DISTRIBUTION OF THE PRINCIPAL MINOR VOLATILES DURING CIDER DISTILLATION IN ‘ALQUITARA’

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A study of minor volatiles from 12 fractions collected during distillation of cider in ‘alquitara’ was carried out. Compounds favouring spirit quality are found in the first half of the distillate. Some compounds imparting aromatic defects could be eliminated by removing a percentage of heads during distillation. In contrast, when distilling ciders without defects, removing heads would not be justified, as their incorporation in the final distillate should lead to obtaining spirits with higher aromatic riches. Tails, however, which are mainly constituted by unpleasant aromas, must be rigorously removed to avoid incorporating compounds that could reduce the quality of the final product.

**Keywords:** cider spirit, distillation, aroma, GC-FID, alquitara

Cider spirit is a characteristic drink of those areas which, owing to their peculiar climate, are apple cider producers. Three stages may be distinguished during its elaboration: raw material selection (apple), cider making (fermentation) and distillation, and a later aging period in oak wood barrels also being customary. These processes are carried out in an artisanal way, thus increasing its valuation when chosen by consumers. In this respect, Regulation (EC, 2008) of the European Parliament and of the Council lays down general rules regarding the definition, description and presentation of spirit drinks and also protects traditional methods through geographical designations, among which ‘Aguardiente de Sidra de Asturias’ is also included.

From the chemical point of view, fresh distillates (those which have not been aged in wood) are characterized by the presence of volatile compounds, since on distilling a hydroalcoholic mixture such as cider, with a boiling point under 100 °C, only some compounds with well-defined characteristics as regards their boiling points and solubility in water and ethanol can be incorporated into the distillate (LÉAUTÉ, 1990; RODRÍGUEZ MADRERA & MANGAS ALONSO, 1996; RODRÍGUEZ MADRERA et al., 2003; 2006). These volatile compounds belong to different chemical families such as alcohols, esters, acids, aldehydes, volatile phenols, etc. and can be found in the spirit in each one of the stages described above, thus enabling us to speak of primary (apple), secondary (fermentation) or tertiary (distillation) aromas (TESEVIC et al., 2005). As an example, compounds such as 1-butanol, ethyl butyrate or hexyl acetate are considered as primary or varietal aroma characteristics from apples (BROWN et al., 1996; SU & WILEY, 1998; LÓPEZ et al., 1998). Likewise, 1-butanol and ethyl caproate levels enable cider brandies to be classified according to the type of cider employed, i.e. cider made from fresh must versus cider made from apple concentrate (RODRÍGUEZ MADRERA & MANGAS ALONSO, 2005). Other compounds, such as higher alcohols, are formed during the fermentation process, the levels of which are closely related to the presence of amino acids (NYKÄNEN, 1986) and

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sugars (Aranda et al., 2005) in the must. The formation of fatty acids and their corresponding ethyl esters also takes place during fermentation, respectively, imparting body and fruity aromas to the spirit (Gay-Belille, 1982; Artajona, 1992). In other cases, the presence of certain compounds in the fresh distillate may be due to their formation in the course of distillation. Thus, for instance, long distillation periods and the copper forming the alambic can favour the formation of acetaldehyde by oxidation of ethanol (Claus & Berglund, 2005; Rodriguez Madrera et al., 2006). On the other hand, the distillation of ciders with residual sugars leads to the formation of furfural as a result of thermal degradation (Da Porto et al., 1996; Rodriguez Madrera et al., 2006).

From a quantitative viewpoint, the most important volatile compounds in fruit spirits are methanol and fusel alcohols (Hernández-Gómez et al., 2003; Soufleros et al., 2004; 2005; Genovese et al., 2004; Schehl et al., 2006; Rodriguez Madrera & Mangas Alonso, 2005). However, these compounds do not have a direct impact on the final quality of cider distillates, which seems to be related to the presence of other compounds at lower concentrations (Guichard et al., 2003).

This paper presents a study of the distribution of minor volatile compounds during distillation of cider in ‘alquitara’, a traditional distillation system characterized by its low rectification capacity.

1. Materials and methods

1.1. Raw material

Cider was produced by means of traditional technology from the juice of a mixture of cider apples with different sensory properties and picked at the optimal maturation stage, thus endowing the resulting juice with an overall acidic nature (pH=3.4). The mixtures of apples were milled in a hammer mill and pressed slowly for two days in traditional hydraulic presses. The presses’ capacity was 15 000 kg and the yield was 70–75%. Fermentation took place in a 25 000 l stainless steel tank and was carried out by the indigenous microflora. Fermentation process took for two months and then the cider was matured for ten months at 12±1 ºC.

1.2. Distillation

The system used to distil the cider consisted of two batteries, each comprising seven alquitaras according to the scheme of distillation described by Rodriguez Madrera and co-workers. (2006). The capacity of the alquitaras, built of 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 ºC to facilitate condensation of the cider spirit. Gas burners were used as heat source.

Distillation takes place in two steps. First, cider is distilled in a pre-concentration step until obtaining an intermediate product with an alcoholic strength of 20% (v/v). Subsequently, distillation of this product was divided into 12 fractions with volumes ranging between 4 and 225 l.

1.3. Chemical analysis

Minor volatiles were analysed with a Hewlett-Packard model 6890 gas chromatograph equipped with a flame ionization detection system (FID). The microfiltered samples were directly injected into the chromatograph (1 µl) and quantitation was 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 separation of volatiles was carried out on a PEG capillary column (TR-Meta WAX, 30 m×0.25 mm i.d.; phase thickness 0.5 μm) supplied by Tecknokroma (Barcelona, Spain). Chromatographic conditions were as follows: oven temperature, initial isotherm at 35 °C (5 min), raised to 60 °C at a rate of 5 °C min⁻¹, raised to 90 °C at a rate of 10 °C min⁻¹ and finally raised to 220 °C at a rate of 8 °C min⁻¹ (15 min); the injector temperature was 260 °C and the detector temperature 275 °C; He was used as carrier gas at 0.8 ml min⁻¹. Injection was carried out in split mode (1/3), and the injection volume was 1 μl (RODRÍGUEZ MADRERA & SUÁREZ VALLES, 2007).

1.4. Other analyses

Alcoholic strength in distillates was determined by direct measurement in an Anton Paar DMA 500 Density Meter (Graz, Austria) and volatile acidity was determined following the methodology described by the OFFICE INTERNATIONAL DE LA VIGNE ET DU VIN (1994).

2. Results and discussion

Table 1 displays the results from the analysis of fractions obtained during distillation. Esters constitute the main group detected in this study, both in terms of number as well as concentration. The evolution during distillation of all of these compounds is similar. Except for 2-phenylethyl acetate and diethyl succinate, the highest concentration of esters is found in the first fractions, with a maximum concentration of less than 5% of the distilled volume. Recovery of each of these esters was higher than 77% before distilling being 25% of the total volume, which allows us to consider these analytes as typical products from heads. On account of their boiling point (b.p. ethyl palmitate 133 °C at 13 mmHg), recovery of esters would be expected to take place in the last stages of distillation. However, the fact that they are soluble in ethanol favours these aromas being pulled at the beginning of distillation, where distilled vapours are richer in ethanol. On the other hand, it was observed that maximum concentrations for these substances are delayed depending on their boiling point. The concentration of esters from fatty acids with less than 12 carbon atoms was higher in the first fraction and that of esters from fatty acids with 12 to 16 carbon atoms was higher in the second fraction, thus giving rise to the distillation curves shown in Fig. 1. The evolution of ethyl esters of fatty acids during distillation fits the expression Y= A + B×Ln (X) where X is the volume percentage distilled, Y is the mass percentage recovered of each ethyl ester and A and B are two characteristic constants for each compound with determination coefficients higher than 95%. From the quantitative point of view, the most important esters were isoamyl acetate, ethyl caprylate, ethyl caprate and ethyl laurate, in agreement with previous characterization studies on cider spirits (GUICHARD et al., 2003; GENOVESE et al., 2004; RODRÍGUEZ MADRERA & MANGAS ALONSO, 2005). These esters highlight the fruity and sweet notes imparted to the distillate associated with descriptors such as banana, apple, pineapple, brandy, etc. (GAY-BELILLE 1982; LEDAUPHIN et al., 2003; GUICHARD et al., 2003; GENOVESE et al., 2004). On the other hand, 2-phenylethyl acetate with rose odour was observed to behave similarly to long chain fatty acids esters as a consequence of its high boiling point, although it was present in all distilled fractions due to its partial solubility in water. In contrast, diethyl succinate
with a lower b.p. than most of the studied esters, and despite being insoluble in water, was extracted throughout the entire distillation process, thus making it mainly a hearts and tails compound (Fig. 1). The long distillation period required in this type of alambic could favour the esterification of succinic acid, which is present in the cider at a concentration of 0.5 g l\(^{-1}\) (Rodríguez Madrera et al., 2006).

**Table 1.** Chemical composition of fractions recovered during distillation in alquitara (expressed in mg l\(^{-1}\))

<table>
<thead>
<tr>
<th>Compound</th>
<th>Fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethyl butyrate</td>
<td>3.27</td>
</tr>
<tr>
<td>Ethyl 2-methylbutyrate</td>
<td>2.19</td>
</tr>
<tr>
<td>Isoamyl acetate</td>
<td>19.06</td>
</tr>
<tr>
<td>Ethyl caproate</td>
<td>10.28</td>
</tr>
<tr>
<td>Hexyl acetate</td>
<td>0.46</td>
</tr>
<tr>
<td>1,1,3-Triethoxypropane</td>
<td>0.00</td>
</tr>
<tr>
<td>3-Methyl-3-buten-1-ol</td>
<td>0.28</td>
</tr>
<tr>
<td>Ethyl caprylate</td>
<td>35.74</td>
</tr>
<tr>
<td>Cis-3-hexen-1-ol</td>
<td>2.44</td>
</tr>
<tr>
<td>3-Ethoxy-1-propanol</td>
<td>0.80</td>
</tr>
<tr>
<td>1-Octen-3-ol</td>
<td>0.15</td>
</tr>
<tr>
<td>Benzaldehyde</td>
<td>2.67</td>
</tr>
<tr>
<td>1-Octanol</td>
<td>0.79</td>
</tr>
<tr>
<td>Ethyl caprate</td>
<td>35.59</td>
</tr>
<tr>
<td>Diethyl succinate</td>
<td>2.00</td>
</tr>
<tr>
<td>1-Decanol</td>
<td>0.37</td>
</tr>
<tr>
<td>Ethyl laurate</td>
<td>14.37</td>
</tr>
<tr>
<td>2-Phenylethyl acetate</td>
<td>1.19</td>
</tr>
<tr>
<td>Benzyl alcohol</td>
<td>0.26</td>
</tr>
<tr>
<td>Ethyl myristate</td>
<td>2.57</td>
</tr>
<tr>
<td>4-Ethylguaiacol</td>
<td>0.93</td>
</tr>
<tr>
<td>Ethyl palmitate</td>
<td>0.84</td>
</tr>
<tr>
<td>Eugenol</td>
<td>0.00</td>
</tr>
<tr>
<td>4-Ethylphenol</td>
<td>1.71</td>
</tr>
<tr>
<td>Volatile acidity (g l(^{-1}) acetic acid)</td>
<td>0.27</td>
</tr>
<tr>
<td>Ethanol % (v/v)</td>
<td>39.94</td>
</tr>
<tr>
<td>Volume (l)</td>
<td>4.0</td>
</tr>
</tbody>
</table>
The acetal 1,1,3-trietoxypropane, a product derived from acrolein, was not detected until the third fraction, i.e. when distillation was well underway. This fact is worth noting, as 1,1,3-trietoxypropane is the last compound recovered, though neither its boiling point nor its solubility in water seems to justify this fact. A possible explanation could be the oxidation of allyl alcohol present in cider into acrolein, which reacts with ethanol to yield 1,1,3-trietoxypropane. In this respect, the formation of acetaldehyde was also detected as a result of the oxidation of ethanol during distillation (Claus & Berglund, 2005), while longer distillation periods favour the presence of 1,1,3-trietoxypropane in the spirit (Rodríguez Madrera, 2001). Although 1,1,3-trietoxypropane has been described as a marker of the ‘acrolein’ defect in fresh cider spirits (Ledauphin et al., 2003) resulting from the processing of raw material with a deficient fermentation (De Smedt & Liddle, 1976), in no case there is any quantitative data about its levels. To the contrary, the distilled cider was evaluated positively, with fruity notes, pronounced acidity in mouth and without defects, thus the concentrations detected must be considered as usual for this product.

Aliphatic alcohols 1-octanol, 1-decanol, 1-octen-3-ol, cis-3-hexen-1-ol and 3-metil-3-buten-1-ol, low solubility in water, or even insoluble, were observed to behave similarly to the ethyl esters described above. *Cis*-3-hexen-1-ol, with a characteristic green grass odour, was the most abundant of these and was detected throughout the entire distillation because of its partial solubility in water. This contrasts with the behaviour of other alcohols such as 1-octanol and 1-decanol, which are insoluble in water, leading to these compounds being present in heads and hearts at concentrations of more than 95%. Although from the sensorial point of view 1-octanol and 1-decanol are of little interest, 1-octen-3-ol with a mushroom odour and a low threshold indicates raw material with microbiological alterations. As this alcohol is a typical product of heads, the removal of an adequate quantity of heads could help this defect to be eliminated.
With respect to benzyl alcohol and the volatile phenols detected (4-ethylguaiacol, eugenol and 4-ethylphenol), their profile was different to that described for aliphatic alcohols (Fig. 2). They were detected throughout the entire distillation process and their distillation curves fitted the expression \( Y = A \times X^B \) with determination coefficients in all cases higher than 99%. From a sensorial point of view, volatile phenols are usually related to aging in wood (Chatonnet, 1995). Nevertheless, in some cases, these compounds can be present as a result of decarboxylation of \( p \)-cumaric and ferulic acids carried out by \( Saccharomyces cerevisiae \) yeasts to yield 4-ethylphenol and 4-ethylguaiacol. Volatile phenols are responsible for spicy and floral notes (Suárez Lepe, 2002), although in the case of wines an excess can give rise to aromas such as varnish, pharmacy or horse-like odour and inhibit the perception of positive aromas (Cacho Palomar, 2006). In this respect, incorporating an excess of tails in the spirit could cause the occurrence of phenolic flavours unsuitable in a fresh spirit.

![Fig. 2. Distribution curves of 1-octanol, eugenol and 4-ethylphenol during distillation in alquitara.](image)

The moiety of 3-ethoxy-1-propanol has two functional groups (ether and alcohol) and, at least in the case of beer, this compound is formed by yeasts (Irwin, 1992). In cider distillates, it constitutes one of the principal components of tails because its increase during distillation is progressive with a maximum in the last fraction recovered. This behaviour can be explained, on one hand, by its moderate solubility due to both polar groups (ether and alcohol) and, on the other, and perhaps more importantly, by etherification of 1,3-propanediol with a moiety of ethanol. Etherification would justify the continuous increase in 3-ethoxy-1-propanol throughout distillation, a correlation \( (r=0.77) \) existing between levels of 1,3-propanediol in ciders and 3-ethoxy-1-propanol in spirits (data not shown). This is an aromatic compound with fruity odour and a threshold perception of 0.1 mg l\(^{-1}\) in hydroalcoholic mixtures at 14% (v/v) of ethanol with an important olfactory activity in sherries (Mozano et al., 2002). However, the last fraction recovered, with an alcoholic strength of 12.3% (v/v) and a concentration of 3-ethoxy-1-propanol 30 times higher than its threshold, presents a heavy aroma originating from the levels of phenolic compounds and a higher volatile acidity.
3. Conclusions

In general, it may be concluded that compounds favouring spirit quality are found in the first half of cider distillate. Certain compounds, such as 1-octen-3-ol, distilled at the beginning of the process and imparting aromatic defects, can be eliminated by removing a percentage of heads during distillation. However, in the distillation of ciders without defects, removing heads would not be justified and their incorporation into the final distillate should lead to obtaining spirits with a higher aromatic riches. As regards tails, these must be rigorously removed to avoid incorporating compounds that could reduce the quality of the final product, since, as was detected, the last fraction is mainly constituted by unpleasant aromas.

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