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Floral aroma improvement of Muscat spirits by packed column distillation with variable internal reflux

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ABSTRACT

The organoleptic quality of wine distillates depends on raw materials and the distillation process. Previous work has shown that rectification columns in batch distillation with fixed reflux rate are useful to obtain distillates or distillate fractions with enhanced organoleptic characteristics. This study explores variable reflux rate operating strategies to increase the levels of terpenic compounds in specific distillate fractions to emphasize its floral aroma. Based on chemical and sensory analyses, two distillate heart sub-fractions obtained with the best operating strategy found, were compared with a distillate obtained in a traditional alembic. Results have shown that a drastic reduction of the reflux rate at an early stage of the heart cut produced a distillate heart sub-fraction with a higher concentration of terpenic compounds and lower levels of negative aroma compounds. Therefore, this sub-fraction presented a much more noticeable floral aroma than the distillate obtained with a traditional alembic.

1. Introduction

Wine spirit is an alcoholic beverage obtained from the distillation of fermented grape musts. The quality of the distillate depends on both the raw materials and the distillation process used.

The grape variety used to produce the wine could provide varietal compounds, such as terpenes and terpenols in the case of Muscat or Malvasía grape varieties, that give wine floral aroma characteristics (Etiévant, 1991). *Pisco* is one of the most relevant terpenic spirit, so distillers aim to preserve the floral and fruity aromas, a factor traditionally associated with the variety and quality of grapes (Agosin, Belancic, Ibacache, Baumes, & Bordeu, 2000). However, large chemical composition differences between aromatic *Piscos* have been observed (Cacho, Moncayo, Palma, Ferreira, & Culleré, 2012). Among floral and fruity aroma compounds, linalool is the most relevant compound in *Pisco* (Bordeu, Formas, & Agosin, 2004), although its characteristic aroma is also related to the sensory perception of other molecules (Peña y Lillo, Agosin, Andrea, & Latrille, 2005). In addition, terpenic compounds present high reactivity in catalyzed and hot acid media (Iwai et al., 2014; Ohta, Morimitsu, Sameshima, Samuta, & Ohba, 1991; Osorio, Pérez-Correa, Belancic, & Agosin, 2004) and tend to distil in early fractions of the distillation (Peña y Lillo et al., 2005), thus these compounds cannot be easily concentrated in the heart cut (commercial distillate fraction). Muscat distillates such as *Pisco* contain other non-terpenic compounds with important sensory attributes (Herraiz, Reglero, Herraiz, & Loyola, 1990), whose distillation behaviors vary throughout the process (Jouret, Cantagrel, & Galy, 1998).

The traditional distillation with a copper *Charentais* alembic (French Style) allows limited intervention during the distillation process (only the heating power in the boiler can be manipulated) to modify the composition of the distillate. A more flexible system is the batch distillation column (German Style) in which the reflux rate can be varied in a wide range. However, none of these systems allows a rapid variation of the internal reflux of the system during distillation. An interesting alternative is the use of a boiler coupled with a rectification column, equipped with an internal partial condenser that allows rapid control of the reflux rate of the column by manipulating the cooling flow rate (García-Llobodanin, Roca, López, Pérez-Correa, & López, 2011).

Several studies have compared the spirits obtained by classical alembics and columns with an internal partial condenser. Kiwi and pear fermented juices and grape pomace have been tested with both methods of distillation (Arrieta-Garay et al., 2013;

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Arrieta-Garay, Blanco et al., 2014; Arrieta-Garay, López-Vázquez et al., 2014) and showed that column distillates presented better fruit and floral characteristics and less solvent-like and toxic compounds (head compounds). In addition, García-Llobodanin et al. (2011) found differences between both methods. The partial reflux column system produced heart fractions of distillate with high levels of esters and higher alcohols, although they observed a lack of reproducibility of the distillation. No previous studies have tested specific variable reflux policies focused on concentrating or removing specific positive or negative compounds in certain distillate fractions.

Therefore, the aim of this study was to develop variable reflux strategies to concentrate terpenic compounds in the heart fraction of the distillate. Hence, non-aromatic wine was doped with several terpenic compounds to study the extraction/distillation kinetics. Moreover, using chemical and sensory analyses, Muscat wine (non- doped) spirits obtained with the optimum column strategy and with a traditional alembic were compared.

2. Material and methods

2.1. Wines

Experiments were performed at the Department of Chemical Engineering of the Rovira i Virgili University. Two white wines were used: a *Vitis vinifera* Macabeo produced in the experimental cellar "Mas dels Frares" of the University (Tarragona, Spain), and a *Vitis vinifera* Muscat kindly donated by Dalmau Hermanos y Cía. Suc. S.A. (Tarragona, Spain). The basic oenological parameters of Macabeo and Muscat wines were: alcohol degree 10.8 and 12.6% (v/v), pH 3.31 and 3.32, and glucose + fructose concentration <0.10 and 0.43 g/L, respectively. Since Macabeo wine contains very low amounts of terpenic compounds, it was doped with six representative terpenic compounds; limonene, linalool, α-terpineol, β-citronellol, geraniol and nerol, all of them of food grade quality (Sigma-Aldrich; Saint Louis, USA). The doses were 4 mg/L for the three most volatile compounds (limonene, linalool, α-terpineol) and 6 mg/L for the others, according to their volatility and the results of preliminary tests. These levels are much higher than those usually found in Muscat wine; the aim was to enhance the sensitivity of the chemical analysis to clearly observe the impact of the different strategies on the evolution of the terpenic compounds during distillations. Physical-chemical characteristics and terpenic compound levels of the wines (doped Macabeo and Muscat) before distillation are shown in Table 1.

2.2. Distillation systems

Column distillation system assays were performed in a distillation boiler (50 L) heated with two electrical resistances and coupled with a stainless steel distillation column with a copper mesh. The distillation column was equipped with a total condenser (on the top) and a partial condenser with variable flow (controlled with a peristaltic pump) to control the internal reflux of the column. In addition, the system was equipped with several temperature sensors (in the boiler, at different levels of the distillation column and in the partial cooling water system). Details of the distillation column have been previously described in García-Llobodanin et al. (2011). The process was controlled with Lab-view software (LabVIEW 8.6.1, National Instruments). Before experimentation, the peristaltic pump of the partial condenser was calibrated between 0 and 200 mL/min.

Traditional distillation system assays were performed in a 20 L copper *Charentais* alembic heated by an electrical hotplate.

2.3. Distillation processes

First, column distillation assays were performed with doped Macabeo wine, in order to determine the behavior of the terpenic compounds and other relevant compounds. Then, based on the obtained results, column and alembic distillation assays were performed with Muscat wine.

For column distillation, 25 L of wine (Macabeo or Muscat) were placed in the boiler. In case of Macabeo wine, terpenic compounds were added 12 h before distillation. Total condenser's cooling flow rate was constant at 1.7 L/min. Partial condenser's cooling flow rate ranged from 0 to 180 mL/min and was modified during distillation according to two different strategies (STR-1 and STR-2) detailed in Table 2. Electrical resistances operated at a constant power of 2400 W until the temperature below the partial condenser raised to 72 °C; then the power was reduced and kept constant at 960 W. The first 200 mL of distillate were collected in 50 mL fractions and the rest in 100 mL fractions until 3500 mL of distillate. Temperatures were monitored and recorded every 16 s at different points of the distillation systems.

For traditional distillation, 12.5 L of Muscat wine and 5 g of pumice stones were placed in the copper *Charentais* alembic boiler. Total condenser cooling flow rate was constant at 1.8 L/min. Electrical hotplate operated at a constant power of 2900 W until the first drop, then the power was reduced and kept constant at 2333 W (both values were calculated without considering heat loss). As in column distillations, first 200 mL of distillate were collected in 50 mL fractions and the rest in 100 mL fractions until 2600 mL of distillate.

Distillation assays were performed in duplicate for doped Macabeo wine and in triplicate for Muscat wine. Head cuts were decided by sensorial analysis.

2.4. Chemical analysis of wines and distilled fractions

Analyses of wine ethanol content and distillation residues were determined by ebulliometry (electronic ebulliometer, GAB instruments), wine glucose + fructose concentration by enzymatic bioanalysis (R-Biopharm AG) and wine pH with a pH-meter (Crison

Table 1
Terpenic compounds proprieties and their concentrations in the wines before distillation.

Compound	Molar mass[a] (g/mol)	Boiling point[a] (°C)	Vapor pressure[b] (mmHg at 95 °C)	Log $K_{o/w}$[a]	Doped Macabeo wine[c]	Non-doped Muscat wine[c]
Limonene	136	176	56.8	4.57	4.12 ± 0.07	n.d.
Linalool	154	197	22.8	2.97	4.03 ± 0.06	2.10 ± 0.00
α-Terpineol	154	220	7.11	2.98	4.23 ± 0.20	2.52 ± 0.14
β-Citronellol	156	224	6.74	3.91	6.07 ± 0.19	1.60 ± 0.08
Geraniol	154	230	5.38	3.56	6.13 ± 0.13	0.306 ± 0.028
Nerol	154	225	6.11	3.47	6.11 ± 0.11	0.117 ± 0.002

[a] Data extracted from EPI Suite database (Environmental Protection Agency & U. S., 2012).
[b] Vapor pressures were calculated with ASPEN PLUS V8.4 software.
[c] Concentrations are expressed in mg/L.

Table 2
Doped Macabeo distillation kinetics of both strategies.[a]

Fraction name	Distillation accumulated volume (mL)	Strategy 1 (STR-1)					Strategy 2 (STR-2)				
		P.C.[b] flow rate (mL/min)	Alcohol content (% v/v)	P.C.[b] temperature (°C)	P.C.[b] removed heat (kJ/min)	ΣHead compounds[c] (g/hLa.a.)	P.C.[b] flow rate (mL/min)	Alcohol content (% v/v)	P.C.[b] temperature (°C)	P.C.[b] removed heat (kJ/min)	ΣHead compounds[c] (g/hLa.a.)
F1	100	100	83.3 ± 0.2	75.3 ± 0.2	17.5 ± 2.4	646 ± 86	180	83.1 ± 0.5	74.3 ± 2.1	28.3 ± 7.2	834 ± 96
F2	200	100	87.0 ± 0.3	74.2 ± 0.3	18.3 ± 0.7	651 ± 82	120	89.3 ± 0.6	74.2 ± 0.1	20.8 ± 0.1	1077 ± 301
F3	500	50	87.0 ± 0.9	75.2 ± 0.0	9.46 ± 0.39	226 ± 10	100	90.5 ± 0.4	74.5 ± 0.1	19.3 ± 0.3	250 ± 52
F4	800	75	88.8 ± 0.4	74.7 ± 0.3	14.0 ± 0.2	143 ± 24	25	79.3 ± 1.5	79.4 ± 2.1	4.34 ± 0.23	58.2 ± 1.4
F5	1100	100	90.5 ± 0.1	74.4 ± 0.2	18.8 ± 0.7	97.5 ± 16.0	15	70.4 ± 1.5	84.3 ± 1.3	2.15 ± 0.31	46.2 ± 0.6
F6	1400	50	84.8 ± 0.4	76.0 ± 0.4	9.59 ± 0.35	41.1 ± 0.7	50	82.0 ± 0.6	77.2 ± 0.1	9.70 ± 0.13	42.9 ± 2.1
F7	1700	25	69.9 ± 0.9	83.8 ± 0.0	4.69 ± 0.11	37.8 ± 0.1	15	66.6 ± 0.3	84.9 ± 1.3	2.16 ± 0.17	43.2 ± 2.7
F8	2000	50	74.7 ± 0.4	80.5 ± 0.3	9.92 ± 0.25	37.3 ± 0.6	25	66.8 ± 1.4	85.9 ± 0.3	4.60 ± 0.01	39.1 ± 1.6
F9	2300	25	61.8 ± 0.6	87.5 ± 0.4	4.84 ± 0.10	32.5 ± 9.5	50	74.0 ± 1.1	81.0 ± 0.1	10.1 ± 0.0	49.5 ± 1.8
F10	2600	75	76.0 ± 2.8	79.0 ± 1.8	15.1 ± 0.3	50.4 ± 0.8	75	82.5 ± 2.4	77.1 ± 1.0	15.2 ± 0.0	63.6 ± 15.5
F11	2900	50	59.0 ± 1.8	87.5 ± 0.8	10.6 ± 0.4	49.8 ± 3.8	25	53.4 ± 3.0	89.4 ± 0.1	5.03 ± 0.04	45.8 ± 2.1
F12	3200	25	38.8 ± 1.5	91.7 ± 0.3	5.39 ± 0.17	51.1 ± 11.3	75	70.6 ± 0.9	81.9 ± 0.6	15.7 ± 0.0	61.3 ± 9.2
F13	3500	0	20.4 ± 1.0	92.1 ± 0.3	0	63.6 ± 3.0	0	23.6 ± 3.8	91.5 ± 1.1	0	60.8 ± 6.5

[a] Mean and standard deviations were calculated with two replicates.
[b] P.C: partial condenser.
[c] Σ acetaldehyde, methyl acetate, acetal, ethyl acetate and methanol.

Basic 20). For distilled fractions, ethanol content of each sample was analyzed with an electronic density meter (Anton Paar DSA 5000M).

Volatile compounds of wines before distillation and distillation residues were extracted with dichloromethane and analyzed by gas chromatography, using a methodology adapted from Ferreira, López, Escudero, and Cacho (1998). For the liquid-liquid extraction, in a 12-mL glass tube, 10 mL of wine were added with 2.5 g of ammonium sulfate and 0.5 mL of dichloromethane. As internal standard, 50 μL of 2-octanol (400 mg/L) solution was added. The extraction was carried out for 1 h in an orbital shaker at 110 rpm. Extractions were done in duplicate.

In the case of distilled fractions, first four samples were grouped in 100 mL fractions, and the rest in 300 mL fractions. For all fractions, 50 μL of the internal standard solution were added to 1 mL of each sample (previously adjusted to 40% v/v of alcohol). In addition, Muscat heart fractions of column and alembic distillations were extracted with dichloromethane to obtain enough instrumental sensibility for terpenic compounds using a methodology adapted from Guichard, Lemesle, Ledauphin, Barillier, and Picoche (2003) and Lukić et al. (2010). For the liquid-liquid extraction, 100 mL of distillate (adjusted to 40% v/v of alcohol), 200 mL of water, 30 g of sodium chloride and 10 mL of dichloromethane were added in a 500 mL separating funnel. As internal standard, 100 μL of 2-octanol (3900 mg/L) solution was used, and the extraction was carried out for 1 h in an orbital shaker at 110 rpm. Dichloromethane extracts were concentrated with a 20 cm Dufton column in a bain-marie at a constant temperature of 50 °C, until the extracted became 0.5 mL. Extractions were done in duplicate.

2.5. Chromatographic analysis

Chromatographic analysis was carried out by using a gas chromatograph equipped with a flame ionization detector (GC-FID) (Agilent 6890) and an automatic sampler (Agilent 7683). The capillary chromatographic column was a polar column MetaWAX (60 of length, 0.25 mm ID and 0.5 μm of phase thickness) from Teknokroma (Barcelona, Spain). The temperatures of the injector and detector were 250 °C and 260 °C, respectively. Separations were performed using two different methods. Quantification was performed by interpolation into calibrations built with synthetic solutions doped with all the analytes at different levels. For liquid-liquid extractions, calibration curves were built by the extraction of synthetic solutions doped with the volatile compounds. Concentration ranges of the calibration solutions were selected according to typical levels in commercial spirits (Christoph & Bauer-Christoph, 2007).

2.5.1. Chromatographic method for major and most volatile compounds

For the analysis of acetaldehyde, methyl acetate, acetal, ethyl acetate, methanol, ethyl butyrate, 1-propanol, 2-methyl-1-propanol, 1-butanol, ethyl hexanoate, 2-methyl-1-butanol, 3-methyl-1-butanol, 1-hexanol, ethyl lactate and ethyl octanoate, the injection (2 μL) was done in split mode (1:5) and was performed with an oven temperature program of: 40 °C (5 min), 7 °C/min up to 100 °C (15 min), 3 °C/min up to 140 °C and 2 °C/min up to 200 °C (5 min). The carrier gas was helium with a column-head flow ramp of 0.5 mL/min (28 min) and 5 mL/min^2 up to 1.1 mL/min (67 min).

2.5.2. Chromatographic method for heavier and minor volatile compounds

For the analysis of 2-butanol, isoamyl acetate, limonene, acetoin, furfural, acetic acid, linalool, ethyl decanoate, α-terpineol, β-citronellol, nerol, geraniol and β-phenylethanol, the injection (2 μL) was done in splitless mode, with an oven temperature ramp of 40 °C (7 min), 2 °C/min up to 140 °C and 6 °C/min up to 220 °C (20 min). The carrier gas was helium at a constant column-head flow of 1 mL/min.

2.6. Muscat spirits sensory analysis

Spirit aroma analysis was performed in a panel room with 18 experienced assessors. The assessors had previously attended a 30 min training session to set the tasting descriptors. Distilled Muscat heart cuts (column and alembic) were analyzed by the following ortonasal and retronasal attributes: floral, fruit, sweet, burn/smoke and pungent/solvent notes. In order to scale the tasting descriptors, the training session was done with a neutral Muscat distillate as base spirit (with low terpenic compounds concentrations, e.g. linalool less than 0.25 g/hL a.a.) by spiking each attribute in two different levels according to the concentration range of the spirit samples: food grade quality terpenic compounds, for floral notes; food grade quality isoamyl acetate (Sigma-Aldrich, Saint Louis) and commercial apple juice, for fruit notes; 1% of column tail fraction, for sweet notes; 3% of column tail fraction, for burn/smoke notes; and 3% of column head fraction, for

pungent/solvent notes. Sensory analysis was performed with a 4 point-scale (0 = not detected; 1 = weakly detected-hardy recognizable; 2 = clear-but not intense; 3 = intense), processed by using the modified frequency expressed as MF(%) = [F(%)·I(%)]1/2, where I(%) is the average intensity expressed as percentage of the maximum intensity and F(%) is the detection frequency of an attribute in percentage (Campo, Ferreira, Escudero, & Cacho, 2005).

2.7. Statistical analysis

For comparison of column distillation strategies and alembic distillation, ANOVA was applied to data and compared by Fisher's least significant difference (LSD) test at $p < 0.05$. For the sensory preference test, a Sign test between samples was done. Both statistical analyses were performed with the STATISTICA 7.0 statistical package. Principal component analysis (PCA) and ANOVA at $p < 0.1$ were applied for the 4 point-scale sensory analysis, using the Product Characterization tool of XLSTAT-sensory 2016 statistical ad-in for Microsoft Office.

3. Results and discussion

3.1. Distillation kinetics and fractions of Macabeo distillations

Table 2 shows, for both distillation strategies and for each fraction, the alcoholic content, the temperature under the partial condenser, the exchanged heat by the partial condenser (measured by the increment of outlet and inlet cooling flow temperatures) and the total contents of head compounds (acetaldehyde, methyl acetate, acetal, ethyl acetate and methanol). In an ideal system, the heat exchanged by the partial condenser will be directly related to the dew point of the gas-liquid mixture. For high cooling flow rates, the mixture above the condenser should be enriched in ethanol, the major light volatile compound. Given that batch distillation is a discontinuous process, the depletion of ethanol and other compounds (in the boiler) cause that at different distillation times the same cooling flow rate produces fractions with different compositions. In addition, as can be seen in Table 2, the temperature reading below the condenser was lower than expected, according to the equilibrium of the water/ethanol ratio of the mixture. This difference may be caused by the down-flowing condensed liquid in contact with the temperature sensor.

The total content of head compounds in each fraction (Table 2) helped to define the head/heart cut, avoiding high levels of head compounds in the heart fraction. Thus, the sum of the first three fractions (F1-F3) was assigned to the head fraction (Head) and the next nine fractions (F4-F12) to the heart fraction (Heart) (usual fraction used to elaborate spirits). Moreover, two heart fractions were separated (Heart-1: F4-F7; and Heart-2: F8-F12). This cut was established according to the levels of terpenic compounds throughout the distillation, between distillation fractions whose contents decreased to very low values in both strategies (F7-F8), as can be seen in Fig. 1 (behavior discussed in the following sections). According to preliminary studies, the 13th fraction (F13) had an alcoholic content lower than 40% (v/v) and it was considered as a distillation tail.

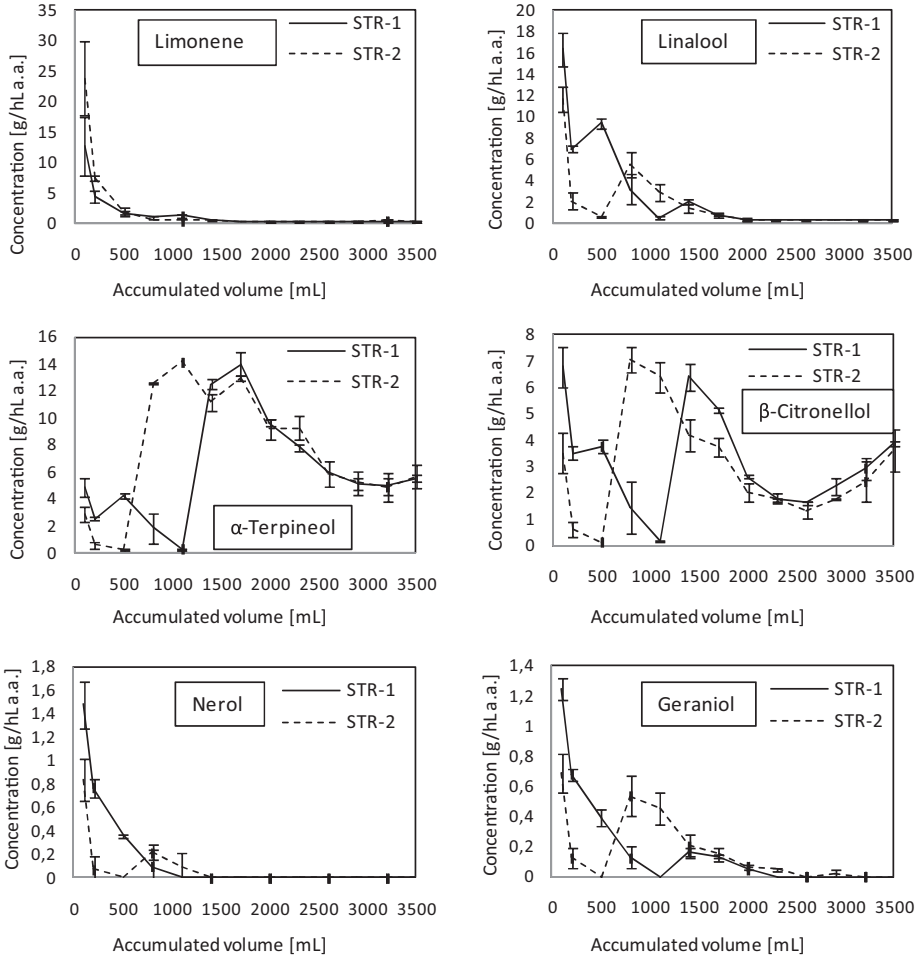

Fig. 1. Limonene, linalool, α-terpineol, β-citronellol, nerol and geraniol average concentrations throughout the column distillation process performed with doped Macabeo wine. Standard deviation was calculated with two replicates.

Table 3
Average concentrations (g/hL a.a.) of volatile compounds of both strategies (STR-1 and STR-2 of Macabeo distillations) in fractions (Head, Heart, Heart-1, Heart-2).[a]

Compound	Head		Heart		Heart-1		Heart-2	
	STR-1	STR-2	STR-1	STR-2	STR-1	STR-2	STR-1	STR-2
Terpenic compounds								
Limonene	4.31 ± 1.37	7.23 ± 0.71	0.630 ± 0.147	0.416 ± 0.012	0.885 ± 0.188	0.482 ± 0.001	0.355 ± 0.102	0.359 ± 0.021
Linalool	10.3 ± 0.0 b	3.02 ± 0.42 a	1.01 ± 0.25	1.44 ± 0.27	1.68 ± 0.49	2.75 ± 0.63	0.288 ± 0.001 a	0.315 ± 0.008 b
α-Terpineol	3.99 ± 0.00 b	0.836 ± 0.194 a	6.79 ± 0.01 a	9.56 ± 0.04 b	6.66 ± 0.19 a	12.6 ± 0.2 b	6.93 ± 0.18	6.91 ± 0.02
β-Citronellol	4.30 ± 0.05 b	0.856 ± 0.21 a	2.67 ± 0.15 a	3.47 ± 0.12 b	3.13 ± 0.38 a	5.37 ± 0.49 b	2.17 ± 0.09	1.84 ± 0.14
Nerol	0.658 ± 0.031 b	0.174 ± 0.056 a	0.014 ± 0.019	0.036 ± 0.021	0.026 ± 0.037	0.078 ± 0.046	d.-n.q.	n.d.
Geraniol	0.616 ± 0.045 b	0.153 ± 0.037 a	0.060 ± 0.015	0.170 ± 0.044	0.105 ± 0.029	0.339 ± 0.088	0.011 ± 0.001	0.025 ± 0.011
Esters								
Ethyl butyrate	1.14 ± 0.00 a	1.26 ± 0.02 b	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Isoamyl acetate	4.25 ± 0.68	5.69 ± 0.08	d.-n.q.	d.-n.q.	d.-n.q.	d.-n.q.	n.d.	n.d.
Ethyl hexanoate	3.30 ± 0.04	2.45 ± 1.19	d.-n.q.	d.-n.q.	d.-n.q.	d.-n.q.	n.d.	n.d.
Ethyl octanoate	2.77 ± 0.20	2.69 ± 0.32	d.-n.q.	0.097 ± 0.031	d.-n.q.	0.209 ± 0.062	d.-n.q.	d.-n.q.
Ethyl decanoate	1.04 ± 0.10	0.897 ± 0.140	0.056 ± 0.038	0.109 ± 0.037	0.027 ± 0.038	0.133 ± 0.029	0.087 ± 0.039	0.089 ± 0.043
Higher alcohols								
2-Butanol	d.-n.q.	0.044 ± 0.063	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
1-Propanol	17.2 ± 0.4 b	12.4 ± 1.0 a	14.3 ± 0.0 a	16.2 ± 0.5 b	15.5 ± 0.2 a	18.4 ± 0.5 b	12.9 ± 0.2	14.3 ± 0.5
2-Methyl-1-propanol	35.9 ± 1.1 b	24.8 ± 1.2 a	14.0 ± 0.1 a	16.7 ± 0.1 b	20.9 ± 0.3 a	26.6 ± 0.5 b	6.70 ± 0.03	8.13 ± 0.52
1-Butanol	0.355 ± 0.013	0.427 ± 0.485	0.132 ± 0.038	0.200 ± 0.008	0.255 ± 0.075	0.432 ± 0.008	d.-n.q.	d.-n.q.
2-Methyl-1-butanol	49.3 ± 1.2 b	21.8 ± 0.7 a	20.3 ± 0.2 a	25.3 ± 0.5 b	30.2 ± 0.1 a	43.5 ± 1.2 b	9.63 ± 0.42	9.73 ± 0.76
3-Methyl-1-butanol	234 ± 5 b	96.4 ± 1.2 a	121 ± 1 a	152 ± 2 b	167 ± 1 a	247 ± 7 b	71.4 ± 3.6	71.5 ± 4.7
1-Hexanol	1.10 ± 0.04 b	0.225 ± 0.03 a	0.508 ± 0.014 a	0.672 ± 0.028 b	0.759 ± 0.022 a	1.23 ± 0.05 b	0.239 ± 0.005 b	0.188 ± 0.013 a
Head compounds								
Acetaldehyde	188 ± 30	278 ± 80	17.9 ± 4.9	5.74 ± 0.12	34.1 ± 9.2	10.9 ± 0.7	0.491 ± 0.46	1.32 ± 0.22
Methyl acetate	0.739 ± 0.099	1.03 ± 0.59	0.365 ± 0.516	0.577 ± 0.272	0.344 ± 0.486	0.123 ± 0.174	0.388 ± 0.548	0.969 ± 0.371
Acetal	27.6 ± 8.4	40.3 ± 18	2.50 ± 1.07	0.785 ± 0.004	4.83 ± 2.09	1.70 ± 0.03	d.-n.q.	d.-n.q.
Ethyl acetate	146 ± 1	167 ± 9	11.0 ± 0.2 b	8.16 ± 0.41 a	14.5 ± 0.1 b	7.94 ± 0.11 a	7.30 ± 0.40	8.34 ± 0.68
Methanol	29.9 ± 1.8	38.9 ± 3.2	32.2 ± 1.7	35.2 ± 2.7	29.1 ± 0.1 b	27.2 ± 0.0 a	35.5 ± 3.6	42.1 ± 5.3
Tail compounds								
Ethyl lactate	d.-n.q.	0.061 ± 0.086	2.70 ± 0.29	2.84 ± 0.57	0.786 ± 0.091 a	1.81 ± 0.29 b	4.75 ± 0.5	3.73 ± 0.85
Furfural	n.d.	d.-n.q.	0.848 ± 0.041	0.877 ± 0.312	0.146 ± 0.059	0.151 ± 0.107	1.61 ± 0.15	1.50 ± 0.51
β-Phenylethanol	0.300 ± 0.031	0.204 ± 0.099	2.73 ± 0.10	2.41 ± 0.29	0.681 ± 0.013 a	1.37 ± 0.02 b	4.93 ± 0.21	3.31 ± 0.60
Other compounds								
Acetic acid	10.5 ± 3.2	4.21 ± 0.81	3.57 ± 0.26	4.10 ± 0.43	1.57 ± 0.01 a	3.12 ± 0.00 b	5.72 ± 0.55	4.94 ± 0.84

[a] Different letters after standard deviation in the same row indicate a significant difference ($p < 0.05$) with respect to both strategies (STR-1 and STR-2) at the same fraction. Means and standard deviations were calculated with two replicates.

3.2. Aroma compounds of doped Macabeo distillations

Table 3 shows the average concentrations of each volatile compound analyzed (terpenes, alcohols, esters, and head and tail compounds) on Head and Heart (Heart-1 + Heart-2) described in the previous section. The behavior of compounds during distillation and their concentrations in the different fractions depended on the physical-chemical characteristics of the compounds such as boiling point, volatility and solubility. Thus, more volatile compounds (such as acetaldehyde, methyl acetate, acetal, ethyl acetate) were mainly distilled in the first fractions. However, some compounds with high boiling points were distilled by steam stripping effect due to their high solubility in ethanol (such as higher alcohols and terpenic compounds), especially in heart fractions.

On the other hand, compounds with high molecular weight and/or that are highly soluble in water tended to distil in the tail fraction (such as β-phenylethanol and ethyl lactate), where water percentage and temperature were higher. These behaviors can be more clearly observed in Table 4, which shows the distilled mass percentage in each fraction (Head and Heart (Heart-1 + Heart-2)) with respect to the total distilled for each compound and group of compounds.

3.2.1. Terpenic compounds of Macabeo distillation

Regarding the behavior of terpenic compounds, Fig. 1 shows the levels throughout the distillation of limonene, linalool, α-terpineol, β-citronellol, nerol and geraniol.

Limonene is the terpene that presents the highest vapor pressure and lowest water solubility values among the terpenic compounds studied (Table 1); therefore, it tended to distil at the beginning of the distillation. In addition, the high reactivity of this compound in acid medium and at high temperatures can transform or degrade limonene to other terpenic compounds during distillation (Iwai et al., 2014). Therefore, no tested strategy was able to concentrate this compound in the heart fractions.

Linalool is a monoterpene with an alcohol group and it has the second highest vapor pressure (Table 1), therefore, it tended to distil in the first fractions. Fig. 1 shows how a higher partial cooling flow rate at the beginning of the distillation (STR-2) can reduce the linalool extraction in the head fractions (fractions not used for spirits production). Later, linalool concentration in the heart fractions can be significantly increased with a drastic reduction of the cooling flow rate.

α-Terpineol, β-citronellol, geraniol and nerol present similar boiling points and vapor pressures (Table 1). Unlike the previous compounds, these compounds were mainly distilled in heart fractions for both strategies (Fig. 1). STR-2 achieved lower concentrations in the first fractions (with a higher reflux rate) and higher concentrations in the following fractions (with a drastic reflux rate reduction). However, geraniol and nerol showed much lower levels and after the middle of the process, they were no longer quantifiable.

Iwai et al. (2014) and Ohta et al. (1991) showed that limonene, geraniol and nerol are precursors of α-terpineol and other minor terpenic compounds in hydrothermal and catalyzed acid media. This would explain the low concentrations of limonene, geraniol and nerol; and the slow reduction of α-terpineol levels throughout the distillation. These tendencies are confirmed in Table 3. Except

Table 4
Distilled mass percentages (%) of volatile compounds of both strategies (STR-1 and STR-2 of Macabeo distillations) in fractions (Head, Heart, Heart-1, Heart-2).[a]

Compound[b]	Head		Heart		Heart-1		Heart-2	
	STR-1	STR-2	STR-1	STR-2	STR-1	STR-2	STR-1	STR-2
Limonene	60.1 ± 1.9 a	79.9 ± 1.8 b	39.9 ± 1.9 b	20.1 ± 1.8 a	29.1 ± 1.9 b	10.8 ± 0.9 a	10.7 ± 0.0	9.3 ± 1.0
Linalool	69.6 ± 5.1 b	32.6 ± 1.4 a	30.4 ± 5.1 a	67.4 ± 1.4 b	26.2 ± 5.5 a	59.3 ± 2.4 b	4.2 ± 0.4 a	8.0 ± 1.0 b
α-Terpineol	11.6 ± 0.1 b	2.0 ± 0.4 a	88.4 ± 0.1 a	98.0 ± 0.4 b	45.0 ± 1.0 a	59.9 ± 0.9 b	43.4 ± 1.1 b	38.1 ± 0.4 a
β-Citronellol	26.5 ± 0.7 b	5.3 ± 1.0 a	73.5 ± 0.7 a	94.7 ± 1.0 b	44.7 ± 3.2 a	67.6 ± 1.7 b	28.8 ± 2.4	27.1 ± 2.7
Nerol	92.1 ± 11.2	54.1 ± 7.4	7.9 ± 11.2	45.9 ± 7.4	7.9 ± 11.2	45.9 ± 7.4	d.-n.q.	n.d.
Geraniol	69.8 ± 6.7 b	17.2 ± 0.4 a	30.2 ± 6.7 a	82.8 ± 0.4 b	27.4 ± 6.6 a	76.3 ± 0.9 b	2.8 ± 0.1	6.5 ± 1.3
ΣTerpenic compounds	**32.5 ± 1.7 b**	**15.7 ± 1.2 a**	**67.5 ± 1.7 a**	**84.3 ± 1.2 b**	**39.1 ± 2.7 a**	**55.9 ± 0.0 b**	**28.4 ± 1.0**	**28.4 ± 1.2**
Ethyl butyrate	100	100	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Isoamyl acetate	100	100	d.-n.q.	d.-n.q.	d.-n.q.	d.-n.q.	n.d.	n.d.
Ethyl hexanoate	100	100	d.-n.q.	d.-n.q.	d.-n.q.	d.-n.q.	n.d.	n.d.
Ethyl octanoate	100 b	86.6 ± 2.2 a	d.-n.q.	13.4 ± 2.2	d.-n.q.	13.4 ± 2.2	d.-n.q.	d.-n.q.
Ethyl decanoate	81.6 ± 9.5	65.8 ± 4.0	18.4 ± 9.5	34.2 ± 4.0	4.2 ± 6.0	19.4 ± 0.2	14.1 ± 3.5	14.8 ± 3.8
Σ Esters	**98.0 ± 1.4**	**93.6 ± 1.2**	**2.0 ± 1.4**	**6.4 ± 1.2**	**0.5 ± 0.7**	**4.9 ± 0.7**	**1.5 ± 0.7**	**1.5 ± 0.5**
2-Butanol	d.-n.q.	100	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
1-Propanol	21.2 ± 0.3 b	15.0 ± 0.7 a	78.8 ± 0.3 a	85.0 ± 0.7 b	44.3 ± 0.6	44.7 ± 0.2	34.4 ± 0.3 a	40.4 ± 1.0 b
2-Methyl-1-propanol	36.3 ± 0.7 b	25.4 ± 1.1 a	63.7 ± 0.7 a	74.6 ± 1.1 b	49.1 ± 0.7 a	55.0 ± 0.9 b	14.6 ± 0.0	19.6 ± 2.0
1-Butanol	38.1 ± 7.6	28.1 ± 27.4	61.9 ± 7.6	71.9 ± 27.4	61.9 ± 7.6	71.9 ± 27.4	d.-n.q.	d.-n.q.
2-Methyl-1-butanol	35.2 ± 0.2 b	16.5 ± 0.3 a	64.8 ± 0.2 a	83.5 ± 0.3 b	50.0 ± 0.6 a	66.2 ± 1.7 b	14.8 ± 0.4	17.3 ± 2.0
3-Methyl-1-butanol	30.1 ± 0.1 b	12.7 ± 0.1 a	69.9 ± 0.1 a	87.3 ± 0.1 b	50.0 ± 0.8 a	65.3 ± 2.1 b	19.8 ± 0.7	22.1 ± 2.2
1-Hexanol	32.5 ± 0.1 b	7.1 ± 1.1 a	67.5 ± 0.1 a	92.9 ± 1.1 b	52.2 ± 0.3 a	78.8 ± 2.7 b	15.3 ± 0.2	14.0 ± 1.6
Σ Higher alcohols	**30.7 ± 0.2 b**	**14.5 ± 0.2 a**	**69.3 ± 0.2 a**	**85.5 ± 0.2 b**	**49.6 ± 0.8 a**	**62.9 ± 1.8 b**	**19.8 ± 0.6**	**22.6 ± 2.0**
Acetaldehyde	70.3 ± 2.3 a	91.4 ± 2.5 b	29.7 ± 2.3 b	8.6 ± 2.5 a	29.3 ± 2.0 b	7.5 ± 2.4 a	0.4 ± 0.3	1.0 ± 0.1
Methyl acetate	58.5 ± 58.8	28.4 ± 2.7	41.5 ± 58.8	71.6 ± 2.7	20.4 ± 28.8	5.2 ± 7.4	21.2 ± 30.0	66.3 ± 10.0
Acetal	71.6 ± 2.6 a	91.4 ± 3.6 b	28.4 ± 2.6 b	8.6 ± 3.6 a	28.4 ± 2.6 b	8.6 ± 3.6 a	d.-n.q.	d.-n.q.
Ethyl acetate	74.7 ± 0.5 a	82.4 ± 0.2 b	25.3 ± 0.5 b	17.6 ± 0.2 a	17.2 ± 0.1 b	7.9 ± 0.2 a	8.0 ± 0.4 a	9.7 ± 0.0 b
Methanol	17.2 ± 0.0 a	20.2 ± 0.3 b	82.8 ± 0.0 b	79.8 ± 0.3 a	38.9 ± 2.0 b	28.6 ± 1.7 a	43.9 ± 2.0	51.2 ± 1.4
Σ Head compounds	**57.8 ± 1.1 a**	**70.2 ± 3.3 b**	**42.2 ± 1.1 b**	**29.8 ± 3.3 a**	**28.3 ± 1.3 b**	**13.1 ± 2.2 a**	**14.0 ± 2.4**	**16.7 ± 1.2**
Ethyl lactate	d.-n.q.	0.4 ± 0.6	100	99.6 ± 0.6	15.1 ± 0.1 a	29.5 ± 0.8 b	84.9 ± 0.1 b	70.1 ± 0.2 a
Furfural	n.d.	d.-n.q.	100	100	9.0 ± 4.0	7.5 ± 3.1	91.0 ± 4.0	92.5 ± 3.1
β-Phenylethanol	2.4 ± 0.2	1.9 ± 0.7	97.6 ± 0.2	98.1 ± 0.7	12.6 ± 0.8 a	26 ± 3.2 b	85.0 ± 0.6 b	72.2 ± 2.5 a
Σ Tail compounds	**1.1 ± 0.1**	**0.9 ± 0.5**	**98.9 ± 0.1**	**99.1 ± 0.5**	**13.2 ± 0.3 a**	**25.1 ± 1.6 b**	**85.8 ± 0.4 b**	**74.0 ± 1.1 a**
Acetic acid	39.1 ± 5.6 b	19.0 ± 1.5 a	60.9 ± 5.6 a	81.0 ± 1.5 b	13.9 ± 2.2 a	28.7 ± 3.0 b	46.9 ± 3.4	52.3 ± 1.5

[a] Different letters after standard deviation in the same row indicate a significant difference ($p < 0.05$) with respect to both strategies (STR-1 and STR-2) at the same fraction. Means and standard deviations were calculated with two replicates.
[b] Compounds sums collect the compounds located above each sum row until next bold type text.

for limonene, the concentrations of terpenic compounds were significantly lower in STR-2 Head than in the STR-1. In STR-2, Heart and Heart-1 had significantly higher levels of α-terpineol and β-citronellol, in relation to STR-1. In addition, linalool levels in Heart-2 of STR-2 were also higher than in Heart-2 of STR-1. Besides, Table 4 shows the extraction mass yields of these terpenic compounds and their sum. Most of the terpenic compounds were distilled in the Heart (67.5% in STR-1 and 84.3% in STR-2) and especially in Heart-1 (39.1% in STR-1 and 55.9% in STR-2). However, nerol and geraniol were concentrated in Heads due to their subsequent degradation during distillation. In turn, linalool showed significant differences between both strategies, presenting higher extraction mass yields in STR-2 Heart, Heart-1 and Heart-2. In summary, a drastic cooling flow rate reduction after high reflux levels favors the recovery of terpenic compounds in the heart fractions.

3.2.2. Other volatile compounds in Macabeo distillations

The chemical group of esters was responsible for the fruity aroma notes (Christoph & Bauer-Christoph, 2007). As can be seen in Table 3, the esters were presented mainly in the Head and its contents in Heart were very low for most of them. These compounds have a limited solubility in water and their hydrophobicity constants (log $K_{o/w}$) ranged between 1.85 (ethyl butyrate) and 4.79 (ethyl decanoate), so these were distilled in the first moments of the process by steam stripping. This behavior is consistent with that observed by Jouret et al. (1998) and Peña y Lillo, Latrille et al. (2005). The ester with the highest boiling point, ethyl decanoate, was the only detected in all heart fractions. In addition, ethyl octanoate was detected in the Heart of the distillation STR-2, although the amount detected was very low. In the case of ethyl decanoate, the distilled mass percentage (Table 4) with STR-2 was around 16% more than with STR-1.

The group of higher alcohols is characterized by an alcoholic and malty odor (Rouseff & Perez-Cacho, 2007). Their hydrophobicity constants (log $K_{o/w}$) ranged between 0.25 and 2.03 and their boiling points between 97.2 and 157.6 °C (values for 1-propanol and 1-hexanol, respectively). Consequently, the levels of higher alcohols were higher in the Head (due to their low boiling points) and in Heart-1 (due to their water solubility) (Table 3). Low levels in Heart-2 of all compounds could be due to their depletion in the boiler. Like terpenic compounds and esters, STR-2 produced lower higher alcohol levels in Head and higher levels in Heart and Heart-1 than STR-1, due to the cooling flow differences. Table 4 illustrates that 62.9% of the higher alcohols were concentrated in STR-2 Heart-1 compared to 49.6% in STR-1 Heart-1.

The most undesirable and toxic compounds in distillates have low boiling points and tend to concentrate in the first fractions. As shown in Table 3, significant differences between strategies were only observed for ethyl acetate (glue-solvent aroma) in Heart and Heart-1, and for methanol (the most relevant toxic compound) in Heart-1; both cases showed lower levels in STR-2 than in STR-1. Methanol is the only head compound which maintained a similar concentration through the distillation. Its contents were much lower than the legal limit of 200 g/hL a.a. for wine spirits (European Commission, 2008). In addition, tail fraction (F13) had

Table 5
Aroma threshold, concentration and odor activity value of the most relevant aroma compounds with respect to column Heart-1 and Heart-2 and Alembic Heart done with Muscat wine.[a]

Compound	Aroma[b] threshold	Concentration (mg/L alc. 40% v/v) and odor activity values[c] (u.a.) Heart-1	Heart-2	Alembic Heart
Linalool	1.00[d]	8.81 ± 1.52 c (8.81)	2.74 ± 0.30 a (2.74)	5.58 ± 0.46 b (5.58)
α-Terpineol	300[d]	8.36 ± 0.78 b (0.028)	7.80 ± 0.59 b (0.026)	5.92 ± 0.03 a (0.020)
β-Citronellol	1.00[d]	0.335 ± 0.045 b (0.335)	0.195 ± 0.039 a (0.195)	0.260 ± 0.017 a (0.260)
Nerol	40.0[d]	0.387 ± 0.055 b (0.010)	0.193 ± 0.038 a (0.005)	0.356 ± 0.017 b (0.009)
Geraniol	3.00[d]	1.06 ± 0.15 b (0.352)	0.550 ± 0.114 a (0.183)	1.15 ± 0.07 b (0.384)
Acetaldehyde	19.2[e]	103 ± 15 b (5.36)	22.5 ± 4.7 a (1.17)	413 ± 34 c (21.5)
Acetal	0.719[e]	26.0 ± 14.5 a (36.2)	4.40 ± 1.86 b (6.12)	40.1 ± 4.5 b (55.7)
Ethyl acetate	50.0[f]	16.5 ± 0.8 a (0.330)	11.6 ± 2.1 a (0.232)	124 ± 5 b (2.47)
Isoamyl acetate	0.245[e]	0.693 ± 0.114 c (2.83)	0.025 ± 0.004 a (0.100)	0.282 ± 0.035 b (1.15)
Ethyl butyrate	0.0095[e]	n.q.	n.q.	n.q.
Ethyl hexanoate	0.030[e]	d. - n.q.	n.q.	4.90 ± 0.36 (163)
Ethyl octanoate	0.147[g]	2.80 ± 0.61 a (19.0)	d. - n.q.	10.9 ± 0.8 b (74.5)
Ethyl decanoate	0.420[h]	2.15 ± 1.21 a (5.13)	d. - n.q.	4.57 ± 0.07 b (10.9)
Ethyl lactate	100[i]	n.q.	73.8 ± 9.9 (0.738)	55.9 ± 29.9 (0.559)
Furfural	20.4[f]	2.63 ± 0.18 a (0.129)	8.27 ± 0.72 b (0.406)	3.55 ± 0.69 a (0.174)
β-Phenylethanol	2.60[e]	2.04 ± 0.10 a (0.783)	3.69 ± 0.40 a (1.42)	11.6 ± 1.7 b (4.46)

[a] Different letters after standard deviation in the same row indicate a significant difference ($p < 0.05$) in respect to heart fractions. Means and standard deviations were calculated with tree replicates.
[b] Aroma thresholds are expressed in [mg/L] in wine spirit.
[c] Odor activity values are shown in brackets expressed in units of aroma (u.a.).
[d] Referenced in Cacho, Moncayo, Palma, Ferreira, and Culleré (2013).
[e] Referenced in Willner, Granvogl, and Schieberle (2013).
[f] Referenced in Clutton and Evans (1978).
[g] Referenced in Poisson and Schieberle (2008).
[h] Referenced in Pino, Tolle, Gök, and Winterhalter (2012).
[i] Referenced in Christoph and Bauer-Christoph (2007).

higher relative methanol levels in all experiments due to ethanol depletion (data not shown), a behavior experimentally observed and simulated by Carvallo, Labbe, Pérez-Correa, Zaror, and Wisniak (2011). Acetaldehyde and ethyl acetate had high concentrations in the initial wine and both were concentrated in the Head, so the total distilled mass percentage of head compounds (Table 4) mostly refers to them. As can be seen, except for methyl acetate and methanol, head compounds were mostly extracted in the Head. Moreover, except in the case of methyl acetate, we have found significant differences between strategies in Head, Heart and Heart-1 in most head compounds and their sum, where STR-2 presented the best behavior with a lower extraction in Heart and Heart-1.

The tail compounds group has high boiling points and high water solubility, and they can be generated during the process. Therefore, these compounds were distilled at the end of the distillation (Table 3). STR-2 obtained higher concentration of ethyl lactate (possible formation from lactic acid) and β-phenylethanol (rose aroma) in Heart-1 due to the lower cooling flow rates. In addition, there was no furfural in the Head, since this compound is generated during distillation by Maillard reactions (Mottram, 2007). Distilled mass percentages (Table 4) were the same in both strategies, where most of tail compounds were extracted at the end of the Heart (85.8 and 74.0% in Heart-2 for STR-1 and STR-2, respectively).

Finally, STR-2 showed higher distilled mass percentages (Heart and Heart-1) and concentration (Heart-1) values for acetic acid than STR-1. Acetic acid has a vinegar-like, pungent aroma and is a precursor of ethyl acetate (glue-solvent aroma). Although, its concentration should not be a problem with an undamaged initial wine.

3.3. Comparison of column and alembic Muscat distillations

According to the results obtained with the doped Macabeo wine, STR-2 was chosen as the most suitable distillation strategy for terpenic wines. Therefore, STR-2 and alembic were compared in non-doped Muscat wine distillations.

3.3.1. Chemical analysis of Muscat distillations

Table 5 shows alcohol content, levels of most relevant compounds and calculated odor activity values of Muscat distillation fractions: column Heart-1 and Heart-2, and Alembic Heart. Odor activity values (OAV) were calculated using the odor thresholds found in bibliography.

The compounds behavior of the column distillation was not affected by the change of the raw material. Otherwise, alembic distillations had much lower internal refluxes than column distillation process, since their rectification (with a constant power heat in the boiler) only depends on the environmental temperature and on the alembic-head design. Thus, lower contents and a uniform distribution of ethanol during alembic distillation avoid the fluctuations of other volatile compounds.

Alembic distillations had much lower head compounds content in the first fractions (data not shown) due to its low rectification. However, head compound levels decreased steadily throughout alembic distillation and this behavior increased acetaldehyde, acetal and ethyl acetate levels in the Alembic Heart (Table 5). The content of terpenic compounds and isoamyl acetate was higher in column Heart-1, since a low amount of these compounds was extracted in the first fractions (compared with alembic). In addition, total column heart cut (Heart-1 + Heart-2) also had higher terpenic compounds levels. In both processes, linalool was the only terpenic compound above its aroma threshold and was much higher in Heart-1 (Table 5). Distillation times were 4.29 ± 0.54 and 7.41 ± 0.42 h for alembic and column distillations, respectively, since initial wine volume and reflux differences are remarkable. Thus, high distillation time increased furfural concentration in Heart-2 by Maillard reactions (Mottram, 2007). Ethyl ester compounds tended to distil with high refluxes (column first fractions), as had been observed with Macabeo wine experiments. However, higher ethyl ester levels were found in alembic heart cut, due to their low refluxes and distillation time. In addition, compounds levels were in line with the range observed in commercial *Piscos*, however, linalool and α-terpineol levels in column Heart-1 were around their maximum published values (Cacho et al., 2012).

Moreover, terpenic compounds can be produced by bound monoterpenes (non-volatiles) present in wine during distillation, as boiler conditions favor acid hydrolysis of glycosides (Strauss & Williams, 1983). Therefore, mass balance deviation (data not shown) helps to estimate formed or degraded amounts of each compound, calculated for each compound as the percentage of the difference between the mass sum of the free compound in all the outputs (Head + Heart + Residue) and the mass of the free compound in the initial wine. Muscat wine is known for its high contents of bound and free terpenic compounds (Dziadas & Jeleń, 2010), not like Macabeo wine which had not detectable free terpenic compounds until it was doped. Therefore, Muscat should have a higher mass balance deviation of terpenes, since bound compounds were released. However, Muscat distillation STR-2 had a mass balance deviation of linalool and α-terpineol significantly lower than Macabeo STR-2, probably because of the wine concentration differences. Otherwise, Muscat residues had much more linalool (1.5 times) and α-terpineol (9.3 times) than Macabeo ones, which suggest a release of free terpenic compounds from the remaining precursors after distillation.

3.3.2. Sensory analysis of Muscat distillations

Modified frequency MF (%) ratings (Fig. 2) showed higher ratings of floral notes in Heart-1 (terpenic compounds), of fruit notes in Alembic Heart (ester compounds), and of sweet and burn/smoke notes in Heart-2 (tail compounds). These results were consistent with the aroma descriptors associated to the chemical composition data. However, assessors found higher levels of retronasal pungent/solvent notes in Heart-1 and Heart-2, and higher sweet notes in Heart-1, than in Alembic Heart. Due to its lower degree of rectification throughout the process, Alembic Heart had a more complex and uniform aroma composition and some synergistic or antagonistic aroma interaction may have occurred (Peña y Lillo, Agosin et al., 2005; Peña y Lillo, Latrille et al., 2005; Styger, Prior, & Bauer, 2011).

In addition, ANOVA differenced the 3 samples as follows: Alembic Heart had significant high fruit notes and low sweet notes values; Heart-1 had significant high floral notes and low burn/smoke notes values; and Heart-2 had significant high sweet and burn/smoke notes and low fruit notes values. In order to emphasize the sensory differentiation between samplers, the tasting panel results were also analyzed by PCA product characterization (Fig. 3) according to ANOVA analysis. 2 principal components

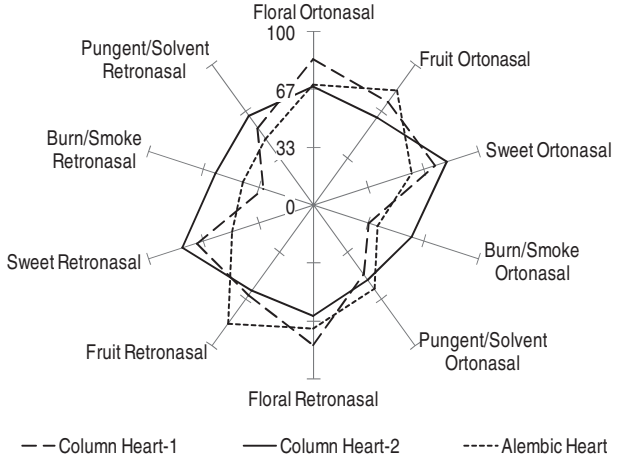

Fig. 2. Graph of mean sensory modified frequency MF (%) ratings of studied Muscat wine spirits, obtained by a sensory descriptive analysis performed with 18 experienced assessors.

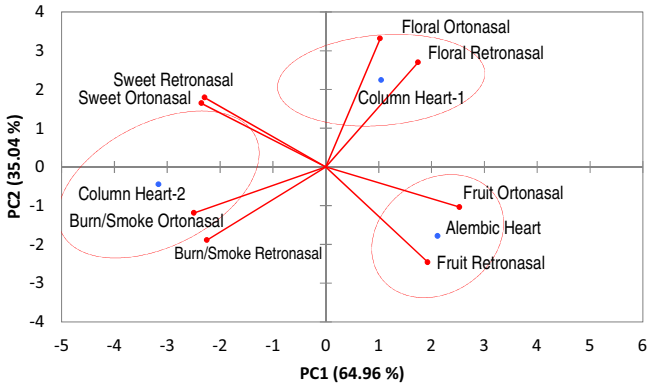

Fig. 3. Biplot with 95% confidence ellipses for the sensory profiles obtained by PCA of the studied Muscat wine spirits with 18 experienced assessors.

(PC1 and PC2) covered the 100% of the variance. Pungent/solvent descriptor was not considered as had not significant differences. PC1 axis places fruit and floral notes descriptors against sweet and burn/smoke descriptors. Thus PC1 shows good separation between heart and tail compounds and indicates the quality of the tail-cut. Moreover, PC2 places the floral and sweet notes descriptors in the same quadrant. This behavior coincides with the MF ratings. Linalool's sweet-like aroma could be easily confused with the sweet notes descriptor (Rouseff & Perez-Cacho, 2007). Besides descriptors, the 3 analyzed spirits were clearly differentiated in the PCA biplot. Heart-1 presented high intensities of floral notes, Heart-2 presented high intensities of burn/smoke notes and Alembic Heart presented high intensities of fruit notes, confirming the explained MF ratings and chemical analyses. Sweet notes vector was placed between Heart-1 and Heart-2, according to the aroma confusion between linalool and tails sweet-like perception.

Finally, there were no significant differences in the sensory preference test (data not shown).

4. Conclusions

High internal refluxes of the distillation column at the first distillate fractions allowed a lower extraction of terpenic compounds in the head fraction. In addition, a drastic reduction of the internal reflux during distillation of the heart enhanced the recovery of terpenic compounds, producing a distillate rich in floral aromas. Furthermore, a drastic cooling flow reduction increased the presence of higher alcohols and esters, and decreased the head compounds in the heart fractions. These behaviors observed for negative and positive aroma compounds allowed to obtain a heart sub-fraction with high quality aroma characteristics and better characteristics than the classical alembic product. This study could help the industry to introduce new premium products with differentiated characteristics in the market.

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