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Aromatically Enhanced Pear Distillates from Blanquilla and Conference Varieties Using a Packed Column

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Supporting Information

ABSTRACT: Pear distillates are generally produced from the Bartlett variety because of its rich aroma. In this study, a chemical and sensorial comparative examination of pear distillates from the three main varieties grown in Spain (Bartlett, Blanquilla, and Conference) using two distillation systems (copper Charentais alembic and packed column) was undertaken. Volatile compounds were identified by gas chromatography to differentiate the spirits according to pear variety and distillation method. The Bartlett distillates from both distillation systems possessed higher ethyl ester and acetate and lower *cis*-3-hexen-1-ol and 1-hexanol concentrations. Despite these differences, a sensory analysis panel could distinguish only the Bartlett alembic distillate from the alembic distillates of the other varieties. In contrast, the panel rated the packed-column distillates equally. Therefore, less aromatic pear varieties can be used to produce distillates with aromatic characteristics similar to those of the Bartlett variety if a suitable distillation process is used.

KEYWORDS: *alembic, packed column, pear spirit, aromas, alcoholic beverages, volatile composition*

INTRODUCTION

After grape, pear is one of the fruits most commonly used to produce distillates in many countries around the world. The cultivated varieties of pear differ by region. According to recent data, pear varieties have remained relatively stable in Spain over the past 40 years.[1] In Europe, the Conference and Bartlett varieties are the most abundantly produced, followed by the Italian variety Abate F and the Spanish variety Blanquilla. Spain is also the second-largest producer of the Conference and Bartlett varieties and the largest producer of the Blanquilla variety.

Given its rich aromatic content, Bartlett is the variety most frequently used to produce pear distillates in Central Europe.[2] The production of pear distillates using other local varieties can help to reduce the surplus of this fruit and provide a product with high added value. However, few studies have been published in the literature on pear distillates from varieties other than Bartlett. Those papers have focused on studying the reducing methanol content,[3,4] the effect of bottle color on the aroma and taste of the distillate,[5] and the composition of a commercial pear essence derived from a distilled pear wine.[6]

The Blanquilla and Conference pear varieties are less aromatic than the Bartlett variety; therefore, it is necessary to apply different fermentation and distillation procedures to improve the aromatic profiles of their spirits. Recently, some studies[7−9] have analyzed the potential of the Blanquilla variety to produce commercial distillates. In particular, they focused on the impact of fermentation, distillation, and raw materials on the aromatic profile of the final product. They found that (1) pH reduction during fermentation significantly increased the concentration of most of the longer chain alcohols and decreased the concentration of ethyl acetate; (2) the concentration of some undesirable compounds (methanol, ethyl acetate, and furfural) decreased or did not change when the lees were present during distillation in a copper alembic; and (3) the concentrations of some desirable compounds (ethyl decanoate and ethyl-2-*trans*-4-cisdecadienoate) increased in the presence of lees. Hence, it can be assumed that, in a copper alembic, the distillation of pear wine with its lees leads to a higher quality product. Finally, the pear distillates produced with a tray column contained significantly higher concentrations of most of the long-chain ethyl esters (C6−C12) than those obtained after a double distillation with a Charantais alembic.

García-Llobodanin et al.[10] analyzed the reproducibility of Conference pear distillate composition from Charentais alembic and packed distillation columns. They found that packed columns can produce aromatically enhanced distillates, although the process is much less reproducible than alembic distillation. Nevertheless, the column-distilled spirits contained 4 times more esters, 20% more long-chain alcohols, 40% less acetaldehyde, and 10% less methanol than alembic spirits. Therefore, we reasoned that pear distillates can be produced from Conference and Blanquilla varieties with aromatic characteristics similar to those of Bartlett pear distillates by

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Table 1. Average Concentrations (g/hL pa) of the Macroconstituents Present in Distillates Obtained from the Blanquilla, Conference, and Bartlett Pear Varieties for Each Distillation Process (Copper Charentais Alembic and Packed Column)[a]

compound	copper Charentais alembic			packed column		
	Blanquilla	Conference	Bartlett	Blanquilla	Conference	Bartlett
ethanol % v/v	64.90 ± 0.15	59.30 ± 0.49	70.60 ± 0.46	67.63 ± 1.14	73.80 ± 0.60	68.90 ± 1.31
methanol	598.34 ± 8.70a,a	549.80 ± 29.86b,a	114.28 ± 5.72c,a	532.84 ± 9.46a,b	503.85 ± 47.17ab,a	450.40 ± 5.55b,b
ethyl acetate	73.21 ± 5.87a,a	34.71 ± 3.75b,a	52.64 ± 2.38c,a	152.56 ± 10.34a,b	268.10 ± 10.34b,b	153.39 ± 49.46a,b
acetaldehyde	0.67 ± 0.16a,a	0.32 ± 0.13b,a	0.54 ± 0.07ab,a	1.87 ± 0.19a,b	0.83 ± 0.10b,b	1.41 ± 0.22c,b
1,1-diethoxyethane (acetal)	1.25 ± 0.19a,a	0.74 ± 0.07b,a	0.31 ± 1.04c,a	2.48 ± 1.04b,b	0.70 ± 0.42a,a	0.42 ± 0.05a,a
Σ acetaldehyde + 1,1-diethoxyethane	**1.92 ± 0.05a,a**	**1.07 ± 0.22b,a**	**0.85 ± 0.09c,a**	**4.35 ± 0.68a,b**	**1.54 ± 0.17b,a**	**1.82 ± 0.24b,b**
1-propanol	46.61 ± 7.19	100.42 ± 13.03	20.98 ± 2.34	nd[b]	nd	nd
2-methyl-1-propanol	68.55 ± 0.52a,a	70.80 ± 1.52a,a	96.36 ± 1.41b,a	74.73 ± 0.77a,a	71.87 ± 3.26a,a	96.80 ± 4.33b,a
1-butanol	2.17 ± 0.03a,a	2.93 ± 0.11b,a	4.07 ± 0.20c,a	4.79 ± 0.20a,b	3.17 ± 0.25b,a	5.23 ± 0.13a,b
2-butanol	125.46 ± 2.76a,a	165.54 ± 6.61b,a	119.66 ± 5.06a,a	267.58 ± 7.46a,b	254.63 ± 18.36a,b	215.65 ± 6.70b,b
allylic alcohol	1.14 ± 0.00a,a	0.53 ± 0.02b,a	2.10 ± 0.12c,a	0.44 ± 0.02b,b	0.71 ± 0.06a,b	0.63 ± 0.02a,b
2-methyl-1-butanol	58.99 ± 0.73a,a	58.99 ± 2.30a,a	81.31 ± 3.84b,a	66.75 ± 1.83a,b	63.18 ± 4.58a,a	85.07 ± 2.46b,a
3-methyl-1-butanol	189.44 ± 1.80a,a	194.05 ± 7.01a,a	203.43 ± 10.13a,a	200.99 ± 5.63a,a	196.54 ± 14.51a,a	211.19 ± 5.84a,a
Σ higher alcohols[c]	**320.29 ± 7.01a,a**	**327.3 ± 10.96a,a**	**387.27 ± 10.26b,a**	**347.7 ± 9.00a,b**	**335.47 ± 8.15a,a**	**398.92 ± 10.99b,a**
ethyl lactate	44.06 ± 0.81a,a	27.17 ± 1.66b,a	39.41 ± 2.65c,a	27.99 ± 1.90b,a	35.97 ± 4.55b,b	61.30 ± 2.47c,b
1-hexanol	9.80 ± 0.05a,a	9.79 ± 0.34a,a	1.65 ± 0.11b,a	9.01 ± 0.40a,b	8.90 ± 0.62a,b	2.02 ± 0.09a,b
isobutyraldehyde	1.11 ± 0.10a,a	0.74 ± 0.13b,a	0.36 ± 0.03c,a	3.95 ± 0.25b,a	5.07 ± 0.46b,b	2.06 ± 0.03c,b

[a]Different letters before the comma in the same row indicate a significant difference ($p \leq 0.05$) with respect to the pear variety (comparison between Blanquilla, Conference, and Bartlett pear spirits). Different letters after the comma in the same row indicate a significant difference ($p \leq 0.05$) with respect to the distillation system (within the same pear variety). [b]nd, not determined. [c]Σ 2-methyl-1-propanol, 1-butanol, allylic alcohol, 2-methyl-1-butanol, 3-methyl-1-butanol.

using this distillation system. In this paper we produced pear distillates from the three main pear varieties grown in Spain (Blanquilla, Conference, and Bartlett) using two distillation systems (copper Charentais alembic and packed column). The volatile compositions of the distillates were determined by gas chromatography, and significant differences among distillates were assessed through analysis of variance (ANOVA) and principal component analysis (PCA). In addition, a sensory panel graded the spirits according to preference.

■ MATERIALS AND METHODS

Pear Juices. Blanquilla, Conference, and Bartlett pear juices were donated by S.A.T. Nufri, Lleida, Spain. The fruits selected had ripened to a similar extent. After the fruit had been selected and cleaned, the pear juices were obtained by mashing and pressing. The juices were frozen at −20 °C until use.

Fermentation. Fermentation was carried out in 200 L stainless steel tanks. A volume of 150 L of each juice was inoculated with *Saccharomyces cerevisiae* (BDX, ENOFERM, France) at 12 ± 1 °C. The inoculum was prepared according to the instructions provided by the supplier, in a dose of 25 g of yeast/hL of pear juice. The initial densities of the Blanquilla, Conference, and Bartlett pear juices were 1.040, 1.0285, and 1.053 g/mL, respectively. When the medium density reached 1040 g/L, 300 mg/L of diammonium hydrogen phosphate (Scharlau, Barcelona, Spain) was added as a nitrogen source. Fermentation was monitored daily by measuring the temperature and density, and when the density reached a plateau, the pear ferment was stored at 4 °C until distillation. The final densities of the Blanquilla, Conference, and Bartlett fermented pear juices were 1.007, 1.005, and 1.007 g/mL, respectively.

Distillation Procedure. *Alembic Distillation.* The pear wine was double-distilled with its lees to obtain the pear spirit. A volume of 12 L of pear wine was first distilled in a 20 L copper Charentais alembic. The base of the boiler was heated with an electric heater, and tap water was used to cool the total condenser. The distillation rate during the first distillation was approximately 14 mL/min. The first 1.2 L of distillate was used in the second distillation, which was carried out in a 2 L copper Charentais alembic. In this case, the average distillation rate was 3 mL/min. Distillations and redistillations were performed in triplicate, although the products of the first distillations were combined and split into three equal volumes before redistillation. After a distillation finished, the alembic was cooled, washed, and air-dried before the next distillation was performed. The ethanol content of each sample was determined using an Anton Paar DSA 5000 M density meter (Anton Paar GmbH, Graz, Austria). On the basis of sensory analysis, the head fractions were defined as the first 35, 30, and 20 mL for the Bartlett, Blanquilla, and Conference distillates, respectively. The heart fractions included the portions from 35 to 550 mL, from 30 to 500 mL, and from 20 to 350 mL for the Bartlett, Blanquilla, and Conference distillates, respectively.

Packed-Column Distillation. The packed-column distillation equipment consisted of a 50 L cylindrical stainless steel boiler (49 cm in height, 37 cm outer diameter (o.d.)) with two 1.2 kW electric heaters and a copper rectification column (5.25 cm o.d.) packed with 10 cm of copper mesh (Amphora Society, http://www.amphora-society.com/). The column details have been described in García-Llobodanin et al.[10] The boiler was loaded with 36 L of pear wine with its lees, except the Bartlett wine, which was mixed with water (21 L of pear wine and 15 L of water) to prevent problems with the electric heaters due to its high levels of suspension solids. The heating and partial condenser cooling rates of the distillation column were adjusted to obtain a distillate flow rate of 6 mL/s. Each pear wine was distilled in triplicate. For the distillations of Bartlett pear wine, the first four samples were of 25 mL each, followed by samples of 100 mL, up to a total volume of 1500 mL. For the distillations of Blanquilla pear wine, four samples of 25 mL distillate were collected first, followed by two samples of 50 mL and samples of 100 mL, until 1000 mL of total volume was collected. For the distillations of Conference pear wine, the first four samples were of 25 mL each, the next two were of 100 mL, the next three were of 200 mL, and the last ones were of 100 mL each, until a total volume of 2000 mL was collected. The ethanol

Table 2. Average Concentrations (g/hL pa) of Microconstituents (Acetates and Esters) Present in Distillates Obtained from the Blanquilla, Conference, and Bartlett Pear Varieties for Each Distillation Process (Copper Charentais Alembic and Packed Column)[a]

	copper Charentais alembic			packed column		
compound	Blanquilla	Conference	Bartlett	Blanquilla	Conference	Bartlett
isobutyl acetate	0.01 ± 0.01a,a	0.05 ± 0.02b,a	0.11 ± 0.02c,a	<LOD[b]	<LOD	<LOD
butyl acetate	<LOD	<LOD	0.12 ± 0.12b,a	0.12 ± 0.03a,b	0.07 ± 0.01b,b	0.12 ± 0.01a,a
isoamyl acetate	0.68 ± 0.22a,a	1.09 ± 0.14b,a	1.73 ± 0.54c,a	1.30 ± 0.01a,b	1.22 ± 0.20a,a	3.26 ± 0.20b,b
hexyl acetate	0.02 ± 0.01b,a	<LOD	<LOD	0.03 ± 0.00a,a	<LOD	<LOD
Σ acetates of higher alcohols	**0.72 ± 0.19a,a**	**1.14 ± 0.09b,a**	**1.96 ± 0.08c,a**	**1.45 ± 0.19a,b**	**1.29 ± 0.06a,a**	**3.39 ± 0.38b,b**
ethyl butyrate	0.10 ± 0.09a,a	0.12 ± 0.12a,a	0.47 ± 0.11b,a	0.43 ± 0.11a,b	0.46 ± 0.11b,a	0.51 ± 0.28a,a
ethyl hexanoate	0.28 ± 0.06a,a	<LOD	0.16 ± 0.14c,a	0.30 ± 0.03a,a	0.29 ± 0.03a,b	0.27 ± 0.02a,b
ethyl octanoate	0.38 ± 0.12a,a	0.48 ± 0.12a,a	1.16 ± 0.14b,a	0.64 ± 0.06a,b	0.67 ± 0.06a,b	1.96 ± 0.01b,b
ethyl decanoate	0.17 ± 0.06a,a	0.33 ± 0.09a,a	2.14 ± 0.37b,a	0.32 ± 0.06a,b	0.52 ± 0.06a,b	4.47 ± 0.06b,b
ethyl-2-*trans*-4-*cis*-decadienoate	0.14 ± 0.09a,a	0.17 ± 0.06a,a	1.03 ± 0.52b,a	0.23 ± 0.01a,b	0.25 ± 0.01a,b	2.31 ± 0.04b,b
ethyl dodecanoate	0.37 ± 0.01a,a	0.33 ± 0.06a,a	1.95 ± 1.00b,a	0.73 ± 0.01a,b	0.67 ± 0.01b,b	2.36 ± 0.20c,b
Σ ethyl esters C6−C12[c]	**1.34 ± 0.08a,a**	**1.31 ± 0.17a,a**	**6.44 ± 0.18b,a**	**2.22 ± 0.21a,b**	**2.40 ± 0.07a,b**	**11.37 ± 0.68b,b**
ethyl tetradecanoate	0.03 ± 0.00a,a	0.05 ± 0.03b,a	0.12 ± 0.03c,a	0.05 ± 0.01a,a	0.07 ± 0.01a,a	0.54 ± 0.04b,b
ethyl hexadecanoate	0.21 ± 0.04a,a	0.02 ± 0.01a,a	0.66 ± 0.20b,a	0.58 ± 0.10a,a	0.35 ± 0.10a,a	5.84 ± 0.68b,b
ethyl octadecanoate	<LOD	<LOD	<LOD	<LOD	<LOD	0.08 ± 0.01b,b
ethyl 9-octadecenoate	0.12 ± 0.12a,a	0.03 ± 0.01b,a	0.17 ± 0.10a,a	0.26 ± 0.06a,a	0.31 ± 0.06a,b	0.52 ± 0.20b,b
ethyl 9,12-octadecadienonate	<LOD	<LOD	0.09 ± 0.03b,a	0.03 ± 0.03a,a	0.04 ± 0.03a,a	0.33 ± 0.12b,b
ethyl 9,12,15-octadecatrienoate	<LOD	<LOD	<LOD	0.06 ± 0.05a,b	0.09 ± 0.05a,b	0.20 ± 0.10b,b
Σ ethyl esters C14−C18	**0.36 ± 0.11a,a**	**0.10 ± 0.01b,a**	**1.05 ± 0.19c,a**	**0.99 ± 0.20a,b**	**0.86 ± 0.18a,b**	**7.51 ± 1.47b,b**
isoamyl decanoate	0.04 ± 0.01a,a	0.05 ± 0.02a,a	0.05 ± 0.05a,a	0.02 ± 0.00b,b	0.04 ± 0.00a,b	0.04 ± 0.02a,a
isoamyl dodecanoate	<LOD	<LOD	<LOD	<LOD	<LOD	0.04 ± 0.01b,a
diethyl succinate	0.33 ± 0.04a,a	0.14 ± 0.05b,a	0.39 ± 0.04a,a	0.67 ± 0.16a,b	0.36 ± 0.03b,b	1.14 ± 0.12c,b

[a]Different letters before the comma in the same row indicate a significant difference ($p \leq 0.05$) with respect to the pear variety (comparison between Blanquilla, Conference, and Bartlett pear spirits). Different letters after the comma in the same row indicate a significant difference ($p \leq 0.05$) with respect to the distillation system (within the same pear variety). [b]LOD, detection limit. [c]Σ ethyl hexanoate, ethyl octanoate, ethyl decanoate, ethyl-2-*trans*-4-*cis*-decadienoate, ethyl dodecanoate.

content of each sample was determined using the Anton Paar DSA 5000 M density meter. On the basis of sensory analysis, the head fractions were defined as the first 75 mL of distillate. The heart fractions included the portions from 75 to 800 mL for Bartlett, from 75 to 900 mL for Blanquilla, and from 75 to 1200 mL for Conference. In all cases, the remainder was the tail fraction. The alcoholic yields of the heart fractions were 51.6, 56.7, and 55.0% for Bartlett, Conference, and Blanquilla pear distillates, respectively.

Analysis of the Distillates. The heart fractions were analyzed by direct injection of the rough distillate into a gas chromatograph with a flame ionization detector (GC-FID). Analyses were carried out using two different columns. A CP123 Wax-57 CB capillary column (Varian Medical Systems Barcelona, Spain; 50 m × 0.32 mm internal diameter (i.d.) × 0.2 μm in film thickness) on a CG Agilent 6890 (Agilent Technologies, Waldbronn, Germany) was equipped with a split/splitless injector with an electronic flow control (EFC), and a FID was used to evaluate the macroconstituents (methanol, longer chain alcohols, acetaldehyde, 1,1-diethoxyethane, ethyl acetate, ethyl lactate, 1-hexanol, isobutyraldehyde, 2-butanol, and allylic alcohol). The conditions have been reported in a previous publication.[11] The remaining compounds were separated using a Supelcowax 10 capillary column (30 m, 0.32 mm, 0.25 μm in film thickness; Supelco Inc., Bellefonte, PA, USA) in a CG Varian CP3900 (Varian Medical Systems, Barcelona, Spain), using the method described in López-Vázquez et al.[12] The analytes were identified by comparing their retention times to those of pure standards. To verify the FID dosage of some compounds, an Agilent 6890 gas chromatograph equipped with a mass spectrometric detector model 5973N was employed (Agilent Technologies). Samples were analyzed in triplicate.

Statistical Analysis. One-way ANOVA was applied to the data from the GC analysis, and means were compared by Fisher's least significant difference (LSD) test at $p \leq 0.05\%$ to assess whether the variety of pear or the distillation system led to any significant composition differences. The variables that showed significant differences were used in the PCA. All statistical analyses were performed with the SPSS statistical package (version 15.0, SPSS Inc., Chicago, IL, USA).

Sensory Analysis. The spirits were tested for flavor quality using order-of-preference tests. All heart fractions were diluted with Milli-Q-treated water (Millipore Corp., Bedford, MA, USA) to an ethanol content of 40% v/v. The panel was composed of 16 consumers with experience in tasting distillates. They were asked to separately evaluate the aroma and the taste of the spirits. The results were analyzed using the Friedman statistical test.[13]

RESULTS AND DISCUSSION

Fermentation. The initial sugar concentrations were 73.50, 53.25, and 94 g/L for the Blanquilla, Conference, and Bartlett juices, respectively. These were fermented for 6 days at 12 ± 1 °C. The alcoholic strengths were 4.28, 2.99, and 5.12 (% v/v) for the Blanquilla, Conference, and Bartlett varieties, respectively.

Table 3. Average Concentrations (g/hL pa) of Microconstituents (Minor Alcohols, Monoterpenols, and Other Compounds) Present in Distillates Obtained from the Blanquilla, Conference, and Bartlett Pear Varieties for Each Distillation Process (Copper Charentais Alembic and Packed Column)[a]

	Copper Charentais alembic			Packed-column		
compound	Blanquilla	Conference	Bartlett	Blanquilla	Conference	Bartlett
Alcohols						
trans-3-hexen-1-ol	0.08 ± 0.06a,a	0.08 ± 0.04a,a	<LOD[b]	0.07 ± 0.01a,a	0.09 ± 0.02a,a	0.03 ± 0.03b,b
cis-3-hexen-1-ol	1.18 ± 0.04a,a	0.69 ± 0.14b,a	0.05 ± 0.04c,a	0.45 ± 0.05a,b	0.79 ± 0.06b,a	0.08 ± 0.02c,a
trans-2-hexen-1-ol	0.19 ± 0.06a,a	0.13 ± 0.06b,a	<LOD	0.09 ± 0.01a,b	0.15 ± 0.02b,a	0.01 ± 0.01c,a
1-pentanol	0.03 ± 0.01a,a	0.53 ± 0.20b,a	0.02 ± 0.01a,a	0.39 ± 0.04a,b	0.38 ± 0.04a,a	0.35 ± 0.03a,b
1-heptanol	0.02 ± 0.02a,a	0.03 ± 0.04a,a	0.02 ± 0.01a,a	0.03 ± 0.01a,a	0.02 ± 0.01a,a	0.03 ± 0.02a,b
1-octanol	0.17 ± 0.01a,a	0.31 ± 0.13b,a	0.18 ± 0.10a,a	0.66 ± 0.05b,b	0.30 ± 0.03a,a	0.25 ± 0.06a,a
1-nonanol	0.18 ± 0.03a,a	0.25 ± 0.13b,a	<LOD	0.25 ± 0.02a,b	0.22 ± 0.02a,a	0.07 ± 0.02b,b
1-decanol	0.04 ± 0.01a,a	0.10 ± 0.01b,a	0.07 ± 0.03a,a	0.24 ± 0.03a,b	0.13 ± 0.03b,a	0.18 ± 0.12ab,b
benzylic alcohol	0.60 ± 0.11a,a	1.20 ± 0.14b,a	0.31 ± 0.04c,a	0.68 ± 0.12a,a	1.39 ± 0.04b,a	0.52 ± 0.20a,b
2-phenylethanol	1.93 ± 0.13a,a	1.64 ± 0.22a,a	1.02 ± 0.27b,a	1.11 ± 0.20a,b	0.75 ± 0.12b,b	1.11 ± 0.06a,b
Σ linear alcohols (C7−C10)*	**0.41 ± 0.02a,a**	**0.69 ± 0.10b,a**	**0.27 ± 0.08c,a**	**1.18 ± 0.04a,b**	**0.67 ± 0.03b,a**	**0.53 ± 0.09b,b**
Other Compounds						
furfural	0.20 ± 0.04a,a	0.27 ± 0.04a,a	0.29 ± 0.03a,a	0.14 ± 0.01a,a	0.18 ± 0.00a,a	1.14 ± 0.04b,b
3-ethoxy-1-propanol	<LOD	<LOD	0.07 ± 0.02b,a	<LOD	0.02 ± 0.01a,b	0.09 ± 0.01b,a
3-hydroxy-2-butanone	3.11 ± 0.59b,a	0.86 ± 0.35a,a	0.81 ± 0.05a,a	0.96 ± 0.14a,b	0.83 ± 0.29a,a	0.38 ± 0.13b,b
Monoterpenols						
trans-furan linalool oxide	0.09 ± 0.03a,a	0.08 ± 0.01a,a	0.07 ± 0.03a,a	0.10 ± 0.02a,a	0.11 ± 0.02a,a	0.20 ± 0.05b,b
cis-furan linalool oxide	0.04 ± 0.02a,a	0.07 ± 0.06a,a	0.06 ± 0.04a,a	<LOD	0.06 ± 0.02a,a	0.44 ± 0.15b,b
linalool	0.07 ± 0.02a,a	0.26 ± 0.08b,a	0.06 ± 0.02a,a	0.07 ± 0.01b,a	0.28 ± 0.03a,a	0.27 ± 0.10a,b
citronellol	0.05 ± 0.04a,a	0.03 ± 0.00b,a	0.04 ± 0.01ab,a	0.05 ± 0.01a,a	0.03 ± 0.01b,a	0.07 ± 0.05c,b
geraniol	0.05 ± 0.01a,a	0.09 ± 0.06b,a	0.02 ± 0.06c,a	0.05 ± 0.02a,a	0.04 ± 0.02a,b	0.32 ± 0.06b,b
hotrienol	0.05 ± 0.05a,a	0.06 ± 0.03b,a	0.04 ± 0.01c,a	0.06 ± 0.01a,a	0.05 ± 0.00a,a	0.09 ± 0.01b,b
Σ monoterpenols	**0.34 ± 0.03a,a**	**0.59 ± 0.07b,a**	**0.30 ± 0.08a,a**	**0.32 ± 0.06a,a**	**0.57 ± 0.07b,a**	**1.40 ± 0.34c,b**

[a]Different letters before the comma in the same row indicate a significant difference ($p \leq 0.05$) with respect to the pear variety (comparison between Blanquilla, Conference, and Bartlett pear spirits). Different letters after the comma in the same row indicate a significant difference ($p \leq 0.05$) with respect to the distillation system (within the same pear variety). [b]LOD, detection limits. [*]Σ 1-heptanol, 1-octanol, 1-nonanol, 1-decanol.

Major Volatile Compounds in Pear Distillates. Table 1 shows the average concentrations of macroconstituents and the ANOVA test results for the spirits grouped according to pear variety and distillation system. In general, the impact of the distillation system was higher than the impact of variety on the macroconstituent composition of the pear distillates produced in this study. According to Table 1, the ethanol contents of the respective heart fractions were higher in packed-column distillates, except for those obtained from the Bartlett variety. In contrast, methanol concentrations were lower in the packed-column distillates, except for the Bartlett variety, confirming the findings of previous studies.[8−10] With regard to pear variety, methanol content was significantly higher in the distillates of Blanquilla pears. The average concentrations of ethyl acetate in our distillates ranged between 34.7 and 268.10 g/hL of pure alcohol (pa). The alembic distillates contained levels much lower than the perception threshold (180 g/hL pa, according to Soufleros et al.[2]), whereas column distillates contained levels close to the perception threshold. The range of acetaldehyde concentrations was much lower than the perception threshold of 30−50 g/hL pa proposed by Odello et al.[14] In addition, the distillates produced by alembic distillation had lower amounts than the column distillates. With regard to pear variety, the Blanquilla distillates showed the highest concentrations of acetaldehyde.

Pear variety had a more significant effect on 1,1-diethoxyethane content than the distillation system. Blanquilla distillates contained 2−3 times more 1,1-diethoxyethane than distillates made from the other varieties. The longer chain alcohol composition was also significantly different between distillates from different varieties, except for 3-methyl-1-butanol. The total concentration of longer chain alcohols is higher in the Bartlett pear distillates, mainly due to the levels of 2-methyl-1-propanol (isobutanol) and 2-methyl-1-butanol. The concentrations of longer chain alcohols in Blanquilla and Conference spirits were similar to those reported in previous studies.[7−10] Postel et al.[15] proposed the use of the concentration ratios between [3-methyl-1-butanol]/[2-methyl-1-butanol] and [2-methyl-1-butanol + 3-methyl-1-butanol]/[2-methyl-1-propanol] to characterize different types of wines and spirits. In our distillates, the first ratio applied to the Conference and Blanquilla varieties had values in the range of 3.0−3.3, whereas the ratio for the Bartlett variety was 2.5. In turn, the second ratio had values close to 3 for the Bartlett distillates and around 3.6 for the Blanquilla and Conference distillates. Thus, the use of these ratios would distinguish Bartlett distillates from those of the Blanquilla and Conference varieties.

All of the distillates contained low concentrations (<62 g/hL pa) of ethyl lactate, suggesting that bacterial spoilage did not occur during fermentation.[16] The smell of this compound is similar to a mixture of sour milk and raspberry and can be unpleasant at concentrations >150 g/hL pa.[17] Concentrations of 1-hexanol in our pear distillates ranged between 1.65 and 9.80 g/hL pa, below the level at which an unpleasant herbal smell is noticeable.[12] The impact of pear variety on 1-hexanol concentrations was more significant than the impact of the distillation system. Both Bartlett distillates possessed concentrations <2.5 g/hL pa, which, according to Galy et al.,[18] are associated with herbaceous and rancid aromas. However, the Blanquilla and Conference distillates contained 1-hexanol concentrations above this threshold. In turn, isobutyraldehyde concentrations were affected by both pear variety and distillation system. Blanquilla and Conference distillates possessed higher concentrations than Bartlett distillates; however, the concentration of isobutyraldehyde in the packed-column Bartlett distillate was higher than that of Blanquilla and Conference alembic distillates.

Minor Volatile Compounds in Pear Distillates. The composition of microconstituents was mostly defined by the distillation system. Most microconstituent concentrations observed in the Bartlett alembic distillates were similar to those observed in the packed-column distillates from the Blanquilla and Conference varieties. For example, the levels of acetates of longer chain alcohols, which supply the distillates with apple−banana fruity scents, are similar in these distillates (Tables 2 and 3).[19] The major compound in this family, isoamyl acetate, was present in high concentrations in Bartlett distillates, although its concentrations in Blanquilla and Conference column distillates were similar to that in the Bartlett alembic distillate. Similarly, both pear variety and distillation system affected the concentrations of high molecular weight ethyl esters (Table 2). Nevertheless, when a packed column was used, the concentrations in Blanquilla and Conference distillates were similar to those in the alembic Bartlett distillate. Monoterpenols are regarded as positive aromas because they supply floral nuances.[20] In alembic distillates, the Conference variety had the highest monoterpenol concentration, whereas the Bartlett column distillate had concentrations almost 5 times higher than that of the Blanquilla variety (Table 3). Hence, both pear variety and distillation system were important in this case as well.

Other minor compounds also proved to be strongly affected by the distillation system. Concentrations of diethyl succinate (Table 2) were 2 times higher in column distillates than in alembic distillates for the Blanquilla and Conference varieties and 5 times higher for the Bartlett variety. Similarly, the concentration of furfural (Table 3) in the column Bartlett distillate was 4 times higher than the other distillates. Moreover, Blanquilla and Conference column distillates showed the smallest concentrations of furfural. In turn, the Blanquilla alembic distillate possessed the highest concentration of 3-hydroxy-2-butanone, whereas the concentration in the Blanquilla column distillate was similar to that of the Conference and Bartlett alembic distillates (Table 3).

Other families of microconstituents were less affected by the distillation system (see Table 2). Low molecular weight ethyl esters contribute fruity aromas,[2] and ethyl-2-*trans*-4-*cis*-decadienoate is particularly important because it gives pear distillates their characteristic and pleasant pear-like aroma.[5] These esters are much more concentrated in Bartlett distillates than in distillates of the other varieties, and they are more concentrated in column distillates than in alembic distillates. However, Blanquilla and Conference column distillates do not have levels as high as those found in the Bartlett alembic distillate.

In this study, ethyl octanoate was the major ester in the Blanquilla and Conference varieties, whereas ethyl decanoate was most abundant in the Bartlett pear distillates. The concentration of ethyl decanoate commonly found in Bartlett pear brandy is between 1.0 and 1.5 g/hL pa.[21] In this study, the ethyl decanoate levels for the Blanquilla and Conference varieties were below this value, whereas the concentration for the Bartlett variety was greater.

Linear alcohols from C7 to C10 are rather fruity−floral compounds derived from the decomposition of fatty acids during fermentation.[19] Our results show that pear variety had a strong influence on the concentrations of these alcohols. Conference distillates contained similar concentrations from both distillation systems (Table 3). Nevertheless, for the Bartlett and Blanquilla varieties, the distillates produced with the column possessed higher concentrations of linear alcohols than the distillates obtained with the alembic. The same trend is observed for benzylic alcohol (Table 3). When Conference pears were distilled in the alembic, the levels of 1-pentanol were significantly higher than in the column distillate. However, all column spirits contained similar amounts of 1-pentanol (Table 3).

C6 compounds, such as 1-hexanol, *cis*-3-hexen-1-ol, and *trans*-2-hexen-1-ol, contribute to herbaceous notes in the spirit aroma. *cis*-3-Hexen-1-ol was the most abundant hexenol in all pear distillates, and concentrations of this compound were higher in distillates from the Blanquilla and Conference varieties than from Bartlett pears (Table 3). C6 alcohols in concentrations >12 mg/L contribute fatty notes to the aroma of brandies.[22] However, none of the levels in our distillates surpassed this threshold. In addition, the distillation system influenced only the *cis*-3-hexen-1-ol concentration in the Blanquilla distillates: the levels were higher for the spirits produced in alembic.

With regard to minor alcohols, 2-phenylethanol was present at the highest concentration (Table 3). It is produced by yeast during fermentation and is derived from L-phenylalanine. In its pure form, it has a pleasant aroma resembling that of rose.[23] Therefore, it is regarded as a favorable compound in spirits when present at low concentrations. This compound is also a typical tail product; therefore, a high concentration in the heart fraction is indicative of bad heart/tail cut supervision.[16] The levels found in the distillates produced in this study (<2 g/hL pa) indicate that the tail fraction was well separated.

PCA. PCA was separately applied to the heart fractions of the distillates obtained by both systems of distillation. The concentrations of the volatile compounds with significant differences ($p < 0.05$) by ANOVA were used. The compounds with concentrations lower than the detection limits (isobutyl acetate, butyl acetate, hexyl acetate, ethyl hexanoate, ethyl octadecanoate, ethyl 9,12-octadecadienoate, ethyl 9,12,15-octadecatrienoate, isoamyl dodecanoate, *trans*-3-hexen-1-ol, *trans*-2-hexen-1-ol, 1-nonanol, 3-ethoxy-1-propanol, and *cis*-furan linalool oxide) were not considered. In the alembic distillates, principal component 1 (PC1) accounted for 61.31% of the total variance, whereas principal component 2 (PC2) accounted for 30.59%. In the column distillates, PC1 explained 64.55% and PC2 25.20% of the variance. Figure 1 represents the plot of the two main components (PC1 vs PC2). In this figure, three clusters of samples are clear, and the data plot is more compact for the alembic cluster than for the column cluster. This supports our previous observation that alembic distillation is more reproducible.[10] Tables 1 and 2 of the Supporting Information PCA show the loading matrix of compounds for the distillations in the alembic and the column, respectively.

In both cases, PC1 showed good separation between Bartlett spirits (right side) and the spirits of the other varieties (left side). In addition, PC2 mainly differentiated the Conference

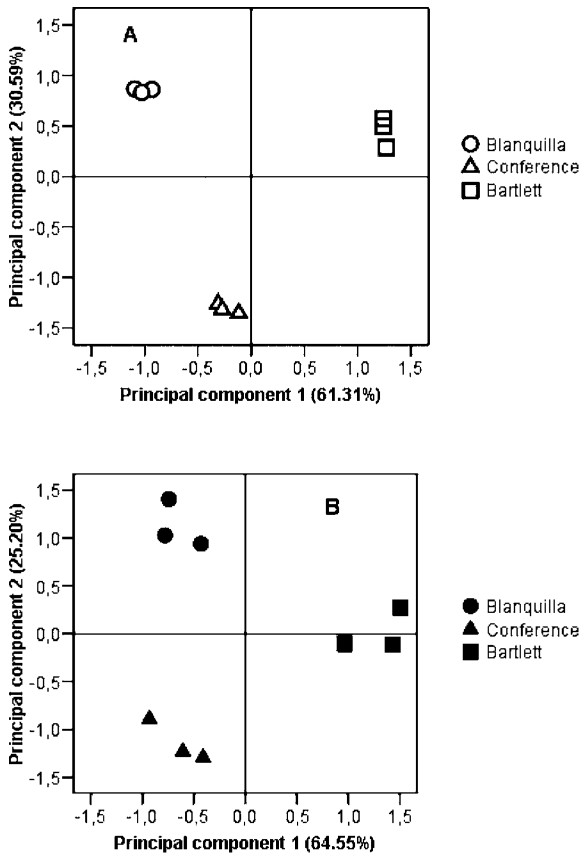

Figure 1. Principal component analysis of the volatile compound composition of the pear spirits: (A) PCA loadings of Blanquilla (○), Conference (△), and Bartlett (□) spirits distilled in a copper Charentais alembic; (B) PCA loadings of Blanquilla (●), Conference (▲), and Bartlett (■) spirits distilled in a packed column.

distillates (bottom) from those of the other varieties (top). For both distillation systems, PC1 was defined by almost the same class of compounds, mainly ethyl esters (ethyl-2-*trans*-4-*cis*-decadienoate, ethyl decanoate, ethyl dodecanoate, ethyl octanoate, ethyl tetradecanoate, and ethyl hexadecanoate), longer chain alcohols (2-methyl-1-butanol and 2-methyl-1propanol), C6 alcohols (1-hexanol and *cis*-3-hexen-1-ol), isoamyl acetate, and methanol. Most of these volatile compounds were desirable, and their concentrations in the Bartlett pear spirits were higher (except for the C6 alcohols and methanol, which were lower). In column distillations, PC1 was also characterized by higher levels of ethyl esters such as ethyl-2-*trans*-4-*cis*-decadienoate (0.992), ethyl decanoate (0.990), and ethyl dodecanoate (0.987). The recovery of these compounds in the heart fraction was always more effective in column distillations.

The compounds in alembic PC2 most representative of a pear variety were linear alcohols and monoterpenols (mainly linalool). PC2 separated the Conference alembic spirits from the other two, largely because of the higher concentrations of these compounds.

To determine whether the distillation system had any influence, a PCA was applied to the volatile compounds that had a significant difference (determined by ANOVA, $p < 0.05$) between the two distillation systems. These compounds were 2-phenylethanol, ethyl acetate, acetaldehyde, 1-hexanol, isobutryaldehyde, ethyl octanoate, ethyl decanoate, ethyl-2-*trans*-4-*cis*-decadienoate, ethyl dodecanoate, and diethyl succinate. The first two principal components (PC1 and PC2), which explained 56.65 and 25.92% of the variance, respectively (see Table 3 in the Supporting Information), are depicted in Figure 2. This figure shows that PC1 separated spirits mainly by the variety of pear, whereas PC2 separated them mainly as a function of the distillation system. Bartlett variety distillates differed from the rest because they had higher concentrations of ethyl esters, which contributed positively to PC1 (ethyl-2-*trans*-4-*cis*-decadienoate, ethyl decanoate, ethyl dodecanoate, and ethyl octanoate). Figure 2 also shows that the Blanquilla and Conference distillates were clustered together in PC1. On the other hand, isobutyraldehyde, ethyl acetate, acetaldehyde, and 2-phenylethanol were the compounds that contributed to PC2. The first three compounds presented positive values, whereas the value for 2-phenylethanol was negative. The spirits produced by column distillation were located in the positive quadrant of PC2, because they had higher concentrations of these first three compounds. Although significant differences were observed in the concentration of ethyl esters when the two methods of distillation were compared, especially for the Bartlett spirits (Table 2), these differences were not evident in the PCAs. Consequently, ethyl esters could only differentiate Bartlett spirits from the other two.

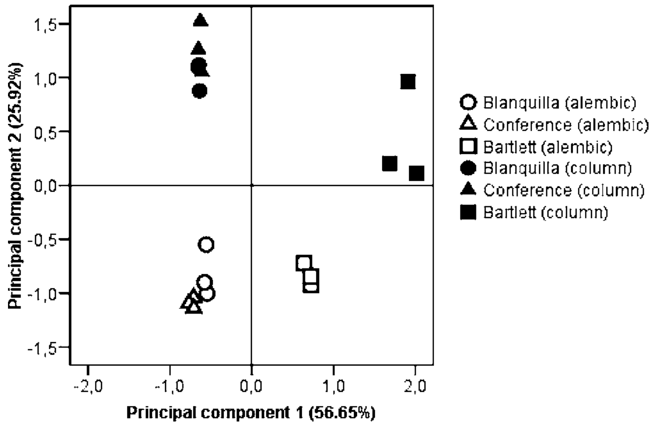

Figure 2. Principal component analysis of the volatile compound composition of the pear spirits (Blanquilla (○, ●), Conference (△, ▲), and Bartlett (□, ■) distilled in a copper Charentais alembic (open symbols) or in a packed column (solid symbols).

Sensory Analysis. Considering aroma, the three alembic pear spirits were not significantly different ($p < 0.05$). However, significant differences ($p < 0.05$) in taste were observed between the Bartlett pear spirit and the other two. In turn, a sensory analysis of the column spirits showed no significant differences in taste or aroma ($p < 0.05$).

The Bartlett variety was preferred when distilled in alembic because of its aromatic intensity, whereas the other alembic-distilled varieties did not have a sufficiently intense aroma. In contrast, for the column-distilled spirits, no significant differences were found. This could be due to the fact that the spirits distilled in the column had a significantly higher concentration of favorable aromatic compounds (C6−C12 ethyl esters) that imparted a fruitier aroma (compared to the alembic-distilled spirits).

From the volatile compounds identified, it was possible to differentiate the spirits by pear variety and distillation method. The statistical analyses (ANOVA and PCA) suggested that the major difference in aroma among these three varieties could be attributed to the variation in the intensity of fruity and floral attributes, principally due to ethyl esters (C6−C12) and acetates (especially the isoamyl acetate content) that were present in higher concentrations in the Bartlett pear spirits. The concentrations of C6 alcohols (1-hexanol and *cis*-3-hexen-1-ol) were lower in Bartlett pear spirits, which minimized the herbaceous aromas. Ethyl esters (C6−C12) also contributed to the differences found between the distillation methods. The spirits obtained with the distillation column had significantly higher concentrations of these compounds. Finally, the sensory analysis confirmed that among the alembic-distilled pear spirits, the Bartlett pear tasted better, whereas column-distilled spirits were indistinguishable in terms of taste and aroma. Our future research will focus on developing operating policies for packed-column distillation to intensify the fruit aromas of Blanquilla and Conference varieties.

■ ASSOCIATED CONTENT

Supporting Information

Principal component analysis data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

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■ ABBREVIATIONS USED

EFC, electronic flow control; GC-FID, gas chromatograph with a flame ionization detector; LSD, Fisher's least significant difference; PCA, principal component analysis.

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