JOURNAL OF AGRICULTURAL AND FOOD CHEMISTRY

Pear Distillates from Pear Juice Concentrate: Effect of Lees in the Aromatic Composition

L. García-Llobodanin, I. Achaerandio, M. Ferrando, C. Güell, and F. López*

Unitat d'Enologia del CeRTA (Generalitat de Catalunya), Departament d'Enginyeria Química, Universitat Rovira i Virgili, Av. Països Catalans 26, 43007 Tarragona, Spain

Pear juice obtained from pear concentrate was fermented at room temperature using *Saccharomyces cerevisiae* (BDX, ENOFERM, France) as the fermentation microorganism. During the fermentation process, total sugars were measured. High performance liquid chromatography analyses were used to monitor the fermentation process and to characterize the pear wine. The pear wine obtained was distilled with its lees using three different equipments: a glass alembic (a glass pot still coupled to a glass column), a copper alembic, and a glass alembic with the addition of 5 g/L of copper shavings to the pot still. The same distillations were repeated with the wine without its lees (separated by decanting). Several distillation fractions were collected, up to a total of 500 mL of distillate. Gas chromatography was used to identify and quantify the volatile compounds in each fraction, and the methanol and ethanol contents. Based on these results, the heart fraction was defined. ANOVA tests were performed on the heart fractions to determine quantitative differences between some volatile compounds depending on the equipment used and the presence or absence of the wine lees. From this series of ANOVA tests, it can be concluded that the concentrations of the compounds that are considered to have a negative effect on the quality of the distillates (methanol, ethyl acetate, furfural) decrease or do not change when they are distilled in the presence of lees and in the copper alembic. In addition, the concentrations of the positive compounds (ethyl decanoate and ethyl-2-*trans*-4-*cis*-decadienoate) increase in the presence of lees for all of the equipment tested. So, it can be assumed that the distillation of pear wine with its lees in copper alembic leads to a better quality product.

KEYWORDS: Pear distillates; fermentation; distillation; aromatic composition

INTRODUCTION

According to the European Council Regulation (N° 1576/89), fruit spirits are alcoholic beverages "produced exclusively by the alcoholic fermentation and distillation of fleshy fruit or must of such fruit, with or without stones." They are produced and consumed in many different countries all over the world, and they all have their own organoleptic characteristics that depend on the process and the raw materials used. The most common are the ones made from grapes. However, many other fruits are also used to produce spirits and spirit drinks (i.e., cherries, pears, blackberries, and plums). The quality of spirits depends mainly on their volatile composition (*1*). Some of these volatile compounds are favorable (i.e., ethylic esters of long-chain fatty acids), others are toxic (i.e., furfural, methanol), and others are favorable at low concentrations, although they are responsible for off-flavors when the concentration increases (i.e., higher alcohols, acetaldehyde, ethyl lactate). Thus, the volatile composition of a distilled beverage is a complex matrix of different compounds and depends on the raw matter used, the fermentation, and the distillation processes (*2*).

Several publications on grape distillates describe their volatile composition (*3*−*6*), the various distillation methods (*7*), and the effect of the storage conditions of the raw matter, fermentation conditions, and distillation methods on the final product (*8*−*10*). However, only a few publications have been found on pear distillates (*11*−*13*). The information available on this topic is very scarce, and studies on how the distillation equipment and conditions affect their composition and final quality have never been published.

The aim of this research work is to test if different distillation equipments and the presence or absence of the wine lees during the distillation process affect the quality of the pear distillates obtained. To this end, pear juice from pear concentrate was fermented and then distilled with and without its lees using a glass alembic (a glass pot still coupled to a glass column), a copper alembic, and a glass alembic with the addition of copper shavings. The volatile composition of the different distillation fractions collected was analyzed by gas chromatography (GC).

MATERIALS AND METHODS

Pear Juice Preparation. Pear concentrate of 73 °Brix from *Blanquilla* variety (donated by Indulleida S. A. Alguaire, Lleida) was diluted with water until a juice of 18° Brix was obtained. This juice

* Author to whom correspondence should be addressed [telephone +34 (977) 558-503; fax +34 (977) 559-621; e-mail francisco.lopez@urv.cat].

10.1021/jf0633589 CCC: $37.00
Published on Web 03/30/2007

was characterized by high performance liquid chromatography (HPLC) and by measuring the °Brix, pH, amount of total sugars, and density.

Fermentation Process. A volume of 40 L of pear juice (18 °Brix) was fermented in a 100 L stainless steel tank at room temperature. The microorganism used was *Saccharomyces cerevisiae* (BDX, ENOFERM, France). The inoculum was prepared in accordance with the instructions provided by the supplier, in a dose of 25 g of yeast/hL of pear juice. After the inoculation, ACTIFERM1, composed by thiamin and ammonium and amine nitrogen (Martin Vialatte Enologie, France), was added as a nitrogen source, again in accordance with the dose and instructions provided by the supplier. When the medium density reached 1040 g/mL, a second nitrogen source was added: ACTIFERM2, composed by ammonium phosphate and sulfate (Martin Vialatte Enologie, France), following the same instructions. The fermentation was done in duplicate.

To monitor the process, samples were collected at different fermentation times. For each one, the temperature was measured and the pH monitored with a Crison Basic 20 pH meter. Total and viable yeasts were counted using a Neubauer chamber. Each sample was mixed with 1/10 of its volume of methylene blue, to differentiate viable (uncolored) from nonviable (colored) cells. The density was measured using a Class H Ludwig Schneider densimeter, and total sugars were determined with a GAB kit for sugar analysis (GAB Sistemática Analítica S.L., Spain). Finally, all of the samples were subjected to HPLC analysis.

HPLC Analysis. HPLC analysis was used to characterize the pear juice and the pear wine, and also to monitor the fermentation process. The HPLC equipment was an Agilent 1100 Series with HP Chemstation software (Agilent, Waldbron, Germany) for data acquisition. Sugars, glycerol, and ethanol were measured using a refractive index detector (Agilent, Waldbron, Germany). The column was a Transgenomic ICSepICE COREGEL-87H3, at an oven temperature of 50 °C. The injection volume was 20 μL. The mobile phase was a solution of pH = 2.20 prepared with concentrated H_2SO_4 (95−97%) in Milli-Q water. The flow rate was 0.6 mL/min. All of the samples and the mobile phase were filtered before the analysis using cellulose acetate filters (Teknokroma) with a pore size of 0.45 μm. Samples were analyzed in duplicate.

Distillation Process. The pear distillates were obtained by simple batch distillation of the pear wine in the presence of its lees. Three different distillation equipments were used: a glass alembic (a glass pot still coupled to a glass column), a copper alembic, and a glass column with the addition of 5 g/L of copper shavings to the glass pot. The operation conditions were the same in all cases: 1 L of pear wine was distilled at a flow rate of 2 mL/min, using water as the refrigerant and an electric heater as the heat source. For each equipment, the distilled fractions were collected in glass bottles and kept in the freezer until they were analyzed by GC. The first four fractions were of 25 mL each, and the following ones were of 50 mL each until a total distilled volume of 500 mL had been collected. The distillations in each equipment were performed in duplicate.

A second series of distillations was carried out under the same conditions described above, but without the lees of the pear wine. The first distillation fraction collected was of 5 mL, the second of 20 mL, the third of 275 mL, the fourth of 50 mL, and the fifth of 150 mL. The distillations in each equipment were performed in duplicate.

GC Analysis. Gas chromatography was used to quantify the methanol in the wine (because HPLC analysis gives less exact concentration values), and also to characterize the different samples collected during the distillations. The method used by Cortés et al. for determining volatile compounds in *orujos* was adapted to determine the volatile composition, and the methanol and ethanol content in each sample (*5*). The equipment used was an Agilent 6890N with a flame ionization detector, automatic injector, and HP Chemstation software (Agilent, Waldbron, Germany) for the data analyses. The column was a Teknokroma TR-MetaWax capillary column (polyethyleneglycol stationary phase; 30 m × 0.25 mm × 0.5 μm). The injection volume was 1 μL in split 1:5 mode at an injector temperature of 250 °C. The carrier gas was helium at a column flow rate of 1.1 mL/min. The oven temperature was programmed at 40 °C for 6 min, then increased to 80 °C at a rate of 1.5 °C/min and from 80 to 200 °C at 3 °C/min. The detector temperature was 260 °C, with a H_2 flow rate of 40 mL/min and an air flow rate of 350 mL/min. Helium was used as the auxiliary gas, at a flow rate of 25 mL/min.

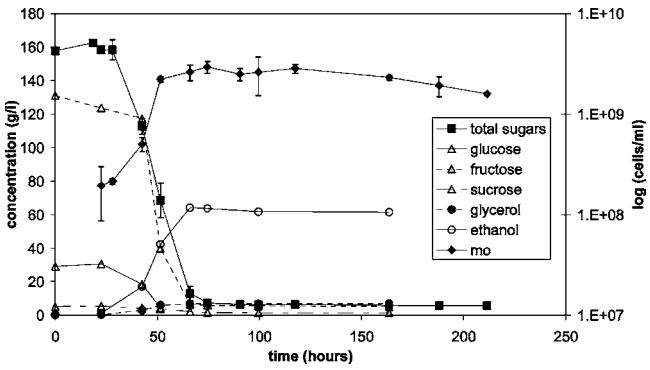

Figure 1. Total microorganisms growth, sugars consumption, and ethanol and glycerol formation during the fermentation process.

The internal standard was 4-methyl-2-pentanol (Fluka) for all of the compounds except ethanol, for which it was acetonitrile (J.T. Baker) (*14*). A solution containing these two standards was prepared and mixed at a ratio of 1/10 for each sample. Each sample was injected by duplicate.

ANOVA Tests. One-way analysis of variance (ANOVA) was used to ascertain if the type of equipment employed and the presence of lees during the distillation cause any significant difference in the composition of the heart fraction (significant at 5% level). Statistical analyses were performed by means of the SPSS statistical package (version 13.0).

To compare the different distillation equipment, a first series of tests was applied to each compound of the heart fraction from the wine distilled with lees, for all of the equipment. The same procedure was used for the heart fractions from the wine distilled without lees.

A second series of tests was applied to each compound of the heart fractions from the wine distilled with and without lees in the distillation equipment. These tests show whether there is any significant difference between the distillations with and without lees.

RESULTS AND DISCUSSION

Fermentation Process. The pear juice prepared had 18 °Brix, a pH of 4.75, and a density of 1.090 g/mL. **Figure 1** shows the total microorganism growth and the total sugar consumption (average of two fermentations). There was a lag period of about 24 h, after which the yeasts grew using the sugars present in the medium.

After 65 h of fermentation, the microorganisms reached the stationary phase. At the beginning of this period, sugars were still being consumed (as a source of carbohydrates for the living cells), but after 90 h of fermentation their concentration was practically constant at 6 g/L. After 150 h of fermentation, the yeast concentration slowly started to decrease, probably due to cell lysis. The number of non-viable microorganisms was counted between the 65th hour and the end of the fermentation. It remained almost constant throughout the process, at values that ranged from 1.8×10^8 to 2.8×10^8 cells/mL. **Figure 1** also shows the sugar concentrations (average of two injections) of the pear juice and their consumption during the fermentation process. Fructose is the main sugar. Its concentration in the pear juice is 125 g/L, followed by glucose (30 g/L), and finally sucrose (5 g/L). The data obtained by HPLC confirm the results found using the GAB kit for sugar analysis, but they also provide new information about the different sugar concentrations.

Glucose was the most rapidly consumed sugar. It reached a concentration of less than 0.1 g/L (not detectable) in less than 65 h of fermentation. This agrees with the fact that *Saccharomyces cerevisiae* strains are mostly glucophilic, and they utilize glucose faster than other sugars such as fructose or sucrose (*15*).

Fructose and sucrose were not completely consumed during the fermentation and reached a concentration of 5.1 and 1.3 g/L, respectively, by the end of the process.

The formation of glycerol and ethanol during the fermentation is shown in **Figure 1**. Ethanol was produced during the microorganism growth phase and reached a value of 62 g/L (8 alcoholic degrees). This value is within the alcoholic degree range suggested by Lèauté for wines that will undergo a subsequent distillation process (*16*). Glycerol concentration increased during the microorganism growth phase, going from 0.1 to 6.7 g/L in the first 65 h of fermentation. After that, its value remained constant until the end of the fermentation.

The GC analyses of the pear wine revealed a methanol concentration of 3.8 ± 0.1 mg/L.

The density decreased during the fermentation process and reached a constant value of 1.02 g/mL after 65 h of fermentation, which is the time at which microorganisms reached the stationary phase.

The temperature was between 20 and 25 °C, except for the period between 50 and 65 h of fermentation, when it was 28 °C. The pH decreased from 4.75 to 4.52 during the fermentation process.

Because both fermentations showed the same behavior throughout the process, only one of them was used to perform all of the distillations.

Distillation Process. In every distillation process, the head and the tail (corresponding to the beginning and the end of the distillation, respectively) must be discarded. The main objective of this separation is to ensure that the heart fraction has a low concentration of toxic and sensorially negative compounds, acceptable concentrations of ethanol, and compounds that can impart a favorable aroma and flavor to the spirit. To define the optimum heart fraction, the compound profiles during the distillation processes and their total amount in the distillates must be determined.

Figure 2 shows the concentration profiles of the different compounds during each distillation process for the wine distilled with lees (each result is the mean of two distillations and two GC injections). In **Figure 2A**, it can be seen that methanol concentration increased from values around 10−15 mg/L in the first fraction to values around 40−55 mg/L in the middle of the distillation, and then remained constant or slowly decreased until the end of the process. Léauté suggests that because of its low boiling point (65.5 °C), and high solubility in water and ethanol, methanol distills in the head and heart of the distillate only (*16*). However, studies made by Hernández-Gómez et al. on melon fruit distillates found methanol in all of the distillation fractions (*17*). They indicated that this behavior is only to be expected due to the formation of azeotropic mixtures. Apostolopoulou et al. also found methanol in all of the fractions (heads, hearts, and tails) of traditional Greek distillates (*18*). Finally, Glatthar et al. found the same behavior for pear distillates (*11*). So, our results are in agreement with these last publications. As far as ethanol is concerned, the first fraction contained the highest concentration (around 700 g/L). Next, it rapidly decreased until it reached a constant value of 15−17 g/L in the last four fractions.

In **Figure 2B**, the profiles of the total higher alcohols (1-propanol, 2-methyl-1-propanol, 1-butanol, 2-methyl-1-butanol, 3-methyl-1-butanol, and 1-hexanol) and total esters (methyl acetate, ethyl acetate, ethyl decanoate, and ethyl-2-*trans*-4-*cis*-decadienoate) are shown. For all of the equipment tested, the first fraction contained the highest concentration of higher alcohols. This concentration decreased from the second fraction on until it reached a nondetectable value (less than 1 mg/L) after the 10th fraction. This behavior is expected for higher alcohols because they have a relatively low boiling point and are soluble in alcohol, but at the same time are completely or partially soluble in water, so they distill at the beginning and in the middle fractions of the distillate (*16*). The behavior of esters was similar to that of higher alcohols, but the total concentration decreased more drastically, reaching a nondetectable value (less than 1 mg/L) after the sixth fraction. Esters can be divided into two groups. On the one hand, ethyl and methyl acetate, which are negative compounds when present in high concentrations (i.e., the maximum concentration of ethyl acetate permitted by "The Regulating Council for the Specific Denomination of Galician Orujo" is 300 g/hL a.a.), are similar to acetaldehyde (low boiling point and soluble in alcohol). They are expected to distill at the beginning of the distillation. On the other hand, ethyl decanoate and ethyl-2-*trans*-4-*cis*-decadienoate are favorable compounds derived from fatty acids. They have relatively high boiling points and are completely or partially soluble in ethanol, so they are expected to distill between the beginning and the middle of the distillation (*16*). This expected behavior is observed in all of the distillations performed (data not shown).

Figure 2C shows that for all of the equipment used, the highest acetaldehyde concentration was found in the first fraction, decreasing drastically in the subsequent ones until it reached a constant value of around 1 mg/L. This behavior agrees with the fact that acetaldehyde has a low boiling point (21 °C) and is soluble in ethanol, so it is expected to distill in the first fractions (*16*). On the other hand, the behavior of furfural is quite the opposite. Its concentration was very low in the first fractions and increased until it reached a maximum in the seventh fraction. After that, it slowly decreased until the end of the distillation. This behavior is coherent with the fact that it has a high boiling point (167 °C) and is also very soluble in water, so its concentration is expected to increase from the middle of the heart to the tails (*16*).

Phenethyl alcohol was also monitored during the distillation processes. Its profile was similar to that of furfural. Its concentration increased to a maximum value in the sixth or seventh fraction, and then slowly decreased until the end of the distillation (data not shown). This behavior is expected because phenethyl alcohol has a high boiling point (higher than water) and is partially soluble in water, so it distills mainly during the middle and the end of the distillation (*16*).

To define the best separation volume for the heads and tails, a mass balance was applied to each compound, to determine the mass present in the total 500 mL distilled with each equipment. The mass is related to the total ethanol volume to obtain the concentration in grams per hectoliter of absolute alcohol of each compound. **Table 1** shows these results.

Ethanol. Ethanol content is obviously of utmost importance in alcoholic drinks. During the first distillation of wine, the alcoholic content of the heart should be around 28% (v/v) (*16*). In fact, commercial pear beverages are available that have a concentration of 20−22 alcoholic degrees. So, the possibility of getting a commercial beverage from a single distillation is extremely interesting from the practical and economic point of view. If we consider all of the distillation fractions, this value was not reached with any of the three distillation equipments. So, it is essential that the last fractions of distillate (which have the lower alcoholic content) be eliminated.

Methanol. According to the European Council Regulation (N° 1576/89), the limit of methanol in fruit spirits is 1000 g/hL

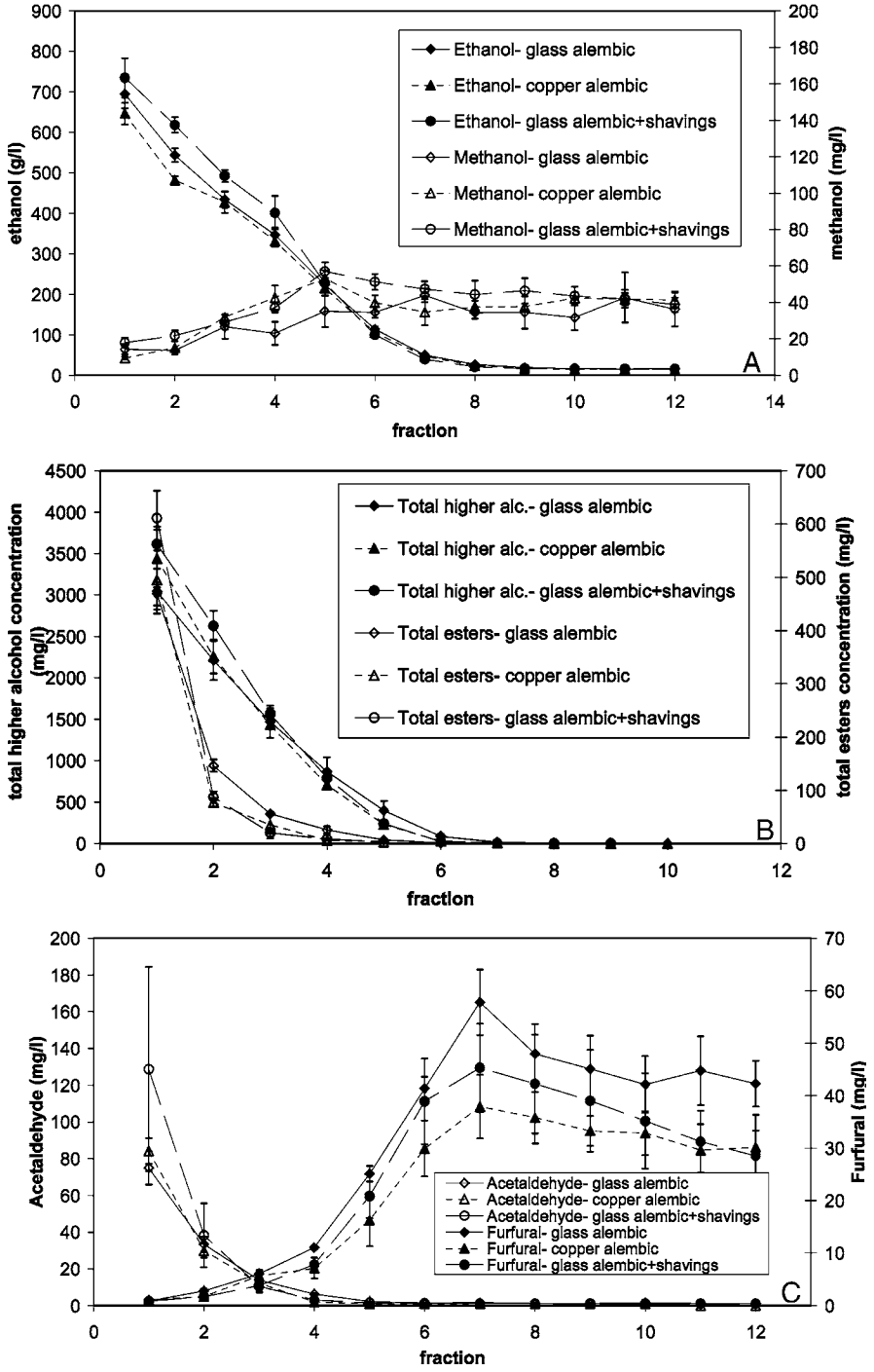

Figure 2. Concentration profiles of the different compounds during each distillation process for the wine distilled with lees. (**A**) Ethanol and methanol; (**B**) total higher alcohols and total esters; and (**C**) acetaldehyde and furfural.

a.a. The values obtained in the three distillation equipments tested were much lower than this. This may be due to the fact that the concentration of pectic substances in our fermentation medium is very low because the pear juice used was obtained from pear concentrate (which is depectinized as part of its production process). Therefore, because the methanol produced during fermentation is derived from the degradation of pectic substances, it could be the cause of the low methanol concentration in our distillates (*14*).

Acetaldehyde. Acetaldehyde is formed from the fermented raw materials, and its concentration increases during the distillation process (*19*). It can provide the beverage with a fruity character when present in low concentrations, but for higher ones it provides a sharp smell (*18*). The official limits adopted by the European Council (N° 1576/89) for fruit distillates are 73−500 g/hL a.a., much higher than the concentration found in our distillates (4−5 g/hL a.a.) (*19*).

Furfural. Furfural is produced by the degradation of fermentable sugars (pentoses) caused by heating in acid conditions and/or the Maillard reaction (*18*). It has a smell that is reminiscent of bitter almonds and it is toxic (reference dose: 3 μg/kg bw/day), so its presence in beverages is not desired. Its concentration in pear brandy is around 2 g/hL a.a., which is considerably lower than the concentration obtained in our distillations. This agrees

Table 1. Mean Concentrations (g/hL a.a.) and Standard Deviations of the Main Volatile Compounds in the Wine Distilled with Its Lees, for Each Distillation Process (Glass Alembic, Copper Alembic, Glass Alembic with Copper Shavings)

compound	glass alembic	copper alembic	glass al with shaving[a]
ethanol (% v/v)	18.9 ± 1.0	17.7 ± 1.0	20.0 ± 1.2
methanol	17.6 ± 3.5	21.4 ± 2.2	21.2 ± 2.4
acetaldehyde	4.0 ± 0.5	4.0 ± 0.5	5.0 ± 2.0
furfural	18.9 ± 2.1	14.3 ± 2.3	14.4 ± 3.1
acetal	0.3 ± 0.1	0.3 ± 0.1	0.6 ± 0.1
methyl acetate	0.2 ± 0.0	0.2 ± 0.0	0.3 ± 0.0
ethyl acetate	16.7 ± 1.0	15.2 ± 2.2	16.4 ± 1.4
phenethyl alcohol	27.4 ± 5.3	28.9 ± 3.5	27.2 ± 3.8
1-hexanol	1.2 ± 0.5	1.4 ± 0.5	1.4 ± 0.5
1-butanol	3.9 ± 2.2	4.0 ± 2.1	4.4 ± 0.8
2-methyl-1-butanol	23.8 ± 2.0	24.2 ± 1.2	22.1 ± 3.8
3-methyl-1-butanol	134.7 ± 18.6	140.8 ± 13.6	136.8 ± 6.8
1-propanol	26.3 ± 3.6	27.6 ± 2.7	26.9 ± 0.8
2-methyl-1-propanol	37.7 ± 4.1	38.8 ± 2.7	37.2 ± 1.0
total higher alcohols	**226.3 ± 30.5**	**235.4 ± 22.4**	**227.4 ± 13.1**
ethyl decanoate	1.3 ± 0.1	1.3 ± 0.3	1.1 ± 0.1
ethyl-2-*trans*-4-*cis*-decadienoate	0.8 ± 0.1	0.8 ± 0.1	0.7 ± 0.1

[a] al = alembic.

with the results found by Cortés et al. in industrial (0.5−2.0 g/hL a.a.) and homemade (up to 8.5 g/hL a.a.) Galician *orujos* (*5*). These results confirm the need to remove the last fractions of distillate to obtain a better quality product.

Esters. They are in the fruit or are formed during the fermentation of the raw material. Long-chain esters contribute to the fruity aroma of the spirits, so their presence in the final product is highly desirable (*19*). Ethyl-2-*trans*-4-*cis*-decadienoate, in particular, is one of the most important aroma compounds in pears, imparting to all its derivatives (such as pear distillates) a very characteristic and pleasant pear-like aroma (*12*). The concentration of ethyl-2-*trans*-4-*cis*-decadienoate in pear brandy ranges between 5.0 and 5.3 g/hL a.a. This value is well above the concentration found in our distillates. Cortés et al. found that the mean concentration of ethyl decanoate in *orujos* is 13.3 g/hL a.a. for industrial samples, and 33.7 g/hL a.a. for homemade samples (*5*). This concentration is much higher than the one found in our distillates. However, Souflero et al. found concentrations between 0.8 and 2.0 g/hL a.a. in samples of blackberry distillate (*mouro*). In addition, the concentration commonly found in pear brandy is between 1.0 and 1.5 g/L a.a. (*20*), which is in good agreement with our results (*19*). On the other hand, short-chain esters usually originate from bacterial spoilage and have a negative influence on the sensory quality of the spirits, giving nuances of dissolvent, glue, or rancid butter. For example, concentrations higher than 180 g/hL a.a. of ethyl acetate add acidic character and even solvent nuances to the spirit (*18*, *19*). In our distillations, the concentrations of these types of esters are quite low.

Higher Alcohols. Higher alcohols are formed during the fermentation process. They make an important contribution to the aroma profile of distillates, imparting a flavoring aroma and essential character (*19*). For this reason, the European Council Regulation (N° 1576/89) demands a minimum total amount of these compounds of 140 g/hL a.a. However, high amounts can have a negative effect on the distillate flavor, giving a pungent smell and taste (*14*, *15*). For this reason, the "Regulating Council for the Specific Denomination of Galician Orujo" fixes the maximum amount for the sum of higher alcohols at 600 g/hL a.a. (*10*). Our distillates respect the requirements of the European legislation, and at the same time are in agreement with the values that are commonly found in pear brandy (155−246 g/hL a.a.) (*18*). Within the higher alcohols, the concentration of isoamyl alcohols (2-methyl-1-butanol and 3-methyl-1-butanol) must be controlled because they can give disagreeable odors (*10*). Their perception threshold is 6 g/hL a.a., which is much lower than the values recorded for our distillates. However, commercial samples of pear distillate show a concentration of 2-methyl-1-butanol of 67 g/hL a.a. (*19*). Another source (*20*) shows that pear brandy has a 2-methyl-1-butanol concentration of 30−45 g/hL a.a., while 3-methyl-1-butanol ranges from 110 to 120 g/hL a.a. These data reveal that the concentration of 2-methyl-1-butanol in our samples is well below the commercial standards. Nevertheless, the concentration of 3-methyl-1-butanol (135−141 g/hL a.a.) is some way above the observed range in commercial samples, meaning that some of the first fractions should be separated from the distillates to avoid disagreeable odors.

Phenethyl Alcohol. It derives from L-phenylalanine through the metabolic reaction of the yeast during carbonic anaerobiosis (*19*). When present in low concentrations, phenethyl alcohol provides the distillates with a pleasant floral aroma resembling that of a rose (*18*). Because it is a typical tail component, it should be present in distillates in low concentrations, so it is an indicator of good (or bad) tail fraction separation. Soufleros et al. state that the distillation technique and the type of alembic used seem to play a significant role in the phenethyl alcohol concentration in distillates (*19*). The influence of the distillation system on the phenethyl alcohol concentration was confirmed by Cortés et al. during their study of Galician *orujos* (*5*). However, they believe that this is related to how the tail fraction is used and not to the material of the distillation equipment. In our distillates, the distillation equipment used did not seem to affect the phenethyl alcohol concentration. This is probably because the distillation method was the same (simple batch distillation) and the fractions collected were also the same.

The phenethyl alcohol concentration of commercial samples of pear brandy ranges between 0.5 and 2.0 g/hL a.a. (*20*). These values are much lower than the ones obtained in our distillates. Soufleros et al. found concentrations between 0.0 and 12.7 g/hL a.a. in blackberry distillates (*mouro*) (*19*). Apostolopoulou et al. found, for *tsipouro*, a phenethyl alcohol concentration between 3.0 and 7.2 g/hL a.a. in industrial samples and between 1.0 and 9.9 g/hL a.a. in homemade samples (*18*). Cortés et al. studied homemade and industrial orujos and found phenethyl ethanol concentrations of 0.0−18.7 and 1.2−5.9 g/hL a.a., respectively (*5*). All of these results agree with the fact that the phenethyl alcohol concentration in our samples is too high, even compared to homemade fruit distillates. For this reason, the last fractions need to be separated if the concentration is to be closer to the concentrations of commercial samples.

On the basis of the previous results, it was decided to remove the first fraction of each distillation (25 mL) and the four last ones (total volume of 200 mL). The remaining fractions were put together, as the heart of the distillate (total volume of 275 mL). All of the heart fractions (of the three equipments tested) were analyzed by GC. **Table 2** shows the results of these GC analyses for each distillation process of the wine distilled with lees (distillations and GC analyses were done in duplicate).

The same distillations were repeated using the pear wine without the lees. The profiles obtained for the compounds analyzed were the same as for those of the distillations of pear wine with lees, although there are some quantitative differences (data not shown). **Table 3** shows the results of the GC analyses of the hearts of each distillation process for the wine distilled without lees.

Table 2. Mean Concentrations (g/hL a.a.) and Standard Deviations of the Main Volatile Compounds in the Heart Fraction of the Wine Distilled with Its Lees for Each Distillation Process (Glass Alembic, Copper Alembic, Glass Alembic with Copper Shavings)[a]

compound	glass alembic	copper alembic	glass al with shaving[b]
ethanol (% v/v)	22.9 ± 0.3	26.5 ± 3.9	24.1 ± 0.9
methanol	21.2 ± 2.8 a	18.5 ± 2.2 a	21.8 ± 1.5 a
acetaldehyde	3.3 ± 0.6 a	1.9 ± 0.2 b	3.0 ± 0.9 ab
furfural	14.8 ± 2.9 a	11.3 ± 1.1 a	11.5 ± 1.5 a
ethyl acetate	8.0 ± 0.4 a	2.2 ± 0.1 b	3.2 ± 0.1 c
phenethyl alcohol	18.3 ± 0.7 a	20.8 ± 3.3 a	20.4 ± 1.4 a
1-hexanol	1.3 ± 0.6 a	1.2 ± 0.5 a	1.5 ± 0.4 a
1-butanol	3.4 ± 2.1 a	2.9 ± 1.6 a	4.7 ± 1.2 a
2-methyl-1-butanol	15.7 ± 0.9 a	14.1 ± 0.9 a	18.3 ± 1.3 b
3-methyl-1-butanol	159.3 ± 3.1 a	138.1 ± 11.4 b	140.1 ± 9.0 b
1-propanol	35.7 ± 1.5 a	33.1 ± 2.6 a	35.6 ± 1.8 a
2-methyl-1-propanol	38.7 ± 2.3 a	31.4 ± 2.5 b	36.4 ± 2.4 a
total higher alcohols	**252.8 ± 9.9**	**219.6 ± 18.9**	**235.0 ± 15.6**
ethyl decanoate	0.7 ± 0.1 a	0.6 ± 0.1 a	0.6 ± 0.1 a
ethyl-2-*trans*-4-*cis*-decadienoate	1.4 ± 0.4 a	1.4 ± 0.2 a	1.2 ± 0.0 a

[a] Different superscripts indicate significant differences ($p \leq 0.05$) between parameter values. [b] al = alembic.

Table 3. Mean Concentrations (g/hL a.a.) and Standard Deviations of the Main Volatile Compounds in the Heart Fraction of the Wine Distilled without Its Lees for Each Distillation Process (Glass Alembic, Copper Alembic, Glass Device with Copper Shavings)[a]

compound	glass alembic	copper alembic	glass al with shaving[b]
ethanol (% v/v)	24.2 ± 1.5	22.6 ± 0.2	24.5 ± 0.1
methanol	30.2 ± 1.6 a	23.8 ± 2.9 b	29.2 ± 3.8 ab
acetaldehyde	3.5 ± 0.8 a	3.3 ± 0.7 a	2.3 ± 0.2 b
furfural	17.1 ± 0.6 a	10.9 ± 1.3 b	16.3 ± 1.3 a
ethyl acetate	10.0 ± 3.2 a	3.6 ± 0.9 b	3.5 ± 0.5 b
phenethyl alcohol	18.4 ± 0.8 a	21.9 ± 1.6 b	19.4 ± 2.3 ab
1-hexanol	4.4 ± 0.2 a	4.9 ± 0.3 b	5.3 ± 0.5 b
1-butanol	6.8 ± 0.6 a	7.2 ± 0.2 a	8.3 ± 0.2 b
2-methyl-1-butanol	16.7 ± 2.8 ab	16.0 ± 0.9 a	19.0 ± 0.9 b
3-methyl-1-butanol	168.7 ± 6.0 a	170.0 ± 11.5 a	152.7 ± 9.6 b
1-propanol	35.9 ± 1.1 a	38.6 ± 2.2 a	37.6 ± 2.0 a
2-methyl-1-propanol	37.9 ± 1.5 a	37.4 ± 2.3 a	38.7 ± 0.6 a
total higher alcohols	**266.1 ± 12.1**	**269.0 ± 17.0**	**256.2 ± 13.3**
ethyl decanoate	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0
ethyl-2-*trans*-4-*cis*-decadienoate	0.5 ± 0.6 a	0.7 ± 0.1 a	0.6 ± 0.1 a

[a] Different superscripts indicate significant differences ($p \leq 0.05$) between parameter values. [b] al = alembic.

ANOVA Tests. The first series of ANOVA tests for the pear wine distilled with lees (**Table 2**) shows that the concentrations of ethyl acetate and 3-methyl-1-butanol in the heart of the distillates were significantly lower ($p < 0.05$) when distilled in the presence of copper (copper alembic and glass alembic with copper shavings). In addition, the concentrations of 2-methyl-1-propanol were significantly lower ($p < 0.05$) when distilled in the copper alembic. The concentrations of 2-methyl-1-butanol and acetaldehyde were also lower when distilled in the copper alembic. For the rest of the compounds, no significant differences were detected.

For the wine distilled without lees (**Table 3**), the concentration of ethyl acetate was significantly lower ($p < 0.05$) for the distillations in the presence of copper. On the contrary, the concentration of 1-hexanol was significantly higher ($p < 0.05$) when distilled in the same devices. The concentration of 1-butanol was significantly lower ($p < 0.05$) for the copper alembic and the glass alembic. However, the concentration of 3-methyl-1-butanol was significantly higher ($p < 0.05$) for these devices. Finally, the furfural concentration was significantly lower ($p < 0.05$) for the distillation in the copper alembic.

Considering that ethyl acetate and furfural are negative compounds for a distillate, and higher alcohols have no major influence in this case (because their concentration is within the accepted range for the three equipments tested), the copper alembic seems to be the best equipment for performing the distillations, either with or without lees.

The second series of ANOVA tests focused on comparing the distillations with and without lees for each equipment. For the distillation in the glass alembic, the concentrations of methanol, 1-butanol, 3-methyl-1-butanol, and 1-hexanol were significantly lower ($p < 0.05$) when the distillation was carried out in the presence of lees. On the contrary, ethyl decanoate and ethyl-2-*trans*-4-*cis*-decadienoate concentrations significantly increased in the presence of lees ($p < 0.05$). In the case of the copper alembic, acetaldehyde, ethyl acetate, 1-propanol, 2-methyl-1-propanol, 1-butanol, 3-methyl-1-butanol, and 1-hexanol concentrations diminished when the distillation was carried out in the presence of lees ($p < 0.05$); on the other hand, ethyl decanoate and ethyl-2-*trans*-4-*cis*-decadienoate concentrations significantly increased in the presence of lees ($p < 0.05$). Finally, for the glass alembic with copper shavings, methanol, 2-methyl-1-propanol, 1-butanol, 1-hexanol, and furfural concentrations significantly decreased when the distillation was carried out in the presence of lees ($p < 0.05$). On the contrary, ethyl-decanoate and ethyl-2-*trans*-4-*cis*-decadienoate concentrations significantly increased in the presence of lees ($p < 0.05$). The compounds that were not mentioned in the previous analysis underwent no significant changes in their concentration.

From this series of ANOVA tests, it can be concluded that the compounds that are considered to be negative for the quality of the distillates (methanol, ethyl acetate, furfural) diminish or do not change their concentrations when they are distilled in the presence of lees, for all of the equipment tested. In addition, the positive compounds (ethyl decanoate and ethyl-2-*trans*-4-*cis*-decadienoate) increase their concentrations in the presence of lees for all of the equipment tested. So, it can be assumed that distillation in the presence of lees leads to a better quality product.

LITERATURE CITED

(1) Schehl, B.; Lachenmeier, D.; Senn, T.; Heinisch, J. Effect of the stone content on the quality of plum and cherry spirits produced from mash fermentations with commercial and laboratory yeast strains. *J. Agric. Food Chem.* **2005**, *53*, 8230−8238.

(2) Rodríguez-Madrera, R.; Blanco-Gomis, D.; Mangas-Alonso, J. Influence of distillation system, oak wood type, and aging time on volatile compounds of cider brandy. *J. Agric. Food Chem.* **2003**, *51*, 5709−5714.

(3) Ebeler, S.; Terrien, M.; Butzke, C. Analysis of brandy aroma by solid-phase microextraction and liquid-liquid extraction. *J. Sci. Food Agric.* **2000**, *80*, 625−630.

(4) Dieguez, S. C.; De la Peña, M. L. G.; Gomez, E. F. Approaches to spirit aroma: Contribution of some aromatic compounds to the primary aroma in samples of Orujo spirits. *J. Agric. Food Chem.* **2003**, *51*, 7385−7390.

(5) Cortés, S.; Gil, M. L.; Fernández, E. Volatile composition of traditional and industrial Orujo spirits. *Food Control* **2005**, *16*, 383−388.

(6) Diéguez, S. C.; De la Peña, M. L. G.; Gómez, E. F. Volatile composition and sensory characters of commercial Galician orujo spirits. *J. Agric. Food Chem.* **2005**, *53*, 6759−6765.

(7) Cortella, G.; Da Porto, C. Design of a continuous distillation plant for the production of spirits originating from fermented grape. *J. Food Eng.* **2003**, *58*, 379−385.

(8) Da Porto, C. Volatile composition of 'grappa low wines' using different methods and conditions of storage on an industrial scale. *Int. J. Food Sci. Technol.* **2002**, *37*, 395−402.
(9) Du Plessis, H. W.; Steger, C. L. C.; Du Toit, M.; Lambrechts, M. G. The occurrence of malolactic fermentation in brandy base wine and its influence on brandy quality. *J. Appl. Microbiol.* **2002**, *92*, 1005−1013.
(10) Cortés, S.; Gil, M. L.; Fernández, E. The influence of redistillation in the distribution of volatile components of marc spirit (Aguardiente) and its repercussion on the aromatic quality. *Sci. Aliment.* **2002**, *22*, 265−275.
(11) Glatthar, J.; Senn, T.; Pieper, H. J. Investigations on reducing the methanol content in distilled spirits made of Bartlett pears. *Dtsch. Lebensm.-Rundsch.* **2001**, *97*, 209−216.
(12) Cigic, I. K.; Zupancic-Kralj, L. Changes in odour of Bartlett pear brandy influenced by sunlight irradiation. *Chemosphere* **1999**, *38*, 1299−1303.
(13) Tucker, A. O.; Maciarello, M. J.; Rose, J. The composition of a commercial 'pear essence' derived from fermentation of 'Bartlett' pears. *J. Essent. Oil Res.* **2003**, *15*, 161−162.
(14) Wang, M. L.; Wang, J. T.; Choong, Y. M. Simultaneous quantification of methanol and ethanol in alcoholic beverage using a rapid gas chromatographic method coupling with dual internal standards. *Food Chem.* **2004**, *86*, 609−615.
(15) Wang, D.; Xu, Y.; Hu, J.; Zhao, G. Fermentation kinetics of different sugars by apple wine yeast Saccharomyces cerevisiae. *J. Inst. Brew.* **2004**, *110*, 340−346.
(16) Léauté, R. Distillation in Alambic. *Am. J. Enol. Vitic.* **1990**, *41*, 90−103.
(17) Hernández-Gómez, L.; Úbeda, J.; Briones, A. Melon fruit distillates: comparison of different distillation methods. *Food Chem.* **2003**, *82*, 539−543.
(18) Apostolopoulou, A. A.; Flouros, A. I.; Demertzis, P. G.; Akrida-Demertzi, K. Differences in concentration of principal volatile constituents in traditional Greek distillates. *Food Control* **2005**, *16*, 157−164.
(19) Soufleros, E. H.; Mygdalia, A. S.; Natskoulis, P. Characterization and safety evaluation of the traditional Greek fruit distillate "Mouro" by flavor compounds and mineral analysis. *Food Chem.* **2004**, *86*, 625−636.
(20) Maarse, H.; Visscher, C. Pear Brandy. *Volatile Compounds in Food: qualitative and quantitative data*; Zeist: TNO-CIVO Food Analysis Institute: Netherlands, 1989; pp 169−172.

Received for review November 20, 2006. Revised manuscript received February 13, 2007. Accepted February 15, 2007.

JF0633589