Chemical Aspects of Distilling Wines into Brandy

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Wines for brandy distillation should be made from white grapes by fermentation of juice separated from pomace without adding SO₂ (to minimize aldehyde accumulation) at as low temperature as is practicable (less than 75°F, to minimize fusel oil formation) and should be distilled as soon as fermentation is complete. In California, wines are distilled into brandy in continuous plate columns arranged for separating a low-boiling heads fraction to eliminate aldehydes. Higher alcohols (fusel oil) are the most abundant group of congeners, and ethyl esters of C₈ to C₁₂ fatty acids are next most abundant provided yeast cells are present in the wine distilled. Fatty acid esters and fusel alcohols accumulate in column tray liquids at 100° to 135° proof and distill most rapidly in the earliest fractions of simple pot distillation.

Brandy is a distillate of wine so its initial chemical composition depends on the compounds present in wine being sufficiently volatile to distill. Although ethyl alcohol and water are the two major components of any distilled spirit, aroma and flavor character depend on a multitude of minor compounds usually referred to as congeners or congeners. Some of the congeners are derived directly from the grapes or other fruits that may be used for brandy. The most abundant congeners of brandy are minor products of alcoholic fermentation derived primarily from sugars but in part from components of the fruit. Distillation conditions affect the relative quantities of minor compounds recovered in the distillate, and some arise from chemical reactions during distillation such as heat-induced degradative changes.

Grape brandies and some fruit brandies are traditionally stored in oak casks for varying periods of time for aging or maturation. During
aging in oak many substances are extracted from the wood, some of which react with compounds initially present, especially ethyl alcohol. Thus, the aging process produces a complexity of minor constituents which generally improves the palatability and enhances the aroma and flavor.

The overall chemical composition of brandy is derived from four general sources: the fruit, alcoholic fermentation, distillation, and aging in wood. The scope of this discussion is limited to chemical aspects of the components of wine and their behavior during distillation.

The term brandy as used here refers to distillates of grape wine before aging. Federal regulators require that distillates derived from other fruits must show the name of the fruit, for example, pear brandy.

Wines for Distillation

The production of grape wines destined for distillation into brandy is essentially the same as that for dry white table wines. However there are some desired characteristics of distilling wines which are relatively more significant than those of table wines produced for consumption. White grape varieties are preferred to red or black varieties even though white wines can be prepared from red grapes by separating the juice prior to fermentation. Red varieties tend to impart a measure of coarseness to the distillates and, compared with white varieties, generally lead to greater formation of higher alcohols during fermentation. This seems to occur whether the fruit is processed as white wines (fermentation of separated juice) or as red wines (fermentation of the entire must containing juice, skins, seeds, and pulp). Thus, the preferred procedure for producing distilling wines is to use non-pigmented grapes and to separate the juice from the marc or pomace prior to fermentation.

Sulfur Dioxide and Aldehydes. Sulfur dioxide is commonly added both before and after fermentation in preparing white table wines. It is an effective antioxidant as well as a selective inhibitor of unwanted microorganisms. However, sulfur dioxide, as the bisulfite ion in solution, combines with aldehydes, especially acetaldehyde, during fermentation giving an accumulation of aldehydes in the bound form of aldehyde–sulfurous acid.

\[ \text{CH}_3\text{CHO} + \text{HSO}_3^- \rightleftharpoons \text{CH}_3\text{CHOHSO}_3^- \]

The accumulation of aldehydes as well as the presence of sulfur dioxide itself is undesirable in distilling wines for reasons given later. We have experienced no difficulty in producing sound wines (that is without bacterial contamination or significant oxidation) if good quality fruit is used. However, fruit that is significantly damaged by rain or
other conditions whereby rot or molds have developed and increased polyphenol oxidase yield wines which oxidize and brown badly and are vulnerable to *Acetobacter* and lactic acid bacteria. In this case it is advisable to add 50–75 ppm of sulfur dioxide prior to fermentation. Amerine and Ough (1) showed that moderate levels of sulfur dioxide (50 ppm) increased aldehyde accumulation only slightly over wines fermented without sulfur dioxide.

Acetaldehyde content reaches a maximum at the time of fermentation that shows the most rapid rate of carbohydrate dissimulation, it falls to a low level at the end of fermentation, and then slowly increases (2, 3). Also aldehydes are formed by oxidation as evidenced by browning of wine when exposed to air. For these and other reasons, distillation should be carried out as soon as possible after fermentation is complete.

**Higher Alcohols.** The most abundant, volatile minor products of alcoholic fermentation are the higher alcohols or fusel alcohols. The most important are isoamyl (3-methyl-1-butanol), *d*-active amyl (2-methyl-1-butanol), isobutyl (2-methyl-1-propanol), and *n*-propyl (1-propanol) alcohols. It is now recognized (4, 5, 6, 7) that these higher alcohols are formed by decarboxylation of particular *α*-keto acids to yield the corresponding aldehydes, and these in turn are reduced to the alcohols in a manner analogous to the formation of ethyl alcohol from pyruvic acid.

\[
\text{RCOOH} \rightarrow \text{RCO} + \text{RCH}_2\text{OH}
\]

Higher alcohol formation by yeasts has long been attributed to the transamination of exogeneous amino acids to yield the analogous keto acid. For example:

\[
\text{(transaminase)}
\]
\[
\text{leucine + } \alpha\text{-ketoglutaric acid } \rightarrow \text{ glutaric acid + } \alpha\text{-ketoisocaproic acid}
\]

\[
\text{(decarboxylase)}
\]
\[
\alpha\text{-ketoisocaproic acid } \rightarrow \text{ isovaleraldehyde + CO}_2
\]

\[
\text{(alcohol dehydrogenase)}
\]
\[
\text{isovaleraldehyde + NADH + H}^+ \rightarrow \text{ isoamyl alcohol + NAD}^+
\]

However, now it is well established that the appropriate *α*-keto acids giving rise to a particular higher alcohol arise mostly from carbohydrate sources through the synthetic pathways by which yeast synthesizes its amino acid requirements.
Peynaud and Guimberteau (8) estimated that no more than one-sixth of the leucine and valine in grape musts assimilated during fermentation gave rise to isoamyl and isobutyl alcohols, and since these amino acids are low in grape musts, the formation of higher alcohols by amino acid degradation is negligible. Instead, nearly all of the higher alcohols are derived from carbohydrate. However, Reazin et al. (9), in $^{14}$C tracer studies during fermentation of grain mashes, concluded that the major proportions of higher alcohols were derived from amino acids, and lesser proportions were derived from carbohydrates.

Since the higher alcohols, especially the two amyl alcohols, constitute the most abundant minor components or congeners of brandy and other distilled spirits, they have a very significant effect on the sensory and taste character. Considerable variation in the concentrations of fusel oil alcohols in wines (10) and brandies (11) occurs in practice. Factors influencing the levels of higher alcohols produced during fermentation include composition of raw material, yeast strain (12), temperature of fermentation, suspended matter, and aeration (13, 14). In practice, it is desirable to minimize the formation of higher alcohols, especially the amyls. Although precise control is not fully feasible, highest levels are formed at medium fermentation temperatures of about 75°F (7, 12, 15, 16). The presence of suspended matter and aeration stimulate fusel oil formation (14). So the practice of draining the relatively clear free-run juice several hours after crushing is preferred to using the juice immediately after pressing, which yields more turbid liquid musts.

Several workers have reported the amounts of higher alcohols found in wines (8, 12, 17). While differences as much as fivefold occur considering diverse genera and strains of yeast, the variation is generally less for strains of Saccharomyces cerevisiae. Guymon and Heitz (10) found a mean fusel oil content of 25 grams/100 liters (250 ppm) for 120 samples of California white table wines and 29 grams/100 liters for 130 samples of red table wines. In our pilot plant scale production of experimental distilling wines, we obtain fusel oil levels ranging from about 16–30 grams/100 liters for white varieties with an average of 20. With red varieties, the levels may attain 40 or more grams/100 liters.

The appropriate fusel oil content of brandy distillate, though commercial producers are not in full agreement, ranges from 65 to 100 grams/100 liters at 100° proof (50 vol %). If 100 grams/100 liters is desired as the upper limit, a distilling wine containing 12 vol % ethyl alcohol should thus contain no more than 24 grams of higher alcohols per 100 liters, assuming all of the higher alcohols are recovered in the distillation process.

**Fatty Acids and Their Ethyl Esters.** The normal aliphatic acids and their ethyl esters are often the second most abundant group of congeners
found in distilled spirits. After ethyl acetate, generally caprylate (C₈), caprate (C₁₀), and laurate (C₁₂) esters predominate (18), although those with both fewer and more carbon atoms are found. The amount of suspended yeast cells in the wine at the time of distillation significantly affects the amount of fatty acids and esters in the distillate. The higher molecular weight acids and esters are closely bound to the cells of yeast whereas those with lower molecular weight tend to be secreted into solution (19).

Thus, the concentrations of fatty acids and esters found in brandy distillates are greatly affected by the nature of the wine at the time of distillation, particularly the time interval between fermentation and distillation since most of the yeast cells settle out fairly quickly after fermentation has ceased. Obviously the degree of resuspension of the settled lees into the wine when distilled affects the amount of fatty acids and esters recovered in the distillates. The method and techniques of distillation are also very important since this class of congeners, having relatively high boiling points and weak solubility in water, exhibit wide ranges of volatility as affected by the alcohol content of the liquid volatilized.

The desirable properties of distilling wines include wines: a) made from white varieties by fermentation of separated juice clarified as much as practicable, b) fermented without addition of sulfur dioxide, c) fermented with strains of yeast which form comparatively low amounts of fusel alcohols at temperatures below 75°F, and d) distilled as soon as possible after fermentation.

Distillation

Many processes are used throughout the world for distilling wine into brandy. Continuous distillation in plate columns, discontinuous or batch distillation using pot stills (with and without adjunct rectifying columns), and even distillation apparatuses involving both continuous and discontinuous aspects are used.

In France, the famous cognac brandy is distilled in simple direct-fired pot stills. The Méthode Charentaise (20) includes two successive distillations. In the first, wine is distilled into low wines (brouillis) containing 26–30% alcohol or approximately a threefold concentration. The low wines are redistilled, and three fractions are collected, i.e., a small heads cut amounting to about 1 vol % of the charge; the brandy coeur as the alcohol content decreases from about 80 to 60 vol % average 70 vol %; and the tails (seconde) to recover the remaining alcohol in the charge. The heads and tails fractions are recycled.

In the Department of Gers, the Armagnac brandies are distilled in an apparatus known as the Verdier système. Wine, preheated by con-
Densifying vapor, flows continuously to the top of a short plate column and is partly stripped of alcohol as it transverses the column and flows into the top section of a two-tiered, direct-fired boiler. The vapor generated in the lower section by the furnace is caused to bubble through the liquid layer in the top section and on up the plate column. Vapor from the top (feed) tray is condensed by the preheater and condenser into brandy containing 50–54 vol % alcohol. Intermittently most of the spent wine in the lower level of the boiler is drawn off to waste, and then the same volume of liquid from the upper level is drawn into the lower part. Thus the process is both continuous and discontinuous.

In California, distillation is usually carried out in a continuous single or split column unit as shown in Figure 1. The brandy distillate, at a maximum of 170° proof as required by federal regulations for standards of identity, is drawn as a liquid sidestream from a tray in the middle or upper region of the concentrating section. A small portion of the overhead distillate from the vent condenser is withdrawn as a heads cut at a rate of about 5–15% of the brandy rate to remove most of the low-boiling aldehydes, sulfites, esters, etc. Some producers also separate another small fraction (ca. 10–20%) of the product rate as a low oils or high-boiling stream from a level one or two trays below the brandy tray to

**Figure 1. Single and split columns for brandy distillation**

In Chemistry of Winemaking; Webb, A.; Advances in Chemistry; American Chemical Society: Washington, DC, 1974.
reduce the level of fusel oil in the product. The concentration of higher alcohols in the tray liquids of a concentrating section producing brandy at $168^\circ$-$170^\circ$ proof is usually at its maximum at two trays below the product level. This maximum concentration of higher alcohols is about 2 to 2½ times that of the product and occurs where the tray liquid indicates approximately $120^\circ$-$135^\circ$ proof. Thus the separation of a low oil fraction at a 20% rate should reduce the fusel oil content of the brandy by about 30%. In practice it is usually less. The disadvantage of this technique is that the amount of brandy, produced from prime quality wine, is reduced by the amount of low oil fraction removed which is usually redistilled to recover the alcohol as neutral spirit.

Most distillation units in California have been installed with the capability of producing high proof wine spirit ($189^\circ$-$192^\circ$ proof). Accordingly the concentrating sections may contain 20–40 bubble cap trays whereas only three or four ideal trays are required to concentrate alcohol from 10 to 85 vol % (the strength of beverage brandy distillate). In beverage brandy production practice, perhaps two-thirds of the trays lie between the feed and product trays, and the remaining one-third of the trays at the top are used for concentrating the low-boiling impurities into the heads cut. Recent installations generally provide for at least 12-inch tray spacings.

The stripping or wine section typically contains 18–22 sieve or perforated trays with 15–18 in. tray spacing. Direct or open steam is the usual heat source although one major brandy producer uses reboilers. Column diameters are commonly 5–6 feet though some larger and smaller are in use. Feed rates to the stripping section are typically in the range 3000–8000 gallons/hr.

Some recent developments in design of distilling units include the use of valve and sieve trays in lieu of bubble caps in the concentrating sections, air-cooled instead of water-cooled condensers, stainless steel in lieu of copper construction, energy economizers which incorporate a thermocompressor to transfer heat energy from the bottoms or stillage to the entering steam, and location of distilling units entirely outside of buildings. However, most of these developments pertain to the more elaborate recovery of neutral wine spirit from residue materials.

Some three- and a few four-column units are used. The third column of multicolumn units is generally an aldehyde concentrating column in which the heads cut from the brandy concentrating column is concentrated (Figure 2) as much as 20-fold; the alcohol, stripped of aldehydes and other low-boiling components, is recycled to the main unit. Another three-column arrangement provides for the brandy to be distilled as a top product without a heads cut; the entire brandy is then fed into an aldehyde stripping and concentrating column. The low-boiling substances
are thus removed as the top product of the aldehyde column and the brandy is removed as the bottom stream. A reboiler, to avoid dilution, is therefore required to supply vapor (Figure 3).

Some ingenious designs have been developed for producing beverage brandy with a substantial removal of the amyl alcohols without exceeding 170° proof in the primary distillate. In one such case a low oils cut, about 20% of the brandy rate, is fed into a fusel oil concentrating column to concentrate the alcohol in the low oils from approximately 130° to 190° proof. A fusel oil cut from this column is thus sufficiently concentrated to separate into oil and aqueous layers in a conventional fusel oil decanter (22). The 190° proof alcohol (thus very low in higher alcohols) is recycled to the main column. Another arrangement effects a partial separation of higher alcohols, especially the amyls, by concentrating the brandy well above 170° proof in the primary concentrating column which permits some separation of fusel oil in its decanter; the brandy stream is subsequently reduced to 170° proof or less by blending it with a low proof stream drawn from an appropriate plate low in the heads concentrating column which, of necessity, is heated with open steam.

Only a small amount of pot-still brandy is produced in California. It is used primarily for blending, in small percentages, with continuous still brandy after aging. Equipment used for this purpose consists of pot-rectifiers. In at least one case, the fractionating column is so arranged that it can serve either as the concentrating section for the pot or as a part of a continuous still unit.
Aldehydes and Other Low-Boiling Components. As mentioned, a low-boiling fraction, called heads, is normally taken from the vent condenser during the distillation of wine into brandy. The principal impurities removed are acetaldehyde, diethyl acetal, ethyl acetate, and acetaldehyde-sulfurous acid.

The heads fraction may be highly acidic and corrosive if sulfur dioxide or bisulfite is used in the production or preservation of the wine. The reversible reactions involved are:

$$\text{H}_2\text{O} + \text{SO}_2 \rightleftharpoons \text{HSO}_3^- + \text{H}^+$$

$$\text{HSO}_3^- + \text{CH}_3\text{CHO} \rightleftharpoons \text{CH}_3\text{CHOHSO}_3^-$$

The acetaldehyde-sulfurous acid compound has the properties of a sulfonic acid with C–S linkage rather than an ester structure as once assumed. It is properly 1-hydroxyethane sulfonic acid (23, 24) and is highly acidic (25). Samples of concentrated heads from commercial aldehyde columns having aldehyde contents of 5–13% gave pH values of 0.7–0.9 and contained high levels of copper (25).
Whitmore (26) and Deibner and Bénard (27) claim that sulfonic acids are capable of distilling intact. However, it would seem more likely that at the temperature of the distilling process, 1-hydroxyethane sulfonic acid in the wine would dissociate into the very volatile free acetaldehyde and therefore rapidly distill along with free sulfur dioxide and recombine at the top level of the fractionating column.

Another reaction of interest is the production of acetal by the reaction of 2 moles of ethanol and 1 mole of acetaldehyde. This reaction is strongly catalyzed by hydrogen ion and during distillation depends on the presence of bisulfites or the 1-hydroxyethane sulfonic acid to establish the necessary acidity. Equilibrium is rapidly established at low pHs and the degree of acetalization obviously depends on the concentrations of the two major components, ethanol and water. However, attempts to determine an equilibrium constant are unsuccessful presumably because the reaction proceeds in two steps and the rate-determining step is the formation of hemiacetal from one mole each of ethanol and acetaldehyde (24).

Ethyl acetate is a product of yeasts and a normal component of wine. Its level can be increased by Acetobacter contamination, although most wines showing excess volatile (acetic) acid do not necessarily contain excess ethyl ester initially. It is quite possible to obtain brandy of normal composition and quality by continuous distillation of newly fermented wine containing excess acetic acid, e.g., 0.1%. On the other hand, ethyl acetate can be formed in continuous columns, particularly if the distillation conditions provide for a relatively high ethanol concentration on the feed tray or immediately below. Since acetic acid is weakly volatile in all mixtures of ethanol and water, it does not appreciably distill upward. Therefore there is no opportunity for acetic acid to combine with ethanol in tray liquids normally of high ethanol concentration.

Ethyl acetate is the major low-boiling impurity of heads fractions from continuous columns if bisulfites are absent in the distilling material. A heads fraction from a typical brandy column usually contains less than 1% of these volatile impurities, although the concentrated heads from an aldehyde-concentrating column may contain as much as 10–15% aldehydes. In either case, ethyl alcohol is the major component of the heads cut, and its recovery in usable form has been a troublesome processing problem.

A simple method, based on the strongly reducing conditions during alcoholic fermentation, was developed in our laboratory (25, 29, 30). The heads liquid is recycled into an actively fermenting dilute grape
juice or sweet pomace wash, initially containing sugar equivalent to about 10° Brix. The titratable aldehydes, including acetal, are very effectively reduced to alcohols, and apparently about half of the ethyl acetate present is metabolized. Guymon and Nakagiri (3) found that acetaldehyde or its equivalent concentration of acetal added before fermentation in excess of about 0.1% caused important delays in fermentation. But up to 0.35% acetaldehyde or 0.9% acetal could be added to a vigorous fermentation without significant effect on fermentation rates.

Ethyl acetate, added prior to fermentation in amounts up to 3%, caused delays in the onset of fermentation proportional to the amount added, but once begun, the fermentation rate was unaffected. When the same levels of ethyl acetate were added to an active fermentation, the fermentation period was sluggish.

This simple method of heads disposal by refermentation eliminated the earlier deterrent to taking an adequate cut to control volatile aldehydes to the desired level, now considered to be approximately 10 ppm or less in new brandy distillates.

Other aliphatic aldehydes have been identified and quantitatively measured in various brandies (31, 32). These include small amounts of formaldehyde, propionaldehyde, isobutyraldehyde, isovaleraldehyde, furfural, etc. Furfural is a normal component of pot-still distillates, but its presence in continuous still brandies is negligible before aging in wood.

Higher Alcohols and Fatty Acid Esters. Because of the remarkable utility of gas chromatography for analysis of minor volatile components, an extensive literature on the composition, mechanism of formation, and variables affecting concentration of higher alcohols for various kinds of distilled spirits has appeared during the past 15 years. Reviews include Stevens (33), Suomalainen and Ronkainen (34), Lawrence (35), Webb and Ingraham (5), Guymon (6), Suomalainen et al. (32), and Ayrapa (7). Data generally limited to the influence of distillation will be reported here.

Guymon (21) reported the composition of tray liquids for brandy distilled in continuous column, respectively, at 130°, 170°, and 181° proof. The maximum level of fusel oil occurred on the tray nearest in proof to about 130°. This is the second tray below the product tray for the customary 170° proof of distillation of the product.

Later we measured the concentrations of n-propyl, isobutyl, and the combined isoamyl and active amyl alcohols (3-methyl-1-butyl alcohol and 2-methyl-1-butyl alcohol) in distillation tray liquids using a gas chromatographic method with n-butyl alcohol as the internal standard. The distribution of the higher alcohols in the 14-tray concentrating section of a 12-inch pilot column during a run in which the product from tray 7 was 169° proof is shown in the upper portion of Figure 4. The
Figure 4. Distribution of higher alcohols (above) and ethyl esters of three fatty acids (below) in tray liquids of concentrating section producing brandy at 169° proof from tray No. 7
highest level of \( n \)-propyl and isobutyl alcohols was found on tray number 6 (152° proof) or one tray below the product tray. The more abundant amyls (plotted on a scale one-tenth the size) were most concentrated on tray number 5 (at 135° proof), two trays below the product tray.

Guymon and Crowell (18) developed a quantitative procedure for extracting (with methylene chloride) the ethyl esters of the straight chain fatty acids from brandy or distillates of wine, and concentrating and measuring by programmed temperature gas chromatography the three most abundant ethyl esters: caprylic, capric, and lauric acids. Ethyl pelargonic acid was used as the internal standard.

The lower portion of Figure 4 shows the distribution of three ethyl esters in the same set of tray liquid samples. These high boiling esters tend to concentrate at slightly lower proof and tray levels than the higher alcohols, but they all overlap. Consequently, a fusel oil or low oils layer drawn from a column will include both higher alcohols and these fatty acid esters.

The higher alcohols and ethyl esters for a set of plate samples from a run during which the product at 173° proof was withdrawn as the top product, \textit{i.e.}, from the condenser, are given in Table I. In this case, the higher alcohols and ethyl esters were most concentrated on the two uppermost trays.

\begin{table}[h]
\centering
\begin{tabular}{llllll}
\hline
Tray No. & °Proof & n-Propyl & Iso- & Amyls & Caprylate & Caprate & Laurate \\
\hline
Product  & 173.1 & 26.4 & 30.2 & 134 & 1.6 & 2.3 & 1.1 \\
       14  & 147.5 & 32.2 & 39.6 & 319 & 4.4 & 25.6 & 10.4 \\
       13  & 107.5 & 24.8 & 27.5 & 305 & 2.8 & 14.2 & 13.3 \\
       12  & 74.2  & 13.6 & 13.1 & 150 & 4.3 & 7.7  & 5.5  \\
       11  & 44.2  & 6.5  & 5.9  & 46.6 & 3.6 & 8.9  & 3.5  \\
       10  & 28.8  & Trace & Trace & 11.4 & 1.4 & 3.2  & 1.8  \\
\hline
\end{tabular}
\caption{Distillation of Beverage Brandy Drawn from Condenser}
\end{table}

- Grams per 100 liters at existing proof.

The analyses for higher alcohols in a set of tray samples in which the primary product was drawn as a sidestream at 186° proof, three trays below the top, are given in Table II. Under the operating conditions for this run, all of the higher alcohols were most concentrated in the lower four trays of the section with an increasing percentage of amyl alcohols on the lower trays.

A set of sequential samples taken during the simple batch or pot distillation of a charge of low wines into brandy were analyzed for higher alcohols and fatty acid esters as shown in Table III. These represent the
Table II. Distillation of Wine Spirits as Sidestream Product from Tray 11

<table>
<thead>
<tr>
<th>Tray No.</th>
<th>°Proof</th>
<th>n-Propyl</th>
<th>Iso-Butyl</th>
<th>Amyls</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heads</td>
<td>189.8</td>
<td>—</td>
<td>2.3</td>
<td>—</td>
</tr>
<tr>
<td>14</td>
<td>189.2</td>
<td>—</td>
<td>7.1</td>
<td>2.4</td>
</tr>
<tr>
<td>13</td>
<td>188.6</td>
<td>11.8</td>
<td>11.8</td>
<td>5.9</td>
</tr>
<tr>
<td>12</td>
<td>187.5</td>
<td>19.9</td>
<td>16.4</td>
<td>14.0</td>
</tr>
<tr>
<td>Product</td>
<td>186.0</td>
<td>25.4</td>
<td>25.4</td>
<td>25.4</td>
</tr>
<tr>
<td>11</td>
<td>186.6</td>
<td>25.7</td>
<td>22.2</td>
<td>23.4</td>
</tr>
<tr>
<td>10</td>
<td>184.0</td>
<td>42.5</td>
<td>42.5</td>
<td>64.0</td>
</tr>
<tr>
<td>9</td>
<td>181.9</td>
<td>62.3</td>
<td>65.6</td>
<td>158</td>
</tr>
<tr>
<td>8</td>
<td>179.2</td>
<td>65.0</td>
<td>85.0</td>
<td>207.5</td>
</tr>
<tr>
<td>7</td>
<td>176.8</td>
<td>88.0</td>
<td>110.0</td>
<td>354</td>
</tr>
<tr>
<td>6</td>
<td>171.9</td>
<td>107.5</td>
<td>150.5</td>
<td>688</td>
</tr>
<tr>
<td>5</td>
<td>166.4</td>
<td>120.5</td>
<td>177</td>
<td>1000</td>
</tr>
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<td>4</td>
<td>160.2</td>
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<td>200</td>
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</tr>
<tr>
<td>3</td>
<td>148.5</td>
<td>116</td>
<td>190</td>
<td>2150</td>
</tr>
<tr>
<td>2</td>
<td>128.5</td>
<td>128</td>
<td>208</td>
<td>3210</td>
</tr>
<tr>
<td>1</td>
<td>94.4</td>
<td>53</td>
<td>71</td>
<td>1178</td>
</tr>
</tbody>
</table>

*Grams per 100 liters at existing proof.

Table III. Pot Distillation of Beverage Brandy—Composition of Sequential Samples

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>°Proof</th>
<th>n-Propyl</th>
<th>Iso-Butyl</th>
<th>Amyls</th>
<th>Ethyl Esters</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Caproylate</td>
</tr>
<tr>
<td>Heads</td>
<td>158.6</td>
<td>24.1</td>
<td>49.7</td>
<td>116.5</td>
<td>6.1</td>
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<tr>
<td>Brandy</td>
<td>1</td>
<td>156.4</td>
<td>25.1</td>
<td>49.4</td>
<td>117.2</td>
</tr>
<tr>
<td>fractions</td>
<td>2</td>
<td>153.2</td>
<td>23.7</td>
<td>44.5</td>
<td>115.5</td>
</tr>
<tr>
<td>3</td>
<td>151.4</td>
<td>23.1</td>
<td>41.4</td>
<td>110.8</td>
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</tr>
<tr>
<td>4</td>
<td>149.0</td>
<td>23.0</td>
<td>38.2</td>
<td>108.9</td>
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<tr>
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<td>144.6</td>
<td>19.8</td>
<td>34.4</td>
<td>102.3</td>
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<td>139.8</td>
<td>19.8</td>
<td>28.2</td>
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</tr>
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<td>7</td>
<td>121.8</td>
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<td>19.6</td>
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*Grams per 100 liters at existing proof.
conditions during the second distillation step of the Charente method used for cognac brandies and for the all-malt highland whiskies of Scotland. The unit used was a 350-gallon pot of copper metal heated by steam condensing in a heating coil. Both the higher alcohols and fatty acid esters are distilled over at the highest rate at the start of the run. The ethyl esters of the C₈, C₁₀, and C₁₂ fatty acids, all having boiling points greater than the higher alcohols of fusel oil, distilled over almost completely in the early part of the run so none were detectable in the later product fractions nor in the tails. n-Propyl alcohol distilled over more uniformly than any other component measured.

Though not reported in Table III, a peak for phenethyl alcohol emerged in the gas chromatograms of the ester concentrates of the later brandy fractions and increased in size into the tails fractions. Phenethyl alcohol is barely detectable, if at all, in corresponding concentrates of continuous still brandies.

The behavior of higher alcohols and fatty acid esters during distillation is clarified by Figures 5 and 6, prepared by Unger (36) from vapor–
liquid equilibrium data obtained by Williams (37). The volatility, or concentration of a component in the vapor phase, divided by that in the liquid phase at equilibrium for the several alcohols or esters added in small amounts (less than 1%) to various strengths of ethyl alcohol–water solutions are shown as a function of the proof strengths of the equilibrium liquid. A higher molecular weight and high boiling alcohol such as isoamyl alcohol is markedly less volatile than ethyl alcohol at high proof strengths since isoamyl alcohol is soluble in ethyl alcohol in all proportions. Normal binary solution behavior for isoamyl–ethyl alcohol mixtures is exhibited. But with water, in which isoamyl alcohol is only slightly soluble, the volatility of the isoamyl alcohol is greatly enhanced, characteristic of a partially miscible binary system which exhibits a minimum boiling point azeotrope.
The proof strength at which the volatility curve of a particular component intersects that of ethyl alcohol indicates that proof at which the minor constituent will be concentrated in a fractionating column at the limiting condition of total reflux. For practical conditions, the maximum concentration of a particular congener or minor component occurs at a proof in the column at which its volatility is approximately equal to the internal reflux ratio \( \frac{L}{V} \) where \( L \) is the molal liquid or overflow rate and \( V \) the molal vapor rate). This can be established by the technique of writing material balance or operating line equations with respect to the particular congener, as in the well-known McCabe-Thiele method in which molal liquid and vapor rates are assumed constant. The internal reflux ratio of the column when the data for Table II were taken was approximately 0.70. Reading from the curves of Figure 5 at 0.7 volatility, the maximum concentrations should have been obtained as follows: amyl alcohols, 128° proof; isobutyl alcohol, 158° proof; \( n \)-propyl alcohol, 170° proof. The values agree fairly well with Table II.

Figure 7. Ethyl esters and free fatty acids in methylene chloride extract of brandy. FFAP column, 6 ft × ½ in., programmed linearly from 100–215°C at 7.5°C/min.; 3 μl; internal standard, ethyl pelargonate.
The ethyl esters of caprylic, capric, and lauric acids are not included in Figure 6. However, they should all fall to the left of the curve for ethyl valerate and exhibit a somewhat steeper volatility gradient.

Nordstrom (19) demonstrated that esters are formed primarily by a direct biosynthetic process during fermentation in which acyl-CoA compounds containing the particular fatty acid moiety combine with alcohols of the medium, which explains the predominance of ethyl esters. Ester formation during fermentation does not appear to be direct esterification between alcohols and free fatty acids. However, some direct esterification may occur on the plates of a distilling column where acids and alcohols are most concentrated.

**Free Fatty Acids.** In our gas chromatographic analyses of brandy extracts prepared for fatty acid ester measurements, free fatty acids also emerged as broad tailing peaks at the end of the programmed temperature run. Free fatty acids have been identified as components of various
fermented and distilled beverages by several workers. Nykänen et al. (38) gave quantitative levels of acetic acid and relative proportions of 21 other volatile fatty acids in a variety of brandy, rum, and whiskey samples. They found that acetic, caproic, caprylic, capric, and lauric acids were generally most abundant. They measured acids by gas chromatography after conversion to methyl esters.

Crowell and Guymon (39) developed a gas chromatographic procedure for quantitative measurement of the predominant free fatty acids by successive extractions of brandy with methylene chloride and then with dilute alkali to separate the free acids from esters. The acids were converted to their n-butyl esters for programmed temperature gas chromatography. Figure 7 shows the chromatogram of ethyl esters extracted from a brandy without removing the free acids. Figure 8 shows the ethyl ester chromatogram with the free fatty acids removed and converted to n-butyl esters and chromatographed as shown in Figure 9. Ethyl pelar-
gonate is used as the internal standard for the naturally occurring ethyl esters or for the free acids after conversion to their n-butyl esters.

We found approximately 2-4 grams of caprylic, 2-5 grams of capric, and 1–2 grams of lauric acid/100 liters in our experimental continuous still beverage brandies but usually less than 1 gram of each per 100 liters in unaged commercial brandy distillates (11). New commercial brandy distillates made from fortified wine contain less than those distilled from straight dry wine. Distillates from a continuous vacuum column and a pilot pot still also contain less.

During aging of brandy and other distilled spirits in wood, very significant changes in composition occur, most of which are well known (40, 41, 42, 43). During aging in oak, acids (primarily acetic), esters (primarily ethyl acetate), color, tannin, extract, and other components increase to a degree dependent on the kind and activity of the wood, length of aging, environmental conditions, etc.

**Literature Cited**


Received July 25, 1973.