

Production and Composition of Cider Spirits Distilled in “Alquitara”

ROBERTO RODRÍGUEZ MADRERA,* BELÉN SUÁREZ VALLES, ANA GARCÍA HEVIA,
OVIDIO GARCÍA FERNÁNDEZ, NORMAN FERNÁNDEZ TASCÓN, AND
JUAN JOSÉ MANGAS ALONSO

Área de Tecnología de los Alimentos, Servicio Regional de Investigación y Desarrollo
Agroalimentario (SERIDA), E-33300 Villaviciosa (Asturias), Spain

The capacity of alquitara (a traditional distillation system) to produce cider brandies is evaluated. To do so, the chemical composition of 12 fractions obtained during the distillation process and the cider brandies obtained from five ciders were analyzed (alcohol strength, methanol, volatile substances, furfural, and metals), taking into account European and Spanish legislation. During the course of distillation, an important increase in methanol, furfural, 2-phenylethanol, and metals in the last fractions was observed, while fusel oils were more abundant in the first fractions collected. Only acetaldehyde behaved differently, showing a minimum concentration in the middle fractions that might be explained by its formation on the surface of alquitara. On the other hand, the final distillates obtained by means of this method complied with the considered regulations. Worth highlighting in this regard are the low levels of a potential toxin such as methanol, as well as the detection of a constant ratio for methanol, ethanol, and fusel oil for the pairs of cider/spirits analyzed, which could be interpreted as an indication of good uniformity in the distillation system and method, thus guaranteeing product quality.

KEYWORDS: Cider; distillate; cider brandy; volatile compounds; metals; GC

INTRODUCTION

Cider spirits are popular alcoholic beverages in countries where cider—apple production is relevant. Asturias (Northern Spain) is the main cider-producing region in Spain, with a long-standing tradition in the production of cider distillates, known as “Aguardiente de sidra de Asturias”, as recognized by the European Community in Annex II of Council Regulation (EEC) 1576/89 for geographical designations.

There are several common factors in the production of distillates that are responsible for the sensorial characteristics appreciated in commercial products, such as raw material, distillation, and maturation in wood (when this takes place). Thus, although all spirits are basically constituted by a mixture of ethanol—water, what is responsible for the characteristics of each product are a large number of minor compounds. In the case of the unaged distillate, these are volatile substances present in the fruit, formed either during fermentation or generated during distillation. In this respect, it is well-known that the levels of methanol in alcoholic beverages are related to the pectic substances present in fruit, as well as to the presence of pectin-methylesterases with the capacity to degrade it. Likewise, an intense enzymatic treatment employed in manufacturing apple juice concentrate for cider production results in higher levels of methanol than when fresh must is employed (1). Furthermore,

the higher alcohols formed from amino acids during fermentation (2) are also affected by the yeast strains employed and the fermentation temperature of ciders (3). Finally, off-flavors in Calvados (French cider brandy) such as acrolein (4) could be formed during cider maturation by microorganisms (5).

The aromatic profile of fermented beverages will especially mark the characteristics of commercial spirits; however, the chosen distillation system also plays an important role in the final composition of the distillate. For instance, the extended length of heating in double distillation systems produces cider brandies with higher contents in furfural due to degradation of residual sugars (6), thus imparting a caramel aroma. The composition of distillates likewise varies depending on the material employed in the construction of the distillation system. Cardoso et al. (7) detected lower levels of methanol in distillates obtained using columns filled with porcelain than in distillates using columns filled with copper or aluminum.

On the other hand, traditional practices in the production process increase consumer approval of products. In this sense, alquitara is a traditional distillation system sometimes used in the production of Spanish marc distillates (8). Alquitara is carried out in copper vessels, which consist of a pear-shaped pot at the top coupled to a recipient filled with cool water for condensing the alcoholic vapor.

In this paper, we study the performance of the alquitara distillation system employed as a novel application for obtaining distillates from cider. To do so, we carried out a preliminary

* To whom correspondence should be addressed. Tel: 34-985890066. Fax: 34-985891854. E-mail: rrodriguez@serida.org.

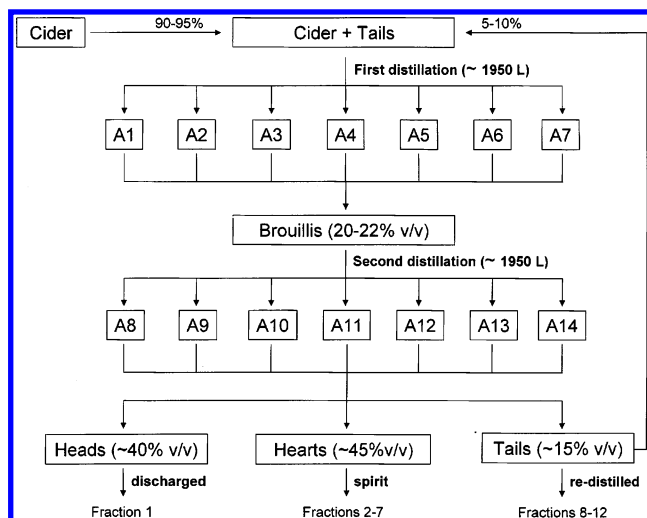


Figure 1. Scheme of distillation in alquitaras. A1–A14, alquitaras with 350 L of total capacity; F1–F12, fractions recovered during the second distillation.

analysis of the chemical composition during the distillation process and subsequently performed a chemical evaluation of the cider spirits thus obtained. Analyses were carried out according to European Union regulation parameters (Council Regulation 1576/89) and Spanish legislation (Real Decreto 1416/82). Volatile compounds were analyzed by gas chromatography with flame ionization detection (GC-FID) and metals (zinc, copper, and lead) by atomic absorption spectroscopy.

MATERIALS AND METHODS

Raw Material. Five ciders (A–E) produced by means of traditional technology were prepared from the juice of a mixture of cider apples with different sensory properties endowing the resulting juice with an overall acidic nature. The mixtures of apples were milled with a hammer mill, pressed slowly for 2 days, and fermented by wild microflora.

Distillation. The system used to distill the ciders consisted of two batteries of seven alquitaras each one. The capacity of the alquitaras, built in copper, was 350 L, resulting in a total volume of 2450 L per battery. The head of each alquitara was cooled with water at 15 °C to facilitate condensation of the cider spirit. Gas burners were used as the heat source.

Distillation took place in two steps. First, ciders were distilled in a preconcentration step until obtaining an intermediate product with an alcohol strength of 20–22% (v/v). Subsequently, distillation of this product, traditionally split into three fractions (heads, hearts, and tails), gave rise to the final product. Heads were discarded, tails were included in subsequent first distillations, and hearts were destined for human consume (**Figure 1**).

In order to study the distillation process of cider in alquitara, the distillate obtained in the second distillation of cider A was divided into 12 fractions (**Figure 1**) with volumes ranging between 4 and 225 L (**Table 3**). To study the chemical composition of cider spirits produced in alquitara, the distillates obtained from each cider were analyzed.

Chemical Analysis. GC. Volatile compounds in ciders and spirits were analyzed in a Hewlett-Packard model 6890 gas chromatograph equipped with a FID system. In both cases, the microfiltered samples were directly injected into the chromatograph (1 μ L) and quantitations were performed according to an external standard method. Standards used were of analytical quality, with at least 99% purity, and were purchased from Sigma-Fluka-Aldrich (Madrid, Spain), Merck (Darmstadt, Germany), and Panreac (Barcelona, Spain). The specific conditions of each method were as follows.

Ciders. Major volatiles in cider were analyzed using a FFAP semicapillary column (TR-FFAP 30 m \times 0.53 mm i.d.; phase thickness, 1.0 μ m) supplied from Tecknokroma (Barcelona, Spain). Injection was carried out in splitless mode (1 min) employing He as the carrier gas

Table 1. Experimental Conditions for the Determination of Cu, Zn, and Pb in Samples

element	wavelength (nm)	linear range (mg/L)	dilution range
Cu	324.8	0.5–5.0	1/2 ^a
Zn	213.9	0.05–1.0	no dilution
Pb	283.3	0.003–0.100	no dilution

^a Diluted with ethanol 40% v/v.

Table 2. HGA 400 Graphite Furnace Parameters Used for Analysis of Pb in Samples^a

step	temperature (°C)	ramp (s)	hold (s)
1	80	5	15
2	100	5	15
3	700	5	15
4	1800	1	6 ^b
5	2500	1	1
6	20	5	10

^a Argon flow rate, 300 mL/min; injection volume, 20 μ L; and spectral bandwidth, 0.7 nm. ^b Gas stop for reading.

at 10 mL/min. The temperature gradient was as follows: oven temperature 40 °C isotherm for 5 min, followed by a linear increase of 4 °C/min until 60 °C. This temperature was raised to 220 °C at a rate of 10 °C/min. Injector and detector temperatures were 240 and 275 °C, respectively.

Distillates. The separation of major volatiles was carried out on a PEG capillary column (TR-Meta WAX, 30 m \times 0.25 mm i.d.; phase thickness, 0.5 μ m) supplied by Tecknokroma (Barcelona, Spain). Chromatographic conditions were as follows: oven temperature, initial isotherm at 60 °C (10 min), raised to 220 °C at a rate of 8.0 °C/min, and final isotherm of 220 °C (15 min); the injector temperature was 260 °C, and the detector temperature was 275 °C; He was used as carrier gas, initially at 0.6 mL/min (5.2 min) and raised to 1.5 mL/min at a rate of 3 mL/min/min. Injection was carried out in split mode (1/20), and the injection volume was 1 μ L.

Atomic Absorption. A Perkin-Elmer (Perkin-Elmer Corp., Norwalk, CT) 3030B atomic absorption spectrometer was used to quantitate copper and zinc using flame atomic absorption spectrometry (FAAS). The 3030B atomic absorption spectrometer fitted to a Perkin-Elmer HG-400 graphite furnace and a Perkin-Elmer AS-40 automatic injector was employed to determine lead by the technique of graphite furnace atomic absorption spectrometry (GFAAS). Experimental conditions for metal determination are shown in **Table 1**. GFAAS temperature programs for lead are presented in **Table 2**. Copper, zinc, and lead were used to prepare a stock solution of ~1000 mg/L following Perkin-Elmer guidelines. The remaining reagents were of analytical reagent grade. Milli-Q treated water (Millipore Corp., Bedford, MA) was used throughout. The working solutions were prepared by suitable dilution from the corresponding stock solution with 40% v/v ethanolic solution.

Samples were diluted to obtain suitable read-outs for proper quantitation. Linear concentration intervals for each element ranged between the detection limit (in concentration units) and a value, which is less than or equal to the maximal concentration, as recommended in the Perkin-Elmer guidelines. All elements were determined from external calibration by matching the alcoholic content in the samples and the standards.

Other Analyses. Density, pH, alcoholic strength, total acidity, and volatile acidity were determined following the methodology described in the Official Analytical Methods AOAC (9). Alcoholic strength in distillates was determined by direct measurement in an Anton Paar DMA 500 Density Meter (Graz, Austria).

RESULTS AND DISCUSSION

Distillation Process. The moderate alcoholic strength of ciders requires a two-step distillation process (preconcentration

and redistillation), as is usual for other raw materials distilled in pot stills. The results of the analyses of the 12 fractions obtained during the second distillation of cider A are shown in **Table 3**.

The European Community Council Regulation (EEC 1576/89) establishes the maximum permissible levels for ethanol and methanol at 86% (v/v) and 1000 g/hL of absolute alcohol (AA), respectively. This regulation further specifies a minimum alcoholic strength by volume for release for human consumption in the European Union of 37.5% (v/v).

The concentration of methanol increases during distillation to decrease notably in the last fraction recovered. This behavior was also observed by the authors in the distillation of ciders using a rectifying column (10) and can be explained by the high solubility of methanol in water. Although its boiling point is lower than that of ethanol, strong hydrogen bonding retains methanol in the water. Nonetheless, the levels of methanol detected in the 12 fractions analyzed, ranging from 11.6 to 87.7 g/hL AA (**Table 3**), were much lower than established European limits.

The alcoholic content of the fractions was not as high as that obtained with other distillation systems in any case. This is due to the poor reflux generated during distillation as a consequence of the small surface at the top of the alquitara; the absence of this phenomenon does not allow the recondensation of water into the pot and the enrichment of volatile fraction in ethanol. This is a disadvantage of the alquitara system, as an important part of volume distillates in this step, more than 50% (375 L from fractions 10 to 12), must be redistilled to achieve a cider spirit or cider brandy with the minimum alcoholic strength required according to the aforementioned regulation, thus increasing energy and economic costs.

Acetaldehyde showed a particular behavior, showing a minimum in fraction 9. Although its low boiling point (21 °C) makes acetaldehyde a typical product of heads (11), this compound is also present in the tails (fractions 10–12) as a consequence of its miscibility in water and its formation during the course of distillation (12).

The presence of acetal in fresh distillates may be due to its formation during the fermentative process or during the course of distillation via the reaction between acetaldehyde and ethanol. From the data obtained, this compound is formed during distillation, since it was not detected in the original ciders. The miscibility of acetal in ethanol and its low solubility in water justify the higher concentration of this compound in the first fractions collected and its progressive decrease, despite the relatively high boiling point (102.7 °C).

The other aldehyde detected was furfural. This compound is more abundant in the last fractions as a consequence of its high boiling point (160 °C) (10, 11). On the other hand, the contamination of fraction 1 with tails from a previous distillation seems the reason for a higher level of this compound in this fraction than in the next.

Higher alcohols are the most important group of volatile substances. The European Community Council Regulation (EEC 1576/89) established the minimum content in volatile substances for cider spirit or cider brandies at 200 g/hL AA. In the fractions recovered for direct consumption (heads, fractions 2–9), this minimum content required is covered by the exclusive presence of 3-methyl-1-butanol, usually the higher alcohol in cider distillates (1, 4, 13). It should further be noted that the values for total alcohols in all of the collected fractions were higher than the minimum requirement. Thus, the use of this distillation

Table 3. Chemical Composition of Fractions Collected during Distillation in Alquitara of Cider A^a

fraction	alcoholic strength ^{**}	volume [*]	acetaldehyde ^{***}	acetal ^{***}	ethyl acetate ^{***}	methanol ^{***}	2-butanol ^{***}	1-propanol ^{***}	2-methyl-1-propanol ^{***}	1-o ^{***}	1-butanol ^{***}	2-methyl-1-butanol ^{***}	3-methyl-1-butanol ^{***}	furfural ^{***}	2-phenyl-ethanol ^{***}	Cu ^{****}	Zn ^{****}	Pb ^{****}	pH	
F1 ^b	39.9	4.0	35.6	10.8	165.8	53.2	19.9	52.0	56.5	21.5	10.3	76.0	385.2	2.3	13.9	4.52	ND	0.09	4.15	
F2 ^c	55.6	21.4	43.0	16.9	210.2	56.9	19.4	54.4	53.3	22.8	10.2	67.3	349.8	1.8	10.9	4.05	ND	0.01	4.32	
F3 ^d	54.0	26.0	34.3	15.1	130.8	57.0	16.4	51.2	45.3	22.9	9.4	56.7	303.8	1.6	13.4	4.19	ND	0.01	4.31	
F4 ^c	51.5	29.7	30.8	15.9	107.4	61.1	15.3	50.9	42.1	24.0	9.2	52.2	283.8	1.6	16.1	4.48	ND	0.01	4.16	
F5 ^c	49.7	29.7	28.7	15.4	98.2	63.1	14.6	50.4	40.2	24.4	8.9	49.4	270.0	1.6	18.4	4.93	ND	0.01	4.17	
F6 ^c	47.1	24.5	24.6	13.3	76.6	63.5	13.3	48.2	36.5	24.3	8.4	44.8	247.7	1.6	21.2	5.24	ND	0.01	4.14	
F7 ^c	45.0	25.4	24.6	12.8	75.1	66.8	13.0	48.5	35.6	25.1	8.3	43.3	240.9	1.6	23.5	5.64	ND	0.02	4.05	
F8 ^c	42.5	26.1	19.9	9.4	51.3	63.5	11.2	43.7	30.6	23.8	7.4	37.3	209.8	1.6	27.5	5.97	ND	0.03	3.97	
F9 ^c	37.6	110.0	19.3	7.4	42.7	69.7	10.5	43.9	28.6	25.5	7.3	34.7	196.7	1.8	35.1	6.27	ND	0.05	3.81	
F10 ^d	27.2	80.0	24.8	4.7	36.4	80.1	8.0	39.3	21.3	26.9	6.0	25.3	145.7	2.1	61.2	6.92	0.04	0.21	3.58	
F11 ^d	20.7	70.0	24.9	2.9	25.2	87.7	6.6	36.3	17.2	28.1	5.3	20.3	116.9	2.5	90.3	7.47	0.04	0.11	3.42	
F12 ^d	12.3	225.0	41.5	2.4	32.9	11.6	5.1	31.8	12.4	31.4	4.4	15.0	80.6	3.4	198.5	7.03	0.06	0.30	3.22	
boiling point ^e	78		20.8	102.7	77	67.4	99.5	97.2	108	96–97	116	128	130	160	220					
solubility in ethanol ^e			m	m	m	m	m	m	m	m	m	m	m	VS	m					
solubility in water (%) ^e	m		m	m	5	10	8	m	5	m	9	4	2	9	2					

^a, expressed in liters; ^{**}, expressed in % (v/v); ^{***}, expressed in mg/100 mL of AA; ^{****}, expressed in mg/L; and ND, not detected. ^b Heads. ^c Hearts. ^d Tails. ^e Data from Windholz, M., Budavari, S., Blumenthal, R. F., Otterbein, E. S., Eds. *The Merck Index*, 10th ed.; Merck & Co., Inc.: Rahway, NJ, 1983; m, miscible; VS, very soluble.

system with Asturian cider should be adequate, at least in this regard.

The evolution of these compounds in the course of distillation was subjected to two profiles clearly marked, generally in accordance to their solubility in water. On the one hand, alcohols with a lower solubility in water, namely, 2-butanol, 2-methyl-1-propanol, 1-butanol, 2-methyl-1-butanol, 3-methyl-1-butanol, and 2-phenylethanol, substantially decrease in concentration during the process, with the exception of 2-phenylethanol, which increases. This may be explained by its high boiling point (220 °C), as observed by other authors (11). On the other hand, alcohols that are miscible in water (1-propanol and 2-propen-1-ol) decrease more slowly during the distillation process (1-propanol) or even increase in the tail fractions (2-propen-1-ol).

Ethyl acetate is the main ester described in cider distillates and may be formed during fermentation or during distillation by esterification of acetic acid with ethanol. Its low boiling point (77 °C) and minor solubility in water (10%) make it a typical product of first fractions during distillation, in this case, fractions 1–7 (total volume 160.7 L), which explains the 24% of total volume distillate, accounting for 50% of the total ethyl acetate recovered during distillation.

Spanish legislation (Real Decreto 1908/84) establishes the limits of zinc and copper in spirits at 10 mg/L of finished product and 1 mg/L for lead. In all cases, it can be stated that their levels increase during the course of distillation. This could be a consequence of a higher level of acids present in the last fractions, as reflected by the lower pH of later fractions (Table 3), which could favor the solubility of metals in the distillate. On the other hand, the higher concentration of copper and lead in the first fraction than in the second could be explained by the contamination of fraction 1 with a small portion of tails, as it was commented for furfural.

Cider Distillates. To obtain a better knowledge of this distillation system, five cider spirits produced according to the methodology presented above were analyzed. The chemical composition of these spirits and their corresponding ciders are given in Tables 4 and 5, respectively.

The methodology employed in the distillation with alquitara is adequate, since it allowed spirits to be obtained with a content in ethanol higher than 37.5% (v/v) (EEC Regulation 1576/89).

On the other hand, as methanol is formed from pectin by the action of pectin-methylesterases, its presence should be related to the raw material. In this respect, the results obtained from this distillation system for cider distillates are in accordance with other spirits obtained from cider (1, 4, 13), showing values clearly below the maximum content of 1000 g/hL of AA in all cases, around 1/11. It should further be pointed out that the analyzed samples presented a similar (methanol in spirit)/(methanol in cider) ratio of around 6–8, which could allow us to estimate the content of this potential toxin prior to distillation. On the other hand, because spirit quality could be established according to cider quality and methodology used in distillation, the constant ratio for ethanol, methanol, and fusel oils for all cider/spirit pairs could be interpreted as indicating a good capacity of alquitara to guarantee the product quality.

The concentrations of acetaldehyde and acetal showed two remarkable facts: on the one hand, the high levels of these compounds in spirits in relation to the low concentration in ciders, and on the other, the similar concentrations in the studied spirits (ranging from 25 to 38 of total acetaldehyde). A reasonable explanation for these findings may lie in the formation of acetaldehyde during distillation on the copper surface, as observed by Claus and Berglund (12), favored by

Table 4. Chemical Composition of Cider Spirits^a

cider spirit	alcoholic strength*	acetaldehyde**	acetal**	ethyl acetate**	methanol**	2-butanol**	1-propanol**	2-methyl-1-propanol**	2-propen-1-ol**	1-butanol**	2-methyl-1-butanol**	3-methyl-1-butanol**	furfural**	2-phenylethanol**	Zn***	Cu***	Pb***
A	46.6	33.9	14.0	89.3	62.6	12.4	45.6	35.4	23.8	8.0	43.3	239.6	1.2	18.4	ND	8.32	0.03
B	44.4	24.2	12.3	91.1	143.0	5.0	48.5	28.2	49.3	14.7	52.3	219.2	1.2	27.8	ND	6.70	0.02
C	43.7	23.1	7.2	51.3	76.4	2.4	41.5	27.6	2.1	8.3	49.9	257.3	2.3	28.4	ND	2.09	ND
D	44.1	23.8	9.7	74.5	116.8	3.9	55.0	25.3	22.7	11.7	50.1	219.0	1.5	26.6	ND	4.92	ND
E	44.9	23.5	11.9	64.2	80.1	9.7	45.6	29.9	12.6	8.5	48.2	245.4	2.1	25.9	ND	3.37	ND

^a, expressed in % (v/v); **, expressed in mg/100 mL of AA; ***, expressed in mg/L; and ND, not detected.

Table 5. Chemical Composition of Ciders^a

alcoholic cider	strength*	density	pH	total acidity**	volatile acidity***	acetaldehyde****	ethyl acetate****	methanol****	2-butanol****	1-propanol****	2-methyl-1- propanol****	2-propen- 1-ol****	1-butanol****	2- and 3-methyl- 1-butanol****	acetoin****	ethyl lactate****	2-phenyl- ethanol****
A	6.5	0.99587	3.71	3.65	1.69	4.6	39.5	38.6	7.9	28.9	20.8	16.9	4.7	157.6	11.1	228.8	127.3
B	6.6	0.99667	3.69	4.30	1.79	2.0	44.4	100.5	2.8	33.3	18.3	26.7	10.3	153.8	3.3	102.2	146.5
C	6.4	0.99718	3.76	3.43	0.98	0.9	30.5	45.3	1.3	22.4	15.8	1.0	4.5	159.6	1.9	54.3	142.7
D	6.4	0.99722	3.72	3.03	0.56	0.9	35.1	62.0	2.1	29.5	13.6	10.1	5.5	140.5	6.6	52.8	136.8
E	6.5	0.99602	3.82	3.53	1.73	1.1	51.3	47.1	16.2	32.9	22.2	28.0	5.5	155.8	ND	113.6	125.5

^a *, expressed in % (v/v); **, expressed in g/L of sulfuric acid; ***, expressed in g/L of acetic acid; ****, expressed in mg/L; and ND, not detected.

the long periods required for distillation, which could also explain the presence of acetaldehyde in the last fractions collected during distillation (Table 3). The values detected in the final spirits are in accordance with those observed by our group in cider brandies (1) and other fruit distillates (11, 12, 14–17), although higher than data reported by Guichard et al. (4) in Calvados. At the levels detected in the five samples, this could impart “green” or fruity notes to the aroma (4, 18).

As was observed above, furfural is a typical product of tails, formed during distillation from residual sugars present in cider. From the health point of view, Subden et al. (19) established a possible relation between a low mutagen content in cider spirits with the presence of furfural and other minor compounds. However, it must be said that the levels in these products are within the range observed for other distillates (11, 14, 20, 21). The five spirits presented similar values, ranging from 5 to 10 mg/L, clearly below the maximum level of 15 mg/L regulated by Spanish law (Real Decreto 250/1988), in accordance with the literature for distillation systems with long heating periods.

As regards the higher alcohols quantitated, 1-propanol, 1-butanol, 2-butanol, 2-methyl-1-propanol, 2-methyl-1-butanol, 3-methyl-1-butanol, and 2-phenylethanol, it should be noted that their concentration is clearly higher than the minimum value accepted by the European Community Council Regulation (200 g/hL of AA), since this value is only surpassed when considering 3-methyl-1-butanol. These alcohols, except for 2-butanol, are formed from amino acids during the course of fermentation of apple juice; their levels in the final distillates thus depend on several factors such as raw material, yeast strains, and fermentation conditions (3). In general, as was observed for methanol and ethanol, the levels of these alcohols in spirits are determined by their concentration in the corresponding cider. Similar ratios to those observed for methanol and ethanol were detected for these alcohols, with the only exception of 2-butanol and 2-propen-1-ol in sample E. In contrast to these alcohols, levels of 2-phenylethanol in spirits were lower than in ciders, as reflected by the ratio for the two concentrations (see Tables 4 and 5), although once again, this ratio showed similar values for the samples studied (0.84 ± 0.1). This low presence of 2-phenylethanol in spirits with respect to other alcohols must be attributed to the fact that this alcohol is predominant in tails, due to its high boiling point, and which furthermore presents low solubility in water, which promotes a low recovery in spirit. This alcohol could contribute to the aroma of this type of distillate with floral or rose notes. Nonetheless, the levels detected in all samples are below the perception threshold (18).

Ethyl acetate is the main ester in many fresh distillates (1, 4, 16, 22), the aroma of which is described as glue/varnish (23). The levels of this compound in distillates are related to the quality of the raw materials used, and as was observed for other compounds, its concentration in the distillates was related to the levels in the cider. Depending on the level in cider, ethyl acetate contributes 11–18% to volatile substances.

Copper from the alquitara is incorporated into the spirit during distillation. The level of this element detected in the cider spirits ranged between 2 and 8 mg/L, in agreement with the published data for other commercial spirits (7, 16, 24), although higher than that detected in whiskies by Adam et al. (25). Lead was likewise detected in three samples, although the values reported for both metals are clearly below the maximum level permitted by Spanish legislation (10 mg/L for copper and 1 mg/L for lead, Royal Decree 1808/1984). Zinc, on the other hand, was not detected in any sample, as was to be expected after observation of the fractions of distillation.

In summary, distillation of ciders in alquitara gives rise to spirits clearly below the maximum permissible limits for methanol, ethanol, furfural, lead, copper, and zinc, whereas minimum values for volatile substances are surpassed. Furthermore, the levels for the analytes studied are in consonance with those of other cider spirits.

However, a major proportion of tails must be separated and redistilled in order to obtain distillates with the necessary alcoholic strength. In this respect, the main disadvantage of alquitara is its high cost in energy. On the other hand, the separation of adequate volumes of tails favored the reduction of furfural and metals in the final product.

LITERATURE CITED

- (1) Mangas, J. J.; Rodríguez, R.; Moreno, J.; Blanco, D. Changes in the major volatile compounds of cider distillates during maturation. *Lebensm.-Wiss. Technol.* **1996**, *29*, 357–364.
- (2) Nykänen, L. Formation and occurrence of flavor compounds in wine and distilled alcoholic beverages. *Am. J. Enol. Vitic.* **1986**, *37*, 84–96.
- (3) Suárez Valles, B.; Pando Bedriñana, R.; Fernández Tascón, N.; González García, A.; Rodríguez Madrera, R. Analytical differentiation of cider inoculated with yeast (*Saccharomyces cerevisiae*) isolated from Asturian (Spain) apple juice. *Lebensm.-Wiss. Technol.* **2005**, *38*, 455–461.
- (4) Guichard, H.; Lemesle, S.; Ledauphin, J.; Barillier, D.; Picoche, B. Chemical and sensorial aroma characterization of freshly distilled Calvados. 1. Evaluation of quality and defects on the basis of key odorants by olfactometry and sensory analysis. *J. Agric. Food Chem.* **2003**, *51*, 424–432.
- (5) Drilleau, J.-F. Pommes et cidres matières premières du Calvados. In *Élaboration et Connaissance des Spiritueux*; Cantagrel, R., Ed.; Lavoisier-Tec & Doc: Paris, 1992; pp 193–200.
- (6) Rodríguez Madrera, R.; Blanco Gomis, D.; Mangas Alonso, J. J. Influence of distillation system, oak wood type, and aging time on composition of cider brandy in phenolic and furanic compounds. *J. Agric. Food Chem.* **2003**, *51*, 7969–7976.
- (7) Cardoso, D. R.; Andrade-Sobrinho, L. G.; Leite-Neto, A. F.; Reche, R. V.; Isique, W. D.; Ferreira, M. C. M.; Lima-Neto, B. S.; Franco, D. W. Comparison between cachaça and rum using pattern recognition methods. *J. Agric. Food Chem.* **2004**, *52*, 3429–3433.
- (8) Orriols, I. Los aguardientes de orujo gallegos. *Vitivinicultura* **1991**, *7*, 58–63.
- (9) AOAC. Beverages: Wines. In *Official Methods of Analysis of the Association of Official Analytical Chemists*; Williams, S., Ed.; AOAC: Arlington, 1984; pp 220–230.
- (10) Rodríguez Madrera, R.; Mangas Alonso, J. J. Obtención de aguardiente de sidra mediante alambique con columna de rectificación. *Alimentaria* **1996**, 89–92.
- (11) Léauté, R. Distillation in alembic. *Am. J. Enol. Vitic.* **1990**, *41*, 90–103.
- (12) Claus, M. J.; Berglund, K. A. Fruit brandy production by batch column distillation with reflux. *J. Food Process Eng.* **2005**, *28*, 53–67.
- (13) Dorey, F.; Lesmele, S.; Le Guennec, S.; Le Querlec, J. F. Dosage des composés volatils du Calvados et des eaux-de-vie de cidre. In *Élaboration et Connaissance des Spiritueux*; Cantagrel, R., Ed.; Lavoisier-Tec & Doc.: Paris, 1992; pp 497–450.
- (14) Filajdic, M.; Djukovic, J. Gas-chromatography determination of volatile constituents in Yugoslav plum brandy. *J. Sci. Food Agric.* **1973**, *24*, 835–842.
- (15) Da Porto, C.; Sensodoni, A.; Battistatta, F. Composition and flavour of muscat of canelli grape distillates obtained using different oenological techniques and unconventional distillation processes. *Ital. J. Food Sci.* **1995**, *1*, 47–56.
- (16) 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.
- (17) Soufleros, E. H.; Mygdalia, A. S.; Natskoulis, P. Production process and characterization of the traditional Greek fruit distillate "Koumaro" by aromatic and mineral composition. *J. Food Compos. Anal.* **2005**, *18*, 699–716.
- (18) Soufleros, E. H.; Natskoulis, P.; Mygdalia, A. S. Discrimination and risk assessment due to the volatile compounds and the inorganic elements present in the Greek marc distillates Tsipouro and Tsipouda. *J. Int. Sci. Vigne Vin* **2005**, *39* (1), 31–45.
- (19) Subden, R. E.; Krizus, A.; Akhtar, M. Mutagen content of Canadian apple eau-de-vie. *Can. Inst. Food Sci. Technol.* **1986**, *19*, 134–136.
- (20) Smedt, P.; de Liddle, P. Place des rhums au sein des eaux-de-vie. *Ann. Technol. Agric.* **1975**, *24*, 269–286.
- (21) 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* **2003**, *16*, 157–164.
- (22) Silva, M. L.; Malcata, F. X. Relationships between storage and conditions of grape pomace and volatile composition of spirits obtained therefrom. *Am. J. Enol. Vitic.* **1998**, *49*, 56–64.
- (23) Caldeira, I.; Belchior, A. P.; Clímaco, M. C.; Bruno de Sousa, R. Aroma profile of Portuguese brandies aged in chestnut and oak woods. *Anal. Chim. Acta* **2002**, *458*, 55–62.
- (24) Cameán, A. M.; Moreno, I.; López-Artíguez, M.; Repetto, M.; González, A. G. Differentiation of Spanish brandies according to their metal content. *Talanta* **2001**, *54*, 53–59.
- (25) Adam, T.; Duthie, E.; Feldmann, J. Investigations into the use of copper and other metals as indicators for the authenticity of Scotch whiskies. *J. Inst. Brew.* **2002**, *108*, 459–464.

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