandies have a far higher ester content than Australian brandies.

The longer column of the Australian pot still would also reduce the ester content.

ALDEHYDES. (Table 5) There is a sharp decrease in the first fractions and this is somewhat more marked in the slow distillation. From the 10th fraction onwards aldehydes increase a gain indicating the modifying influence of the mutual solubilities of alcohol and aldehyde on their distribution.

Any attempt to eliminate aldehydes will have a greater effect in removing esters.

VOLATILE ACIDS. (Table 5) Distilling rapidly there was a sharp decrease in volatile acids in the first few fractions, thus fractions 1 - 4 were high in volatile acids. There is a slight increase in volatile acidity from the 7th fraction, the increase becoming more marked towards the end of the distillation.

Slow distillations show only small amounts of volatile acids in the first few fractions but in the last part of the distillation, marked increases occur. By slowing down the rate of distillation volatile acids tend to accumulate in the tail fraction. This is probably the reason for the difference in volatile acidities of the low wines.

The greater concentration of acids in the pot during the slow distillation must assist in the formation of increased amounts of esters.

EFFECT OF VOLATILE ACIDITY ON ESTER CONTENT.

Graham (5) investigating the effect of volatile acidity on ester content refluxed a sample of dry wine, with and without added volatile acid. After refluxing, the wines were distilled.

Refluxing hastens the process of esterification, the effect being as if the wine had been stored for a long period with consequent ester development.

An increase in volatile acidity of 300% gave only a very slight increase in ester content.

Thus volatile acid has only a small influence on ester production in comparison with other factors.

FACTORS AFFECTING COMPOSITION OF BRANDIES.

(3) METHOD OF DISTILLATION. USE OF LEES.

As pointed out earlier it is customary in the production of Cognac to distil the wine with its own lees. This is supposed to give the brandy a great part of its characteristic bouquet and flavour. In an endeavour to investigate what changes occur distilling on lees Angove (7) made an analysis of the same wine distilled on and off lees.

RESULTS.

TABLE 6. COMPOSITION OF LOW WINES (a) CLEAR WINE AND (b) WINE PLUS LEES.

	ALCOHOL	ACID	ESTERS	ALDEHYDES	SEC. ALCOHOLS	FURFURAL
a.	34.7	155	152	60	245	.4
b.	37.5	205	207	46	260	.6

The presence of lees resulted in a marked increase in acids and esters and slight increases in secondary alcohols and alcohol, also an increase in furfural. There was a definite decrease in the aldehyde content of the low wines.

As lees contain as much as 40% KHT this may account for the increase in acids and esters.

The low wines were then bulked and redistilled. Heads were collected in 2 fractions; the first above 45 O.P. and the second down to 44 O.P. Brandy was cut out at 20 O.P. and the tails collected in 2 fractions; first down to 18 U.P, and the second, down to zero.

TABLE 7. COMPOSITION OF DISTILLATES (BRANDY) (a) CLEAR WINE (b) WINE PLUS LEES.

FRACTION	ALCOHOL		ACID		ESTER		ALDEHYDE		SEC. ALCOHOLS.	
	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)
HEADS 1	80.0	68.4	193	303	328	516	149	147	290	350
HEADS 2	80.6	80.9	56	149	132	266	67	78	390	380
BRANDY	74.9	77.9	48	34	42	45	22	11	300	280
TAILS 1	41.6	57.8	69	46	127	111	3	5	170	90
TAILS 2	12.0	20.3	290	219	469	416	17	16	90	-

The considerable increase in acids and esters that occurred in the low wines of this distillate has disappeared. This would indicate that there must be considerable differences in the acids and esters of the low wines and the brandy distillates.

In each case the acids and esters tend to concentrate in the heads.

If early heads are undesirable in brandy and later heads desirable then the effect of lees is to give a clearer and cleaner separation between the two heads thus more of the heads could be included in the brandy.

The effect of lees summed up by Angove is to cause a marked increase in the ester and a cid content of the low wines, and, in the brandy run, a stronger tendency for these constituents to pass into the heads.

FACTORS AFFECTING THE COMPOSITION OF BRANDIES.

(3) METHODS OF DISTILLATION - EFFECT OF RETURNING HEADS & TAILS TO SUBSEQUENT WINE CHARGES.

The practice of returning the heads and tails from the brandy run to the next low wine charge is an essential part of the production of Cognac.

In his literature review Angove (7) outlines the following procedures that may take place.

(a) The heads and tails may be run back to the next wine charge.

(b) The heads returned to the next brouillis charge and the tails to the next wine charge, or,

(c) High strength tails may be divided into two, the highest strength portion going to the next brouillis charge and the lower strength going to the wine charge; finally,

(d) The heads and tails may be bulked and redistilled and the heads and tails from this going back to the wine charge.

Heath (22) in his project made an analysis of the low wine and brandy fractions of four separate brandy charges. The plan of the experiment is as shown hereunder.

Step (a) Three charges of wine distilled and these bulked and redistilled separating Heads - Brandy - Tails.

(b) Three charges of wine plus feints from (a) distilled to low wines. Redistilled and Heads - Brandy - Tails separated.

(c) Three charges of wine plus feints from (b) distilled to low wines. Redistilled to Heads - Brandy - Tails.

(d) Three charges of wine plus feints from (c) distilled to low wines. Redistilled and Heads - Brandy - Tails separated.

Each brandy charge divided into 5 fractions, viz., Heads 1 and 2 - Brandy - tails 1 and 2.

Before feints were added to the wine they were broken down to the strength of the wine thus preventing increase of alcoholic strength due to the addition of feints.

TABLE 8. EFFECT OF RUN BACK ON COMPOSITION OF SUBSEQUENT FRACTIONS.

b, c and d, representing progressive runbacks.

FRACTIONS.	ALCOHOL				ACIDS				ESTERS				ALDEHYDES				SECONDARY 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 1	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 2	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 1	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 2	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

RESULTS.

LOW WINES - The main constituent affected is the acids where there is a considerable decrease obtained from the first run back (b) but no further change is significant with the run backs from (c) and (d). It appears, therefore, that with the additions of feints an equilibrium is reached with the acid which then distils over unchanged throughout progressive distillations.

Angove (7) also found that there is a decrease in acids and that the successive feints additions had very little more effect than the feints from the first brandy distillation. The same worker also found slight but significant increases in esters, aldehydes, secondary alcohols and furfural. However Heath found that aldehydes decrease slightly and that there is little change in secondary alcohols or furfural.

BRANDY FRACTIONS.

ACIDS. Both workers found that there was a strong tendency for acids to concentrate in tails and heads. The effect of run back is to produce cleaner fractions. First run back markedly reduced acid content but no appreciable change with progressive feints addition as indicated by (c) and (d) in Table 8.

ESTERS. Working independently Angove and Heath found that esters tend to accumulate in the heads and tails and this is further accentuated by run back.

If second heads and first tails were included in the brandy run, the ester content would approach that of French brandy (7).

ALDEHYDES. Heath (22) found that there was a slight cleansing of all fractions down to brandy due to the effect of run back and that the extra aldehyde tended to collect in the tails.

This is contrary to the Angove's results where it was found that aldehydes accumulated in the heads and this was accentuated by run back.

Tails were almost free of aldehyde and they were not affected by run back.

SECONDARY ALCOHOLS. Definitely a head product and there is a complete absence of secondary alcohols in Tails 2. Run back gave a slight increase in the amounts separating in Heads 1.

FURFURAL. This is present in very small amounts. Heath (22) found that run-back reduced the amount of furfural very slightly but Angove (7) reports a slight increase with runback. Furfural is a tails product.

ORGANOLEPTICAL EXAMINATION.

The four brandy fractions (a), (b), (c) and (d) produced by Heath with progressive additions of feints were examined by nose and palate.

The samples (b), (c) and (d) were found to be vastly superior to (a) but there was no noticeable difference between (b), (c) and (d). It therefore claimed that runback improved the spirit by giving it a more balanced character.

FACTORS AFFECTING COMPOSITION OF BRANDY.

(3) Method of Distillation.

(c) Separation of HEADS and TAILS from the Brandy Fraction.

Earlier it was reported that in the production of Cognac only a small fraction of the brandy running was removed as heads (about 5%) but that it was common practice in Australia to remove about 20% of the brandy running.

Graham using data cited by Elliott (24) distilled low alcohol content wines into low wines and then these were bulked and redistilled very slowly dividing the distillate into 3 fractions. These were then analysed.

TABLE 9. ANALYSIS OF THE 3 BRANDY FRACTIONS.
(French Method of Distilling).

No.	STRENGTH % p.f.	ESTERS	ALDEHYDES	VOLATILE ACIDS.
1	129.4	250	35.2	17.6
2	121.2	42.9	10.9	19.3
3	106.0	46.1	4.0	29.8

DISCUSSION OF RESULTS.

ESTERS - The average ester content is 113 as compared to 37, the figure obtained from the same wine, by Australian methods.

The ester content approximates the composition of genuine Cognac.

As can be seen from the Table, the esters concentrate in the early fractions and the exclusion of theheads from the brandy run, explains in some measure, the low ester content of Australian brandies.

ALDEHYDES. The average aldehyde content of the fractions is 16.7 which is slightly lower than that for commercial Australian brandies.

Cognac averages about 25 but the figure varies considerably.

VOLATILE ACID. The average volatile acid content of the fractions is 22 and this is typical of commercial brandies.

Graham quoted 19 as being the averages, obtained by Gerald and Cuniasso, for young Cognacs.

Heath and Angove, similarly analysed fractions and included the second heads and first tails in the brandy run. Their results agreed fairly well with Graham in the ester and aldehyde content of the brandy fraction, but for the volatile acid content, Heath obtained a figure of 13 whilst Angove gave 31 as the figure.

Summing up, the composition of The distillate alters with the method of separation. If run on heads for a relativaly long time, a large proportion of the more volatile constituents are removed giving a more neutral spirit.

CONCLUSIONS. Method of Distillation.

(1) Esters concentrate mainly in the first fractions and the decrease from these to the brandy fraction is most marked.

Aldehydes concentrate in first fractions but there is no marked separation of volatile acids.

(2) Distilling wine with lees caused a marked increase in acid and ester content of low wines, and, in the brandy run, a stronger tendency for these constituents to pass into the head.

(3) Esters are concentrated in theheads - the proportion of heads taken governs the ester content of the brandy to a marked extent.

(4) The use of feints as 'runback' in the low wine charge has a cleansing effect on the resultant distillate causing the heads and tails to pass more and more completely towards the first and last stages of the distillation, thus a much larger brandy cut can be taken. The resultant brandy is richer in aldehydes and esters but the other constituents remain much the same.

(5) With a fast rate of distillation the decrease in alcoholic strength of the first fraction is small with a fairly rapid decrease in the later

fractions. With a slow rate of distillation, the strength falls gradually in increasing amounts from start to finish.

With a slow rate of distillation, the concentration of esters in the early fractions is less marked and there is a slight increase in ester content in the middle fractions.

Rate of distillation has no marked effect on the distribution of aldehyes.

Rate of distillation has a marked effect on distribution of volatile acids. The early fractions tend to be high in volatile acids when distillation is accomplished rapidly; slow distillation gives a tendency for volatile acids to concentrate in thetails, thus assisting in ester formation during the distillation.

FACTORS AFFECTING THE COMPOSITION OF BRANDY.

(4) MATURATION.

Brandy undergoes physical and chemical changes during storage. This change is most marked in brandies containing relatively large amounts of secondary constituents such as volatile acids, higher alcohols, esters. It is therefore evident that the practice of regularly removing heads and tails during distillation will result in a brandy that is thin, lacks Cognac quality and will need little maturation.

The following table sums up the relative effects of the various substances in the brandy after optimum maturation.

FLAVOUR - derived from the presence of small quantities of aldehydes and higher alcohols.

ARMOMA - is due to certain esters produced by the interaction of acids and alcohols.

STRENGTH - depends upon the amount of ethyl alcohol required in the brandy. It has no particular influence on the special characteristics of flavour and aroma and may vary considerably.

SWEETNESS - most spirits as they come from the still are 'dry' and harsh but during the process of maturation acquire a certain 'sweetness' or mellowing.

Liquer brandy has been sweetened by the addition of sugar or other sweetening agents.

COLOUR - Brandy when first distilled is colourless but during ageing it extracts from the wood certain colouring matters.

Caramel is often added to brandies to give a pale brown colour. (25)

In the production of Cognac, the spirit ex still is stored in new casks of Limonsin white oak. Many of the larger Cognac distilleries maintain their own forests of Limonsin oak in order to have suitable and adequate supplies for casks and barrels. The staves are split in the forests and allowed to season for about two years before the casks are made. Cognac casks are never charred. (13)

New barrels are first scalded and then soaked with water and dilute Cognac brandy. Neutral spirits are never, in any circumstances, used for this preliminary soaking of new barrels.

The freshly filled barrels (of about 75 gallons capacity) are first stored in dark rooms, frequently in buildings without windows and on the ground floor. The atmosphere is always damp and consequently the alcohol content decreases rather than increases. After varying periods of time depending on the view of an expert, the Cognac is removed to warm, dry, storage and kept in larger casks at fairly constant temperatures. Very old Cognacs are usually transferred to large glass containers to prevent excessive losses of alcohol. It is estimated that stocks of Cognac maturing in the Charente district is 22,000,000 gallons and the average annual production is about 4,500,000 gallons. These are prewar figures. (8)

Warehouses are under strict Government control and only cane sugar or syrup and caramel are allowed to be added. No neutral spirit, brandy from another district or any other flavours are permitted. Cognac may legally contain 2% cane sugar or syrup.

There is a limit to which any brandy may be aged in wood. Up to fifty years is considered sufficiently long for a good Cognac to develop to perfection. Once bottled they undergo no further maturation.

Changes During Maturation.

Substances derived from the wood include acids, colouring matter, tannin and the amounts are proportional to the darkening of the brandy spirit.

During ageing there is a slight increase in total acid, furfurals and in solids.

The loss in weight under Australian conditions is considerable and due to differential loss of water there is a small increase in proof. However this does not occur where brandies of high proof are stored for very long periods, particularly under relatively higher humidity conditions. (1)

The chemical changes are due to oxidation alcoholysis and exterification. Bellet (26) found that the total ester content remained essentially constant but the more volatile esters rose very slowly at the expense of the less volatile esters of the higher alcohols. The consequent liberation of higher alcohols is termed 'alcoholysis'. Some of the higher alcohols released are converted to aldehydes. The secondary importance of oxidation, and the relatively greater importance of alcoholysis gives reasons why the rapid oxidation of new brandies by the introduction of oxygen or ozone under pressure has not been successful.

Jocelyn and Amerine (1) point out that one of the most apparent changes is in the ratio of esters to total acids. In the new brandy the esters are usually present in larger amounts, but during the ageing in barrels, the ester increase is much less than the total acid increase; after a year or so in storage these values are not so far apart. Generally however the esters still exceed the total acids.

Graham (5) when studying changes in ester content during storage found that there was a marked decrease in esters in those fractions high in esters; but where the ester content is low the change is relatively insignificant. A freshly distilled brandy spirit with an ester content above 100 is liable to a loss of esters and this decrease may be as high as 30%.

This could be due to evaporation losses but is more probably due to a reversion of esters to alcohols and acids to form the equilibrium constant.

$$\frac{\text{MOLECULES OF ESTERS} \times \text{MOLECULES OF WATER}}{\text{MOLECULES OF ALCOHOL} \times \text{MOLECULES OF ACID}} = K.$$

which occurs when two thirds of the equilibrium mixture is esterified.

Graham assumed therefore that brandies are much higher in esters when newly distilled than is shown by the published analysis of brandies.

As Graham conducted his experimental work in glass stoppered bottles the results obtained may not necessarily occur under practical conditions. However it is possible that very volatile or unstable esters newly formed would disappear on ageing.

The period of maturation therefore depends on:-

(1) Method by which brandy has been distilled and the resultant chemical composition
(2) Type of container in which brandy undergoes maturation
(3) Whether it is to be used pure or blended with a neutral spirit and if blended - in what proportion

SUMMARY.

The foregoing has been an attempt to explain the essential differences in the manufacture of Cognac and brandy making as practised in Australia.

It has been shown that:-

(1) type of grape
(2) manufacture of the base wine
(3) type of still
(4) distilling wine with lees
(5) rate of distillation
(6) incorporation of feints into the next low wine charge
(7) method of separating heads from the brandy run
(8) method of maturation

can modify the composition of the resultant brandy.

Although comparisons have been made between Australian brandy and Cognac, the comparison is not a fair one as they are two distinct types of brandies. However while a comparatively neutral brandy is satisfactory, perhaps even ideally suited, for Australian conditions and consumption, it may be necessary for Australian distillers to modify their procedures in order to comply with the overseas demand for a heavier bodied brandy requiring lengthy maturation.

The Influence of Organic and Inorganic Nitrogen Compounds in the Must on the Composition of the Distillate.

This part of the project can be conveniently divided into three headings:-

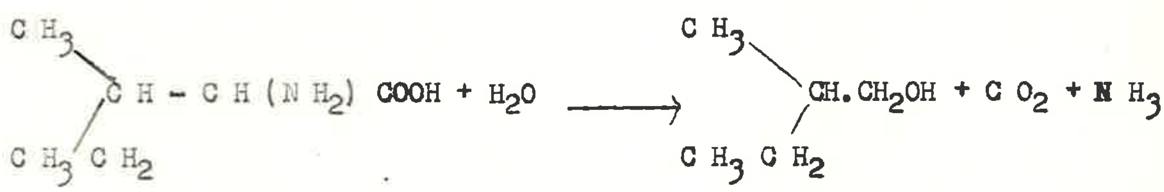
(1) A literature review of the subject

(2) Experimental work

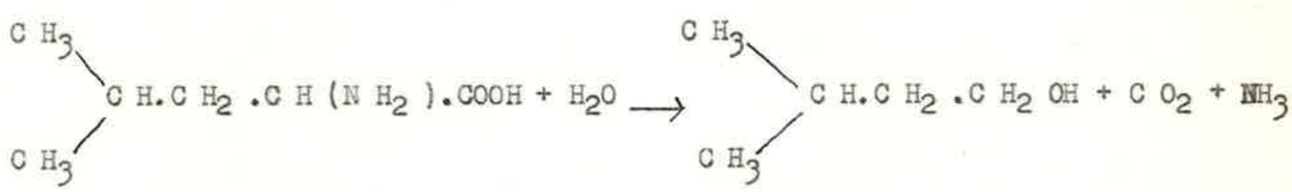
(3) Conclusions drawn from the results.

The influence of Organic and Inorganic nitrogen compounds in the must on the composition of the distillate could be quite important in the production of a neutral spirit necessary for fortifying certain types of wine. It could possibly offer an explanation in the use of lees which are distilled with the wine in the production of Cognac.

Although little experimental evidence is available concerning the source of the compounds which make up fusel oil (the higher alcohols), it is believed that certain of them arise from nitrogen metabolism on the part of the yeast. For example, amyl alcohol and iso amyl alcohol may be derived from the hydrolytic decarboxylation and de-amination of the amino acids iso leucine and leucine, respectively:



iso leucine amyl alcohol



leucine isoamyl alcohol

The amounts of the two alcohols produced depends upon the concentration of the specific amino acids present and the yeast employed (11).

The broad definition of an amino acid is any organic acid with one or more substituent amino groups, however it is more usually employed to include those substances which are constituents of proteins.

Chemically, the important amino acids are alpha amino acids; that is, the $-NH_2$ group is attached to the carbon atom adjacent to the terminal carboxyl group

$$\begin{array}{c} R.C.COOH \\ | \\ NH_2 \end{array}$$

Much of the nitrogen matter present im must is assimilated by the yeast during alcoholic fermentation. During the final stages of fermentation however, organic nitrogen is slowly liberated from the yeast cells into the wine; this is due to autolysis.

Niehaus (4) found that the total nitrogen content of young South African wines increased during long storage on the gross lees.

Muth and Malseh in 1934 determined different fractions of Nitrogen in musts and wines and found that NH_3 and protein represented quite small fractions of the total nitrogen present. By far the greater portion of the nitrogen in the wine was in the form of amino acids and substances of intermediate complexity corresponding to peptides and peptones which were precipitated by phospho tungstic acid, but not by 80% alcohol and sodium sulphite (9).

Nitrogen used by the yeasts is obtained from inorganic and organic sources. The best source of inorganic nitrogen is obtained from ammonia and its salts; nitrates are usually suitable for growth but the fermentative powers of some yeasts may be greatly reduced. Nitrites are toxic to the yeasts.

Of the organic nitrogenous matter those assimilated by yeasts are low molecular weight substances such as albumoses, polypiptides, amino acids and their amides.

Niels Nielsen cited by Jorgensen and Hansen (10) found that yeasts most frequently absorb only one of the two optically active forms of an amino acid, alpha amino acid.

THE BREAKDOWN OF AMINO ACIDS BY YEASTS.

AMINO ACID.	COMPOUNDS PRODUCED
SERINE	Ethyline glycol.
VALINE	Iso buthy alcohol, NH_2, CO_2
LEUCINE	Iso amylamine, CO_2, unidentified products.
ISO LEUCINE	Methylethyl pyruvic acid, NH_3 Amylamine, CO_2.
NOR LEUCINE	n-Amyl alcohol, NH_3, CO_2.

This Table was adapted from "Bacterial Chemistry and Physiology" Porter 1946.

It can be seen from this Table that amino acids can breakdown to give higher alcohols.

Quoting directly from Jocelyn and Amerine (1), "the higher alcohols are known collectively as "fusel oil" and are homologes of ethyl and methyl alcohol.

The proportions of the various higher alcohols present in brandy is not constant due to differences in the composition of the raw material, to the use of various types of yeasts and of degrees of purity of the strain, to the extremely variable fermentation conditions, to the methods of distillation and to various other factors. As far as brandy is concerned, comparative analysis of spirits produced from raw materials of known composition, with a uniform method of fermentation and distillation would do much to elucidate the problem of the relative proportions of the higher alcohols present, and the factors which influence their formation.

Yeasts will preferentially assimilate inorganic nitrogen compounds such as ammonium phosphates and ammonium sulphate and the production of higher alcohols is reduced."

The addition of an organic source of nitrogen should give a heavier bodied brandy.

BOILING POINTS OF IMPORTANT HIGHER ALCOHOLS.

PROPYL	97.8° C
LSO PROPYL	82.5
BUTYL	117
ISO BUTYL	107
n - AMYL	137.8
ISO AMYL	130.5
HEXYL	155.2
HEPTYL	176.3
2, 3 BUTYLENE, GLYCOL	184

The tails or aftershots contain the major portion of the higher alcohols and consequently they will come over towards the end of distillation.

Iso propyl alcohol and tertiary butyl alcohol are readily soluble in ethyl alcohol and will come over during the brandy run. In a very weak alcoholic solution some of thehigher boiling point higher alcohols will also tend to come over early because they are relatively insoluble in water compared to ethyl alcohol and do not suffer a reduction of vapour tension due to water admixture as does alcohol. (27)

These secondary constituents in brandy are never objectionable when in a pure state but their reactions with acids constitutes esters of flavouring substances which add considerably to the fullness and aroma of brandy.

EXPERIMENTAL WORK.

By the addition of inorganic and organic sources of nitrogen to the must before fermentation it was hoped to ascertain the effect on the composition of the resultant distillate.

Up to date it has been found impossible to obtain satisfactory results when using the British Government Laboratory Method as laid down by Allen (16) in the analysis of higher alcohols. A criticism of this method will be given in an appendix to the project.

It is hoped to obtain the necessary reagents to determine the higher alcohol content of the distillate by either the Allen-Marquardt or Gerard and Cuniasse method. There are, however, serious objections to the Gerard and Cuniasse analysis for higher alcohols.

Conclusions will be given in the appendix.

APPARATUS AND MATERIAL.

(1) STILL. Quick-fit glass still with two litre boiler heated by an electric hot plate with simmerstat regulator. Boiler lagged with glass wool. Due to the exposed position of the still it was impossible to maintain a constant rate of distillation. To distil 400 mls. of spirit took between $2\frac{1}{4}$ - $3\frac{1}{2}$ hours.

(2) GRAPE JUICE - A mixture of Pedro - Mataro and Grenache grape juice.

(3) YEAST CULTURE - S. ellipsoideus, port type (from the Waite Institute)

(4) Peptone - Davis's Commercial - the nitrogen content was determined by Kjeldahl method.

(5) A.R. Ammonium Phosphate.

(6) A.R. Ammonium Sulphate.

(7) Standard Mixture of Higher Alcohols. This was prepared by weighing out 1 gm. propyl alcohol, 2 gms butyl alcohol (should be iso butyl alcohol but this was impossible to obtain). 3 gms amyl alcohol, and 1 gm. capryl alcohol. This was dissolved in 100 mls 50%. Absolute alcohol, aldehyde free 14.29 mls. of this taken and diluted to 100 mls with aldehyde free absolute alcohol. This was the Standard solution from which the working solution was prepared.

METHODS OF ANALYSIS.

WINE.

ALCOHOL	-	Ebulliometer and Churchward's Tables for Dry Wines. Expressed as % proof.
TITRATABLE ACIDITY	-	Direct titration. Phenol Red as an outside indicator. Expressed as gms/100 mls. as Tartaric Acid.
VOLATILE ACID	-	Sellier tube method and titration using phenolphthalein. Expressed as gms/100 mls. as Acetic Acid.
ESTERS	-	A.O.A.C. method (14), modified by standing for 12 hours with N/10 NaOH instead of refluxing. Expressed as parts of ethylacetate/100,000 parts A.A.
SUGAR	-	Reducing - Lane & Eynon. Expressed as gms/100 mls reducing sugar.

SPIRIT.

ALCOHOL	-	Sikes Brass Hydrometer % proof.
ACIDS	-	Direct titration using phenol phthalein. Parts of acetic acid/100,000 parts A.A.
ALDEHYDES	-	Jaulmes and Espezel (15) Parts of acetaldehyde/100,000 parts A.A.
SECONDARY ALCOHOLS	-	British Government Laboratory Method, but using butyl alcohol instead of iso butyl alcohol. Expressed as parts of secondary alcohol/100,000 parts A.A.

OUTLINE OF EXPERIMENT.

The grape juice was blended and given a coarse filtration through glass wool.
Beaume of grape juice 11.7°.

Amounts of ammonium phosphate, ammonium sulphate and peptone containing the same percentage of nitrogen were added to the grape juice and this was seeded with 2% yeast culture and allowed to ferment.

OUTLINE OF EXPERIMENT.

Including the controls all samples were in triplicate.

Ammonium phosphate 21.22% nitrogen added at the rate of 1.5 gms/ litre.

Ammonium sulphate 21.22% nitrogen added at the rate of 1.5 gms/ litre.

Peptone 14.45% nitrogen added at the rate of 2.2005 gms/ litre.

As the weather remained cold, fermentation was very slow and the must had to be aerated several times to accelerate fermentation and to get the residual sugar down to a reasonable level. Fermentation was carried out in ½ gallon jars containing 1800 mls juice.

After fermentation the pH of all the wines were adjusted to pH 3.2 using $1N H_2SO_4$

Duplicates of the wine were fined with bentonite and 1200 mls of the wine were used for distillation. The third jar of the experimental series was not fined and was distilled on gross lees.

SAMPLE	ALCOHOL % p.f.	pH before Adjustment	TITRATABLE ACIDITY	VOLATILE ACIDITY	ESTERS	SUGAR
A control	21	3.4	.75	.042	87.56	.2150
B "	21.1	3.46	.74	.042	87.56	.2025
C "	21.9	3.46	.75	.048	84.37	.2100
A phosphate	20.7	3.42	.76	.048	96.72	.2000
B "	21.2	3.4	.76	.048	109.0	.2000
C "	21.6	3.42	.75	.048	106.9	.2100
A sulphate	21.68	3.28	.72	.051	113.6	.2075
B "	21.64	3.28	.72	.051	113.9	.2050
C "	21.9	3.26	.71	.051	112.5	.2075
A peptone	21.16	3.5	.72	.075	196.3	.2050
B "	21.52	3.52	.73	.075	200.4	.2150
C "	21.52	3.52	.72	.069	257.6	.2100

DISCUSSION.

There appears to be no significant difference between the fermentation rates but this may be due to the fact that they were all fermented at low temperatures. Perhaps ammonium sulphate gave a slightly more efficient alcohol production pH.

Ammonium sulphate gave a big reduction in pH, while peptone raised the pH slightly above the control. Ammonium sulphate is the salt of a weak base and a strong acid and on hydrolysis there would be a slight reversion to the strong acid thus lowering the pH. Peptone on being decomposed by the yeast would yield amino acids and finally higher alcohols and ammonia. Ammonia on being released would raise the pH slightly.

TITRATABLE ACIDITY.

There is not a great difference between the titratable acidities of any of the samples. However there does appear to be some correlation between titratable acidity and volatile acidity. Where the titratable acidity is low, compared with the controls, the volatile acidity is relatively higher.

It is difficult to account for the relatively low titratable acidity of the wines fermented with ammonium sulphate.

Peptone has shown a slight reduction in titratable acidity.

VOLATILE ACIDITY.

Wines fermented with ammonium sulphate have shown a slight increase over the controls.

Peptone has given a significant increase in volatile acidity.

ESTERS.

Peptone has given a decided increase in ester content in the wine over the controls. Throughout the whole series where there has been a rise in the volatile acid content, there has also been a rise in the ester content.

REDUCING SUGAR.

There appears to be no significant differences between the sugar content of the various samples. Owing to the exigencies of time it was not possible to let the wines ferment right out.

DISTILLATION.

1200 mls of each lot of wine were taken and the third jar in each series was distilled on lees. In the Table this is Sample C in each case.

The still was fitted with a Quick fit rectifying column which was not entirely desirable as it may have caused too much refluxing of the higher alcohols, particularly those with a high boiling point.

Although the regulator on the simmerstat controlling the temperature of the hot plate was set on a constant figure, the rate of distillation fluctuated considerably.

400 mls. of the distillate was collected in each instance and the spirit analysed.

ANALYSIS OF SPIRIT.

SAMPLE	ALCOHOL % proof	TITRATABLE ACIDITY	ESTERS	ALDEHYDES	HIGHER ALCOHOLS.
A Control	64.6	97.52	81.06	69.36	
B	64.8	103.7	83.18	96.93	
C *	65.6	110.1	84.4	125.1	
A phosphate	62.8	69.13	74.99	93.26	
B	63.5	61.49	77.59	122.6	
C *	65.0	54.28	87.68	63.27	
A sulphate	65.1	67.74	85.15	97.03	
B	64.9	66.01	84.03	89.1	
C *	64.6	65.01	83.45	45.78	
A peptone	63.1	87.34	77.98	115.9	
B	63.4	81.7	82.58	84.55	
C *	64.3	68.58	83.83	62.04	

* Distilled on lees.

DISCUSSION.

Alcohol - There are considerable differences in the strength of alcohol which is not entirely due to the original strength of the wine. Probably rate of distillation played some part in the variance of the strength of the distillate.

Titratable Acidity. This represents volatile acidity for the most part as there would be little or no entrainment of fixed acid when using a rectifying column. There appears to be a decrease in volatile acids in all samples when compared with the controls - the wines fermented with ammonium phosphate giving the least volatile acidity.

Esters. There are no significant differences in the ester content of any of the distillates. This is rather surprising in view of the increased ester content of some samples of the wine, particularly those fermented with ammonium phosphate.

Aldehydes. Again no significant differences except perhaps those fermented on lees (see later)

Higher Alcohols. Not determined as method unsatisfactory.

DISTILLATION ON LEES.

Represented by C – the third jar in the triplicate of each experiment.

Titratable Acidity.

No significant differences. With the exception of the control those distilled on lees may have given slightly less volatile acidity than those distilled with wine only.

Esters. No significant differences.

Aldehydes. With the exception of the control all wines distilled on lees gave a considerably lower aldehyde content than those distilled with wine only

DIFFERENCE DUE TO ESTER CONTENT IN THE WINE AND IN THE DISTILLATE.

It is difficult to give a reasonable explanation for this difference. A possibility may be that the esters were high boiling point esters which would come over in the ordinary distillation apparatus fitted with a splash head used in the analysis of ester content of the wines, but with a still fitted with a reflux column would remain behind in the ~~distillate~~.

REMARKS.

The conclusions drawn from the results of the analyses of wine and spirit are in some instances hardly justifiable but nevertheless it is felt that it may give an indication of a trend in a certain direction which can be proved or disproved by other workers.

A summary and conclusion will be given in the appendix to this project as definite conclusions cannot be made until an analysis is made of the higher alcohol content of the spirit.

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