This thesis studies the feasibility of using a discontinuous packed column distillation system in order to produce spirit drinks with improved quality.

The experimental work was focused on comparing distillates obtained with this distillation system with those obtained with traditional copper alembic (charantais). Experiments considered different pear varieties (Conference, Blanquilla and Barlett), fruit fermented from Kiwi (Hayward variety) and grape pomace from different varieties (mainly Albariño and Catalán Roxo). Obtained distillates have been compared and analyzed - from a chemical and sensory point of view - according to the raw material, fermentation yeast and distillation system used.

The obtained results consistently support the use of the packed column as an alternative to the traditional system in order to obtain distillates with improved organoleptic and chemical features.

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Doctoral Thesis 2014

Yanine Arrieta Garay

Influence of a packed distillation column on volatile composition and sensory profile of spirit drinks: Application to pear, kiwi and grape pomace

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Application to pear, kiwi and grape pomace

Thesis submitted by

Yanine Arrieta Garay

To obtain the degree of
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Tarragona, July 2014

Yanine Arrieta Garay

Influence of a packed distillation column on volatile composition and sensory profile of spirit drinks:

Application to pear, kiwi and grape pomace

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Supervised by
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Departament d'Enginyeria Química
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Tarragona
2014

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To my parents and my siblings,

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Abstract

This thesis studies the possibility of using a discontinuous distillation system that consists of a packed column with a copper mesh that allows increasing the separation efficiency of ethanol and other volatile compounds in fermented fruits and grape pomace. In this experimental work the packed column has been compared with a traditional copper alembic (*charantais*). The raw materials employed have been fermented pear from three different varieties (*Blanquilla*, Conference and Bartlett), fermented kiwi (Hayward variety), and grape pomace (mainly *Albariño* and *Catalán* Roxo varieties). The distillates obtained by the two methods were compared both analytically and sensorially.

The obtained results have shown that packed column distillation improves the aromatic profile of less aromatic pear varieties, such as *Blanquilla* and Conference, thus making possible to obtain similar distillates as with the Bartlett pear, a more aromatic variety. Regarding kiwi distillates, the products obtained with the packed column have been better appreciated by consumers, featuring aromatic profiles with higher concentration of positive aromas, and less negative aromas. With respect to grape pomace distillates, the trend has been similar to fruit distillates. Finally, it is worth to remark the greater yield obtained in recovered ethanol, thus allowing an increased productivity by means of packed column distillation.

Resumen

En esta tesis se ha estudiado la posibilidad de emplear un sistema de destilación discontinuo que consiste en una columna empacada de un relleno formado con una malla de cobre que permite aumentar la eficacia de separación, tanto del etanol como de otros compuestos volátiles de fermentados tanto de frutas como de orujos del sector vitivinícola. En el trabajo experimental este sistema se ha comparado con la destilación tradicional con alambique tipo *charantais* construido en cobre. Las materias primas empleadas han sido fermentados de pera de tres variedades diferentes (Blanquilla, Conferencia y Bartlett), fermentados de kiwi de la variedad Hayward, y orujos de uva principalmente de las variedades Albariño y Catalan Roxo. Los destilados obtenidos por los dos procedimientos han sido comparados tanto analíticamente como sensorialmente.

Los resultados obtenidos han mostrado que con la columna empacada, los destilados de variedades de peras menos aromáticas, como son la Blanquilla y la Conferencia, pueden mejorar su perfil aromático, y obtener productos similares a los de la pera Bartlett, más aromática. Respecto los destilados de kiwi, los productos obtenidos con la columna empacada han sido mejor valorados por los consumidores, presentando perfiles aromáticos con más concentración de aromas positivos, y menores aromas negativos. Respecto los destilados de orujo la tendencia mostrada ha sido similar a los destilados de frutas. Finalmente destacar el mayor rendimiento obtenido en etanol recuperado en la destilación con columna, permitiendo aumentar también la productividad mediante el empleo de la columna empacada.

Resum

En aquesta tesis s'ha estudiat la possibilitat d'emprar un sistema de destil•lació discontinu que consisteix en una columna de rebliment, formada d'una malla de coure, que permet augmentar l'eficàcia de separació, tant de l'etanol com d'altres compostos volàtils de fermentats de fruites como de vinasses del sector vitivinícola. En el treball experimental aquest sistema s'ha comparat amb la destil•lació tradicional amb alambí tipus charantais construït en coure. Las matèries primeres emprades han estat fermentats de pera de tres varietats diferents (Blanquilla, Conferencia i Bartlett), fermentats de kiwi de la varietat Hayward, i vinasses de raïm principalment de les varietats Albariño i Catalan Roxo. Els destil•lats obtinguts pels dos procediments han estat comparats tant analíticament como sensorialment.

Els resultats obtinguts han mostrat que amb la columna de rebliment, els destil•lats de varietats de peres menys aromàtiques, como són la Blanquilla i la Conferencia, poden millorar el seu perfil aromàtic, i obtenir productes similars als de la pera Bartlett, més aromàtica. Respecte els destil•lats de kiwi, els productes obtinguts amb la columna de rebliment han estat millor valorats pels consumidors, presentant perfils aromàtics amb més concentració d'aromes positius, i menors d'aromes negatius. Respecte els destil•lats de brisa la tendència mostrada ha estat similar als destil•lats de fruites. Finalment destacar el major rendiment obtingut en la destil•lació amb columna en etanol recuperat, permetent augmentar també la productivitat mitjançant la utilització de la columna de rebliment.

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Chapter 1

Introduction

Within the European Union, together with Italy and France, Spain is one of the major fruit and wine producing countries (52.600.000 l of wine in 2013 year, according to *Observatorio Español del Mercado del vino*), thanks to its Mediterranean climate. Fruit beverages correspond to an important line among the different fruit-derived products exploited in industry. According to the Spanish Food Code (CAE), drinks are classified in three categories: non-alcoholics, alcoholics and water, being the spirits drinks within the group of alcoholic beverages.

The alcoholic beverage industry must deal with continuos changes in the preferences of consumers demanding increasingly better quality products in terms of aroma and authenticity. However, the producers often lack the tools for adapting their products to the new requirements in the fast and efficient way required by a competitive market. There are many factors that can influence on the chemical composition of the final product and, therefore, on the sensory character of distillates. These include the typology of the raw material, the fermentation process, which is conditioned by the type of yeast used, as well as the distillation process, in which the equipment used directly affects on the final quality of the distillate.

Every year large amounts of different local fruits are wasted since the surplus cannot be directly consumed by the market and because some fruits do not fulfil market requirements (second or third quality fruits). On the one hand, one of the most produced fruit in Spain is pear (mainly *Blanquilla* and Conference varieties). On the other hand, the production of kiwifruit (*Actinidia chinensis*) has increased considerably the last years, mainly in Galicia. Although some alternatives to direct consumption have already been exploited (jams, fruit concentrates, fruit juices, nectars, purées, preserves, etc.), a large amount of fruit is still left in the fields to rot or to be collected and later disposed as waste. These practices create both an environmental and an economic problem. As a result, it is necessary to find alternatives to the generated surpluses and to develop new added-value products. Within this context, the distillation of these fruits and the traditional vinification of by-products could represent a potential solution to the problem and could have an important influence on the economy of the country.

The main aim of this thesis is to study the feasibility of using a batch packed column distillation system on grape pomace distillates (*orujo*) and fruit distillates, as an alternative to traditional *Charentais* alembic.

1.1 Spirit drinks

According to the European Regulation (EC) No 110/2008, article 2, section 1 (EC, 2008), a spirit drink is defined as an alcoholic liquid intended for human consumption, having particular organoleptic qualities, a minimum alcoholic strength of 15 % (v/v), and produced exclusively by the alcoholic fermentation and distillation of fleshy fruit or must of such fruit, with or without added flavorings, and/or by maceration of vegetable substances, and/or the addition of other regulated substances. There are different categories of spirit drinks such as rum, whiskey, grain spirit, wine spirit, brandy, grape marc spirit or grape marc, fruit marc spirit, fruit spirits, cider spirit, cider brandy or perry spirit, juniper-flavored spirit drinks, aniseed-flavored spirit drinks and vodka, among others. Alcoholic beverages are produced according to this definition from different fruits.

In Mediterranean countries, the most popular ones are obtained from grape pomace (grape marc). Grape pomace is a solid residue that consists of skins, stalks and seeds left after juice extraction in the winemaking process (Orriols, 1991; Da Porto, 1998; Silva et al., 2000). Galicia is the main grape pomace spirits producing region in Spain, with a long-standing tradition in the production of grape pomace distillates, known as “Orujo de galicia”, as recongnized by the The European community in anex III of regulation (EC, 2008) for geographical indications. This Geographical Indication has 30 distilleries, which have sold a volume of 131.324 liters on the average from 2005 to 2013 (*Datos Orujo de Galicia*). The French, Italian, Portuguese and Greek equivalents spirit drinks produced from grape pomace, are known as “Marc”, “Grappa”, “Bagaçeira” and “Tsipouro”, respectively.

In general, grape pomace is produced from both white and red grapes. The white grape pomace is fermented separately from must before being stored, while the red grape pomace has already undergone alcoholic fermentation with the must and can be distilled inmediately (Bovo et al., 2009; De Pina and Hogg, 1999)

A large number of studies have been published about these beverages in regard to volatile composition (Da Porto, 1998; Apostolopoulou et al., 2005; Da Porto and Decorti, 2009), storage conditions (Da Porto, 2002; Silva and Malcata, 1998), enzymatic treatment (Zocca et al., 2008, 2007) fermentation conditions (Iacumin et al., 2012; Bovo et al., 2014) and distillation of the raw material (Da Porto and Decorti, 2008; Da Porto et al., 2010).

Regarding Galician *orujo*, similar studies have been carried out about raw material treatment and storage conditions (Cortés Diéguez et al., 2001; Cortés et al., 2010; Orriols and Bertrand, 1990) and the influence of grape variety and distillation technology on the volatile composition of *orujo* (Cortés and Fernández, 2011; Cortés et al., 2005; Diéguez et al., 2005, 2003; López-Vázquez et al., 2010a; Orriols, 1991; Orriols et al., 1997a, 1997b; Orriols et al., 2008a; 2008b, 2008c). The results of these studies showed differences in the primary aromas of *orujo* from several grapevine varieties including *Treixadura*, *Godello*, *Albariño*, *Mencía*, *Catalán Roxo*, *Loureira*, *Dona Branca* and *Torrontés* (López-Vázquez et al., 2010b; Orriols et al., 1997a; Versini et al., 1995). Certain compounds as methanol, 1-hexanol, 1, propanol, ethyl lactate and ethyl acetate were higher in spirits from industrial origin, whereas 2-phenylethanol was higher in traditional ones (Cortés et al., 2005). These chemical differences determined the sensorial properties of *orujo* spirits, specially at taste level (Cortés et al. 2005; Orriols et al., 2008a, 2008b); Grape marc stored in plastic sacks produced distillates of good quality but poor aroma, plastic drums were related with high content of ethyl esters and higher alcohols in distillates, whereas concrete containers favored the methanol production (Cortés et al., 2010). In addition, the composition of Galician *orujos* and grappas (Italian grape marcs) was compared, the later had low contribution of the majority volatile compounds (Cortés et al., 2011; Versini el al., 2004).

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 the region. According to recent data, pear varieties have remained relatively stable in Spain over the last 40 years , (interpera 2010). 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 single producer of *Blanquilla* variety.

Given its rich aromatic content, Bartlett is the variety most frequently used to produce pear distillates in Central Europe (Soufleros et al., 2004). The studies on Bartlett variety in the last years have focused on the reduction of methanol content (Andraous et al., 2004; Glatthar et al., 2001) the effect of bottle color on the aroma and taste of the distillate (Cigic and Zupancic-Kralj, 1999), and the composition of a commercial pear essence derived from a distilled pear wine (Tucker et al., 2003). 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. For instance, Versini et al. (2012) studied the aroma fraction of Italian distillates of wild (Pyrus amygidaliformis, Vill., namely ‘Pirastru’) and cultivated (Pyrus communis, L. cvs. ‘Coscia’, ‘Precoce di Fiorano’ and ‘Butirru de Austu’) pear varieties grown in the northern part of the island of Sardinia.

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 (García-Llobodanin et al., 2010a, 2010b, 2007) 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)* the pH reduction during fermentation significantly increased the concentration of most of the higher alcohols and decreased the concentration of ethyl acetate; *(2)* the concentration of some compounds (methanol, ethyl acetate, furfural) decreased or did not change when the lees were present during distillation in a copper alembic; and *(3)* the concentration of some desirable compounds (ethyl decanoate and ethyl-2-*trans*-4-*cis*-decadienoate) 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 *Charentais* alembic.

García-Llobodanin et al. (2011) 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 higher alcohols, 40% less acetaldehyde and 10% less methanol than alembic spirits.

On the other hand, in recent years, the production of kiwifruit (*Actinidia chinensis*) has increased considerably in Spain, harvesting today 931 ha, being within the top ten global producers. According to statistics of the Spanish Goverment, the national production of kiwi reaches up to 23,000 tm per year (Agronota, 2012). **Table 1.1** shows the production in the European Union including Spain, during the years 2008-2011.

Table 1.1. Kiwi fruits production (tons) in the European Union during 2008- 2011.

Country	2008	2009	2010	2011
Italy	473,955	447,608	415,877	431,558
Greece	84,300	104,000	116,310	140,400
France	65,670	76,171	70,719	73,395
Portugal	15,506	26,927	23,903	23,473
Spain	17,709	18,800	25,676	23,327
other countries	301	508	480	545
total production in the EU	**657,441**	**674,014**	**652,965**	**692,698**

Source: (FAO, 2012)

In Spain, Galicia is the main kiwi-producing region, producing 66.7 % of the total amount harvested each year. Although Kiwifruit is mainly eaten fresh, other uses have increased their importance recently. The availability of fruits in different ways throughout the year, and the use of those which cannot meet the standard required for the fresh fruit market, estimated as of 10% of annual production (Interempresas, 2011), made necessary to look for some alternatives to fresh consumption such as nectar, jam, preserves, and kiwi-based Syrups (Bortolini et al., 2001; Luh and Wang, 1984; Nunes Damaceno, 2007).

Regarding alcoholic beverages using kiwifruit, studied in Europe are scarce. The most of the published studies have been performed in Asia, mainly focused in kiwifruit wine (Heatherbell, 1975, Lodge, 1981, Withy and Lodge, 1982, Lodge et al., 1986, Craig, 1988). In more recent years, research on kiwi wine has been focused on quality (Peng et al., 2006), fermentation conditions (Jang et al., 2007), and fruit maturity (Towantakavanit et al., 2011). Only three papers have been found regarding kiwi wine and kiwi distillates in Europe. Soufleros et al. (2001) evaluated the composition of volatile compounds, organic acids, sugars and glycerol in a kiwifruit wine. They found that wines from kiwifruit had higher concentrations of methanol, lower concentrations of esters and similar concentrations of higher alcohols when compared with grape wines. Sensidoni et al. (1997) obtained spirits of kiwi from the distillation of the product obtained from the fermentation of kiwi juice enriched with rectified grape must and addition of pectolytic enzymes. In their research, the distillation was performed at two different operating pressures: reduced and atmospheric. The obtained distillates at reduced pressure were aromatically better; however the characteristic aroma of the kiwi fruit was not detected in either of the distillates. In a previous study in our laboratory, the aromatic composition of kiwi distillates fermented with two different strains of *Saccharomyces cerevisiae* was assessed (López-Vázquez et al. 2012), contributing fundamental knowledge to help developing a distillate of kiwi wine.

1.2 Distillation techniques and systems

Distillation is the technique used to carry out the separation, by the application of heat, of the volatile components from a liquid mixture. Wine is composed mainly by water and ethanol; however, there are approximately 300 minority volatile compounds which will distill differently depending on their boiling point, solubility in ethanol and water, and variation of ethanol content in the vapour during distillation (Léauté, 1990).

Two distillation systems can be used for distillates production: the batch distillation and the continuous distillation. Batch distillation is a term used for a distillation that entails distilling a mixture to obtain three component fractions known as the heads, hearts and the tails. Each of these fractions contains different amounts and types of compounds. The heads contain higher concentration of low boiling point components, (acetaldehyde, acetone, esters) and are unfit for consumption. The heart, the middle fraction, has lower concentrations of all the undesired compounds, and eventually becomes the potable product, whereas the tails fraction has an unpleasant aroma character, due to the higher concentration of fusel alcohols and other compounds with boiling points higher than ethanol (Bernot et al., 1990; Orriols et al., 1991; Versini et al., 1991).

The distillation equipments that are most frequently used for the production of distilled drinks (see **Figure 1.1**) are copper *Charentais* alembic (French style) and batch distillation columns (German style). Copper alembic has been generally utilized in small commercial and artisanal distilleries and medium-sized distilleries, in the production of *Orujo*, where the still is usually heated by direct fire. These systems are discontinuous, and they consist of a copper boiler, a column of rectification (optional, not being usual), a partial condenser and a total condenser

(Silva et al., 2000). German style has been used for fruit brandy (Claus and Berglund, 2005), and consists of a copper pot still fitted with column plates and a dephlegmator. The purpose of the column dephlegmator is to partially condense the distillate vapor, returning a portion of it as counter current distillate to be re-distilled. The plates in the column are usually copper sieves trays, which the distillate vapors can pass through as they rise through the column. The counter current distillate drains back down and sits on the next lower plate to be re-distilled therefore increasing the efficiency of separation of different components. This process is called reflux and rectification (Claus and Berglund, 2001).

Figure 1.1. Distillation equipment employed in fruit spirits. (A) copper alembic, (B) distillation column (Holstein type).

Both distillation methods are based on the same theoretical principles, i.e. mass and energy balances, heat and mass transfer, and vapour–liquid equilibrium (Kister, 1992, García-Llobodanin et al., 2011).

The effect of distillation equipments on distillates quality have been studied for several raw material, such as pear spirits (García-Llobodanin et al., 2011, 2010b), cachaça (Reche et al., 2007; Serafim et al., 2012), cider Brandy (Rodríguez-Madrera et al., 2003) and melon spirits (Hernández-Gómez et al., 2003).

Recently, a novel type of batch distillation column has been configured by our research group (García-Llobodanin et al., 2011). This batch distillation system consists of a cylindrical stainless steel boiler with two electric heaters, a copper rectification column packed with copper mesh (Amphora Society, http://www.amphorasociety.com/). The column also included a partial condenser with two coils as well as a total condenser and a condensate reservoir (**Figure 1.2**). This packed distillation column had more difficult to operate reproducibly vs. traditional alembics but the spirits obtained with this rectification column were more concentrated in ethanol than alembic distilled spirits.

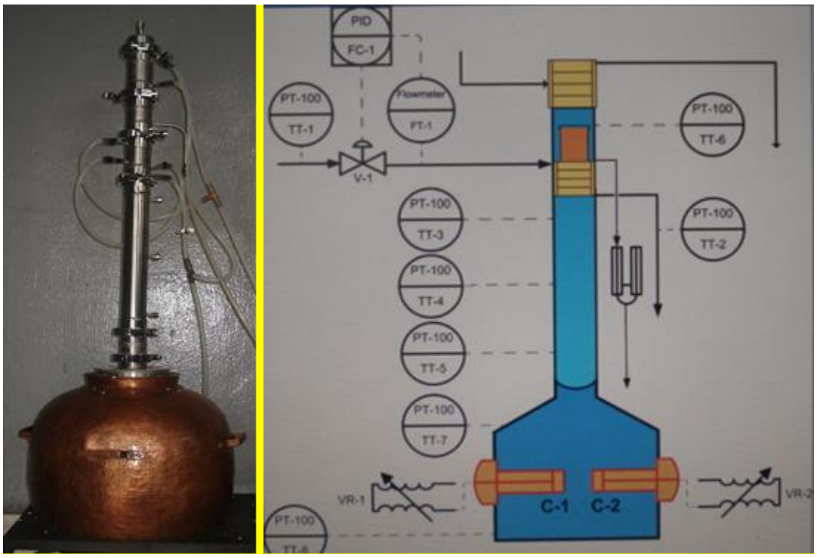

Figure 1.2. Equipment and schema of the batch distillation system with a packed column used by García Llobodanin et al., 2011.

1.3 Volatile compounds in distillates

A spirit drink consists mainly of water and ethanol, at an average of 50%. However, as mentioned previously, there are hundreds of minor components that will define its quality and sensory character. These compounds can be split into several groups according to their chemical nature in alcohols, esters, fatty acids, aldehydes and acetates (Nykänen, 1986; Lehtonen et al., 1983). The most abundant volatile compounds in the spirit drinks are higher alcohols (also known as fusel oils), fatty acid esters, together with acetaldehyde and methanol. Fusel alcohols, fatty acid esters and acetaldehyde are mainly resulting from yeast and bacteria metabolism during the fermentation step (Nykänen, 1986; Nykänen and Nykänen, 1991; López-Vázquez et al., 2010b) while methanol is derived from enzymatic degradation of grape pectins (Hang and Woodams, 2008). In addition to these compounds there are other compounds, the terpenes, whose presence in spirits is very important from the sensory point of view (Versini et al., 1993) and intense fruity floral bouquet (Tomasi et al., 2000).

1.4 Objectives

The aim of this thesis is to study the feasibility of using a batch packed distillation column in order to produce fruit distillates and grape pomace distillates (*Orujos*) with improved quality with respect to the traditional distillation with a *Charentais* alembic.

To this end, the following objectives were raised:

- To produce pear distillates with less aromatic varieties, such Conference and *Blanquilla*, with these two distillation systems and to compare them with pear distillates obtained from the Bartlett variety, both from the analytical and organoleptic points of view, in the same conditions of fermentation and distillation. The aim is to assess the viability of leveraging surpluses of these two less aromatic varieties in order to obtain distillates comparable to Bartlett pear distillates.

- To study the impact of these two distillation systems on the volatile composition and sensory profile of kiwi distillates obtained under different fermentation conditions.

- To study the impact of these two distillation systems on the volatile composition and sensory profile of grape pomace distillates from *Albariño* and *Catalán Roxo* varieties.

- To study the impact of both distillation systems on the volatile composition and sensory profile of grape pomace distillates from *Xenérico* (mix of varieties) at semi-industrial scale, in order to adjust the distillation process to procedures used in Galician distilleries.

Chapter 2

Materials and methods

2.1 Raw materials

The experiments of this thesis were carried out in the distillery of *Estación de Viticultura e Enoloxía de Galicia* (EVEGA, Leiro, Ourense, Spain) and the facilities of the URV (experimental cellar of *Mas dels Frares* and the laboratories of the *Grup d'Investigació en Tecnologia d'Aliments*).

The raw materials used in this thesis were:

- Natural pear juice from *Blanquilla*, Conference and Bartlett varieties donated by S.A.T. Nufri, Lleida, Spain
- Kiwi fruits of the Hayward variety grown in the southwest of Galicia (Spain) in the 2010 harvest.
- White grape pomace from *Albariño* (*Vitis vinifera* L.) supplied by Bodega As Laxas (Arbo, Pontevedra, Spain) from 2009 and 2010 harvest.
- *Catalán Roxo* (*Vitis Labrusca*) grape provided by different growers of the Ulla region (A Coruña, Spain, harvests 2009 and 2010), from which fermented grape pomace was obtained.
- Grape pomace (plurivarietal) referred to as *Xenérico* (mixture of varieties from EVEGA) from 2010 harvest.

2.2 Fermentation

Pear juices. The selected fruits 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 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 on a daily basis by measuring the temperature and density. 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.

Kiwi fruits. The kiwi fruits used in this study had ripened to a similar extent. Kiwi fruits were transported to *Estación de Viticultura e Enoloxía de Galicia* (EVEGA) and processed as follows: kiwi fruits were sorted by size and manually washed with plenty of running water in order to remove foreign material from the skin (pesticides, hairs, particles). Next, the kiwi fruits were crushed using an ENO-2 crusher (Magusa, Vilafranca del Penedés, Spain). The mash obtained was divided into 3 batches of 200 kg and put into 3 plastic fermentation tanks of 200 L followed by the addition of 35 mg/L of SO_2. Three kiwi fermentations were carried out: KL1, fermented with L1 yeast (*S. cerevisiae* EC1118, an active dry yeast from Lallemand, Zug, Switzerland), KL2, fermented with L2 yeast (a *S. cerevisiae* strain isolated as a major yeast from previous kiwi fermentations in EVEGA cellar), and KL3, a spontaneous fermentation (L3 yeast). L1 yeast was rehydrated for 20 min in 250 mL of sugared water at 37°C, acclimated in 1 L of kiwi juice and added to the fermentation tank at a concentration of 4.1×10^7 cells/mL, according to the instructions provided by the supplier. L2 yeast was previously grown in Yeast Extract Peptone Dextrose (YEPD) medium [1% (w/v) yeast extract, 2% (w/v) peptone and 2% glucose (w/v)] at 28 °C for 24 h, and the cells were recovered by centrifugation, washed with sterile water, and added into other kiwi tank at a concentration of 4.1 x 10^7 cells/mL. The remaining container was allowed to ferment spontaneously. All fermentations were performed in a room acclimated at 20ºC. The evolution of the fermentations was monitored by measurement of density until it reached a plateau. After 3 days of fermentation, samples were taken for microbiological control. The fermented kiwi mashes were stored at 4 ºC until distillation.

Grape pomaces. All grape pomaces were obtained after standard winemaking procedures, in correspondence to the type of grape (white grape pomace or red grape pomace). Grape pomace from *Albariño* and *Catalán Roxo* were separated from the grape fruits before the fermentation and briefly pressed. Grape pomace from *Xenérico* was fermented as red grape pomace and collected immediately after mashes were crushed and pressed. Each grape pomace was fermented separately in plastic tanks. Some fermentation (*Catalán Roxo* 2009 harvest and *Xenérico* 2010 harvest) were carried out spontaneously while commercial or autochthonous yeast strains were used as inoculum in the rest of them[1]. The spontaneous fermentations were named S1 and S2, as shown in **Table 2.1.**

The fermentation conditions for each grape pomace are detailed in **Table 2.1**. The commercial yeast strains (BDX and QA23) were rehydrated in 250 ml of sugared water at 37ºC for 20 min and added to the containers at the concentration showed in **Table 2.1**, according to the instructions provided by the supplier. The native yeast strain (XG3 and Sc24) were prepared following the procedure described in fermentation of kiwi fruits for L2 yeast and added to the containers at the concentration showed in **Table 2.1** for each type of grape pomace. In all cases the yeast inoculum was spread in the bottom, middle and top of containers during the filling process with marc and mixed to ensure its homogeneous distribution in the pomace. Then, the containers were hermetically closed and the fermentation and storage were performed at room temperature until distillation.

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[1] Commercial yeast: *Saccharomyces cereviseae* Uvaferm BDX and QA23 (active dry yeasts from Lallemand). Autoctonous yeast: *Saccharomyces cerevisiae* XG3 and Sc24 (from EVEGA yeast collection).

The evolution of the fermentation was monitored on a daily basis by measuring the temperature and density. When the density reached a plateau the fermentations were stopped by adding 50 mg/L of SO_2. The obtained ferments were stored at 4 ºC until distillation.

Table 2.1. Fermentation conditions for grape pomaces

Grape pomace (harvest)	Number of fermentations	Batch amount (kg) *	Yeast strain	Concentration of yeast (cells/mL)	T (ºC)
Albariño (2009)	6	50	XG3	1×10^6	20±5
	6	50	BDX	2.5×10^6	20±5
Albariño (2010)	5	50	XG3	1×10^6	20±5
	5	50	QA23	1×10^6	20±5
Catalán Roxo (2009)	8	50	S1	-	20±5
Catalán Roxo (2010)	2	200	QA23	1×10^6	20±5
	2	200	Sc24	1×10^6	20±5
Xenérico (2010)	4	200	S2	-	20±5

2.3 Distillation

The obtained ferments were distilled using the studied equipments: a copper *Charentais* alembic and a packed column. (**Figure 2.1).** The main characteristics of each distillation system are summarized in **Tables 2.2** and **2.3** (*Charentais* alembic and packed column, respectively).

Figure 2.1. Distillation equipment used in this thesis. (A) 50 L-alembic charentais, (B) 50 L-packed column. (C) 300 L-alembic charentais, (D) 300 L-packed column.

Table 2.2. Main characteristics of *Charentais* alembic distillations for pear, kiwi and grape pomace

	Capacity (L)	**Load (L, kg)***	**Distillation rate (L/h)**	**Heater**
Pear (first distillation)	20	12	14mL/min	electric
Pear (re-distillation)	2	1.2	3mL/min	electric
Kiwi	50	30	1.61	direct fire
Albariño (2009)	50	22-25	1.76	direct fire
Albariño (2010)	50	22-25	1.6	direct fire
Catalán Roxo (2009)	50	22-25	1.31	direct fire
Catalán Roxo (2010)	50	22-25	1.4	direct fire
Xenérico (2010)	300	200	35	direct fire

* Pear expressed in liters, kiwi and pomace expressed in kg

Table 2.3. Main characteristics of packed column distillations for pear, kiwi and grape pomace

	Capacity (L)	**Load (L, kg)[a]**	**Distillation rate (L/h)**	**Heater**
Pear	50	36, 21[b]	6 mL/s	electric
Kiwi	50	30	1.94	direct fire
Albariño (2009)	50	22-25	1.03	direct fire
Albariño (2010)	50	22-25	1.51	direct fire
Catalán Roxo (2009)	50	22-25	0.68	direct fire
Catalán Roxo (2010)	50	22-25	1.01	direct fire
Xenérico (2010)	300	200	11	direct fire

[a]Pear expressed in liters, kiwi and pomace expressed in kg, [b]for Bartlet pear variety

2.3.1 Alembic distillations

The distillations in alembic were carried out according to the procedure described below.

Pear distillation. The pear wine was double-distilled in the presence of its lees in order 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 in the first distillation was approximately 14 mL/min. The first 1.2 L of distillate were collected and used for 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 re-distillations were performed in triplicate, although the products of the first distillations were combined and then split into three equal volumes before re-distillation. Once a distillation had finished, the alembic was cooled. Then, it was washed and left to dry before the next distillation was performed. Usually only one distillation was performed per day. The head fraction was defined as the first 30, 20 and 35 mL for the *Blanquilla,* Conference and Bartlett distillates, respectively. The heart fraction included the samples from 30 mL to 500 mL, from 20 mL to 350 mL and from 35 mL to 550 mL for the Blanquilla, Conference and Bartlett distillates, respectively.

Kiwi distillation. 30 kg of fermented kiwi were distilled in a 50 L copper *Charentais* alembic. The base of the boiler was heated by an open flame, and tap water was used to cool the total condenser. The heating power was set to obtain an initial average distillation rate of 1.61 L/h. The first 100 mL of distillate were collected as head according an organoleptic analysis; the heart was collected until the ethanol concentration reached 40% v/v, and the tail was obtained until the ethanol concentration reached 28% v/v. Distillations were carried out in triplicate for each wine type. The respective head, heart and tail fractions of the three replicate distillations were mixed for sensorial and analytical analysis.

Grape pomaces distillation. Fermented grape pomaces from *Albariño* and *Catalán Roxo* varieties were distilled separately using a 50 L copper Charentais alembic. For *Xenérico* grape pomace a 300 L copper Charentais alembic was used. Before the distillation of samples of grape pomace, 7-10 L of distilled water had previously been added in order to prevent burning the marc. The operation conditions are detailed in **Table 2.2**. The base of the boiler was heated by direct fire, with natural gas as a heating source, and tap water was used to cool the total condenser. The heating power was set to obtain an initial average distillation rate in the range 1.3-1.8 L/h for *Albariño* and *Catalán roxo* grape pomaces, and 35 L/h for *Xenérico* grape pomace.

Table 2.4 summarizes the head, heart and tail fractions defined for each grape pomace distillates. The heads were the first 200-250, 150 and 300 mL for *Albariño* (2009 and 2010 harvests), *Catalán Roxo* 2009 and *Catalán Roxo* 2010, respectively, and 1.5 L for X*enérico.* The hearts were collected until the ethanol concentration reached 40% v/v, and the tails were obtained until the ethanol concentration reached 28% v/v.

Table 2.4. Volume (ml) collected for different fractions in grape pomace spirits distilled on alembic and column.

Grape pomace (harvest)	**Yeast strain**	**Copper *Charentais* alembic**			**packed-column**		
		Volum colected (mL)			**Volum colected (mL)**		
		Head	Heart	Tail	Head	Heart	Tail
Albariño (2009)	XG3	220	2320	600	240	2320	210
Albariño (2009)	BDX	220	1740	880	280	2290	310
Albariño (2010)	XG3	250	1330	600	250	1500	340
Albariño (2010)	QA23	250	1650	520	240	1590	440
Catalán Roxo (2009)	S1	150	940	610	160	1230	250
Catalán Roxo (2010)	QA23	300	1640	600	290	1910	400
Catalán Roxo (2010)	Sc24	300	1690	610	210	1800	370
Xenérico (2010)	S2	1500	21600	5900	1000	21750	4000

The number of distillations carried out for each grape pomace is detailed below:

- 6 distillations of *Albariño* 2009 and 5 distillations of *Albariño* 2010 for each of their corresponding yeasts. Each distillation was independently subjected to chemical analysis (without mixing).
- 8 distillations of *Catalán Roxo* 2009. Each distillation was independently subjected to chemical analysis.
- 7 distillations of *Catalán Roxo* 2010 for each yeast. In this case, two chemical analyses were performed by mixing the first three distillations and the remaining 4 distillations in separate groups (obtained from the same fermentation batch).
- 2 distillations of *Xenérico.*

2.3.2 Packed-column distillations

The packed column distiller used in this study has been described in chapter 1 (section **1.2**) and has been previously described in Garcia-Llobodanin et al. 2011 (see Figure **1.2)**. The packed column distillations were carried out according to the procedure described below.

Pear distillation. 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 high content 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 *Blanquilla* pear wine, first, four samples of 25 mL of distillate were collected, followed by two samples of 50 mL and then samples of 100 mL each, until the total volume collected reached 1000 mL. For the distillations of Conference pear wine, the first four samples were of 25 mL each, the fifth and sixth were of 100 mL, the next three were of 200 ml and the last ones collected were of 100 mL each, for a total volume of 2000 mL. For the distillations of Bartlett pear wine, the first four samples were of 25 mL each, followed by samples of 100 mL each up to a total volume of 1500 mL. The head fraction was defined as the first 75 mL of distillate. The heart fraction included samples from 75 mL to 900 mL for Blanquilla, from 75 mL to 1200 mL for Conference and from 75 mL to 800 mL for Bartlett. In all cases, the rest was the tail fraction.

Kiwi distillation. 30 kg of fermented kiwi were distilled in a packed column with a 50 L copper boiler. The first 140 mL of distillate were collected as head, the heart was collected until the ethanol concentration reached 40% v/v, and the tail was obtained until the ethanol concentration reached 28% v/v. Distillations were carried out in triplicate for each wine type. The respective head, heart and tail fractions of the three replicate distillations were mixed for sensorial and analytical analysis.

Grape pomace distillation. Fermented grape pomaces of *Albariño* and *Catalán Roxo* varieties were distilled in a small packed column with a 50 L copper boiler, while the *Xenérico* grape pomace was distilled with a 300 L copper boiler. The operation conditions and the amounts of each fermented grape pomace used for distillation are detailed in **Table 2.3**.

Based on an organoleptic analysis, distillation products were separated in three fractions: heads, hearts and tails. And they were defined as summarized in **Table 2.4**. The heads collected ranged between 150 to 300 mL for *Albariño* and *Catalán Roxo*, while for *Xenérico* it was 1000 mL. The hearts were collected until the ethanol concentration reached 40% v/v, and the tails were obtained, until the ethanol concentration reached 28% v/v. The number of distillations and the number of samples for chemical analysis were carried out with the same procedure followed with the alembic (section **2.3.1**).

2.4 Classical chemical Analysis

The classical chemical parameters were determined according to the o*rganisation Internationale de la Vigne et du Vin*, OIV (OIV, 2009) and the Official Journal of the European Communities (ECC, 1990). The methods used are summarized in **Table 2.5.**

2.5 Gas-chromatography analysis

The concentrations of volatile compounds were expressed in grams of solute in 100 hL of pure alcohol (g/hL p.a.) following the CE Regulation 2870/2000 (EC, 2000), laying down community reference methods for the analysis of the spirits drinks.

The head, heart and tail fractions of each obtained distillate were analysed 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) equipped with a split/splitless injector with an electronic flow control (EFC), and a FID was used to evaluate the macroconstituents (methanol, higher alcohols, acetaldehyde, 1,1-diethoxyethane, ethyl acetate, ethyl lactate, 1-hexanol, isobutyraldehyde, ethyl formate, methyl acetate, 2-propenal, 2-butanol and allylic alcohol). The conditions have been reported in López-Vázquez et al. (2010b). The remaining compounds were separated using a Supelcowax 10 capillary column (30 m, 0.32 mm, 0.25 μm film thickness; Supelco Inc., Bellefonte, PA, USA) in a GC Varian CP3900 (Varian Medical Systems Barcelona, Spain), using the method described in López-Vázquez et al. (2010a). 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.

Table 2.5. Classical chemical analysis

Chemical parameter	Method	Applied to
citric acid (g/L)	Enzymatic-spectrophotomety, LISA 200 autoanalyzer, TDI, Barcelona, Spain	Kiwi mash, kiwi wine
malic acid (g/L)	Enzymatic-spectrophotomety, LISA 200 autoanalyzer, TDI, Barcelona, Spain	Kiwi mash, kiwi wine
density (g/mL)	Anton Paar DMA 5000 density meter (Anton Paar GmbH, Graz, Austria)	Kiwi mash, kiwi wine, pear juices, fermented pear juices
alcoholic strength (%V/V)	Steam-distillation of kiwi wine made alkaline by a suspension of calcium hydroxide	Kiwi wine
alcoholic strength (%V/V)	Anton Paar (DMA 5000 density meter (Anton Paar GmbH, Graz, Austria)	Kiwi, pear, and grape pomace spirits
total sugars (g/L)	GAB kit for sugar analysis (GAB Sistemática Analítica S.L., Spain).	Pear juice, pear ferments, kiwi mash
reduced sugars (g/L)	Cupric-alkaline method	Kiwi wine
total acidity (g/L tartaric acid)	Acid−alkali titration, Crison TitroMatic 1S, Barcelona, Spain	Kiwi mash, kiwi wine
volatile acidity (g/L acetic acid)	Titration of the volatile acids separated by steam-distillation with sodium hydroxide	Kiwi wine
pH	Crison micropH 2000, Barcelona, Spain	Kiwi mash, kiwi wine

2.6 Sensory analysis

The sensory analysis of the distillates was carried out in two steps: order-of-preference tests and quantitative descriptive analysis (QDA). All distillates (the heart fractions) were diluted with Milli-Q treated water (Millipore Corp., Bedford, MA, USA) to an ethanol content of 40% v/v.

The samples were served in AFNOR glasses and labeled with random numbers at room temperature. The distillates obtained from *Catalán Roxo* 2009 harvest were not subjected to sensory analysis due to excessively high values of ethyl acetate, above the maximum permitted (250 g/hL) by the Regulation of the Geographic Indication of the spirits and Traditional Liqueurs from Galicia and its Regulating Council (DOG nº 10, 2012).

2.6.1 Order-of-precedence test

The main objective of the order-of-precedence test was to determine significant differences between samples distilled with alembic and those distilled with packed column. To this end, the consumers were asked to rank by preference the distillates evaluating separately aroma and taste, awarding the following score: 1 the most preferred, 2 to the second and so on up to 4 or 6 (depending on the number of samples), being the higher score the least preferred. The results were analyzed using the Friedman statistical test (Jellinek, 1981). The number of consumers for each sensory analysis is detailed below.

- **Pear distillates.** The panel was composed of 16 consumers with experience in tasting distillates.
- **Kiwi distillates.** The panel was composed of 37 consumers (26 males and 11 females) ranged between 18 and 60 years old.
- **Distillates obtained from *Albariño* 2009 harvest.** Two series were realized, composed of 37 consumers each one (27 men and 10 women).
- **Distillates obtained from *Albariño* 2010 harvest.** Two series were realized, both composed of 37 consumers, one of 27 men and 8 women and another one of 26

men and 11 women.

- **Distillates obtained from *Catalán Roxo* 2010 harvest.** Two series were realized, one composed of 37 consumers (27 men and 5 women) and the other one composed of 37 consumers (26 men and 11 women).
- **Distillates obtained from *Xenérico* 2010 harvest.** One serie composed of 36 consumers (25 men and 11 women) was realized.

2.6.2 Quantitative descriptive sensory analysis (QDA)

The second evaluation was a descriptive sensory analysis performed by a trained panel (five people) with experience in the assessment of distillates. This analysis was not made with the pear distillates. Previously, the most representative descriptive attributes of the distillates were defined in an initial tasting session according to the method described in the ISO 13299:2003 norm. The chosen attributes were aroma and taste descriptors. This test consisted in a preliminary round table discussion, where the panellists defined the terms: 11 aroma descriptors grouped by common categories (floral, fruity, vegetal/herbaceous, spicy, positive general impression, solvent, rancid, oxidized, pungent, burnt/smoky, negative general impression) and 8 taste descriptors (astringency/bitterness, mellowness, sweet, harmony, alcoholic, persistence, pungent and general quality in mouth), as shown in **Annex I**. Then, an individual smelling and tasting of the samples was carried out by the panellist in order to qualify the distillates. All samples were assessed in one formal session that lasted 3 h with several breaks.

The intensities of the descriptors were rated on a discontinuous scale from 0 to 5. A zero score indicated that a descriptor was not perceived and a score of 5 indicated the highest intensity.

2.7 Statistical analysis

The data concerning volatile compounds in the heart fractions of the different distillates obtained were statistically analyzed by One-way analysis of variance (ANOVA) and principal component analysis (PCA). Means were compared by Fisher’s least significant difference (LSD) test at $p \leq 0.05\%$ in order to assess whether the distillation system led to any significant differences in the composition. For kiwi distillates, ANOVA was not realized due to the limited number of samples. More details of PCA analysis are given in each section. All statistical analyses were performed with the SPSS statistical package (version 15.0, SPSS Inc., Chicago, IL, USA).

Chapter 3

Results and discussion

3.1 Pear distillates

3.1.1 Abstract

Pear distillates are generally produced from the Bartlett variety because of its rich aroma. In this study, a chemical and sensory 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 fruity ethyl ester and acetates 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.

3.1.2 Fermentation

The initial sugar concentrations were 73.50, 53.25, and 94 g/L for the *Blanquilla*, Conference, and Bartlett juices, respectively. The juices 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.

3.1.3 Chemical composition of pear distillates

Major volatile compounds. **Table 3.1** 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 analyzed pear distillates. According to **Table 3.1**, the ethanol content 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. (García-Llobodanin et al., 2011, 2010a, 2010b). With regard to pear variety, methanol content was significantly higher in distillates from *Blanquilla* pears. The average concentration of ethyl acetate in our distillates ranged between 34.7 and 268.10 g/hL of pure alcohol (p.a.). The alembic distillates contained levels much lower than the perception threshold [180 g/hL p.a., according to Soufleros et al. (2004), 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 p.a. proposed by Odello et al. (1997). In addition, the distillates produced by alembic distillation had lower amounts of this compound than the column distillates. With regard to pear variety, *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 obtained from the other varieties. The higher alcohols composition was also significantly different between distillates from different varieties, except for 3-methyl-1-butanol. The total concentration of higher alcohols was 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 (García-Llobodanin et al., 2011, 2010a, 2010b, 2007). Postel and Adam (1990) 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 of ethyl lactate (<62 g/hL p.a.), suggesting that bacterial spoilage did not occur during fermentation (Apostolopoulou et al., 2005). The smell of this compound is similar to a mixture of sour milk and raspberry and can be unpleasant at concentrations above 150 g/hL p.a. (López-Vázquez, 2011). Concentrations of 1-hexanol in our pear distillates ranged between 1.65 and 9.80 g/hL p.a., below the level at which an unpleasant herbal smell is noticeable (López-Vázquez et al., 2010a). The impact of pear variety on 1-hexanol concentrations was more significant than the impact of the distillation system. Both Bartlett distillates possessed concentrations lower than 2.5 g/hL p.a., which, according to Galy et al. (2008), 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.

Table 3.1. Average concentrations (g/hL p.a.) and standard deviations 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]

	copper *Charentais* alembic			**packed-column**		
Compound	***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±10.34^{a},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	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 acetal. + 1,1-dieth.	**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	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±0.20^{a},b	3.17±0.25b,a	5.23±0.13^{a},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*	**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≤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≤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.

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 (**Tables 3.2**, **3.3**). For example, the levels of acetates of longer chain alcohols, which supply the distillates with apple-banana fruity scents (Versini et al., 2009), were similar in these distillates. 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 of the Bartlett alembic distillate. Similarly, both pear variety and distillation system affected the concentrations of high molecular weight ethyl esters (**Table 3.2**). 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 (Falqué et al., 2001). 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 3.3**). 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 3.2**) were 2 times higher in column distillates than in alembic distillates for the *Blanquilla* and Conference varieties, and five times higher for the Bartlett variety. Similarly, the concentration of furfural (**Table 3.3**) in the column Bartlett distillate was four 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 3.3**).

Other families of microconstituents were less affected by the distillation system (see **Table 3.2**). Low molecular weight ethyl esters contribute to fruity aromas (Soufleros et al., 2004), and ethyl-2-*trans*-4-*cis*-decadienoate is particularly important because it gives pear distillates their characteristic and pleasant pear-like aroma (Cigic and Zupancic-Kralj, 1999). 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 the 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 p.a. (Maarse and Visscher, 1989). 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 (Versini et al., 2009). 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 3.3**). 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 3.3**). 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 3.3**).

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 3.3**). C6 alcohols in concentrations higher than 12 mg/L contribute with fatty notes to the aroma of brandies

(Ebeler et al., 2000). 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 respect to minor alcohols, 2-phenylethanol was present at the highest concentration (**Table 3.3**). 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 (Gerogiannaki, 2009). 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 (Apostolopoulou et al., 2005). The levels found in the distillates produced in this study (<2 g/hL p.a.) indicate that the tail fraction was well separated.

Table 3.2. Average concentrations (g/hL p.a.) and standard deviations of microconstituents (acetates and esters) present in distillates obtained from *Blanquilla*, Conference, and Bartlett pear for each distillation process (copper *Charentais* alembic and packed-column).[a]

	copper *Charentais* alembic			**packed-column**		
Compounds	***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.

Table 3.3 Average concentrations (g/hL p.a.) and standard deviations 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]

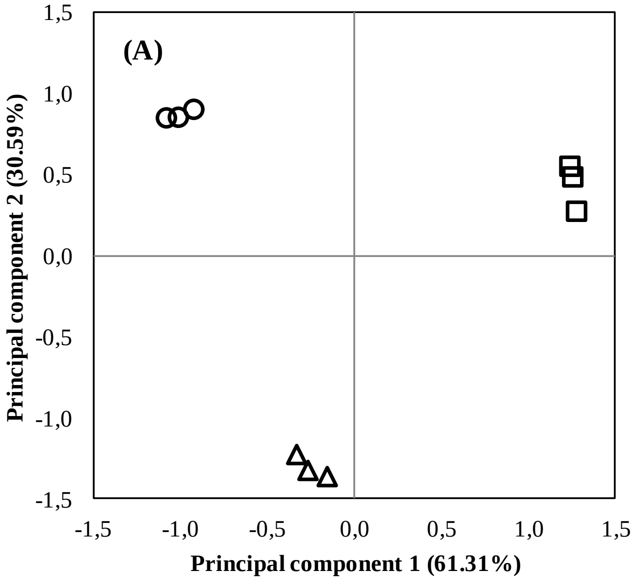
	copper *Charentais* alembic			packed-column		
Compounds	***Blanquilla***	**Conference**	**Bartlett**	***Blanquilla***	**Conference**	**Bartlett**
Alcohols						
trans-3-hexen-1-ol	0.08±0.06a,a	0.08±0.04a,a	<LOD	0.07±0.01a,a	0.09±0.02a,a	0.03±0.03b,b
cis-3-hexen-1-ol	1.18±0.04a,a	0.69±0.14b,a	0.05±0.04c,a	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)[c]	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 limit. [c]Σ 1-heptanol, 1-octanol, 1-nonanol, 1-decanol.

3.1.4 PCA analysis

PCA was separately applied to the heart fractions of the distillates obtained by both distillation systems. 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 column distillates, PC1 and PC2 explained 64.55% 25.20% of the variance, respectively. **Figure 3.1** plots 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 previous observation that alembic distillation is more reproducible (García-Llobodanin et al., 2011). **Tables 3.4** and **3.5** 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 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.



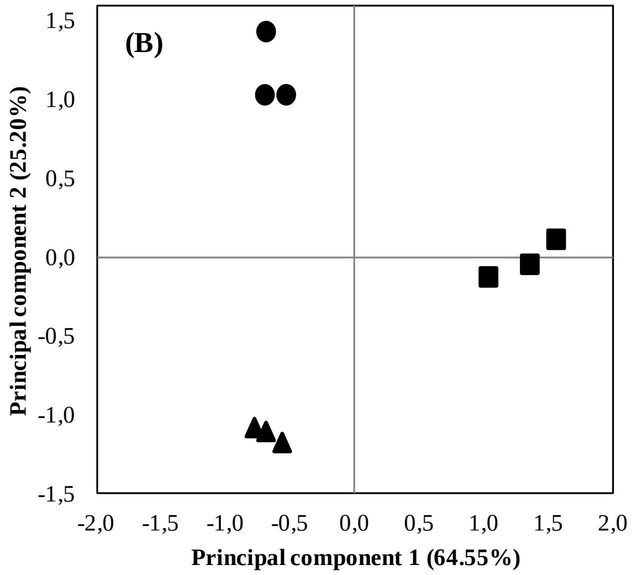


Figure 3.1. Principal components analysis of the volatile composition of the pear distillates: (A) PCA loadings of *Blanquilla* (○), Conference (△), and Bartlett (□) distilled in a copper *Charentais* alembic; (B) PCA loadings of *Blanquilla* (●), Conference (▲) and Bartlett (■) distilled in a packed column.

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

Table 3.4. PCA results for the average volatile compounds in the pear distillates produced from the *Blanquilla*, Conference and Bartlett pear varieties distilled in copper *Charentais* alembic.

Principal Component	Compound	Loading	Variance explained (%)	Total variance (%)
PC1	ethyl tetradecanoate	992	61.31	61.31
	cis-3-hexen-1-ol	-984		
	1-butanol	982		
	Isoamyl acetate	978		
	ethyl octanoate	967		
	methanol	-966		
	ethyl decanoate	962		
	ethyl-2-*trans*-4-*cis*-decadienoate	954		
	1,1-diethoxyethane (acetal)	-952		
	2-methyl-1-butanol	951		
	isobutyraldehyde	-950		
	ethyl butyrate	950		
	2-methyl-1-propanol	947		
	1-hexanol	-942		
	ethyl dodecanoate	932		
	2-phenylethanol	-866		
	ethyl hexadecanoate	770		
	3-hydroxy-2-butanone	-758		
	allylic alcohol	743		
PC2	ethyl lactate	971	30.59	91.90
	1-pentanol	-960		
	linalool	-955		
	ethyl acetate	910		
	1-octanol	-893		
	benzylic alcohol	-857		
	1-decanol	-850		
	diethyl succinate	842		
	ethyl 9-octadecenoate	838		
	geraniol	-831		
	acetaldehyde	795		
	Hotrienol	-786		
	citronellol	766		

In order to assess the influence of the distillation system, 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, isobutyraldehyde, 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 3.6**), are depicted in **Figure 3.2**.

Table 3.5. PCA results for the average volatile compounds in the pear distillates produced from the *Blanquilla*, Conference and Bartlett pear varieties distilled in packed column.

Principal Component	Compound	Loading	Variance explained (%)	Total variance (%)
PC1	ethyl-2-*trans*-4-*cis*-decadienoate	0.992	64.55	64.55
	ethyl decanoate	0.990		
	ethyl dodecanoate	0.987		
	isoamyl acetate	0.986		
	1-hexanol	-0.975		
	geraniol	0.943		
	ethyl lactate	-0.939		
	ethyl tetradecanoate	0.934		
	ethyl octanoate	0.890		
	2-methyl-1-propanol	-0.881		
	2-methyl-1-butanol	0.864		
	3-hydroxy-2-butanone	0.852		
	ethyl hexadecanoate	0.850		
	diethyl succinate	-0.849		
	cis-3-hexen-1-ol	0.816		
	hotrienol	0.734		
	citronellol	-0.718		
	ethyl 9-octadecenoate	0.968		
	isobutyraldehyde	0.958		
	furfural	0.953		
	trans-furan linalool oxide	0.953		
	methanol	0.950		
PC2	acetaldehyde	0.951	25.20	89.75
	allylic alcohol	-0.931		
	1-decanol	0.906		
	1-octanol	0.798		
	1,1-diethoxyethane (acetal)	0.798		
	linalool	-0.779		
	Isoamyl decanoate	-0.766		
	benzylic alcohol	-0.748		
	ethyl acetate	-0.742		
	ethyl butyrate	0.718		
	1-butanol	0.715		
	2-phenylethanol	0.686		

Table 3.6. PCA results for the average volatile compounds in the pear spirits produced from the Blanquilla, Conference and Bartlett pear varieties distilled in packed column and copper *Charentais* alembic.

Principal Component	**Compound**	**Loading**	**Variance explained (%)**	**Total variance (%)**
PC1	ethyl-2-*trans*-4-*cis*-decadienoate	0.987	56.65	56.65
	ethyl decanoate	0.984		
	ethyl dodecanoate	0.961		
	ethyl octanoate	0.949		
	1-hexanol	-0.916		
	ethyl lactate	0.833		
	diethyl succinate	0.772		
PC2	isobutyraldehyde	0.950	25.92	82.57
	ethyl acetate	0.931		
	acetaldehyde	0.737		
	2-phenylethanol	-0.685		

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 3.2** also shows that *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 3.2**), these differences were not evident in the PCAs. Consequently, ethyl esters could only differentiate Bartlett spirits from the other two.

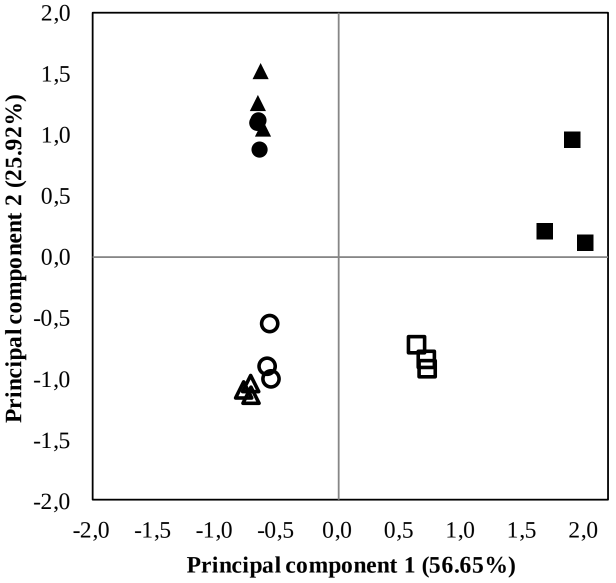


Figure 3.2. Principal components analysis of the volatile composition of the pear distillates *Blanquilla* (○, ●), Conference (△, ▲), and Bartlett (□, ■) distilled in a copper *Charentais* alembic (open symbols) or in a packed column (solid symbols)**.**

3.1.5 Sensory analysis

Considering aroma, the three alembic pear distillates 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 identified volatile compounds, it was possible to differentiate the distillates 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 distillates, 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.

3.2 Kiwi distillates

3.2.1 Abstract

In order to investigate the impact of the distillation system and yeast strain on the chemical and aromatic profile of kiwi distillates, three fermentations of kiwi fruits were carried out: two with selected yeasts (KL1 and KL2) and one spontaneous (KL3). The obtained kiwi wines were distilled using two different distillation systems (*Charentais* alembic and packed column) and the resulting distillates were analysed by direct injection gas chromatography. Kiwi distillates obtained with the packed column had the highest concentrations of esters c6-c10 and monoterpenols, while the alembic distillates had the highest concentrations of ethyl acetate, methyl acetate and higher alcohols. Three principal components derived from the chemical composition data explained 96.6% of the variance. Principal component 1 differentiates alembic distillates from packed column distillates, principal component 2 distinguishes KL3 distillates and principal component 3 distinguishes KL1 distillates. Kiwi spirits distilled with the packed column were preferred by consumers. The predominant sensory descriptors in packed column kiwi distillates were floral, fruity and spicy, while burnt/smoky and pungent were the principal aroma descriptors in alembic distillates. Moreover, significantly higher ethanol yields and ethanol strengths were obtained with the packed column distillation system. The observed influence of the yeast strains on preference and ethanol yields were minor.

3.2.2 Fermentation process

The kiwi mash had a total sugar content of 101.4 g/L, an initial pH of 3.27, and a density of 1046 g/mL. The total acidity was 11.5 g/L tartaric acid, and an initial concentration of 4.8 g/L of citric acid and 1.2 g/L of malic acid. Fermentations took 4-6 days to complete. In the analysis of isolated yeasts for spontaneous fermentation, the *S. cerevisiae* strain named as XXII in previous studies (Blanco et al., 2011) appeared as the dominant yeast (frequency 82%). *S. cerevisiae* XXII had been found as a resident strain in EVEGA winery and its profile is similar to that of the commercial strain Excellence XR (Blanco et al., 2012). The characteristics of the final kiwi ferments are summarized in **Table 3.6**.

Table 3.7. Physical and chemical characteristics of Kiwi wine.

Yeast	L1	L2	L3
citric acid (g/L)	0.84	0.80	0.88
density(g/mL)	0.99365	1.00806	1.0087
alcoholic strength (%v/v)	5.4	5.5	5.4
reduced sugars (g/L)	5.2	5.6	5.8
total acidity (g/L tartaric acid)	10.7	9.6	10.1
volatile acidity (g/L acetic acid)	2.82	3.59	3.13
pH	3.95	4.01	3.91
malic acid (g/L)	6.5	4.8	6.1

3.2.3 Distillation

Table 3.7 shows the efficiency of the two distillation systems, measuring ethanol recovery in the heart fraction. For alembic distillation, the average heart ethanol yield was 51.1 %, with an average alcoholic strength of 44.9 % v/v. For the column distillations, the average heart ethanol yield was 79.6% with average alcoholic strength of 54.4 % v/v. No effect of the yeast strains on the ethanol productivity in the heart fraction was observed.

Table 3.8. Ethanol balance in both distillation systems for kiwi distillates

	Copper *Charentais* alembic			**Packed-column**		
	yeast strain			**yeast strain**		
	L1	**L2**	**L3**	**L1**	**L2**	**L3**
Heart alcoholic strength (% v/v)	44.8±0.4	45.1±0.5	44.8±0.4	54.4±1.1	55.3±3.3	53.4±2.3
Heart ethanol yield (%)	52.5±2.7	50.8±2.3	49.9±2.6	77.7±2.6	82.0±4.6	79.0±3.6
Heart total higher alcohols (g/hL p.a.)	768.4±0.1	786.4±0.5	813.1±0.3	567.5±0.5	553.2±1.1	565.6±0.6
total higher alcohols recovered (g/100 L real distillate)	403.4±0.06	399.5±0.26	405.7±0.13	440.4±0.28	454.7±0.23	446.8±0.43
Heart 1-hexanol (g/hL p.a.)	3.59±0.01	3.72±0.01	4.05±0.01	2.61±0.01	2.54±0.03	2.75±0.01
Total 1-hexanol recovered (g/100 L real distillate)	1.45±0.01	1.89±0.01	2.02±0.01	2.03±0.01	2.09±0.03	2.17±0.01
Heart total linear alcohols (g/hL p.a.)	0.55±0.04	0.68±0.10	0.82±0.09	0.39±0.05	0.46±0.04	0.49±0.04
Total linear alcohols recovered (g/100 L real distillate)	0.29±0.01	0.35±0.03	0.41±0.02	0.30±0.02	0.38±0.04	0.39±0.06

3.2.4 Chemical composition of kiwi distillates

Tables 3.9, 3.10 and 3.11 show the average concentration of macroconstituents and microconstituents for the distillates obtained with the alembic and column distillation systems. Data is grouped according to the yeast used in the kiwi fermentation. 58 volatile compounds have been identified and quantified. The results showed differences among the samples according to the distillation system, mainly in ethyl acetate, higher alcohol, 1-hexanol, methyl acetate, the sum of *trans/cis* hexenols, the sum of acetates of higher alcohols, linear alcohols, ethyl esters C6-C12, ethyl esters C14-C18 and monoterpenols. All of these compounds being slightly higher in alembic except esters C6-C12 and monoterpenols.

Table 3.9. Average concentrations (g/hL p.a.) and standard deviations of macroconstituents present in distillates obtained from kiwi fermented with different yeast strains and two distillation systems.[a]

	Copper *Charentais* alembic			**Packed-column**		
	yeast strain			**yeast strain**		
	L1	**L2**	**L3**	**L1**	**L2**	**L3**
ethanol % V/ V	45.2	44.9	44.4	54.2	55.6	53.4
methanol	708.0 ± 0.5	701.3±0.6	699.9±0.2	775.2±0.3	783.2±0.3	776.5±0.1
ethyl acetate	140.0 ± 0.1	166.90±0.01	179.0±0.2	67.80±0.03	70.50±0.03	80.5±0.1
acetaldehyde	12.90 ± 0.01	8.76±0.01	15.30±0.08	11.40±0.01	6.59±0.08	7.71±0.01
1.1-dietoxiethane	7.60 ± 0.01	5.26±0.02	8.49±0.09	10.60±0.01	6.61±0.05	6.81±0.01
Σ acetaldehyde + 1.1-diethoxyethane	**20.50 ± 0.01**	**14.00±0.03**	**23.80±0.17**	**22.00±0.02**	**13.20±0.14**	**14.50±0.02**
1-propanol	40.90 ± 0.01	28.20±0.14	23.10±0.02	37.20±0.02	25.20±0.01	20.80±0.01
2-methyl-1-propanol	240.0 ± 0.1	239.8±0.1	328.7±0.1	175.5±0.1	171.4±0.3	227.9±0.3
1-butanol	3.86 ± 0.01	3.82±0.01	3.40±0.01	3.25±0.01	3.15±0.01	2.78±0.01
2-butanol	5.06 ± 0.01	5.09±0.01	4.07±0.03	2.38±0.01	1.87±0.01	1.50±0.01
allylic alcohol	0.10 ± 0.01	0.14±0.01	0.43±0.01	0.02±0.01	0.13±0.01	0.24±0.03
2-methyl-1-butanol	191.0 ± 0.01	182.6±0.2	179.1±0.1	135.7±0.2	132.0±0.1	119.0±0.1
3- methyl-1-butanol	287.4 ± 0.03	326.8±0.2	274.3±0.1	213.5±0.3	219.5±0.7	193.4±0.2
Σ total higher alcohols[b]	**768.4 ± 0.1**	**786.4±0.5**	**813.1±0.3**	**567.5±0.5**	**553.2±1.1**	**565.6±0.6**
ethyl lactate	20.60 ± 0.02	21.90±0.01	16.10±0.05	18.60±0.04	18.9±0.1	14.40±0.02
1-hexanol	3.59 ± 0.01	3.72±0.01	4.05±0.01	2.61±0.01	2.54±0.03	2.75±0.01
isobutyraldehyde	0.04 ± 0.01	<LOD	<LOD	<LOD	<LOD	<LOD
ethyl formiate	1.55 ± 0.01	0.87±0.18	0.95±0.07	1.27±0.05	0.97±0.01	0.78±0.01
methyl acetate	3.35 ± 0.05	3.71±0.11	4.54±0.01	1.51±0.03	1.54±0.01	1.89±0.01
2-propenal	0.26 ± 0.01	0.42±0.45	0.26±0.01	0.47±0.01	0.21±0.01	0.27±0.04

[a] Results correspond to the average of three replicates of gas-chromatography analysis. [b] Σ 2-methyl-1-propanol, 1-butanol, allylic alcohol, 2-methyl-1-butanol, 3-methyl-1-butanol.

Table 3.10. Average concentrations (g/hL p.a.) and standard deviations of microconstituents (Esters) present in distillates obtained from kiwifruit fermented with different yeast strains.[a]

	Copper *Charentais* alembic			**Packed-column**		
	yeast strain			**yeast strain**		
	L1	**L2**	**L3**	**L1**	**L2**	**L3**
isobutyl acetate	2.12 ± 0.03	2.16±0.03	3.28±0.49	1.40±0.01	1.58±0.03	2.83±0.12
butyl acetate	0.20 ± 0.02	0.09±0.01	0.17±0.04	0.29±0.02	0.08±0.01	0.11±0.01
isoamyl acetate	1.41 ± 0.01	0.67±0.11	1.15±0.02	1.04±0.06	0.35±0.04	0.62±0.02
hexyl acetate	<LOD	<LOD	<LOD	<LOD	0.03±0.01	<LOD
2-phenylethyl acetate	0.22 ± 0.01	0.27±0.01	0.19±0.04	0.13±0.02	0.15±0.01	0.13±0.03
Σ acetates of higher alcohols	3.95 ± 0.06	3.19±0.16	4.79±0.59	2.86±0.10	2.19±0.08	3.69±0.19
ethyl butyrate	0.72 ± 0.01	0.99±0.27	0.71±0.06	0.80±0.07	0.32±0.05	0.39±0.01
ethyl hexanoate	0.32 ± 0.01	0.14±0.01	0.06±0.01	0.69±0.01	0.37±0.01	0.18±0.06
ethyl octanoate	1.01 ± 0.02	1.44±0.04	0.67±0.06	3.08±0.11	3.30±0.01	1.24±0.07
ethyl decanoate	1.95 ± 0.01	3.01±0.09	1.76±0.07	3.90±0.07	7.83±0.01	3.45±0.20
ethyl dodecanoate	0.34 ± 0.01	0.44±0.01	0.51±0.03	0.61±0.01	0.48±0.05	0.55±0.01
Σ ethyl esters C6-C12[c]	3.62 ± 0.05	5.02±0.15	2.99±0.18	8.28±0.19	11.98±0.08	5.43±0.34
ethyl tetradecanoate	0.02±0.01	0.05±0.02	0.04±0.01	0.04±0.01	0.01±0.01	0.01±0.01
ethyl hexadecanoate	<LOD	0.01±0.01	<LOD	0.01±0.01	<LOD	0.01±0.01
ethyl octadecanoate	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
ethyl 9-octadecenoate	0.01±0.01	<LOD	0.10±0.02	0.05±0.01	<LOD	<LOD
Ethyl 9.12-octadecadienonate	0.16±0.01	0.06±0.02	0.04±0.01	0.18±0.02	<LOD	<LOD
Ethyl 9.12.15-octadecatrienoate	0.26±0.01	0.26±0.05	0.16±0.01	0.13±0.01	0.14±0.01	0.19±0.01
Σ ethyl esters C14-C18	0.45±0.04	0.38±0.10	0.34±0.05	0.39±0.06	0.16±0.02	0.21±0.03
isoamyl octanoate	<LOD	0.07±0.01	0.15±0.01	0.09±0.01	0.15±0.01	0.09±0.01
diethyl succinate	1.71±0.01	2.41±0.15	1.08±0.08	1.28±0.13	1.63±0.06	1.29±0.01

[a]Results correspond to the average of three replicates of gas-chromatography analysis. [b] LOD, detection limit. [c]Σ ethyl hexanoate, ethyl octanoate, ethyl decanoate, ethyl dodecanoate.

Table 3.11. Average concentrations (g/hL p.a.) and standard deviations of microconstituents (minor alcohols, monoterpenols and other compounds) present in distillates obtained from kiwi fermented with different yeast strains.[a]

	Copper *Charentais* alembic			**Packed-column**		
	yeast strain			**yeast strain**		
	L1	**L2**	**L3**	**L1**	**L2**	**L3**
trans-3-hexen-1-ol	0.10 ± 0.01	0.09 ± 0.01	0.20 ± 0.03	0.07 ± 0.01	0.08 ± 0.01	0.11 ± 0.01
cis-3-hexen-1-ol	0.09 ± 0.01	0.10 ± 0.05	0.10 ± 0.01	0.04 ± 0.01	0.06 ± 0.01	0.08 ± 0.01
trans-2-hexen-1-ol	0.06 ± 0.01	0.06 ± 0.01	0.05 ± 0.01	0.04 ± 0.01	0.02 ± 0.01	0.03 ± 0.02
Σ *trans/cis* hexenols	**0.24 ± 0.03**	**0.25 ± 0.07**	**0.36 ± 0.04**	**0.15 ± 0.03**	**0.16 ± 0.03**	**0.23 ± 0.04**
1-pentanol	0.34 ± 0.01	0.40 ± 0.09	0.40 ± 0.06	0.33 ± 0.02	0.38 ± 0.01	0.46 ± 0.02
1-heptanol	0.07 ± 0.01	0.08 ± 0.03	0.07 ± 0.01	0.06 ± 0.02	0.07 ± 0.01	0.09 ± 0.01
1-octanol	0.28 ± 0.01	0.33 ± 0.04	0.30 ± 0.05	0.20 ± 0.02	0.22 ± 0.01	0.19 ± 0.01
1-nonanol	0.11 ± 0.01	0.20 ± 0.02	0.28 ± 0.01	0.10 ± 0.01	0.12 ± 0.01	0.13 ± 0.01
1-decanol	0.10 ± 0.01	0.07 ± 0.02	0.17 ± 0.02	0.03 ± 0.01	0.04 ± 0.01	0.07 ± 0.01
benzylic alcohol	0.35 ± 0.01	0.29 ± 0.01	0.61 ± 0.01	0.15 ± 0.03	0.15 ± 0.02	0.47 ± 0.04
2-phenylethanol	14.51 ± 0.02	16.03 ± 1.30	17.94 ± 0.16	8.33 ± 1.18	10.04 ± 0.01	12.12 ± 0.51
Σ linear alcohols [b]	0.55 ± 0.04	0.68 ± 0.10	0.82 ± 0.09	0.39 ± 0.05	0.46 ± 0.04	0.49 ± 0.04
			Other compounds			
Benzaldehyde	0.14 ± 0.01	0.13 ± 0.03	0.13 ± 0.01	0.12 ± 0.01	0.10±0.01	0.11±0.01
Furfuraldehyde	1.15 ± 0.06	0.82 ± 0.01	0.22 ± 0.02	1.35 ± 0.10	1.12±0.01	0.61±0.01
3-ethoxy-1-propanol	0.26 ± 0.01	<LOD	<LOD	0.13 ± 0.05	<LOD	<LOD
1-octen-3-ol	0.05 ± 0.01	0.07 ± 0.01	0.02 ± 0.01	0.03 ± 0.01	0.04±0.01	0.03±0.01
3-hydroxy-2-butanone	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
			Monoterpenols			
trans-furan linalool oxide	0.42 ± 0.01	0.47 ± 0.04	0.35 ± 0.01	0.51 ± 0.01	0.50 ± 0.01	0.53 ± 0.05
cis-furan linalool oxide	0.15 ± 0.01	0.19 ± 0.01	0.10 ± 0.01	0.65 ± 0.01	0.96 ± 0.01	0.87 ± 0.09
Linalol	0.34 ± 0.01	0.43 ± 0.01	0.38 ± 0.01	0.37 ± 0.01	0.50 ± 0.01	0.46 ± 0.01
α-terpineol	0.04 ± 0.01	0.08 ± 0.01	0.06 ± 0.01	0.08 ± 0.01	0.11 ± 0.01	0.10 ± 0.01
Citronellol	0.06 ± 0.01	0.18 ± 0.01	0.12 ± 0.01	0.07 ± 0.01	0.15 ± 0.01	0.12 ± 0.01
Nerol	0.02 ± 0.01	0.02 ± 0.01	0.03 ± 0.01	0.01 ± 0.01	0.02 ± 0.01	0.02 ± 0.01
Geraniol	0.13 ± 0.01	0.29 ± 0.01	0.23 ± 0.01	0.21 ± 0.02	0.29 ± 0.02	0.30 ± 0.02
Hotrienol	0.29 ± 0.01	0.31 ± 0.06	0.19 ± 0.01	0.16 ± 0.03	0.18 ± 0.01	0.21 ± 0.01
Σ monoterpenols	**1.45 ± 0.15**	**1.96 ± 0.16**	**1.45 ± 0.13**	**2.06 ± 0.23**	**2.71 ± 0.31**	**2.61 ± 0.28**

[a] Results correspond to the average of three replicates of gas-chromatography analysis. [b] Σ 1-heptanol, 1-octanol, 1-nonanol, 1-decanol.

3.2.5 PCA analysis

To simplify the analysis, the concentrations of higher alcohols, *cis* and *trans* hexenols, linear alcohols and monoterpenols were grouped as family sums. Three principal components (see **Table 3.12**) explained 96.6 % of the total variance. As seen in **Figure 3.3**, PC1 accounts for 40.4% of the total variance and clearly differentiates the spirits according to the distillation system. PC1 is characterized with positive loadings of 2-phenylethyl acetate, the sum of higher alcohols, ethyl acetate, 1-hexanol, methyl acetate, 2-phenylethanol and the sum of linear alcohols, and negative loading of methanol. PC2, accounts for 35.4% of the total variance and distinguishes KL3 distillates. It was characterized with positive loadings of benzyl alcohol, isobutyl acetate and sum of *trans/cis* hexenols, and negative loadings of ethyl octanoate, furfural and ethyl hexanoate. Finally, PC3 accounts for 20.9% of the total variance and distinguishes KL1 distillates. It was characterized with positive loadings of ethyl 9,12 octadecadienoate, isoamyl acetate and 3-ethoxy-1-propanol, and with negative loadings of the sum of monoterpenols and ethyl decanoate. As shown in **Figure 3.3**, the spirits obtained with the packed column are situated on the negative side of PC1, and those obtained with alembic are situated on the positive side. This separation is due to the fact that spirits obtained with the packed-column had lower values of ethyl acetate, methyl acetate and 2-phenylethyl ethanol, indicating a better head/heart and heart/tail fractions separation during distillation (Apostolopoulou et al., 2005). In addition, the methanol content was slightly higher in the distillates obtained with the packed column (around 10%), although they did not surpass the maximum limit according to the European Council Regulation EC nº 110/2008 (1000 g/hL p.a.). Moreover, the concentration of alcohols (higher alcohols, hexanol and linear alcohols) in distillates obtained with the distillation column was lower than that obtained with the alembic (around 30%) (**Table 3.9** and **3.11**). This difference is mainly due to the dilution effect in the higher and minor alcohols, since the ethanol yield in the heart fraction obtained in the column was 30% higher than the one obtained in alembic (**Table 3.8**). Kiwi spirits obtained with the alembic were richer in 2-phenyethyl acetate, a compound that contributes to the flowery aroma of the distillates (Soufleros and Bertrand, 1987) (**Table 3.10**). However, the values obtained were below the perception threshold of 2 g/hL p.a. (Odello et al., 1997).

Figure 3.3A shows that KL3 spirits are situated on the positive side of PC2, whereas KL1 and KL2 spirits are on the negative side. KL3 spirits are richer in benzyl alcohol, isobutyl acetate and *trans/cis* hexenols (between 100 and 40 % for alembic and between 200 and 45% for column). The concentration of short-chain ethyl esters (ethyl hexanoate and ethyl octanoate) is lower for KL3 spirits in comparison to KL1 and KL2 spirits (in the range of 40 to 80%). Similar results were found for Mencía wines from spontaneous fermentations dominated by the same yeast XXII: the content of ethyl hexanoate and ethyl octanoate were lower than for wines obtained with other yeasts (Blanco et al., 2012). Moreover, KL3 distillates have lower concentrations of furfural than KL1 and KL2 spirits (see **Table 3.11**).

Figure 3.3B shows that KL1 distillates are situated on the positive side of PC3, while KL2 and KL3 distillates are on the negative side. KL1 distillates have higher concentrations of isoamyl acetate (around 50 and 40% more than KL2 and KL3 respectively), ethyl 9,12-octadecadienoate and 3-ethoxi-1-propanol. The production of high amounts of isoamyl acetate by *S. cerevisiae* EC1118 was previously reported by Gobbi *et al.* (2013).

As shown in **Figure 3.3** the distillation system also influences PC2 and PC3. Column distillates have lower values of PC2 and PC3, mainly due to their higher concentrations of short-chain ethyl esters (ethyl hexanoate and ethyl octanoate) and monoterpenols (see **Table 3.12**).

Table 3.12. PCA results for the average volatile compounds in the kiwi distillates distilled in a *Charentais* alembic and a packed column.

Principal Component	**compound**	**loading**	**variance explained (%)**	**total variance (%)**
PC1	2-phenylethyl acetate	0.961	40.36	40.36
	methanol	-0.904		
	Σ higher alcohols	0.898		
	ethyl acetate	0.895		
	1-hexanol	0.850		
	methyl acetate	0.838		
	2-phenylethanol	0.794		
	Σ linear alcohols	0.766		
PC2	benzyl alcohol	0.972	35.40	75.76
	isobutyl acetate	0.969		
	furfural	-0.899		
	Σ *trans/cis* hexenols	0.789		
	ethyl octanoate	-0.779		
	ethyl hexanoate	-0.692		
PC3	isoamyl acetate	0.926	20.87	96.63
	ethyl 9,12-octadecadienoate	0.899		
	3-ethoxy-1-propanol	0.894		
	Σ monoterpenols	-0.698		
	ethyl decanoate	-0.624		

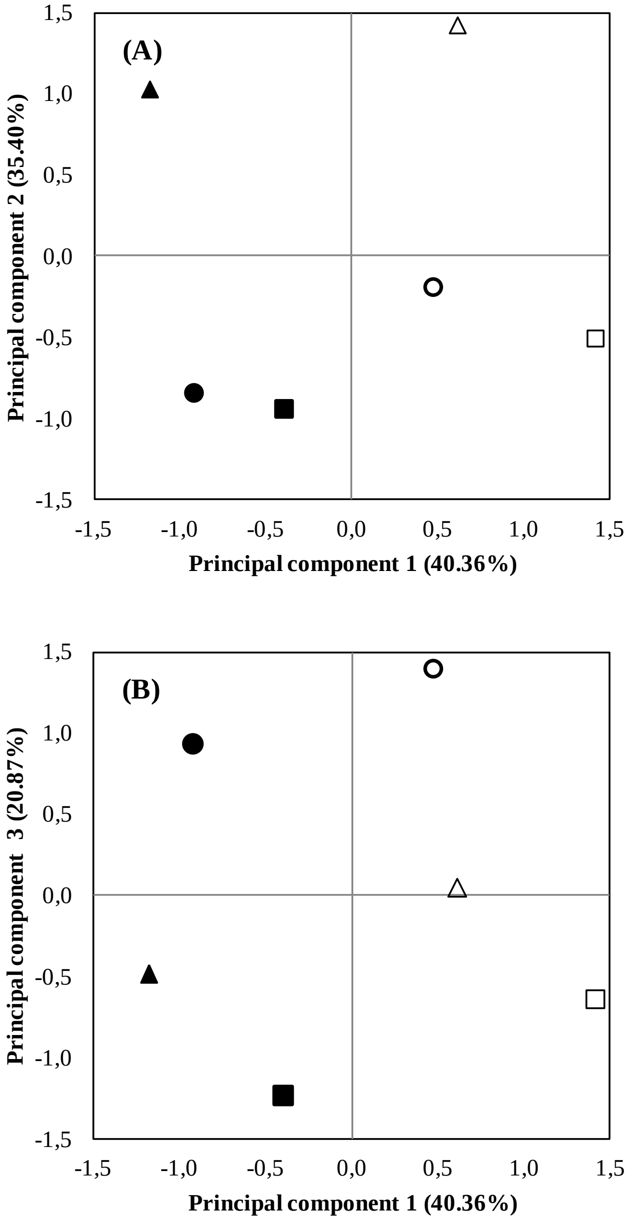


Figure 3.3. Principal component analysis of the volatile composition of the kiwi distillates. (A) PC1 vs PC2; (B) PC1 vs PC3. Yeast L1 (○,●), yeast L2 (□, ■), and yeast L3 (△, ▲), Alembic distillates (open symbols) and packed-column distillates (solid symbols).

3.2.6 Sensory analysis

A preference test did not show any significant tasting difference among the kiwi distillates obtained in this study (Friedman test $p < 0.05$). In turn, the aroma of column distillates was preferred ($p < 0.05$) against alembic distillates when L1 and L2 yeasts were used for fermentation. However, the distillates obtained from L3 yeast showed no significant aroma differences ($p < 0.05$) between alembic and column distillates.

The results of the descriptive test with expert panellists for the aromatic profile of all distillates are shown in **Figure 3.4**. The aroma descriptors corresponding to spirits distilled with alembic were evaluated with higher negative characteristics, being associated with burnt/smoky and pungent flavours (see **Figure 3.4**). The kiwi distillates obtained with column were associated to floral, fruity and spicy aroma (see **Figure 3.4**). Like the consumers panel, the expert panellists did not find a clear difference in taste (results not shown). This sensory result is in agreement with the PCA analysis. Defects found in alembic distillates could be mainly due to high concentrations of ethyl acetate and methyl acetate, since it has been reported that methyl acetate contributes to a pungent aroma when the concentration of ethyl acetate is high (López-Vázquez 2011). In this case, ethyl acetate concentration in distillates obtained with the alembic (140g/hL to 179g/hL p.a.) was near the perception threshold 180g/hL p.a. (Soufleros et al., 2004), whereas the values obtained with the column (67.8 to 80.5 g/hL p.a.) were much lower (see table 3). Probably, the rectification in the packed column helped to increase these compounds in the head fraction, reducing the concentration in the heart fraction (García-Llobodanin et al., 2010b).

Floral and fruity aromas identified in column distillates could be related to ethyl esters of middle-chain fatty acids (Lukić et al., 2012), such us ethyl hexanoate, ethyl octanoate and ethyl decanoate which were two or three times higher in the distillates obtained with the column than in those obtained with the alembic (see **Table 3.10**). Specifically, ethyl hexanoate is described as apple, banana, violets, strawberry and anise (Lambrechts et al., 2000; Peña y Lillo et al., 2005), ethyl octanoate (ethyl caprylate) as pineapple and pear, and ethyl decanoate as sweet, oily-nut like and floral (Lambrechts et al., 2000; Li et al., 2008). These results support previous studies with fruit spirits suggesting that distillations in batch stills coupled to a reflux column preserve better the delicate fruit essence compared to distillations in alembics (García-Llobodanin et al., 2010b; 2011; Claus et al., 2005).

The higher floral character in column distillates might be also due to the fact that the sum of monoterpenols concentrations was higher for distillates produced with the column compared to those produced in the alembic (see table 5). Like in the C6-C12 ethyl esters case, the reflux column recovers more these aroma compounds in the heart cut.

Results obtained in this study show that the distillation system has a stronger influence than the yeast strain on the floral and fruity character of the kiwi distillates. Compared with alembic spirits, the packed column spirits presented higher amounts of compounds associated with favourable aromas (floral and fruity), such as C6-C10 esters and monoterpenols, and lower amounts of compounds associated with organoleptic defects (pungent), such as ethyl acetate and methyl acetate. Moreover, the distillates obtained with the packed column were preferred by a consumer panel and higher ethanol recoveries were achieved.

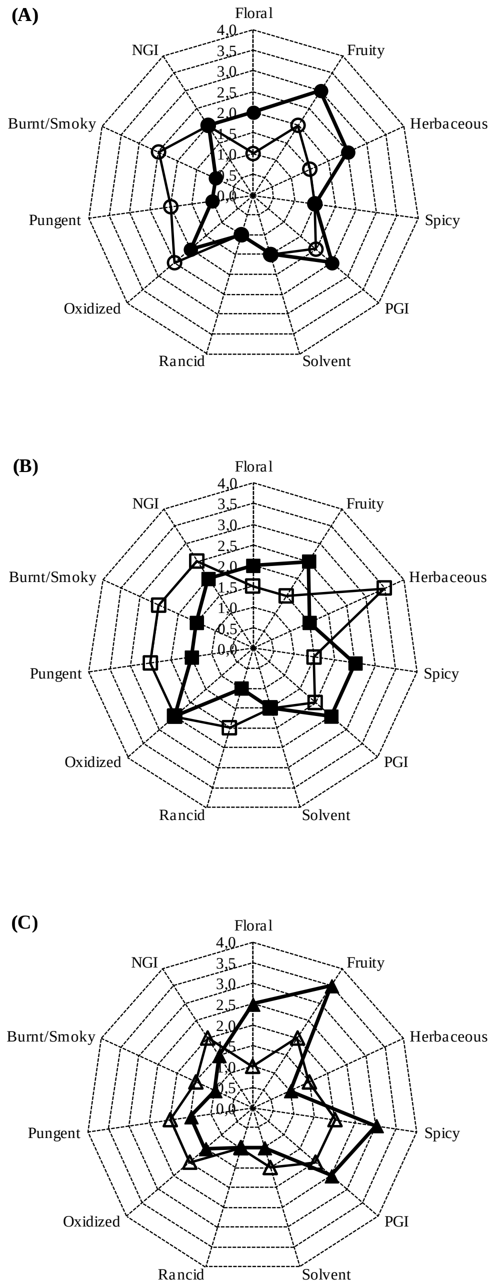


Figure 3.4. Comparison of the aroma profile for kiwi distillates distilled using either a packed-column (solid symbol) or an alembic (open symbol). (A) yeast L1; (B): yeast L2; (C): yeast L3. PGI, positive general impression; NGI, negative general impression.

3.3 Grape pomace distillates

3.3.1 Abstract

This section presents the results of the work performed during two campaigns with two varieties of grape pomace (*Albariño* and *Catalán Roxo*) at pilot scale. There has also been a study on industrial scale with grape pomace named *Xenérico*, which is a mixture of different pomace varieties, mostly *Albariño*.

Results showed that the use of an adequate distillation system, such as a packed column, in the production of “Orujo” distillates improved the chemical composition of the distillate and, therefore, its sensory quality. This system increased the concentration of esters and, therefore the fruity aroma, and reduced organoleptic defects such as oxidized and solvent notes with respect to the distillates obtained with the *Charentais* alembic. On the other hand, some yeast strains allow obtaining distillates with favorable attributes and higher ethanol yield.

3.3.2 Fermentation process

The microbiological control was carried out only in the samples where the grape pomace was inoculated with yeast strains, but not in spontaneous fermentation (*Catalán Roxo* 2009 and *Xenérico* 2010).

The yeast population present in grape pomaces before inoculation and fermentation were 2.3 x 10^5 ufc/ mL, 7 x 10^6 ufc/ mL and 1.1 x 10^6 ufc/ mL for *Albariño* 2009, *Albariño* 2010 and *Catalán Roxo* 2010, respectively.

After inoculation, grape pomaces were allowed to ferment and then stored until distillation. Pomace samples from each container were taken before distillation. The results showed that, in the case of *Albariño* 2009, in all *S. cerevisiae* XG3 fermentations the inoculated strain was the dominant yeast even after the storage period, except in one experiment (XG3-5), where a different strain of *S. cerevisiae* (strain IV) was isolated. In addition, a non-*Saccharomyces* yeast species appeared with a higher frequency than *Saccharomyces*. The later was characterized as *Pichia membranifaciens*, a film forming yeast that has oxidative activity (Fleet 2003), suggesting that anaerobic conditions were not adequately kept in this container. This yeast is considered a common food spoilage species (Loureiro et al., 2003) and its presence has been also reported at the end of fermentations of Prosecco marc (Bovo et al. 2009). Based on this result, XG3-5 was not considered for chemical analysis and ethanol yield, in order to avoid misleading conclusions.

3.3.3 Distillation

Tables 3.13 to 3.17 show the efficiency in pure ethanol recovery in the heart fraction with respect to the total ethanol recovered by the two distillation systems (%), as well as the efficiency in the pure ethanol expressed in litres per 100 kg of grape pomace distilled in the heart fraction. In all cases the packed column showed higher ethanol strength and ethanol yield in comparison to the alembic, mainly for *Catalán Roxo* 2009, 2010 where these differences were significant (around 10-15%). In addition, recovered higher alcohols, linear alcohols, and monoterpenols are shown in **Tables 3.13 to 3.17**. The significant differences were obtained mainly in monoterpenols for *Albariño* 2010, *Catalán Roxo* 2010 and *Xenérico* with higer values in column-distilled. Nevertheless, in all cases the recovery of higher alcohols and linear alcohols was slightly greater when packed column was used in comparison to alembic. On the other hand, comparing the ethanol yield in distillates fermented with inoculated yeast, in almost all cases the authochonous yeasts (XG3 and Sc24) allowed obtaining greater ethanol yield than the commercial yeasts (BDX and QA23), within the same grape pomace variety and harvest.

Table 3.13. Ethanol balance in both distillation systems for *Albariño* grape pomace distillates (2009 harvest).[a]

	Copper *Charentais* alembic		**Packed-column**	
	yeast strain		**yeast strain**	
	XG3 (n=5)	**BDX (n=6)**	**XG3 (n=5)**	**BDX (n=6)**
Heart ethanol alcoholic strength (%v/v)	61.92±4.50a,a	50.68±3.14a,b	75.80±3.86b,a	75.2±4.55b,a
Heart ethanol yield (%)	81.2±8.33a,a	65.66±6.5a,b	86.7±2.91a,a	83.91±2.6b,a
Heart ethanol yield (L a.a. /100 kg grape pomace)	7.89±0.59a,a	5.87±0.61a,b	8.28±0.60a,a	8.93±0.46b,a
Total higher alcohols recovered (g/100 L real distillate)	469.3±48.3a,a	367.2±61.8a,b	409.7±51.4a,a	397.1±60.4a,a
Total higher alcohols recovered (g/100 kg grape pomace)	40.46±2.9a,a	32.8±7.19a,b	37.4±7.03a,a	42.2±5.18a,a
Total linear alcohols recovered (g/100 L real distillate)	0.30±0.75a,a	0.23±0.04a,b	0.21±0.04b,a	0.21±0.03a,a
Total linear alcohols recovered (mg/100 kg grape pomace)	29.2±10.1a,a	20.55±8.2a,b	19.97±9.04b,a	22.33±5.11a,a
Total monoterpenols recovered (g/100 L real distillate)	1.35±0.24a,a	1.05±0.16a,b	1.0±0.12b,a	1.16±0.20a,b
Total monoterpenols recovered (mg/100 kg grape pomace)	131.7±18.29a,a	93.92±13.04a,b	100.2±13.85b,a	124.13±19.2b,b
Total 1-linalool recovered (g/100 L real distillate)	0.45±0.04a,a	0.39±0.06a,a	0.37±0.02b,a	0.40±0.04a,a
Total 1-linalool recovered (mg/100 kg grape pomace)	43.4±2.26a,a	35.2±5.45a,b	37.6±4.45b,a	42.9±4.6b,b

[a] Different letters before the comma in the same row indicate a significant difference ($p \leq 0.05$) with respect to the distillation system (within the same yeast strain). Different letters after the comma in the same row indicate a significant difference ($p \leq 0.05$) with respect to the yeast strain (within the same distillation system).

Table 3.14. Ethanol balance in both distillation systems for *Catalán Roxo* grape pomace distillates (harvest 2009).[a]

	Copper *Charentais* alembic (n=8)	**Packed- Column (n=8)**
Heart ethanol alcoholic strenght (%v/v)	46.33±5.42a	61.16±8.75b
Heart ethanol yield (%)	53.81±15.6a	71.39±6.92b
Heart ethanol yield (L a.a. /100 kg grape pomace)	2.08±0.89a	3.76±1.36b
Total higher alcohols recovered (g/100 kg grape pomace)	8.44±3.13a	12.11±4.22a
Total linear alcohols recovered (mg/100 kg grape pomace)	72.6±25.3a	115.1±51.2a
2-phenylethanol recovered (mg/100 kg grape pomace)	461.7±150.7	541.4±262.4
Total monoterpenols recovered (mg/100 kg grape pomace)	116.9±40.5a	236.1±45.6b

[a] Different letters before the comma in the same row indicate a significant difference ($p \leq 0.05$) with respect to the distillation system (within the same yeast strain). Different letters after the comma in the same row indicate a significant difference ($p \leq 0.05$) with respect to the yeast strain (within the same distillation system).

Table 3.15. Ethanol balance in both distillation systems for *Albariño* grape pomace distillates (harvest 2010).[a]

	Copper *Charentais* alembic		**Packed-column**	
	yeast strain		**yeast strain**	
	XG3(n=5)	**QA23(n=5)**	**XG3(n=5)**	**QA23(n=5)**
Heart ethanol alcoholic strenght (%v/v)	60.50±1.12a,a	59.56±3.00a,a	69.10±4.23b,a	64.24±3.07a,a
Heart ethanol yield (%)	68.11±6.70a,a	71.08±4.78 a,a	77.52±4.31 a,a	74.76±7.76 a,a
Heart ethanol yield (L a.a. /100 kg grape pomace)	4.21±0.31a,a	4.01±1.00a,a	5.38±0.50b,a	4.54±1.00a,a
Total higher alcohols recovered (g/100 kg grape pomace)	13.81±0.84a,a	14.27±3.65a,a	16.40±1.00a,a	16.23±4.32a,a
Total linear alcohols recovered (mg/100 kg grape pomace)	27.85±10.3 a,a	21.82±5.76 a,a	36.45±5.10 a,a	25.42±6.68 a,a
2-phenylethanol recovered (mg/100 kg grape pomace)	205.4±36.7	158.4±64.5	207.1±65.62	173.4±49.5
Total monoterpenols recovered (mg/100 kg grape pomace)	64.56±25.8 a,a	44.04±19.4 a,b	94.87±43.7 b,a	65.38±7.13 b,b

[a] Different letters before the comma in the same row indicate a significant difference ($p \le 0.05$) with respect to the distillation system (within the same yeast strain). Different letters after the comma in the same row indicate a significant difference ($p \le 0.05$) with respect to the yeast strain (within the same distillation system).

Table 3.16. Ethanol balance in both distillation systems for *Catalán Roxo* grape pomace distillates (harvest 2010). [a]

	Copper *Charentais* alembic		**Packed-column**	
	yeast strain		**yeast strain**	
	QA23 (n=2)	**Sc24 (n=2)**	**QA23 (n=2)**	**Sc24 (n=2)**
Heart ethanol alcoholic strenght (%v/v)	50.30±0.71a,a	50.95±1.34a,a	60.60±1.13b,a	61.05±0.35b,a
Heart ethanol yield (%)	59.72±4.15a,a	68.25±1.51a,b	68.90±8.70b,a	80.23±0.37b,b
Heart ethanol yield (L a.a. /100 kg grape pomace)	3.23±0.37a,a	3.42±0.31a,a	4.55±0.10b,a	5.51±0.42b,a
Total higher alcohols recovered (g/100 kg grape pomace)	12.16±2.03a,a	12.22±0.83a,a	14.44±1.09a,a	14.40±2.24a,a
Total linear alcohols recovered (mg/100 kg grape pomace)	60.54±2.54a,a	60.05±2.57a,a	70.03±11.25a,a	67.65±5.19a,a
2-phenylethanol recovered (mg/100 kg grape pomace)	374.0±165.4	513.3±25.17	435.4±153.8	520.7±76.27
Total monoterpenols recovered (mg/100 kg grape pomace)	70.41±6.64a,a	81.39±10.8a,a	134.2±19.4b,a	138.0±18.5b,a

[a] Different letters before the comma in the same row indicate a significant difference ($p \le 0.05$) with respect to the distillation system (within the same yeast strain). Different letters after the comma in the same row indicate a significant difference ($p \le 0.05$) with respect to the yeast strain (within the same distillation system).

Table 3.17. Ethanol balance in both distillation systems for *Xenérico* grape pomace distillates.[a]

	Copper *Charentais* alembic (n=2)	**Packed-column (n=2)**
Heart ethanol alcoholic strenght (%v/v)	53.95±2.05a	60.6±3.11a
Heart ethanol yield (%)	68.9±4.09a	79.8±0.89a
Heart ethanol yield (L a.a. /100 kg grape pomace)	5.72±0.76a	7.62±0.39a
Total higher alcohols recovered (g/100 kg grape pomace)	15.85±1.44a	21.26±0.31a
Total linear alcohols recovered (mg/100 kg grape pomace)	17.5±1.28a	20.2±4.50^{a}
2-phenylethanol recovered (g/100 kg grape pomace)	381.5±140.3	591.3±219.7
Total monoterpenols recovered (mg/100 kg grape pomace)	25.56±9.86a	66.42±22.07b

3.3.4 Chemical composition of grape pomace distillates

The results obtained for the chemical composition of grape pomace distillates are shown in **Tables 3.18 to 3.26** according to the variety and harvest grape, the distillation system and yeast strain. PCA analysis and sensory analysis are detailed below in sections **3.3.5** and **3.3.6**, respectively.

Table 3.18. Average concentrations (g/hL p.a.) and standard deviations of the macroconstituents present in grape pomace distillates obtained from *Albariño* variety (2009 and 2010 harvest), for each distillation process (copper *Charentais* alembic and packed-column).[a]

Compound	**copper *Charentais* alembic**				**packed-column**			
	yeast strain / harvest				**yeast strain / harvest**			
	XG3 / 2009 (n=5)	**BDX / 2009 (n=6)**	**XG3 / 2010 (n=5)**	**QA23 / 2010 (n=5)**	**XG3 / 2009 (n=5)**	**BDX / 2009 (n=6)**	**XG3 / 2010 (n=5)**	**QA23 / 2010 (n=5)**
metanol	432.8 ±30.04a,a	579.9±33.03a,b	785.2±41.2a,a	714.9 ± 50.9a,a	438.1 ±35.9a,a	616.1 ± 83.9a,b	816.18±33.9a,a	690.4 ± 55.8a,b
ethyl acetate	221.0±58.60a,a	126.4±63.41a,b	169.3±37.2a,a	165.8 ± 24.1a,a	109.4 ±91.5b,a	105.1 ± 78.7a,a	101.09±29.2a,a	109.3 ± 52.3a,a
acetaldehyde	31.96±10.54a,a	23.76±5.84a,a	49.08±5.25a,a	41.61 ± 3.29a,a	21.73 ± 9.54b,a	21.21 ± 4.74a,a	41.26±5.21a,a	38.07 ± 5.39a,a
1,1-dietoxiethane	30.95±14.05a,a	12.84±4.64a,b	24.47±11.6a,a	20.00 ± 6.24a,a	34.39 ± 22.0a,a	30.86 ± 7.79b,a	14.90±5.02a,a	10.88 ± 1.84a,b
Σ acetaldehyde + 1,1-diethoxyethane	**62.92 ±24.41a,a**	**36.61 ±10.47a,b**	**73.55±16.8a,a**	**61.61 ±4.48a,a**	**56.12 ±31.5a,a**	**52.07 ± 1.82b,a**	**56.16±10.2b,a**	**48.95 ± 8.32a,a**
1-propanol	63.26± 4.72a,a	77.43±4.93a,b	69.85±2.30a,a	72.74 ± 2.69a,a	57.24 ± 8.09a,a	72.89 ± 5.96a,b	66.59±2.87a,a	71.6 ± 1.97a,a
2-methyl-1-propanol	134.5±4.01a,a	152.0±23.15a,a	86.48±2.41a,a	90.84 ± 7.16a,a	104.1 ± 25.0b,a	129.5 ± 28.0a,a	79.40±4.36a,a	93.6 ± 4.06a,a
1-butanol	1.06±1.27a,a	0.14±0.04a,a	2.26±0.07a,a	2.28 ± 0.13a,a	0.34 ± 0.13b,a	0.60 ± 1.01a,a	2.14±0.13a,a	2.25 ± 0.08a,a
2-butanol	0.33±0.02a,a	0.32±0.04a,a	0.62±0.15a,a	0.34 ± 0.07a,b	0.24 ± 0.06a,a	0.26 ± 0.06a,a	0.62±0.10a,a	0.35 ± 0.14a,b
allylic alcohol	0.11±0.05a,a	0.03±0.02a,b	0.05±0.02a,a	0.04 ± 0.02a,a	0.05 ±0.05b,a	0.03 ± 0.02a,a	0.03±0.01a,a	0.04 ± 0.02a,a
2-methyl -1-butanol	95.75±4.89a,a	84.93±22.92a,a	40.21±2.37a,a	43.97 ± 4.42a,a	72.02 ± 14.8b,a	69.57 ± 18.1a,a	37.74±1.80a,a	45.19 ± 2.96a,a
3- methyl- 1-butanol	282.9±12.19a,a	244.5±71.44a,a	127.8±10.09a,a	143.2 ± 15.7a,a	218.6 ± 36.9b,a	200.4 ± 53.2a,a	119.51±7.62a,a	144.3 ± 8.96a,a
Σ total higher alcohols[b]	**577.9±18.75a,a**	**559.3±117.5a,a**	**327.3±16.9a,a**	**353.4±29.9a,a**	**452.62±91.2a,a**	**473.2±101.3a,a**	**306.0±15.4a,a**	**357.4 ± 13.5a,a**
ethyl lactate	33.28±7.89a,a	53.89±12.26a,b	51.95±2.48a,a	46.17 ± 4.73a,a	19.74 ± 9.44b,a	19.53 ± 8.45b,a	38.32±6.49b,a	38.9 ± 8.97a,a
1-hexanol	7.47±0.47a,a	7.68±1.10a,a	13.55±1.13a,a	12.40 ± 0.48a,a	5.58 ± 0.88b,a	6.22 ± 0.84b,a	12.59±0.79a,a	12.93 ± 1.43a,a
isobutyraldehyde	0.79±0.66a,a	0.27±0.09a,b	0.28±0.04a,a	0.22 ± 0.03a,a	0.27 ± 0.14b,a	0.25 ± 0.08a,a	0.21±0.04a,a	0.15 ± 0.04a,a
ethyl formiate	2.17±1.22a,a	0.93±0.36a,b	1.96±0.47a,a	1.94 ± 0.16a,a	1.36 ± 0.35b,a	1.033 ± 0.33a,a	1.57±0.25a,a	1.57 ± 0.37a,a
methyl acetate	2.15±0.58a,a	1.62±0.76a,a	3.07±0.76a,a	2.79 ± 0.33a,a	1.15 ± 0.96b,a	1.30 ± 0.86a,a	1.49±0.40b,a	2.05 ± 0.82a,a
2-propenal	0.62±0.30a,a	0.32±0.10a,a	0.54±0.32a,a	0.48 ± 0.16a,a	0.61 ± 0.35a,a	0.67 ± 0.16b,a	0.30±0.11a,a	0.27 ± 0.25a,a

[a] Different letters before the comma in the same row indicate a significant difference ($p \leq 0.05$) with respect to the distillation system (within the same harvest and yeast strain). Different letters after the comma in the same row indicate a significant difference ($p \leq 0.05$) with respect to the yeast strain (within the same harvest and distillation system) [b] Σ 2-methyl-1-propanol, 1-butanol, allylic alcohol, 2-methyl-1-butanol, 3-methyl-1-butanol

Table 3.19. Average concentrations (g/hL p.a.) and standard deviations of the microconstituents (esters) present in grape pomace distillates obtained from *Albariño* variety (2009 and 2010 harvest), for each distillation process (copper *Charentais* alembic and packed-column).[a]

Compound	copper *Charentais* alembic				packed-column			
	Variety / yeast strain				Variety / yeast strain			
	XG3 / 2009 (n=5)	**BDX / 2009 (n=6)**	**XG3 / 2010 (n=5)**	**QA23 / 2010 (n=5)**	**XG3 / 2009 (n=5)**	**BDX / 2009 (n=6)**	**XG3 / 2010 (n=5)**	**QA23 / 2010 (n=5)**
isobutyl acetate	0.18 ± 0.04a,a	0.13 ± 0.04a,a	5.96 ± 0.94a,a	6.42 ± 0.59a,a	0.12 ± 0.05b,a	0.09 ± 0.05a,a	6.03 ± 1.04a,a	5.91 ± 0.70a,a
butyl acetate	<LOD [b]	0.06 ± 0.02a,a	1.37 ± 0.27a,a	0.83 ± 0.35a,a	0.39 ± 0.23b,a	0.26 ± 0.08b,a	2.13 ± 0.60b,a	0.93 ± 0.30a,b
isoamyl acetate	1.28 ± 0.25a,a	0.73 ± 0.32a,a	1.82 ± 0.34a,a	1.42 ± 0.70a,a	1.25 ± 0.64a,a	0.98 ± 0.62a,a	2.18 ± 0.37a,a	1.45 ± 0.47a,b
hexyl acetate	0.05 ± 0.03a,a	0.03 ± 0.02a,a	0.14 ± 0.09a,a	0.12 ± 0.03a,a	0.04 ± 0.02a,a	0.07 ± 0.06a,a	0.20 ± 0.02b,a	0.13 ± 0.04a,a
2-phenylethyl acetate	0.14 ± 0.09a,a	0.13 ± 0.04a,a	0.08 ± 0.01a,a	0.06 ± 0.01a,a	0.11 ± 0.08b,a	0.14 ± 0.07a,a	0.07 ± 0.01b,a	0.07 ± 0.01b,a
Σ acetates of higher alcohols	**1.65 ± 0.48a,a**	**1.08 ± 0.44a,b**	**9.38 ± 1.50a,a**	**8.84 ± 1.52a,a**	**1.91 ± 1.02a,a**	**1.54 ± 0.86a,b**	**10.62 ± 0.61a,a**	**8.49 ± 0.72a,a**
ethyl butyrate	0.46 ± 0.10a,a	0.29 ± 0.13a,a	2.91 ± 1.25a,a	1.0 ± 0.17a,b	0.28 ± 0.09a,a	0.38 ± 0.26a,a	3.58 ± 2.39a,a	1.01 ± 0.49a,b
ethyl hexanoate	2.72 ± 0.32a,a	1.16 ± 0.42a,b	1.46 ± 0.29a,a	1.41 ± 0.56a,a	2.16 ± 0.61b,a	1.14 ± 0.57a,b	1.90 ± 0.19a,a	1.45 ± 0.26a,a
ethyl octanoate	2.92 ± 0.38a,a	1.14 ± 0.39a,b	0.98 ± 0.06a,a	1.40 ± 0.69a,a	3.90 ± 0.50b,a	2.06 ± 0.13b,b	1.68 ± 0.06b,a	1.71 ± 0.16a,a
ethyl decanoate	4.19 ± 0.50a,a	1.93 ± 0.51a,b	0.85 ± 0.10a,a	1.15 ± 0.34a,a	5.53 ± 0.31b,a	3.10 ± 0.46b,b	1.49 ± 0.18b,a	1.52 ± 0.13a,a
ethyl dodecanoate	1.58 ± 0.19a,a	0.82 ± 0.12a,b	0.33 ± 0.04a,a	0.36 ± 0.08a,a	1.94 ± 0.16b,a	1.23 ± 0.17b,b	0.54 ± 0.09b,a	0.44 ± 0.05a,a
Σ ethyl esters C6-C12[c]	**11.87 ± 1.39a,a**	**5.05 ± 1.44a,b**	**3.61 ± 0.45a,a**	**4.32 ± 1.56a,a**	**13.53 ± 1.60b,a**	**7.54 ± 1.33b,b**	**5.61 ± 0.30b,a**	**5.11 ± 0.41a,b**
ethyl tetradecanoate	0.33 ± 0.06a,a	0.17 ± 0.22a,b	0.09 ± 0.01a,a	0.08 ± 0.02a,a	0.38 ± 0.03a,a	0.39 ± 0.08b,a	0.26 ± 0.08b,a	10.11 ± 0.02a,b
ethyl hexadecanoate	2.42 ± 0.83a,a	0.90 ± 0.29a,b	0.36 ± 0.07a,a	0.31 ± 0.10a,a	3.63 ± 0.46b,a	4.38 ± 0.77b,a	1.88 ± 1.0b,a	0.62 ± 0.24a,b
ethyl octadecanoate	<LOD	<LOD	<LOD	<LOD	<LOD	0.07 ± 0.02	<LOD	0.01 ± 0.03
ethyl 9-octadecenoate	0.37 ± 0.16a,a	0.12 ± 0.07a,b	0.09 ± 0.02a,a	0.05 ± 0.03a,a	0.40 ± 0.07a,a	0.43 ± 0.07b,a	0.24 ± 0.08a,a	0.24 ± 0.26b,a
ethyl 9,12-octadecadienonate	2.26 ± 0.77a,a	1.45 ± 0.43a,b	0.69 ± 0.07a,a	0.59 ± 0.20a,a	1.88 ± 0.55a,a	2.16 ± 0.41b,a	1.22 ± 0.23a,a	0.76 ± 0.32a,a
ethyl 9,12,15-octadecatrienoate	1.01 ± 0.43a,a	0.86 ± 0.17a,a	0.36 ± 0.04a,a	0.29 ± 0.05a,a	0.69 ± 0.26a,a	0.87 ± 0.22a,a	0.60 ± 0.07a,a	0.39 ± 0.07a,a
Σ ethyl esters C14-C18	**6.39 ± 2.64a,a**	**3.51 ± 1.0a,b**	**1.6 ± 0.2a,a**	**1.31 ± 0.32a,a**	**6.98 ± 1.38a,a**	**8.30 ± 1.57b,a**	**4.20 ± 1.43b,a**	**2.14 ± 0.46a,b**
isoamyl hexanoate	0.07 ± 0.03a,a	0.03 ± 0.02a,b	<LOD	<LOD	0.04 ± 0.01b,a	0.01 ± 0.02a,a	<LOD	<LOD
isoamyl octanoate	0.04 ± 0.01a,a	0.01 ± 0.0a,b	0.01 ± 0.01a,a	0.02 ± 0.02a,a	0.05 ± 0.02a,a	0.01 ± 0.01a,b	0.03 ± 0.01b,a	0.02 ± 0.01a,a
isoamyl decanoate	0.12 ± 0.03a,a	0.11 ± 0.05a,a	<LOD	<LOD	0.09 ± 0.03a,a	0.09 ± 0.01a,a	<LOD	<LOD
Σ isoamyl esters	**0.22 ± 0.08a,a**	**0.16 ± 0.07a,a**	**0.01 ± 0.01a,a**	**0.02 ± 0.02a,a**	**0.18 ± 0.06b,a**	**0.11 ± 0.04a,a**	**0.03 ± 0.01b,a**	**0.02 ± 0.01a,a**
diethyl succinate	4.58 ± 1.44a,a	4.86 ± 0.61a,a	1.24 ± 0.51a,a	0.84 ± 0.08a,a	2.42 ± 1.10b,a	2.33 ± 1.17b,a	1.23 ± 0.19a,a	0.87 ± 0.30a,a

[a] Different letters before the comma in the same row indicate a significant difference (p≤0.05) with respect to the distillation system (within the same harvest and yeast strain). Different letters after the comma in the same row indicate a significant difference (p≤0.05) with respect to the yeast strain (within the same harvest and distillation system) [b] LOD, detection limit. [c] Σ ethyl hexanoate, ethyl octanoate, ethyl decanoate, ethyl dodecanoate.

Table 3.20. Average concentrations (g/hL p.a.) and standard deviations of the microconstituents (minor alcohols, monoterpenols, and other compounds) present in grape pomace distillates obtained from *Albariño* variety (2009 and 2010 harvest), for each distillation process (copper *Charentais* alembic and packed-column).[a]

Compound	**copper *Charentais* alembic**				**Packed-column**			
	Variety / yeast strain				**Variety / yeast strain**			
	XG3 / 2009 (n=5)	**BDX / 2009 (n=6)**	**XG3 / 2010 (n=5)**	**QA23 / 2010 (n=5)**	**XG3 / 2009 (n=5)**	**BDX / 2009 (n=6)**	**XG3 / 2010 (n=5)**	**QA23 / 2010 (n=5)**
trans-3-hexen-1-ol	0.12 ± 0.01a,a	0.15 ± 0.02a,a	0.14 ± 0.03a,a	0.13 ± 0.01a,a	0.10 ± 0.02a,a	0.13 ± 0.02a,a	0.16 ± 0.03a,a	0.15 ± 0.01a,a
cis-3-hexen-1-ol	0.19 ± 0.03a,a	0.21 ± 0.04a,a	0.42 ± 0.08a,a	0.36 ± 0.03a,a	0.17 ± 0.02a,a	0.20 ± 0.02a,a	0.43 ± 0.08a,a	0.40 ± 0.05a,a
trans-2-hexen-1-ol	0.32 ± 0.14a,a	0.05 ± 0.03a,b	0.35 ± 0.20a,a	0.21 ± 0.07a,a	0.22 ± 0.09a,a	0.12 ± 0.10a,b	0.19 ± 0.04a,a	0.41 ± 0.47a,b
1-pentanol	0.77 ± 0.05a,a	0.77 ± 0.04a,a	0.99 ± 0.10a,a	0.85 ± 0.05a,a	0.63 ± 0.05a,a	0.65 ± 0.04a,a	1.07 ±0.13a,a	0.89 ± 0.07a,a
1-heptanol	0.12 ± 0.04a,a	0.10 ± 0.03a,a	0.19 ± 0.02a,a	0.17 ± 0.01a,a	0.08 ± 0.01b,a	0.08 ± 0.01a,a	0.21 ±0.03a,a	0.17 ± 0.01a,a
1-octanol	0.15 ± 0.04a,a	0.13 ± 0.01a,a	0.17 ± 0.02a,a	0.15 ± 0.01a,a	0.08 ± 0.01b,a	0.07 ± 0.01b,a	0.16 ±0.03a,a	0.15 ± 0.01a,a
1-nonanol	0.08 ± 0.03a,a	0.10 ± 0.01a,a	0.27 ± 0.08a,a	0.21 ± 0.01a,a	0.08 ± 0.02a,a	0.08 ± 0.02a,a	0.25 ± 0.05a,a	0.22 ± 0.02a,a
1-decanol	<LOD [b]	<LOD	0.04 ± 0.01a,a	0.02 ± 0.01a,a	<LOD	<LOD	0.06 ± 0.03b,a	0.02 ± 0.01a,a
benzylic alcohol	0.76 ± 0.35a,a	0.81 ± 0.15a,a	0.67 ± 0.06a,a	0.57 ± 0.13a,a	0.38 ± 0.21b,a	0.38 ± 0.16b,a	0.54 ± 0.11a,a	0.55 ± 0.14a,a
2-phenylethanol	6.90 ± 3.28 a,a	6.83 ± 0.99a,a	4.88 ± 0.65a,a	3.95 ±0.85a,a	2.70 ± 1.34b,a	3.42 ± 1.85b,a	3.85 ± 0.84a,a	3.82 ± 0.97a,a
Σ linear alcohols[d]	**0.37 ± 0.09a,a**	**0.35 ± 0.04a,a**	**0.66 ± 0.07a,a**	**0.54 ± 0.02a,a**	**0.24 ± 0.05b,a**	**0.25 ± 0.03b,a**	**0.68 ± 0.10a,a**	**0.56 ± 0.03a,a**
Other compounds								
benzaldehyde	0.65 ± 0.57a,a	0.13 ± 0.04a,b	0.13 ± 0.02a,a	0.10 ± 0.01a,a	0.54 ± 0.38a,a	0.14 ± 0.07a,a	0.13 ± 0.02a,a	0.09 ± 0.03a,a
furfuraldehyde	<LOD	0.16 ± 0.10a,a	0.05 ± 0.02a,a	0.05 ± 0.02a,a	0.07 ± 0.06a,a	0.33 ± 0.32b,b	0.07 ± 0.01a,a	0.03 ± 0.03a,a
3-ethoxy-1-propanol	0.39 ± 0.10a,a	0.47 ± 0.09a,a	1.14 ± 0.27a,a	0.92 ± 0.19a,a	0.18 ± 0.10b,a	0.30 ± 0.16b,b	0.97 ± 0.23a,a	0.90 ± 0.26a,a
1-octen-3-ol	0.12 ± 0.02a,a	0.10 ± 0.03a,a	0.13 ± 0.01a,a	0.12 ± 0.01a,a	0.09 ± 0.02b,a	0.09 ± 0.02a,a	0.15 ± 0.02a,a	0.12 ± 0.01a,a
3-hydroxy-2-butanone	<LOD	<LOD	0.07 ± 0.04a,a	0.01 ± 0.02a,a	0.12 ± 0.06a,a	0.06 ± 0.04a,a	0.01 ± 0.01a,a	0.04 ± 0.05a,a
Monoterpenols								
trans-furan linalool oxide	0.47 ± 0.06a,a	0.47 ± 0.02a,a	0.23 ± 0.13a,a	0.20 ± 0.04a,a	0.35 ± 0.07b,a	0.41 ± 0.13a,a	0.30 ± 0.10a,a	0.24 ± 0.03a,a
cis-furan linalool oxide	0.20 ± 0.08a,a	0.07 ± 0.05a,b	<LOD	<LOD	0.07 ± 0.05b,a	0.08 ± 0.06a,a	<LOD	<LOD
linalol	0.55 ± 0.03a,a	0.60 ± 0.06a,a	1.02 ± 0.12a,a	0.63 ± 0.33a,a	0.43 ± 0.04b,a	0.48 ± 0.03b,a	1.15 ±0.19a,a	0.74 ± 0.21a,b
α-terpineol	<LOD	<LOD	0.11 ± 0.04a,a	0.08 ± 0.01a,a	0.05 ± 0.01b,a	0.05 ± 0.03a,a	0.14 ± 0.02a,a	0.11 ± 0.01a,a
citronellol	0.08 ± 0.01a,a	0.08 ± 0.01a,a	0.04 ± 0.01a	0.04 ± 0.01a	0.06 ± 0.01a,a	0.06 ± 0.02a,a	0.05 ± 0.01a,a	0.06 ± 0.01a,a
nerol	0.06 ± 0.01a,a	0.04 ± 0.01a,b	0.06 ± 0.01a,a	0.04 ± 0.01a,a	0.03 ± 0.01b,a	0.05 ± 0.01a,b	0.07 ± 0.01a,a	0.06 ± 0.01a,a
geraniol	nd [c]	nd	0.11 ± 0.01a,a	0.09 ± 0.02a,a	nd	nd	0.20 ± 0.03a,a	0.19 ± 0.03a,a
hotrienol	0.23 ± 0.03a,a	0.27 ± 0.03a,a	0.07 ± 0.04a,a	0.07 ± 0.03a,a	0.22 ± 0.03a,a	0.27 ± 0.09a,a	0.07 ± 0.02a,a	0.09 ± 0.01a,a
Σ monoterpenols	**1.67 ± 0.37a,a**	**1.60 ± 0.20a,a**	**1.65 ± 0.20a,a**	**1.15 ± 0.39a,a**	**1.21 ± 0.23b,a**	**1.39 ± 0.38a,a**	**1.98 ± 0.32a,a**	**1.47 ± 0.22a,a**

[a] Different letters before the comma in the same row indicate a significant difference ($p \leq 0.05$) with respect to the distillation system (within the same harvest and yeast strain). Different letters after the comma in the same row indicate a significant difference ($p \leq 0.05$) with respect to the yeast strain (within the same harvest and distillation system) [b] LOD, detection limit. [c] nd, not determined. [d] Σ 1-heptanol, 1-octanol, 1-nonanol, 1-decanol.

Table 3.21. Average concentrations (g/hL p.a.) and standard deviations of the macroconstituents present in grape pomace distillates obtained from the *Catalán Roxo* 2009 and 2010 harvest, for each distillation process (copper *Charentais* alembic and packed-column).[a]

Compound	**copper *Charentais* alembic**			**Packed-column**		
	yeast strain / harvest			**yeast strain / harvest**		
	S1 / 2009 (n=8)	**QA23 / 2010 (n=2)**	**Sc24 / 2010 (n=2)**	**S1 / 2009 (n=8)**	**QA23 / 2010 (n=2)**	**Sc24 / 2010 (n=2)**
methanol	760.7 ± 49.5a	742.5 ± 81.1a,a	720.5 ± 36.5a,a	834.3 ± 77.7b	759.5 ± 87.4a,a	789.9 ± 64.6a,a
ethyl acetate	951.1 ± 388.9a	73.3 ± 38.4a,a	63.0 ± 7.64a,a	366.9 ± 157.3b	38.2 ± 4.95a,a	36.9 ± 13.5a,a
acetaldehyde	83.0 ± 34.4a	28.67 ± 19.1a,a	16.9 ± 2.43a,b	63.4 ± 26.8a	23.4 ± 4.25a,a	19.81 ± 2.05a,b
1,1-dietoxiethane	44.3 ± 23.9a	26.81 ± 5.15a,a	23.4 ± 2.31a,a	63.9 ± 44.2a	30.2 ± 3.34a,a	32.63 ± 4.26a,a
Σ acetaldehyde + 1,1-diethoxyethane	**127.2 ± 58.3a**	**55.5 ± 24.2a,a**	**40.3 ± 4.7a,a**	**127.3 ± 70.9a**	**53.6 ± 7.59a,a**	**52.4 ± 16.3a,a**
1-propanol	106.7 ± 5.09a	75.3 ± 1.57a,a	78.0 ± 3.44a,a	95.6 ± 7.79b	71.8 ± 1.16a,a	71.9 ± 2.66a,a
2-methyl-1-propanol	95.8 ± 15.6a	73.5 ± 8.35a,a	72.1 ± 1.44a,a	68.6 ± 28.5a	51.5 ± 12.88b,a	63.3 ± 3.40a,b
1-butanol	3.99 ± 2.08a	2.68 ± 0.33a,a	2.60 ± 0.07a,a	1.04 ± 1.60b	2.38 ± 0.11a,a	2.40 ± 0.20a,a
2-butanol	1.12 ± 1.36a	0.14 ± 0.01a,a	0.11 ± 0.02a,a	1.10 ± 1.36a	0.11 ± 0.01a,a	0.10 ± 0.03a,a
allylic alcohol	0.37 ± 0.18a	0.07 ± 0.01a,a	0.05 ± 0.01a,a	0.23 ± 0.13a	0.08 ± 0.01a,a	0.06 ± 0.03a,a
2-methyl -1-butanol	39.7 ± 7.73a	49.9 ± 4.20a,a	46.3 ± 0.99a,a	31.0 ± 2.75b	42.7 ± 0.54a,a	42.4 ± 3.71a,a
3- methyl- 1-butanol	158.1 ± 27.0a	173.7 ± 8.51a,a	158.0 ± 2.18a,a	124.4 ± 9.33b	148.4 ± 6.31b,a	145.5 ± 13.4a,a
Σ total higher alcohols[b]	**405.7 ± 54.8a**	**375.3 ± 19.8a,a**	**357.04 ± 8.0a,a**	**322.3 ± 33.3b**	**316.9 ± 18.5a,a**	**325.6 ± 18.1a,a**
ethyl lactate	43.3 ± 19.3a	64.2 ± 35.4a,a	77.7 ± 19.8a,b	82.8 ± 17.21b	47.1 ± 28.7a,a	58.4 ± 8.25a,a
1-hexanol	18.3 ± 2.71a	11.1 ± 0.01a,a	11.5 ± 1.33a,a	13.8 ± 1.68b	10.8 ± 0.21a,a	11.23 ± 0.88a,a
isobutyraldehyde	1.05 ± 0.35a	0.12 ± 0.10a,a	0.17 ± 0.02a,a	0.80 ± 0.47a	0.24 ± 0.02a,a	0.12 ± 0.02a,b
ethyl formiate	4.89 ± 1.98a	2.25 ± 1.02a,a	1.98 ± 0.22a,a	5.11 ± 1.82a	2.36 ± 0.01a,a	2.00 ± 0.01a,a
methyl acetate	17.5 ± 6.36a	1.81 ± 1.22a,a	1.74 ± 0.24a,a	6.76 ± 3.25b	0.65 ± 0.31a,a	1.19 ± 0.40a,b
2-propenal	1.32 ± 0.92a	0.99 ± 0.01a,a	0.94 ± 0.11a,a	1.99 ± 1.65a	1.25 ± 0.20a,a	1.53 ± 0.27a,a

[a] Different letters before the comma in the same row indicate a significant difference ($p \leq 0.05$) with respect to the distillation system (within the same harvest and yeast strain). Different letters after the comma in the same row for 2010 harvest indicate a significant difference ($p \leq 0.05$) with respect to the yeast strain (within the same distillation system) [b]Σ 2-methyl-1-propanol, 1-butanol, allylic alcohol, 2-methyl-1-butanol, 3-methyl-1-butanol

Table 3.22. Average concentrations (g/hL p.a.) and standard deviations of the microconstituents (esters) present in grape pomace distillates obtained from the *Catalán Roxo* variety from 2009 and 2010 harvest, for each distillation process (copper *Charentais* alembic and packed-column).[a]

Compound	**copper *Charentais* alembic**			**packed-column**		
	yeast strain / harvest			**yeast strain /harvest**		
	S1 / 2009 (n=8)	**QA23 / 2010 (n=2)**	**Sc24 / 2010 (n=2)**	**S1 / 2009 (n=8)**	**QA23 / 2010 (n=2)**	**Sc24 / 2010 (n=2)**
isobutyl acetate	1.11 ± 1.42 a	0.38 ± 0.06a,a	0.25 ± 0.01a,a	0.32 ± 0.32a	0.15 ± 0.08a,a	0.19 ± 0.01a,a
butyl acetate	0.28 ± 0.24a	0.16 ± 0.16a,a	0.37 ± 0.29a,a	0.31 ± 0.25a	0.73 ± 0.30b,a	0.62 ± 0.20a,a
isoamyl acetate	2.17 ± 0.84a	0.52 ± 0.28a,a	0.38 ± 0.25a,a	1.72 ± 1.15a	0.45 ± 0.19a,a	0.35 ± 0.02a,a
hexyl acetate	0.32 ± 0.24a	0.03 ± 0.01a,a	0.04 ± 0.03a,a	0.37 ± 0.28a	0.06 ± 0.06a,a	0.07 ± 0.02a,a
2-phenylethyl acetate	0.16 ± 0.13a	0.12 ± 0.01a,a	0.09 ± 0.02a,a	0.07 ± 0.10a	0.12 ± 0.09a,a	0.10 ± 0.01a,a
Σ acetates of higher alcohols	**4.04 ± 2.88a**	**1.20 ± 0.51a,a**	**1.13 ± 0.60a,a**	**2.79 ± 2.09b**	**1.51 ± 0.72a,a**	**1.33 ± 0.25a,a**
ethyl butyrate	1.39 ± 1.16a	0.35 ± 0.12a,a	0.71 ± 0.73a,b	2.03 ± 1.50a	0.25 ± 0.18a,a	0.56 ± 0.23a,a
ethyl hexanoate	1.60 ± 0.97a	1.98 ± 0.95a,a	1.48 ± 1.21a,a	1.59 ± 1.23a	2.45 ± 1.06a,a	1.86 ± 0.27b,a
ethyl octanoate	0.49 ± 0.43a	5.01 ± 1.25a,a	4.41 ± 1.94a,a	1.30 ± 0.56b	5.82 ± 1.15a,a	5.41 ± 0.34b,a
ethyl decanoate	0.46 ± 0.59a	4.26 ± 0.62a,a	4.64 ± 1.09a,a	0.99 ± 0.50a	4.81 ± 0.97a,a	5.13 ± 0.09b,a
ethyl dodecanoate	0.20 ± 0.30a	1.40 ± 0.76a,a	1.31 ± 0.26a,a	0.45 ± 0.18a	1.80 ± 0.20a,a	1.66 ± 0.14a,a
Σ ethyl esters C6-C12[c]	**2.75 ± 2.29a**	**12.65 ± 3.59a,a**	**11.8 ± 4.51a,a**	**4.33 ± 2.48b**	**14.9 ± 3.37a,a**	**14.1 ± 0.84a,a**
ethyl tetradecanoate	0.06 ± 0.12a	0.40 ± 0.04a,a	0.40 ± 0.07a,a	0.18 ± 0.11b	0.36 ± 0.10a,a	0.40 ± 0.04a,a
ethyl hexadecanoate	0.33 ± 0.90a	2.67 ± 0.47a,a	2.85 ± 0.39a,a	0.82 ± 0.70 a	2.34 ± 0.54a,a	2.72 ± 0.03a,a
ethyl octadecanoate	0.01 ± 0.02	0.14 ± 0.04a,a	0.17 ± 0.01a,a	<LOD [b]	0.06 ± 0.02b,a	0.05 ± 0.04b,a
ethyl 9-octadecenoate	0.09 ± 0.17a	0.47 ± 0.13a,a	0.51 ± 0.04a,a	0.19 ± 0.20a	0.34 ± 0.05a,a	0.33 ± 0.10a,a
ethyl 9,12-octadecadienonate	0.27 ± 0.42a	2.26 ± 0.38a,a	2.86 ± 0.02a,a	0.63 ± 1.90a	1.90 ± 0.38a,a	2.14 ± 0.02a,a
ethyl 9,12,15-octadecatrienoate	0.07 ± 0.12a	0.85 ± 0.05a,a	1.09 ± 0.02a,a	0.22 ± 0.69a	0.69 ± 0.19a,a	0.77 ± 0.04a,a
Σ ethyl esters C14-C18	**0.83 ± 1.76a**	**6.80 ± 1.12a,a**	**7.88 ± 0.55a,a**	**2.05 ± 1.94b**	**5.70 ± 1.28a,a**	**6.42 ± 0.17a,a**
isoamyl octanoate	<LOD	0.05 ± 0.01a,a	0.03 ± 0.01a,a	<LOD	0.05 ± 0.01a,a	0.06 ± 0.01b,a
diethyl succinate	2.89 ± 0.58a	1.00 ± 0.44a,a	1.39 ± 0.32a,a	2.32 ± 0.91a	0.89 ± 0.54a,a	0.97 ± 0.20a,a

[a] Different letters before the comma in the same row indicate a significant difference ($p \leq 0.05$) with respect to the distillation system (within the same harvest and yeast strain). Different letters after the comma in the same row for 2010 harvest indicate a significant difference ($p \leq 0.05$) with respect to the yeast strain (within the same distillation system) [b] LOD, detection limit. [c] Σ ethyl hexanoate, ethyl octanoate, ethyl decanoate, ethyl dodecanoate.

Table 3.23. Average concentrations (g/hL p.a.) and standard deviations of the microconstituents (minor alcohols, monoterpenols, and other compounds) present in grape pomace distillates obtained from the *Catalán Roxo* variety (2009 and 2010 harvest), for each distillation process (copper *Charentais* alembic and packed-column).[a]

Compound	copper *Charentais* alembic			Packed-column		
	yeast strain / harvest			yeast strain /harvest		
	S1 / 2009 (n=8)	**QA23 / 2010 (n=2)**	**Sc24 / 2010 (n=2)**	**S1 / 2009 (n=8)**	**QA23 / 2010 (n=2)**	**Sc24 / 2010 (n=2)**
trans-3-hexen-1-ol	021 ± 0.05a	0.09 ± 0.01a,a	0.09 ± 0.01a,a	0.15 ± 0.06b	0.07 ± 0.03a,a	0.07 ± 0.01a,a
cis-3-hexen-1-ol	0.71 ± 0.71a	0.25 ± 0.07a,a	0.25 ± 0.01a,a	0.58 ± 0.46a	0.20 ± 0.05a,a	0.21 ± 0.01a,a
trans-2-hexen-1-ol	0.96 ± 0.83a	0.57 ± 0.13a,a	0.79 ± 0.13a,a	0.65 ± 0.68a	0.76 ± 0.22a,a	0.82 ± 0.20a,a
1-pentanol	0.06 ± 0.03a	0.32 ± 0.37a,a	0.59 ± 0.09a,a	0.15 ± 0.27a	0.57 ± 0.18a,a	0.54 ± 0.06a,a
1-heptanol	0.75 ± 0.07a	0.28 ± 0.01a,a	0.28 ± 0.01a,a	0.60 ± 0.08b	0.25 ± 0.05a,a	0.25 ± 0.01a,a
1-octanol	0.56 ± 0.04a	0.19 ± 0.01a,a	0.18 ± 0.01a,a	0.50 ± 0.13a	0.16 ± 0.05a,a	0.16 ± 0.01a,a
1-nonanol	2.11 ± 0.21a	1.41 ± 0.30a,a	1.30 ± 0.08a,a	1.88 ± 0.70a	1.13 ± 0.17a,a	1.10 ± 0.02a,a
1-decanol	0.08 ± 0.01a	0.01 ± 0.01a	<LOD [b]	0.07 ± 0.04a	<LOD	0.03 ± 0.02a
benzylic alcohol	1.20 ± 0.30a	0.34 ± 0.07a,a	0.48 ± 0.05a,a	0.78 ± 0.30b	0.21 ± 0.10a,a	0.28 ± 0.03a,a
2-phenylethanol	22.2 ± 4.61a	11.58 ± 3.80a,a	15.01 ± 0.77a,a	14.4 ± 5.03b	9.57 ± 3.54a,a	9.45 ± 0.78a,a
Σ linear alcohols[c]	**3.49 ± 0.26a**	**1.89 ± 0.29a,a**	**1.75 ± 0.08a,a**	**3.06 ± 0.92a**	**1.54 ± 0.27a,a**	**1.54 ± 0.04a,a**
Other compounds						
benzaldehyde	0.70 ± 0.72a	0.46 ± 0.22a,a	0.45 ± 0.77a,a	0.43 ± 0.28a	0.30 ± 0.13a,a	0.28 ± 0.05a,a
furfuraldehyde	0.87 ± 0.79a	0.21 ± 0.14a,a	0.46 ± 0.06a,a	1.33 ± 1.35a	1.02 ± 0.01a,a	0.99 ± 0.02a,a
3-ethoxy-1-propanol	1.06 ± 0.31a	0.28 ± 0.07a,a	0.42 ± 0.13a,a	0.71 ± 0.27b	0.23 ± 0.06a,a	0.27 ± 0.02a,a
1-octen-3-ol	0.28 ± 0.04a	0.06 ± 0.01a,a	0.05 ± 0.01a,a	0.23 ± 0.04b	0.04 ± 0.03a,a	0.04 ± 0.01a,a
3-hydroxy-2-butanone	0.11 ± 0.05a	<LOD	0.02 ± 0.03a	0.13 ± 0.05a	0.09 ± 0.02	0.09 ± 0.02a
Monoterpenols						
trans-furan linalool oxide	1.08 ± 0.22a	0.14 ± 0.04a,a	0.16 ± 0.01a,a	1.20 ± 0.71a	0.21 ± 0.10a,a	0.20 ± 0.05a,a
cis-furan linalool oxide	0.01 ± 0.01a	0.08 ± 0.07a,a	0.16 ± 0.06a,a	0.02 ± 0.02a	0.44 ± 0.06b,a	0.54 ± 0.01b,a
linalol	1.37 ± 0.21a	0.70 ± 0.17a,a	0.71 ± 0.07a,a	1.34 ± 0.21a	0.71 ± 0.15a,a	0.78 ± 0.09a,a
α-terpineol	1.65 ± 0.25a	0.51 ± 0.09a,a	0.59 ± 0.08a,a	1.56 ± 0.81a	0.67 ± 0.11a,a	0.70 ± 0.09a,a
citronellol	0.74 ± 0.32a	0.41 ± 0.20a,a	0.43 ± 0.05a,a	0.94 ± 0.22a	0.56 ± 0.04a,a	0.55 ± 0.09a,a
nerol	0.39 ± 0.21a	0.23 ± 0.02a,a	0.21 ± 0.03a,a	0.53 ± 0.10a	0.15 ± 0.09a,a	0.14 ± 0.01a,a
geraniol	0.37 ± 0.23a	0.17 ± 0.06a,a	0.18 ± 0.01a,a	0.64 ± 0.09b	0.30 ± 0.10a,a	0.33 ± 0.01a,a
hotrienol	0.01 ± 0.04a	0.11 ± 0.03a,a	0.12 ± 0.02a,a	0.05 ± 0.05a	0.21 ± 0.04a,a	0.22 ± 0.02b,a
Σ monoterpenols	**5.62 ± 1.06a**	**2.35 ± 0.61a,a**	**2.56 ±0.32a,a**	**6.28 ±2.34a**	**3.25 ± 0.59a,a**	**3.46 ± 0.35a,a**

[a]Different letters before the comma in the same row indicate a significant difference (p≤0.05) with respect to the distillation system (within the same harvest and yeast strain). Different letters after the comma in the same row for 2010 harvest indicate a significant difference (p≤0.05) with respect to the yeast strain (within the same distillation system) [b] LOD, detection limit. [c]Σ 1-heptanol, 1-octanol, 1-nonanol, 1-decanol.

Table 3.24. Average concentrations (g/hL p.a.) and standard deviations of macroconstituents present in grape pomace distillates obtained from *Xenérico* with two distillation systems (copper *Charentais* alembic and packed-column).[a]

Compound	**copper *Charentais* alembic (n=2)**	**packed-column (n=2)**
methanol	297.87 ± 17.28a	299.39 ± 33.0a
ethyl acetate	38.46 ± 21.39a	32.51 ± 24.28a
acetaldehyde	15.56 ± 1.10a	9.31 ± 1.88b
1,1-dietoxiethane	23.38 ± 10.11a	27.29 ± 9.65a
Σ acetaldehyde + 1,1-diethoxyethane	**24.3 ± 2.67a**	**19.50 ± 5.48a**
1-propanol	30.26 ± 4.11a	24.18 ± 2.05a
2-methyl-1-propanol	39.02 ± 5.31a	35.70 ± 6.27a
1-butanol	1.92 ± 0.06a	1.66 ± 0.12a
2-butanol	0.09 ± 0.03a	0.11 ± 0.04a
allylic alcohol	<LOD	0.02 ± 0.02
2-methyl -1-butanol	45.70 ± 1.49a	49.72 ± 3.20a
3- methyl- 1-butanol	160.96 ± 0.73a	167.99 ± 6.70a
Σ total higher alcohols[b]	**277.94 ± 11.7a**	**279.38 ± 18.4a**
ethyl lactate	54.85 ± 0.37a	46.98 ± 15.84a
1-hexanol	3.23 ± 0.48a	3.42 ± 0.54a
isobutyraldehyde	0.03 ± 0.04a	0.19 ± 0.09a
ethyl formiate	0.53 ± 0.08a	1.17 ± 0.66b
methyl acetate	0.66 ± 0.42a	0.22 ± 0.22a
2-propenal	0.28 ± 0.12a	0.25 ± 0.01a

[a]Different letters before the comma in the same row indicate a significant difference ($p \leq 0.05$) with respect to the distillation system. [b]Σ 2-methyl-1-propanol, 1-butanol, allylic alcohol, 2-methyl-1-butanol, 3-methyl-1-butanol

Table 3.25. Average concentrations (g/hL p.a.) and standard deviations of microconstituents (esters) present in grape pomace distillates obtained from *Xenérico* with two distillation systems (copper *Charentais* alembic and packed-column).[a]

Compound	copper *Charentais* alembic (n=2)	packed-column (n=2)
isobutyl acetate	3.50 ± 0.32a	2.83 ± 0.81a
butyl acetate	0.35 ± 0.02a	0.86 ± 0.06a
isoamyl acetate	0.32 ± 0.22a	0.51 ± 0.27a
hexyl acetate	<LOD[b]	<LOD
2-phenylethyl acetate	0.02 ± 0.0.3a	0.06 ± 0.01a
Σ acetates of higher alcohols	**4.20 ± 0.0.6a**	**4.27 ± 0.64a**
ethyl butyrate	0.23 ± 0.12a	0.31 ± 0.12a
ethyl hexanoate	0.87 ± 0.12a	1.47 ± 0.16b
ethyl octanoate	2.87 ± 0.06a	4.09 ± 0.26b
ethyl decanoate	5.36 ± 0.85a	7.37 ± 0.52b
ethyl dodecanoate	1.67 ± 0.06a	2.70 ± 0.29b
Σ ethyl esters C6-C12	**10.78 ± 0.73a**	**15.63 ± 0.91b**
ethyl tetradecanoate	0.36 ± 0.08a	0.43 ± 0.07a
ethyl hexadecanoate	3.49 ± 0.30a	3.87 ± 0.21a
ethyl octadecanoate	0.12 ± 0.01a	0.08 ± 0.03a
ethyl 9-octadecenoate	0.35 ± 0.0.5a	0.45 ± 0.0.1a
ethyl 9,12-octadecadienonate	2.41 ± 0.56a	2.96 ± 0.79a
ethyl 9,12,15-octadecatrienoate	0.97 ± 0.27a	1.23 ± 0.45a
Σ ethyl esters C14-C18	**7.70 ± 1.26a**	**9.01 ± 1.48b**
isoamyl hexanoate	<LOD	0.04 ± 0.01b
isoamyl octanoate	0.10 ± 0.01a	0.05 ± 0.02b
isoamyl decanoate	<LOD	0.09 ± 0.03a
isoamyl dodecanoate	<LOD	0.01 ± 0.00
Σ isoamyl esters	**0.10 ± 0.01a**	**0.19 ± 0.06b**
diethyl succinate	4.96 ± 0.75a	4.74 ± 1.57a

[a] Different letters before the comma in the same row indicate a significant difference ($p \leq 0.05$) with respect to the distillation system. [b] LOD, detection limit. [c] Σ ethyl hexanoate, ethyl octanoate, ethyl decanoate, ethyl dodecanoate

Table 3.26. Average concentrations (g/hL p.a.) and standard deviations of microconstituents (minor alcohols, monoterpenols and other compounds) present in grape pomace distillates obtained from *Xenérico* with two distillation systems (copper *Charentais* alembic and packed-column).[a]

Compound	**copper *Charentais* alembic (n=2)**	**packed-column (n=2)**
trans-3-hexen-1-ol	0.09 ± 0.0.2a	0.10 ± 0.01a
cis-3-hexen-1-ol	0.14 ± 0.0.3a	0.16 ± 0.06a
trans-2-hexen-1-ol	0.07 ± 0.04a	0.12 ± 0.11a
1-pentanol	0.38 ± 0.01a	0.36 ± 0.05a
1-heptanol	0.08 ± 0.01a	0.09 ± 0.01a
1-octanol	0.14 ± 0.07a	0.09 ± 0.03a
1-nonanol	0.07 ± 0.01a	0.07 ± 0.02a
1-decanol	0.02 ± 0.01a	0.02 ± 0.01a
benzylic alcohol	0.02 ± 0.01a	0.08 ± 0.03a
2-phenylethanol	6.67 ± 2.70a	7.16 ± 2.78a
Σ linear alcohols[b]	**0.31 ± 0.06a**	**0.27 ± 0.04a**
	Other compounds	
benzaldehyde	0.11 ± 0.06a	0.13 ± 0.04a
furfuraldehyde	0.16 ± 0.12a	0.58 ± 0.16a
3-ethoxy-1-propanol	0.19 ± 0.01a	0.08 ± 0.03b
1-octen-3-ol	0.03 ± 0.01a	0.03 ± 0.01a
3-hydroxy-2-butanone	0.16 ± 0.03a	0.09 ± 0.01a
	Monoterpenols	
trans-furan linalool oxide	0.07 ± 0.04a	0.10 ± 0.01a
cis-furan linalool oxide	0.01 ± 0.01a	0.27 ± 0.12b
linalol	0.10 ± 0.05a	0.15 ± 0.03a
α-terpineol	0.05 ± 0.03a	0.09 ± 0.04a
citronellol	0.02 ± 0.01a	0.04 ± 0.01a
nerol	0.02 ± 0.01a	0.01 ± 0.01a
geraniol	0.02 ± 0.01a	0.05 ± 0.02a
hotrienol	0.15 ± 0.02a	0.15 ± 0.07a
Σ monoterpenols[e]	**0.44 ± 0.12a**	**0.86 ± 0.23b**

[a] Different letters before the comma in the same row indicate a significant difference ($p \leq 0.05$) with respect to the distillation system. [b] Σ 1-heptanol, 1-octanol, 1-nonanol, 1-decanol.

3.3.5 PCA analysis

Given the variability of raw material (different varieties), vintage, used yeast, as well as the two different distillation systems used in this work, in a first stage, an initial statistical study using principal components was used to determine what analytical parameters are suitable for the determination of the effect of the distillation system in the quality of the final products.

The principal component analysis performed on grape pomace distillates is explained as follows.

Test 1.

First, a preliminary principal component analysis (PCA) was applied to all the obtained grape pomace distillates, considering all measured volatile compounds (geraniol and ethyl acetate were not considered to PCA analysis since the former was not determined in *Albariño* 2009 and the later had excessively high values in *Catalan roxo* 2009). The first three principal components, which explained 54.34% of the total variance, are summarized in **Table 3.27** and plotted in **Figure 3.5**. From these figures, it can be seen that although the separation of the distillates according to the distillation system was not clear, some tendencies were observed.

PC1, characterized positively with higher loadings of monoterpenols (citronellol, a-terpineol, nerol, *trans*-furan-linalool oxide, linalool), linear alcohols (1-heptanol, 1-octanol, 1-nonanol, 1-decanol) and 2-phenylethanol, differentiated the obtained distillates according to the grape variety. *Catalán Roxo* distillates were situated on the positive side, whereas *Albariño* and *Xenérico* disitillates were on the negative side of PC1. Therefore, *Catalán Roxo* distillates had higher concentration of these compounds in comparison to the other distillates. This is in agreement with results obtained in previous studies (López-Vázquez et al., 2010a; Orriols et al., 2008; Versini et al., 1995). Other compounds contributed positively PC1 with lower loadings (1-propanol, methyl acetate, 1-octen-3-ol, ethyl formiate, benzyl acohol, hexanols) and the only compound that contributed negatively to PC1 was 1-pentanol.(see **Table 3.27**).
PC2 did not show clear clusters. However, in almost all cases, a differentiation according to

the distillation system was observed. Column distillates (situated closer to the top of PC2) were differentiated from alembic distillates by higher concentrations of the compounds that contributed positively PC2, which were ethyl esters C6-C12 and C14-C18 (see **Table 3.27** and **Figure 3.5-A**).

PC3 differentiated distillates from the *Albariño* variety obtained from 2009 harvest from those obtained from 2010 harvest, with higher values of the compounds that contributed positively to PC3, which were: higher alcohols (2-methyl-1-butanol, 3-methyl-1-butanol, 2-methyl-1-propanol), isoamyl decanoate, isoamyl hexanoate, hotrienol, 2-phenylethyl acetate, isobutyl acetate and methanol. A difference according to the distillation system was also observed (see **Figure 3.5B**), mainly with the distillates obtained in the 2009 harvest (independently of the variety). In this case, alembic-distilled were located closer to the top of PC3.

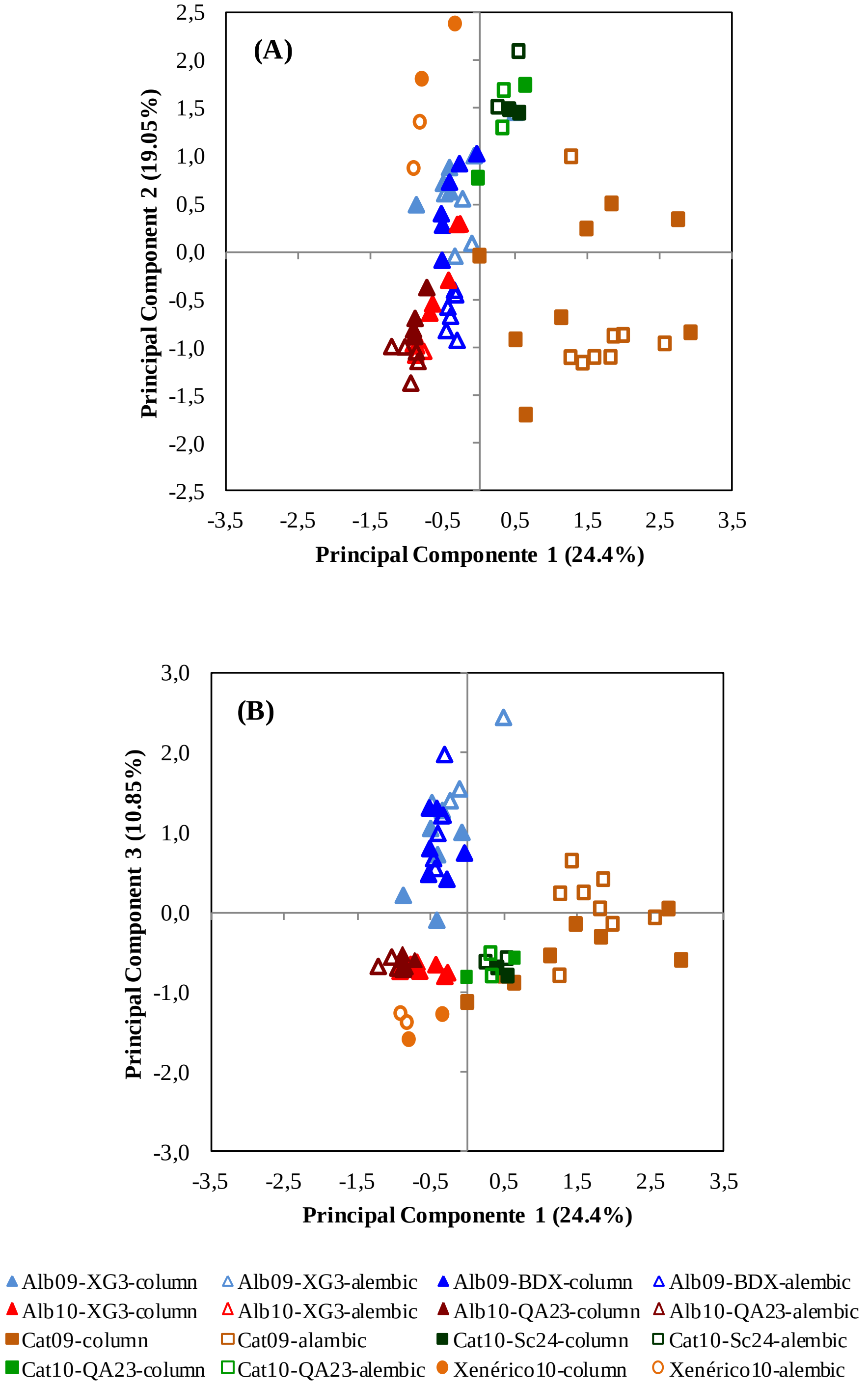


Figure 3.5. Principal component analysis performed in Test 1 for grape pomace distilled in copper *Charentais* alembic (open symbols) and packed-column (solid symbols). (A) PC1 vs PC2, (B) PC1 vs PC3. Alb09: *albariño* 2009; Alb10: *albariño* 2010; Cat09: *catalán roxo* 2009; Cat10: *catalán roxo* 2010.

Table 3.27. PCA results performed in Test 1 for grape pomace distilled in copper *Charentais* alembic and packed-column

Principal Component	Compound	Loading	Variance explained (%)	Total variance (%)
PC1	citronellol	0.928	24.44	24.44
	a-terpineol	0.927		
	1-nonanol	0.926		
	nerol	0.897		
	1-octanol	0.884		
	1-heptanol	0.880		
	2-phenylethanol	0.845		
	trans-furan-linalool oxide	0.799		
	1-decanol	0.764		
	1-pentanol	-0.760		
	allylic alcohol	0.743		
	linalool	0.679		
	1-propanol	0.675		
	methyl acetate	0.647		
	1-octen-3-ol	0.607		
	ethyl formiate	0.596		
	benzyl alcohol	0.573		
	1-hexanol	0.539		
	trans-3-hexen-1-ol	0.505		
	trans-2-hexen-1-ol	0.439		
PC2	ethyl tetradecanoate	0.928	19.05	43.49
	ethyl 9,12-octadecadienoate	0.882		
	ethyl dodecanoate	0.862		
	ethyl 9-octadecenoate	0.855		
	ethyl decanoate	0.851		
	ethyl hexadecanoate	0.834		
	ethyl octanoate	0.797		
	ethyl 9,12,15-octadecatrienoate	0.750		
	ethyl octadecanoate	0,738		
	3-ethoxy-1-propanol	-0.702		
	isoamyl octanoate	0.680		
	cis-furan-linalool-oxide	0.674		
PC3	3-methyl- 1- butanol	0.854	10.85	54.34
	2-methyl-1-butanol	0.849		
	2-methyl-1-propanol	0.834		
	isoamyl hexanoate	0.801		
	isoamyl decanoate	0.779		
	2-phenylethyl acetate	0.644		
	hotrienol	0.554		
	isobutyl acetate	-0.502		
	methanol	-0.447		

Test 2.

In an attempt to improve the differentiation between distillates according to the distillation system, a second principal component analysis was conducted by grouping as family sums corresponding to individual compounds that contributed PC1, PC2 and PC3 in the preliminary analysis. The considered families were: higher alcohols (2-methyl-1-propanol, 2-methyl-1-butanol, 3-methyl-1-butanol), linear alcohols (1-heptanol, 1-octanol, 1-nonanol, 1-decanol), monoterpenols (*trans*-furan linalool oxide, *cis*-furan linalool oxide, linalool, a-terpineol, citronellol, nerol, hotrienol), ethyl esters C6-C12 and ethyl esters C14-C18. Methanol and 2-phenylethanol were considered because they are determinants of the quality on distillates (methanol for its important toxicity level and 2-phenylethanol its organoleptic importance).

Two principal components were obtained (PC1 and PC2), that accounted for 76.03% of total variance (see **Table 3.28** and **Figure 3.6**).

Table 3.28. PCA results performed in Test 2 for grape pomace distilled in copper *Charentais* alembic and packed-column.

Principal Component	Compound	Loading	Variance explained (%)	Total variance (%)
PC1	Σ monoterpenols	0.929	38.86	38.86
	2-phenylethanol	0.928		
	Σ linear alcohols	0.885		
PC2	Σ ethyl esters C6-C12	0.851	37.17	76.03
	Σ ethyl esters C14-C18	0.834		
	methanol	-0.786		
	Σ higher alcohols	0.553		

As in the preliminary analysis (**Test 1**), monoterpenols, 2-phenylethanol and linear alcohols were the compounds that contributted positively to PC1 and they differentiated *Catalán Roxo* distillates from the others. However, a differentiation between the distillates obtained from 2009 harvest (independentely of the variety) according to the distillation system can be observed in **Figure 3.6**. Alembic distillates were situated more to the right side of PC1, indicating higher values of monoterpenols, linear alcohols and 2-phenylethanol in comparison with column distillates.

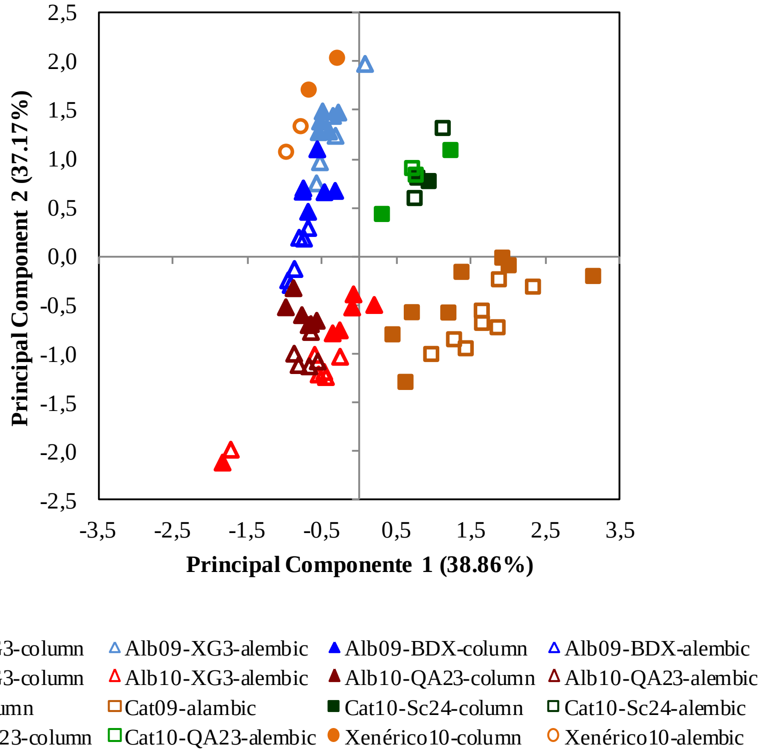


Figure 3.6. Principal component analysis performed in Test 2 for grape pomace distilled in copper *Charentais* alembic (open symbols) and packed-column (solid symbols). Alb09: *Albariño* 2009; Alb10: *Albariño* 2010; Cat09: *Catalán roxo* 2009; Cat10: *Catalán roxo* 2010

PC2 mainly differentiated the distillates according to the harvest. However, it also allowed to separate the distillation system in the distillates obtained from *Albariño* (independently of the harvest) and *Xenérico* varieties (see **Figure 3.6**). Column-distilled were situated more to the top of PC2, indicating higher concentrations of the compounds that contributed positively to PC2, which were ethyl esters C6-C12 and C14-C18 (see T**able 3.28**).

To summarize, the results that emerged from principal component analysis subjecting all the grape pomace distillates considered in this study, indicated the possibility of separating grape pomaces distillates according to the distillation system using a selected subset of variables (higher alcohols, linear alcohols, monoterpenols, ethyl esters C6-C12 and C14-C18, methanol and 2-phenyletanol). However the effect of the grape variety is greater than the distillation system. Accordingly, a third test was carried out, in which PCAs were separately applied to the distillates by variety, considering the above mentioned compounds. The results of these PCAs are explaind as follows.

Test 3.

Albariño 2009 and 2010 harvest

Two principal components were obtained (PC1 and PC2), which explained 50.44 and 24.8% of the total variance, respectively (see **Table 3.29**). As shown in **Table 3.29** and **Figure 3.7**, all the compounds that were correlated with PC2 in **Test 2** were also correlated with PC1 in this PCA analysis, and they differentiated the distillates according to the harvest of grape. In this case, linear alcohols also contributed to PC1. It is also observed that the distillates obtained with the column were located more to the right of PC1 and those obtained with alembic were located more to the left (within the same harvest and yeast strain). Thus, the distillates obtained with the column had higher concentration of ethyl esters C6-C12 and C14-C18 in comparison with those obtained with alembic. PC2, formed positively by 2-phenylethanol and monoterpenols, allowed differentiating the distillation system, locating the distillates obtained with the alembic on the positive side. This difference was clearer in *Albariño* 2009 distillates. Interestingly enough, the recovery of monoterpenols was similar for both distillation systems in the case of *Albariño* 2009, whereas it was higher for packed column in the case of 2010 harvest, as shown in **Tables 3.13** and **3.15**.

Table 3.29. PCA results performed in Test 3 for *Albariño* 2009 and 2010 grape pomace distilled in copper *Charentais* alembic and packed-column.

Principal Component	Compound	Loading	Variance explained (%)	Total variance (%)
PC1	methanol	-0.931	50.44	50.44
	Σ ethyl esters C6-C12	0.860		
	Σ linear alcohols	-0.842		
	Σ higher alcohols	0.809		
	Σ ethyl esters C14-C18	0.736		
PC2	2-phenylethanol	0.894	24.80	75.24
	Σ monoterpenols	0.869		

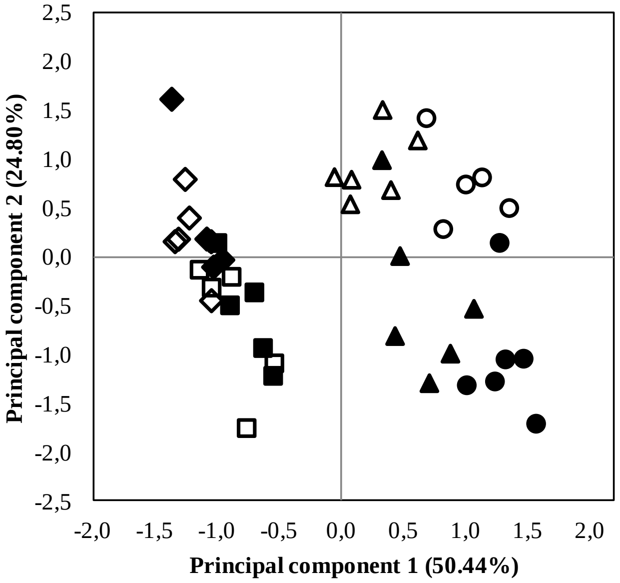


Figure 3.7. Principal component analysis (PC1 vsPC2) performed in Test 3 for *Albariño* 2009 and 2010 grape pomace distillates. *Albariño* 2009: XG3 yeast (○, ●), BDX yeast (△, ▲), *Albariño* 2010: XG3 yeast (◇,◆) QA23 yeast (□,■). Alembic distillates (open symbols) and packed-column distillates (solid symbols).

Catalán Roxo 2009 and 2010 harvest

Two principal components were obtained (PC1 and PC2), which explained 55.05 and 23.95% of the total variance, respectively (see **Table 3.30**). These components are depicted in **Figure 3.8** showing four sets of distillate samples. PC1 separated spirits mainly by the harvest, whereas PC2 separated them mainly as a function of the distillation system. *Catalán Roxo* grape pomace distillates 2009 harvest (right side) differed from *Catalán Roxo* grape pomace spirits 2010 harvest (left side) because they had higher concentrations of monoterpenols, linear alcohols and 2-phenylethanol, which contributed positively to PC1, and *Catalán Roxo* 2010 had higher concentrations of ethyl esters, which contributed negatively to PC1. On the other hand, alembic-distilled grape pomace (top) differed from those column-distilled (bottom) because they had higher concentrations of higher alcohols and lower concentration of methanol, which were the compounds that contributed to PC2. **Figure 3.8** also shows that with PC1 alembic-distilled were located more on the right, with higher levels in ethyl esters C6-C12 and C14-C18, and lower levels in linear alcohols, monoterpenols and 2-

phenylethanol in comparison with column-distilled. This observation was clearer with 2009 harvest.

Table 3.30. PCA results performed in Test 3 for *Catalán Roxo* 2009 and 2010 distilled in copper *Charentais* alembic and packed-column.

Principal Component	Compound	Loading	Variance explained (%)	Total variance (%)
PC1	Σ ethyl esters C6-C12	-0.900	55.05	55.05
	Σ monoterpenols	0.897		
	Σ linear alcohols	0.896		
	Σ ethyl esters C14-C18	-0.864		
	2-phenylethanol	0.805		
PC2	Σ higher alcohols	0.916	23.95	79.00
	methanol	-0.854		

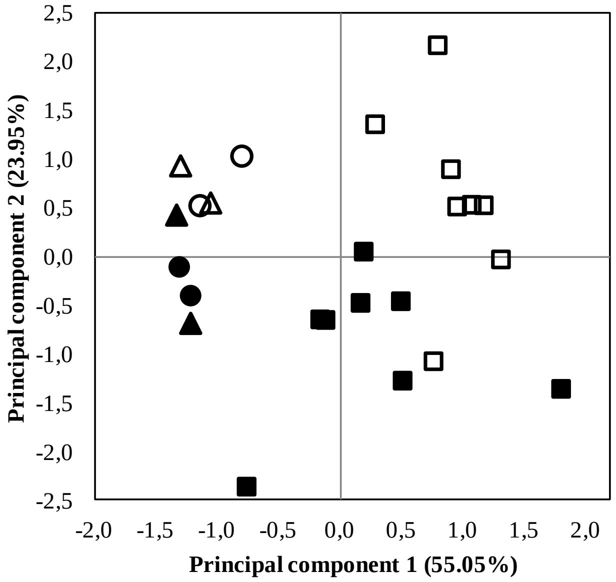


Figure 3.8. Principal component analysis (PC1 vs PC2) performed in Test 3 for *Catalán Roxo* 2009 and 2010 grape pomace distillates. *Catalán Roxo* 2009 (□, ■). *Catalán Roxo* 2010: QA23 yeast (△, ▲), Sc24 yeast (○, ●).Alembic distillates (open symbols) and packed-column distillates (solid symbols).

Test 3 shows that a clear influence of the distillation system was not evident when the two harvests within the same variety (*Albariño* and *Catalán Roxo*) were subjected to PCA. Consequently, a PCA in which the variety and the harvest of grape were separated was performed as described below.

Test 4.

Albariño 2009 harvest

Those compounds that showed significant differences among systems and/or yeasts were considered for PCA, except for those influenced by the cut supervision at the distillation process like diethyl succinate, ethyl lactate and benzyl alcohol. To simplify the analysis, the concentration of ethyl esters C6-C12, acetates of higher alcohols and linear alcohols were grouped as family sums. Two principal components were obtained (PC1 and PC2), which explained 73.75% of the variance (**Table 3.31**). As shown in **Figure 3.9**, the samples can be separated according to yeast used and distillation system. PC1 accounts for 38.70% of the total variance and clearly differentiates the distillates according to the yeast strain. XG3 distillates were located on the positive side of PC1, whereas those from BDX were plotted on the negative side of this component. XG3 distillates were characterized by higher concentrations of ethyl esters C6-C12, isoamyl octanoate, *trans*-2-hexenol and acetates of higher alcohols than the BDX ones. In contrast, BDX distillates were defined by a higher content of methanol and 1-propanol. PC2 accounts for 35.05% of the total variance and differentiates the samples according to the distillation system. Alembic distillates (top) were characterized by higher levels of linear alcohols, linalool, 1-hexanol and 3-ethoxy-1-propanol, whereas column distillates (bottom) were characterized by higher concentrations of ethyl hexadecanoate.

Table 3.31. PCA results for the average volatile compounds in distillates from *Albariño* 2009 grape pomace distilled in copper *Charentais* alembic and packed-column

Principal Component	Compound	Loading	Explained variance (%)	Total variance (%)
PC1	Σ ethyl esters C6-C12	0.922	38.70	38.7
	isoamyl octanoate	0.915		
	methanol	-0.912		
	trans-2-hexen-1-ol	0.809		
	Σ acetates of higher alcohols	0.671		
	propanol	-0.639		
PC2	Σ linear alcohols	0.934	35.05	73.75
	linalool	0.93		
	1-hexanol	0.878		
	ethyl hexadecanoate	-0.796		
	3-ethoxy-1-propanol	0.610		

Albariño 2010 harvest

Two principal components were obtained (PC1 and PC2), which explained 55.02 and 26.53% of the variance, respectively (see **Table 3.32**). These components are depicted in **Figure 3.10**. With PC1, there is a tendency to differentiate the distillates according to the yeast strain, whereas PC2 separated the distillation system. *Albariño* grape pomace distillates obtained with XG3 yeast (right side) differed from those obtained with QA23 (left side) because they had higher concentrations of monoterpenols, methanol and linear alcohols, which contributed positively to PC1; and those obtained with QA23 yeast had higher concentrations of higher alcohols, which contributed negatively to PC1. Regarding the distillation system, column-distilled (top) had higher concentrations of ethyl esters C6-C12 and C14-C18 and lower concentration of 2-phenylethanol in comparison with alembic-distilled. However, the recovered amount of 2-phenylethanol were slightly higher for column-distilled (**Table 3.15**).

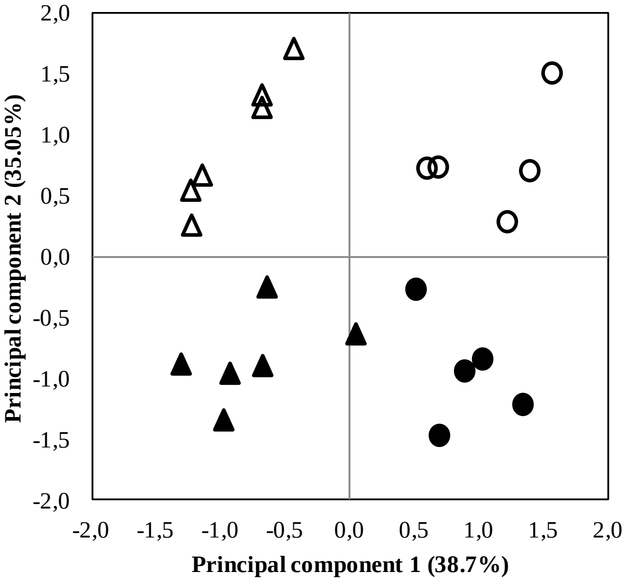


Figure 3.9. Principal components analysis of the volatile composition of *Albariño* 2009 grape pomace distillates: XG3 yeast (○, ●) and BDX yeast (△, ▲). Alembic distillates (open symbols) and packed-column distillates (solid symbols).

Table 3.32. PCA results for the average volatile compounds in distillates from *Albariño* 2010 grape pomace distilled in copper *Charentais* alembic and packed-column

Principal Component	Compound	Loading	Variance explained (%)	Total variance (%)
PC1	Σ monoterpenols	0.933	52.02	52.02
	Σ higher alcohols	-0.917		
	methanol	0.903		
	Σ linear alcohols	0.832		
PC2	2-phenylethanol	-0.827	26.53	78.55
	Σ ethyl esters C6-C12	0.792		
	Σ ethyl esters C14-C18	0.733		

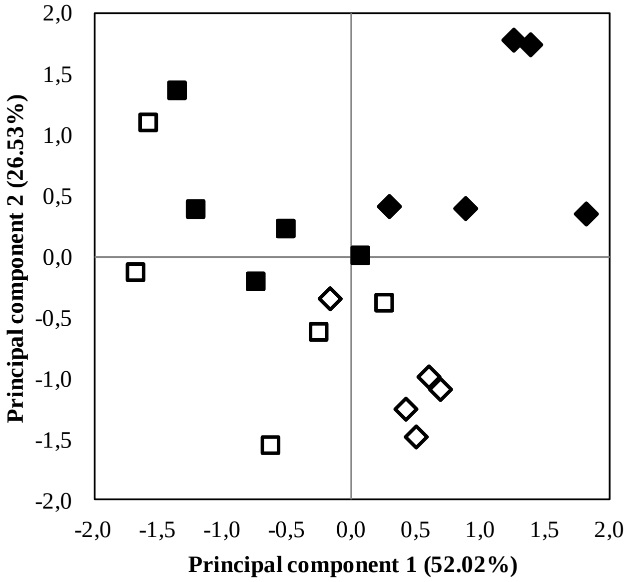


Figure 3.10. Principal components analysis (PC1 vs PC2) of the volatile composition of *Albariño* 2010 grape pomace distillates. XG3 yeast (◊,♦), QA23 yeast (□, ■). Alembic distillates (open symbols) and packed-column distillates (solid symbols).

Catalán Roxo 2009 harvest

Three principal components were obtained (PC1, PC2 and PC3). PC1 and PC2, which explained 31.0 and 30.7% of the total variance, respectively (**Table 3.33**), differentiated the distillates according to the distillation system (**Figure 3.11**). According to PC1, Column distillates (right side) were characterized with higher levels of ethyl esters C6-C12 and C14-C18, whereas alembic distillates (left side) were characterized with higher levels of 2-phenylethanol. According to PC2, alembic-distilled grape pomace (top) differed from those column-distilled (bottom) because they had higher concentrations of higher alcohols and lower concentration of methanol.

Table 3.33. PCA results for the average volatile compounds in distillates from *Catalán Roxo* 2009 grape pomace distilled in copper *Charentais* alembic and packed-column

Principal Component	Compound	Loading	Variance explained (%)	Total variance (%)
PC1	Σ ethyl esters C14-C18	-0.921	31.00	31.00
	2-phenylethanol	0.837		
	Σ ethyl esters C6-C12	-0.605		
PC2	methanol	0.960	30.70	61.79
	Σ higher alcohols	-0.944		
PC3	Σ monoterpenols	0.910	24.31	87.88
	Σ linear alcohols	0.899		

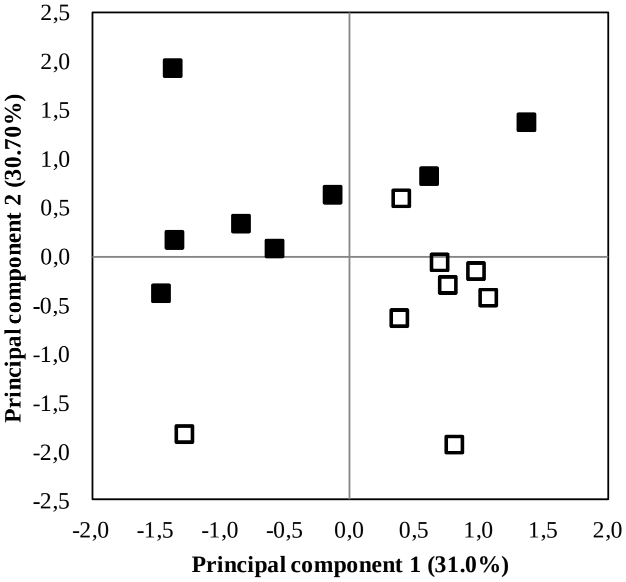


Figure 3.11. Principal components analysis (PC1 vs PC2) of the volatile composition of *Catalán Roxo* 2009 grape pomace distillates. Alembic distillates (open symbols) and packed-column distillates (solid symbols).

Catalán Roxo 2010 harvest

Three principal components were obtained (PC1, PC2 and PC3), whereas only PC1 and PC3 showed a tendency to differentiate the distillates according to the distillation system (See

Figure 3.12). PC2 is not shown in the plot. PC1 was contributed positively by linear alcohols, ethyl esters C14-C18 and 2-phenylethanol (**Table 3.34**), and the distillates obtained with alembic were clustered in right side. PC3 was contributed positively by higher alcohols and negatively by monoterpenols. Alembic distillates were located on the positive side while the column distillates were located on the negative side. This PCA result suggest that alembic-distilled had higher concentrations of alcohols (linear alcohols, higher alcohols and 2-phenylethylethanol) and ethyl esters C14-C18, while column-distilled had higher concentrations of monoterpenols. In this case, esters C6-C12 and methanol did not contribute to differentiate the distillation system. The higher concentration of alcohols in alembic can be associated to the dilution effect since the ethanol yield in the heart fraction obtained in the column was higher than the one obtained in alembic and, therefore, a greater recovery of linear alcohols, higher alcohols and 2-phenylethylethanol was obtained in column-distilled (see **Table 3.16**)

Table 3.34. PCA results for the average volatile compounds in distillates from *Catalán Roxo* 2010 grape pomace distilled in copper *Charentais* alembic and packed-column

Principal Component	Compound	Loading	Variance explained (%)	Total variance (%)
PC1	Σ linear alcohols	0.901	30.08	30.08
	Σ ethyl esters C14-C18	0.896		
	2-phenylethanol	0.875		
PC2	methanol	0.961	29.55	59.63
	Σ ethyl esters C6-C12	0.898		
PC3	Σ higher alcohols	0.925	28.25	87.88
	Σ monoterpenols	-0.742		

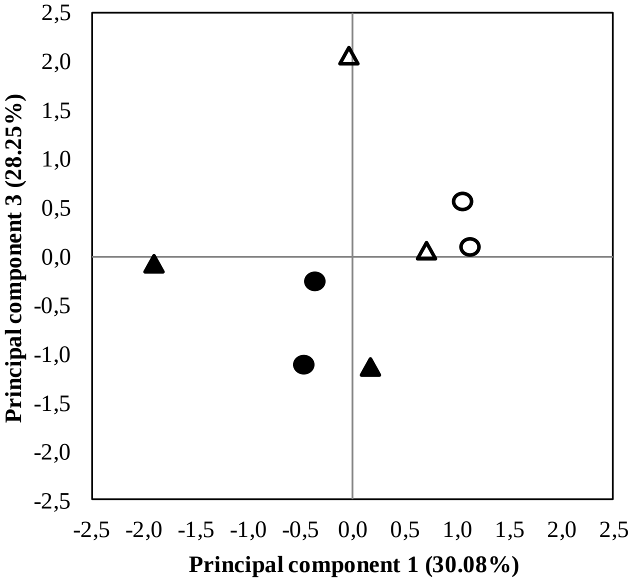


Figure 3.12. Principal component analysis (PC1 vs PC3) of the volatile composition of *Catalán Roxo* 2010 grape pomace distillates. QA23 yeast (△, ▲), Sc24 yeast (○, ●).Alembic distillates (open symbols) and packed-column distillates (solid symbols).

Xenérico

Table 3.35 shows the results of the two principal components obtained (PC1 and PC2), which explained 49.47 and 45.14% of the variance respectively. PC1 and PC2 are depicted in **Figure 3.13**. PC2 shows a differentiation according to the distillation system. Monoterpenols and ethyl esters (C6-C12 and C14-C18) contributed positively to PC2 and *Xenérico* distillates obtained in column were clustered in the right side. This result suggests that packed-column allows obtaining distillates with greater concentration in these compounds; however the number of samples is insufficient to conclude. PC1, composed by the alcohols (higher alcohols, 2-phenylethylethanol, methanol and linear alcohols), did not differentiate any of the distillates.

Table 3.35. PCA results for the average volatile compounds in distillates from *Xenérico* 2010 grape pomace distilled in copper *Charentais* alembic and packed-column

Principal Component	Compound	Loading	Variance explained (%)	Total variance (%)
PC1	Σ higher alcohols	-0.984	49.47	49.47
	2-phenylethanol	0.917		
	methanol	0.887		
	Σ linear alcohols	0.757		
PC2	Σ monoterpenols	0.967	45.14	94.61
	Σ ethyl esters C6-C12	0.963		
	Σ ethyl esters C14-C18	0.871		

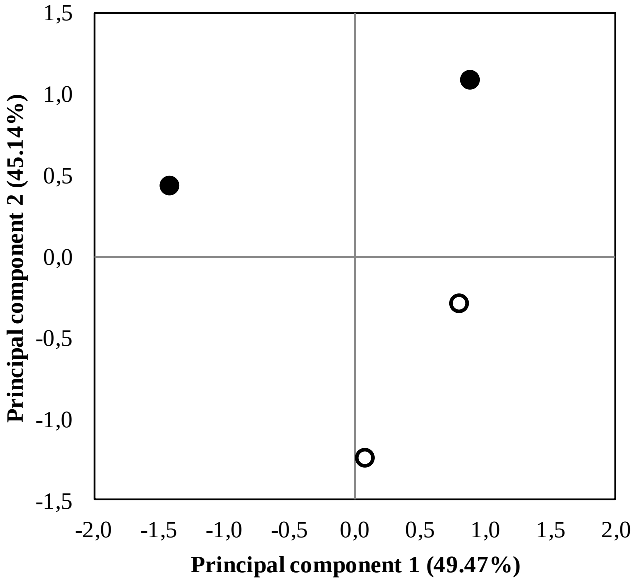


Figure 3.13. Principal component analysis (PC1 vs PC2) of the volatile composition of *Xenérico* 2010 grape pomace distillates. Alembic distillates (open symbols) and packed-column distillates (solid symbols).

3.3.6 Sensory analysis

This section includes the results obtained from sensory analysis (order-of-preference test and quantitative descriptive analysis) for each type of distillate. The results are explained separately by harvest as follows:

Albariño 2009 harvest

The preference test did not show any significant taste and aroma difference (Friedman test $p < 0.05$) among the distillates according to the distillation system and yeast strain. In contrast, a noticeable difference according to the distillations system and/or yeast strain is observed from the results obtained from the descriptive test (**Figure 3.14**). For aroma (**Figure 3.14A**), the distillates obtained from column and XG3 yeast were scored with the highest PGI (Positive General Impression) and described by fruity character. This could be related to ethyl esters C6-C12, and acetates of higher alcohols, which were present in higher concentrations in these distillates (**Table 3.19**). The distillates obtained from alembic and BDX yeast received the lowest scores in some aromas (fruity, herbaceous, and spicy). However, the distillates obtained from XG3 and distilled in alembic had the highest punctuation in oxidized and solvent attributes, which may be due to the fact that this distillate was the only one with concentrations of acetaldehyde (31.96 g/hL) and ethyl acetate (221 g/hL) close to the perception thresholds (30-50 g/hL and 180 g/hL, respectively) (Odello et al. 1997; Soufleros et al. 2004). It can also be noted in **Figure 3.14** that although distillates obtained with alembic had higher concentration of compounds associated with floral nuances (1-linalool and linear alcohol), the difference in these concentrations was not large enough (**Table 3.11**) for the panel to be able to differentiate the distillates according to this character.

The panel of experts was able to differentiate the distillates by taste according to distillation system (**Figure 3.14B**) but not the yeast. Distillates obtained from alembic (independently of the yeast strain) were characterized by the highest scores in astringency and the lowest scores in positive attributes (sweet, harmony, mellowness and general quality in mouth). This result may be attributed to the interactions of the different compounds present in the studied distillates.

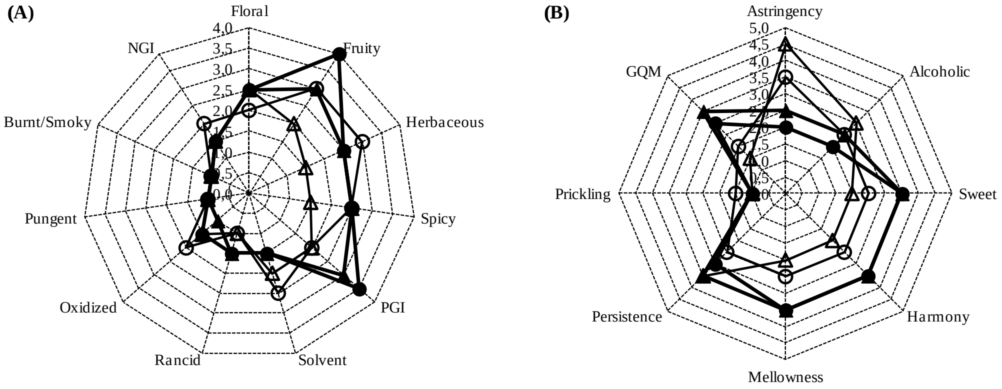


Figure 3.14. Spider diagram of descriptive sensory analysis for *Albariño* 2009 grape pomace distillates: (A) Aroma profile and (B) taste profile. XG3 yeast (○, ●) and BDX yeast (△, ▲). Alembic distillates (open symbols) and packed column (solid symbols). PGI (Positive General Impression), NGI (Negative General Impression), GQM (General Quality in Mouth).

Albariño 2010 harvest

Considering aroma, preference test showed significant difference (Friedman test $p< 0.05$) according to distillation system but not according to yeast strain used. The distillates obtained from column were preferred against alembic. Considering taste, a significant difference between XG3 and QA23 yeasts was found when distilled in alembic (being the XG3 yeast preferred) but not when they were distilled in column. According to distillation system, a significant difference is found when QA23 is used for fermentation (being the column-distilled preferred) but not when XG3 is used.

Similarly as in the preference test, in the aroma descriptive test the panel did not distinguish the distillates according to the yeast. The floral aroma was the only attribute whose score was different according to yeast, being higher with XG3 yeast in comparison with QA23 yeast (**Figure 3.15-A**). This is in agreement with chemical and PCA results since XG3 yeast produced higher amount of monoterpenols and linear alcohols (see **Table 3.20**, and Section **3.3.5**).

Comparing the distillation systems, the distillates obtained with column were in general characterized with fruity, herbaceous and spicy notes, the highest positive general impression (PGI) and the lowest negative characters (oxidized, pungent, solvent, NGI). These negative characters may be attributed to the slighly higher values in alembic-distilled of compounds like the sum of acetaldehyde and 1,1-diethoxyethane (73.55-61.61 g/hL), 2-propenal (0.54-0.38 g/hL), ethyl acetate (169.3-165 g/hL) and methyl acetate (3.07-2.79 g/hL) (**Table 3.18**), which have been associated to these notes in distillates (Odello et al. 1997; Ledauphin et al. 2003; Soufleros et al. 2004; López-Vázquez 2011)

In taste (**Figure 3.15-B**), the only distillate with different scores was the one obtained from the column with XG3 yeast. This distillate was characterized with positive attributes such as sweet, harmony, mellowness and persistence and with the highest general quality in mouth. The astringency and prickling terms were described in all distillates with the same intensity.

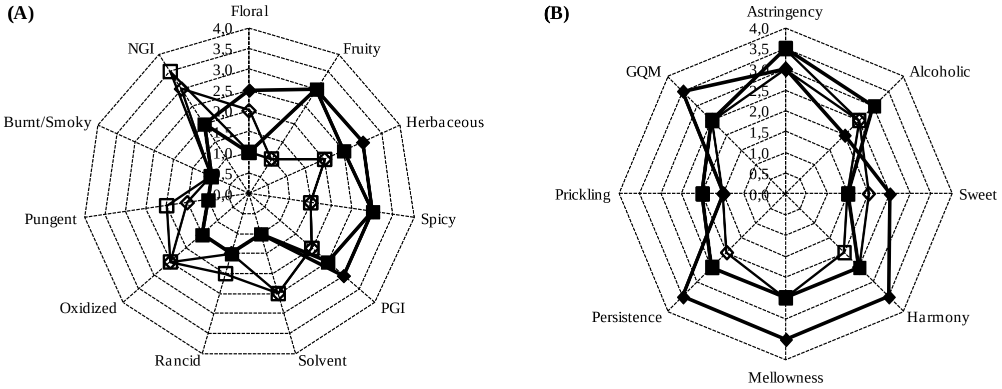


Figure 3.15. Spider diagram of descriptive sensory analysis for *Albariño* 2010 grape pomace distillates: (A) Aroma profile and (B) taste profile. XG3 yeast (◊,♦), QA23 yeast (□, ■). Alembic distillates (open symbols) and packed column (solid symbols). PGI (Positive General Impression), NGI (Negative General Impression), GQM (General Quality in Mouth).

Catalán Roxo 2010 harvest

Preference test did not show any significant aroma and test difference among the distillates obtained from alembic and column from *Catalán roxo* 2010 harvest. However in descriptive test a small difference was observed (**Figure 3.16**). Distillates obtained with column were slightly characterized with positive aromas (floral, fruity), since they had higher concentrations of ethyl esters C6-C12 and monoterpenols, although the differences were not significant ($p< 0.05$) in ANOVA test (**Table 3.22-3.23**). The distillates obtained in alembic were characterized with negatives attributes (solvent, oxidized and NGI). It is interesting to note from **Figure 3.16** that distillates obtained from column had the highest score in burnt/smoky attribute which is usually associated to furfuraldehyde (Oishi et al., 2008) whose concentrations were higher in column-distilled compared to alembic-distilled (**Table 3.23**).

In taste, distillates obtained in column were slightly more harmonic, soft (mellowness attribute) and sweet, with less prickling and scored with higher quality in mouth comparing with alembic-distilled.

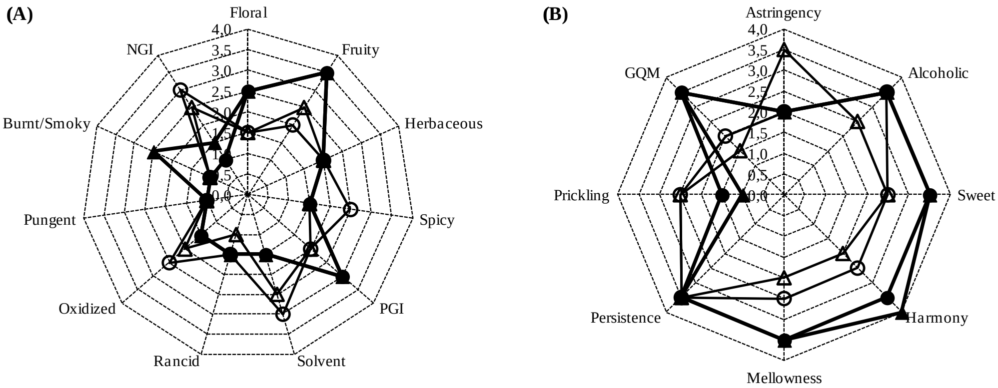


Figure 3.16. Spider diagram of descriptive sensory analysis for *Catalán roxo* 2010 grape pomace distillates: (A) Aroma profile and (B) taste profile. QA23 yeast (△, ▲), Sc24 yeast (○, ●).. Alembic spirits (open symbols) and packed column (solid symbols). PGI (Positive General Impression), NGI (Negative General Impression), GQM (General Quality in Mouth).

Xenérico 2010 harvest

In preference test no significant differences were found (in both aroma and taste) among the distillates obtained from alembic and column. However, in descriptive test, some differences were found in both aroma and taste (**Figure 3.17**). In aroma, distillates obtained with the column were characterized by higher punctuation in fruity, herbaceous, spicy and positive general impression, and lower punctuation in oxidized and negative general impression. Some of the investigated compounds confirm this result. Ethyl esters C6-C12 and monoterpenols, as above mentioned, are positive compounds from sensorial point of view and, according to PCA analysis distillates obtained from column had higher concentrations in these compounds.

It is important to note from **Figure 3.17A** that the compounds obtained from column had the highest punctuation in rancid term, which may be associated with ethyl esters C14-C18 (Salo, 1970) and chemical (**Table 3.25**) and PCA analysis (**Table 3.35** and **Figure 3.13**) showed that these compounds were higher with the column in comparison with alembic.

In taste, distillates obtained with the column were more harmonic, persistent, with less prickling, alcoholic and sweet. Both distillation systems had the same score in general quality in mouth.

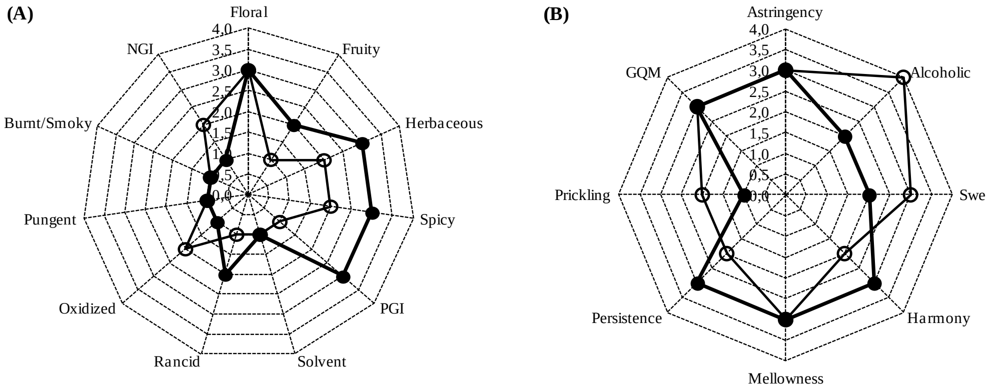


Figure 3.17. Spider diagram of descriptive sensory analysis for *Xenérico* grape pomace distilled in alembic (open symbols) and packed column (open symbol). (A) Aroma profile and (B) taste profile PGI (Positive General Impression), NGI (Negative General Impression), GQM (General Quality in Mouth).

In summary, the use of an adequate distillation system as a packed column in the production of *orujo* distillates allows improving the distillate chemical composition and, therefore, its sensory quality. In this case, packed-column distillation guaranteed a distillate with desirable organoleptic characteristics, standing out the greater production of C6-C12 ethyl esters, which impart fruity notes to distillates. Packed-column enhances positive sensations in mouth and reduces the intensity of negative aromas (oxidized, solvent). Moreover, packed-column distillation combined with an adequate yeast strain (XG3 in this case) resulted in higher ethanol yields.

Chapter 4

Conclusions

The results obtained in this research support the use of packed column as an alternative to traditional alembic in the production of fruit and grape pomace distillates, both from an economic point of view and in terms of the quality of the final product.

The main contributions of this work are summarized as follows.

- The feasibility of improving pear distillates from two pear varieties (*Blanquilla* and Conference) through the use of packed column compared to distillates obtained with traditional alembic has been demonstrated.

- It has been shown that it is possible to minimize the difference in the sensory quality of distillates obtained from less aromatic varieties (*Blanquilla* and Conference) with respect to distillates obtained with the Bartlett pear, a more aromatic variety, using the packed column.

- The feasibility of obtaining good quality kiwi distillates from the sensory point of view has also been demonstrated. In particular, the distillation system has a stronger influence than the yeast strain. Distillation with packed column enhanced the floral, fruity and spicy character of kiwi distillates, associated to ethyl esters C6-C12 and monoterpenols, and reduced the intensity of negative aromas (burnt/smoky, and pungent), with respect to alembic.

- The study with grape pomace was more complex due to variability on the raw material (different harvest and grape pomace variety). Although the effect of the variety and harvest on the volatile composition of the distillates is greater than the distillation system, in general, packed column distillation improved the sensory quality of the distillates. Specifically, the column enhanced the quality in both nose and mouth. Fruity, herbaceous and spicy were the predominant aroma descriptors in grape pomace distilled with column, in contrast to oxidized and solvent aroma descriptors more dominant in grape pomace distilled in alembic.

- The packed column allowed obtaining distillates with greater ethanol yield, thus allowing in many cases to increase the recovery of positive compounds such as monoterpenols, linear alcohols and higher alcohols.

More distillations at semi-industrial scale should be carried out in order to verify the reproducibility in small commercial distilleries. It would also be interesting to detect and quantify other compounds of organoleptic importance that have not been included in this thesis in order to correlate them with sensory analysis.

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Annex I. Descriptive tasting sheet for quality assessment

NAME: ____

SAMPLE: ____________

Score each attribute from **0-5** (0: not perceived, 1: very low, 2: low, 3:medium, 4:high, 5:very high)

Attributes	**Descriptive olfactory phase**	0	1	2	3	4	5
Floral	Intensity of perceived floral aromas (rose, violet, manzanilla, lavanda, honey, etc.)						
Fruity	Intensity of perceived fresh fruity aromas (citrus, banana, apple,pear,melon, etc.)						
Vegetal/herbaceous	Intensity of perceived vegetal aromas (fresh grass, dried vegetals, asparagus, mushroom)						
Spicy	Intensity of perceived spicy aromas (clove, pepper, nutmeg, anise, liquorice, vanilla)						
Positive general impression	Intensity of the perceived positive general aromas						
Solvent	Intensity of aromas associated to nail polish remover, glue, chemical solvents, etc.						
Rancid	Intensity of aromas associated to fat, sweat, leather, etc.						
Oxidized	Intensity of aromas associated to overripe apple, sharp						
Pungent	Perception of heat in the nasal mucus, similar those caused by the vinegar						
Burnt/smoky	Intensity of aroma associated to smoke dried, ash, burnt paper						
Negative general impression	Intensity of the perceived negative general aromas						

Attributes	**Descriptive tasting phase**	0	1	2	3	4	5
Astringency/bitterness	Perceptions of dryness, surlines, and tension of the papillae						
Alcoholic	Taste of alcohol asscociated to the perception of dehydration and heating in mouth						
Sweet	Perception of seewtness						
Harmony	Fresh dynamic acid/sweetness balance, rich and smooth mouth-feel, harmonious						
Mellowness	Tenderness of spirit and mouth volume						
Persistence	Prolonged flavor in the mouth (≥10 to 15 seconds), delicate and refined aftertaste						
Pungent	Agressive, repulsive, abrasive and sharp sensation in mouth						
General quality in mouth	So nearly perfect in all sensory perceptions truly remarkable						