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ORIGINAL RESEARCH ARTICLE

Effects of using cationic exchange for reducing pH on the composition and quality of sparkling wine (Cava)

Arnau Just-Borràs[1], Pere Pons-Mercadé[1], Jordi Gombau[1], Pol Giménez[1], Glòria Vilomara[2], Marta Conde[2], Antoni Cantos[2], Joan Miquel Canals[1] and Fernando Zamora[1*]

[1] Departament de Bioquímica i Biotecnologia, Facultat d'Enologia de Tarragona, Universitat Rovira i Virgili, C/Marcel.li Domingo s/n, 43007 Tarragona, Spain
[2] Juvé & Camps SA, c/Sant Venat, 1, 08770 Sant Sadurní d'Anoia, Barcelona, Spain

ABSTRACT

Climate change is affecting vine and grape physiology and consequently wine composition, causing a decrease in titratable acidity and an increase in ethanol content and pH. These effects are especially problematic in sparkling wines that need higher acidity to maintain an adequate freshness. Therefore, the wine industry is currently using certain procedures for reducing wine pH, among which cation exchange stands out as it is probably the most widely used. To study the influence of cation exchange treatment on the composition and quality of sparkling wines, a grape juice of Macabeo (pH 3.21 and titratable acidity 5.70 g of tartaric acid/L) after settling was treated to obtain a very acidic grape juice (pH 1.9 and titratable acidity 8.70 g of tartaric acid/L). The original grape juice was then blended in different proportions (0-45 %) with a treated grape juice. These different grape juices were used for obtaining their corresponding base wines which in turn were used for elaborating their corresponding sparkling wines using the traditional method. The cation exchange treatment reduced the pH from 3.15 (Control) to 2.87 (45 % of treatment) and increased the titratable acidity from 4.61 (Control) to 7.69 (45 % of treatment). No significant effects were observed on the concentration of any of the protein or polysaccharide fractions and the foaming properties of the base wine or young sparkling wines were not affected; however, cation exchange caused a decrease in foamability and persistence of the foam in older sparkling wines, especially when the proportion of treated grape juice was higher. A trained panel only found clear sensory differences in the acidity of the sparkling wines without the rest of the attributes being affected by the treatment.

KEYWORDS: sparkling wines, cationic exchange, pH, titratable acidity, potassium

*correspondence:
fernando.zamora@urv.cat

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INTRODUCTION

Cava is the name of an AOC of sparkling wines produced in Spain by the traditional method that comprises two fermentation steps (Ministerio De Agricultura y medio ambiente, 2018). The grape juice is transformed into a base wine during the first fermentation of a standard winemaking process. After blending and stabilisation, the base wine is transformed into sparkling wine in a second fermentation called *prise de mousse*. This second fermentation takes place inside the bottle. The sparkling wines age for some time in contact with the lees to benefit from the autolysis process (Maujean, 1989).

The maturity and the healthiness of the grape berries plays a very important role in the final composition and quality of base wines and their corresponding sparkling wines (Cilindre *et al*., 2007). It has been reported that an excess of maturity can seriously affect some factors that are important for sparkling wine quality, such as foamability, titratable acidity and especially pH (Esteruelas *et al*., 2015b; Liu *et al*., 2018). For this reason, sparkling wine producers consider low sugar concentration, high titratable acidity and low pH as the main criteria for determining the harvest dates (Jones *et al*., 2014). High acidity and low pH are needed to maintain the necessary sensory freshness of sparkling wines and both parameters have been reported to be key factors for guaranteeing the correct evolution during aging (Zoecklein, 2002).

In recent years, the increase in temperature and the changes in rainfall distribution caused by climate change are affecting vine and grape physiology and are consequently impacting wine composition and quality (Jones *et al*., 2005; Santos *et al*., 2020; Schultz, 2000). As a consequence of global warming, the grape pulp ripens faster, and the pH and sugar concentration become too high and titratable acidity too low (Godden *et al*., 2015; Mira de Orduña, 2010; Schultz, 2016). Therefore, grapes reach a very high potential alcoholic degree and pH sooner than usual. This phenomenon causes harvest dates to be earlier and makes it much more difficult to pinpoint proper aromatic and pulp maturity, which leads to unbalanced wines (Zamora, 2014). This is an increasing problem in the case of AOC Cava (Esteruelas *et al*., 2015a; Ramos, 2017). Therefore, wineries are very interested in knowing how they can mitigate the effects of climate change on grape and wine composition.

In this new situation, oenologists are looking for strategies to counteract these effects. There seems to be only two possibilities: they can harvest when alcoholic degree and pH are at the correct level and accept that the grapes will not have the correct aromatic and phenolic maturity; or they can wait for adequate maturity and accept that the wines will have high ethanol content and pH.

Neither of these choices is conducive to obtain high quality wines and therefore winemakers are obviously concerned about this problem. Since the lack of real grape maturity cannot be compensated for, most winemakers prefer to wait for the correct grape maturity and then later apply procedures to compensate for the disequilibrium of these unbalanced grapes (Zamora, 2014).

Several practices for reducing sugar in grape juice or ethanol in wines have been proposed, including selecting grape cultivars and clones that ripen later or adapting farming practices to this new situation (Schultz, 2000), selecting yeasts with lower sugar/ethanol transformation yields (Dequin and Barre, 1994), reverse osmosis (Gil *et al*., 2013) or partial evaporation of ethanol from the wine (Takács *et al*., 2007). For more information on these procedures for reducing alcohol, the following reviews are recommended: Saha *et al*. (2013) and Zamora (2016).

The problem of the low titratable acidity of grape juices and wines can be easily solved by adding authorised acids, such as L-(+)-tartaric, citric, lactic or malic acids. Nevertheless, all these organic acids have pK values that are relatively high and therefore they are not efficient enough for lowering the pH. Furthermore, the use of mineral acids is strictly forbidden (International organisation of vine and wine, 2021). In fact, there are only two techniques authorised by OIV for reducing pH: electrodialysis and cationic exchange (International organisation of vine and wine, 2021).

Electrodialysis makes it possible to extract ions, mainly potassium cation and hydroxyl anion, through selective ion exchange membranes under the influence of a continuous electric field (El Rayess and Mietton-Peuchot, 2016; Gonçalves *et al*., 2003; Romanov and Zelentsov, 2007). In contrast, cationic exchange makes it possible to interchange cations, mainly potassium, with protons using cationic exchange resins (Lasanta and Gómez, 2012). Both techniques are very effective and are being increasingly used by wineries; however, cation exchange is probably being more widely used due to its lower cost (Lasanta and Gómez, 2012; Walker *et al*., 2004).

Several studies have been reported about the use of cationic exchange in grape juice and wine and its effects on wine composition and quality (Ibeas *et al*., 2015; Mira *et al*., 2006; Ponce *et al*., 2018). However, to our knowledge, only few of them refer to base wines (Cisilotto *et al*., 2020; Cisilotto *et al*., 2019) and none of them have focused on the effect on sparkling wines produced using the traditional method. Therefore, the aim of this work is to study how applying cationic exchange to the grape juice influences the composition and quality of the base wines and their corresponding sparkling wines after 11 and 20 months of aging. This study was performed by blending treated grape juice with non-treated grape juice in different proportions in order to determine which treatment percentage was the most adequate for obtaining the most balanced sparkling wine.

MATERIALS AND METHODS

1. Experimental design

The experiment was carried out using Macabeo grapes (VIVC Prime name: Viura; VIVC Variety number: 13127) from the 2018 vintage. The grapes were from Juvé & Camps SL

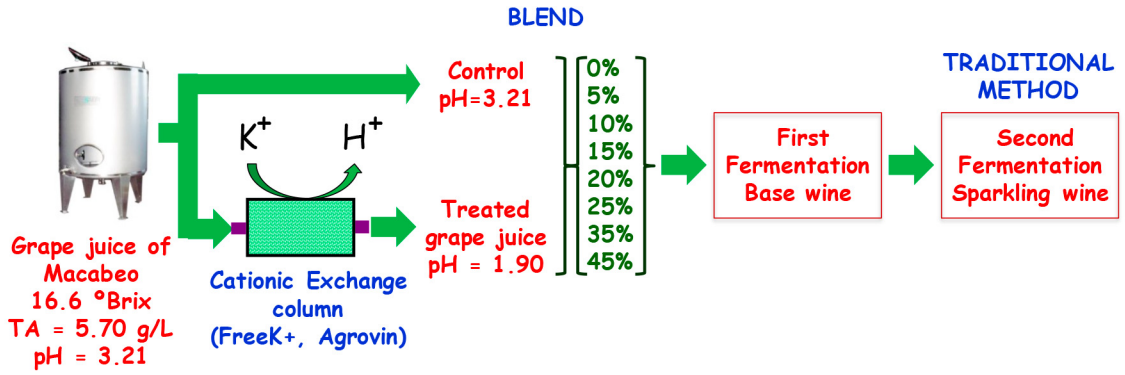

FIGURE 1. Experimental design.

vineyards in Sant Sadurní d'Anoia (AOC Cava, Barcelona, Spain; 41º 26' 47.42'' N and 1º 49' 0.63'' E). The grapes were harvested when the maturity level was adequate for sparkling wine production. Specifically, the maturity parameters of the obtained grape juice were: total sugar concentration: 159 g/L (corresponding to 16.6 ºBrix), titratable acidity: 5.7 g/L (expressed as tartaric acid) and pH: 3.21. The grapes were immediately pressed in a pneumatic press to obtain a yield of 0.6 L/kg of grape juice. The grape juice was immediately sulfited with 100 mg/L of $K_2S_2O_5$ and pectinolytic enzymes (20 mg/L) were added to facilitate settling. After 18 h, clean grape juice (around 70 NTUs) was racked into a stainless steel tank.

Figure 1 shows a schematic diagram of the experimental design.

Around 2,000 L of this grape juice were divided into two parts, and 1,000 L were treated with a cationic exchange column (FreeK+ column, Agrovin, Ciudad Real, Spain) and the other 1,000 L were kept without any treatment. The pH and titratable acidity of the initial grape juice were 3.21 ± 0.01 and 5.70 ± 0.02 respectively. In contrast, the final pH and titratable acidity of the treated grape juice were 1.90 ± 0.02 and 8.70 ± 0.05 respectively. Subsequently, both grape juices, treated and non-treated, were blended in different proportions in order to obtain a set of grape juices with different pH levels. Specifically, the different blends were obtained with the following proportions of treated grape juice: 0, 5, 10, 15, 20, 25, 35 and 45 %. All the different blends were placed in 8-litre alimentary plastic tanks to perform the first fermentation. All the tanks were immediately inoculated with 200 mg/L of selected yeasts (*Saccharomyces cerevisiae*, Lalvin EC1118™, Lallemand, Inc., Montreal, Canadá). The fermentation kinetics were monitored using a digital densimeter (Mettler Toledo-PortableLabTM). All alcoholic fermentations were performed at 16-18 °C. Once alcoholic fermentation was finished, the base wines were racked, sulfited (40 mg/L of $K_2S_2O_5$) and cold stabilised. The entire process was carried out in triplicate.

Once the base wines were stable they were used for producing sparkling wine (Cava) following the traditional method. All the base wines were supplemented with 22 g/L of sucrose, 0.2 mL/L of a liquid riddling agent (Inoclair, Institut Oenological de Champagne, Epernay, France) and $2x10^6$ cells/mL of pre-adapted yeast culture (Saccharomyces cerevisiae - IOC 18-2007; Institut Œnologique de Champagne, Epernay, France). The wines were then bottled in standard green glass bottles (750 mL), crown sealed and stored at 12-15 °C until disgorgement. Eleven and twenty months later, four bottles of each experimental group were disgorged. Three bottles were used for chemical and physical analyses and one bottle was used for the sensory analysis. The second fermentation was monitored by measuring CO_2 pressure accumulation in each bottle following a non-destructive method (L.sensor CO_2-FTSYSTEM). No important differences were found in the internal pressure kinetics during the second fermentation (Data not shown). Only a very small delay was observed in the case of the more acidic samples (35 and 45 %) at the beginning of the second fermentation, but all the samples reached the maximal internal pressure at the same time (around two months).

2. Standard wine analysis

The analytical methods recommended by the OIV were used to determine the ethanol content (pycnometry), residual fermentable sugar concentration (D-glucose + D-fructose enzymatic method), pH, titratable acidity and volatile acidity (International organisation of vine and wine, 2019). The CIELab coordinates were determined following the method described by Ayala *et al*. (1997) using Helios Alpha UV VIS spectrophotometer (Thermo Fisher Scientific Inc., Waltman, MA, USA), and the data were processed using MSCV® software.

3. Sample preparation

All the samples, grape juices, base wines and sparkling wines were centrifuged at 17,000 g (Biofuge Primo centrifuge (Heraeus, Hanau, Germany)) for 15 min in order to obtain limpid liquids and when necessary to eliminate all carbon dioxide.

4. Measurement of the foaming properties

A Mosalux device (Station Oenotechnique de Champagne, Epernay, France) was used to measure HM, the max height of the foam after CO_2 injection through the glass frit, and HS, the stable height during CO_2 injection. HM represents

foamability (the wine's ability to foam) while HS represents foam stability (the persistence of the foam collar or the wine's ability to produce a stable foam). HM and HS are expressed in millimeters.

Base wine and sparkling wine samples were tempered at 18 °C for 24 h before analysis. The foam properties were measured using the Mosalux method (Maujean *et al*., 1990). A glass cylinder placed on a glass frit was filled with 100 mL of the sample. CO_2 was then injected into the glass cylinder through the glass frit with a constant gas flow of 115 mL/min under a constant pressure of 1 bar in the case of base wines and of 2 bar in the case of sparkling wines. Sparkling wines were measured at 2 bars in order to improve the method's sensitivity, because their values are noticeably lower than in base wines.

Calibration of Mosalux was performed using a standard solution composed of absolute ethanol 96 % vol. (17 % v/v), tartaric acid 99.5 % (4 g/L), glycerol 99.5 % (6 g/L) (all purchased from Panreac (Barcelona, Spain)), diethyl phthalate 99.5% (0.5 % v/v), and bovine serum albumin ≥ 98 % (10 mg/L) (both purchased from Sigma–Aldrich (Madrid, Spain)). Sodium hydroxide ≥ 98 % was used to adjust pH to 3.00. The foaming parameters (HM and HS) of this calibration solution were measured at 1 and 2 bar in order to determine a compensatory coefficient to refer all the measurements to 1 bar of pressure. Therefore, the foaming properties of the base wine and sparkling wines can be correctly compared. All measurements were determined in triplicate.

5. Potassium determination

The potassium concentration of the different base wine samples was determined by means of Flame Atomic Emission Spectroscopy (UNICAM969 AA SPECTROMETER) according to an adaptation of the method described by Aceto *et al*. (2002).

6. Acid composition

All the main wine acids were analysed using commercial kits provided by r-Biopharm (Darmstadt, Germany) following the instructions provided by the kit manufacturer. L-Malic, L-Lactic, Acetic and Citric acids were analysed according to the enzymatic methods recommended by the OIV (International organisation of vine and wine, 2019). Specifically, the following enzymatic kits were used for each acid: Art. No. 10139068035 for L-Malic, Art. No. RCS4260 for L-Lactic, Art. No. RCS4226 for Acetic, and Art. No. E1214 for Citric. Succinic acid was also enzymatically analysed according to the method described by Michal *et al.* (1976) using the commercial kit Art. No. 10176281035. Tartaric acid was analysed according to Hill and Caputi (1970) using the colorimetric kit Art. No. E3100.

The main wine acids were analysed using commercial kits provided by r-Biopharm (Darmstadt, Germany) following the instructions provided by the kit manufacturer. Specifically, the following enzymatic kits were used for each acid: Art. No. 10139068035 for L-Malic, Art. No. RCS4260 for L-Lactic, Art. No. RCS4226 for Acetic, Art. No. 10176281035 for Succinic and Art. No. E1214 for Citric. Tartaric acid was analysed using colorimetric kit Art. No. E3100).

7. Polysaccharide extraction and determination by HRSEC-RID

The samples were processed using the methodology described by Ayestarán *et al*. (2004). Briefly, 10 mL of sample in triplicate were concentrated to a final volume of 2 mL using a vacuum evaporator (Univap 148 100ECH; Progen Scientific, London, UK). Total soluble polysaccharides were precipitated by adding 10 mL of cold acidified ethanol (hydrochloric acid 0.3 M in absolute ethanol) and kept for 24 h at 4 °C. The samples were then centrifuged (10,000 g for 15 min) and the supernatants discarded. Finally, the precipitates were dissolved in 1 mL of ultra-pure water, frozen to −20 °C and freeze-dried using a lyophilizer (Telstar LyoQuest HT40, Barcelona, Spain). The soluble fractions were analysed by high-resolution size-exclusion chromatography (HRSEC) in order to determine the molecular distribution and quantify the polysaccharides obtained from the samples. The lyophilized samples were resuspended in 1 mL of 50 mM ammonium formate ≥ 99.0 % (Sigma–Aldrich (Madrid, Spain)) and filtered through 0.22 µm acetate cellulose filters (Merck Millipore, Darmstadt, Germany). Then 100 µL were injected into the chromatographic system. The analyses were carried out in an HPLC Agilent 1200 Series system (Agilent Technologies Inc., Santa Clara, USA) equipped with a G1311A quaternary pump, a G1316A column oven, a G1329A autosampler (Agilent Technologies, Santa Clara, CA, USA) and with a refractive index detector (G1362A - RID). Separation was carried out at 20 °C using two Shodex gel permeation HPLC columns (OHpak SB-186 803 HQ and SB-804 HQ, 300 mm × 8 mm I.D.; Showa Denko, Japan). The mobile phase consisted of an aqueous solution of 50 mM ammonium formate applied with a constant flow of 0.6 mL/min for 60 min, and the cell RID temperature was 35 °C. The molecular weight distribution of the wine fractions was monitored by calibration with a Shodex P-82 pullulan calibration kit (P-5, MW = 5.9 kDa; P-10, MW = 11.8 kDa; P-20, MW = 22.8 kDa; P-50, MW = 47.5 kDa; P-100, MW = 112 kDa; P-200, MW = 212 kDa; P-400, MW = 404 kDa; and P-800, MW = 788 kDa) purchased from Waters (Barcelona, Spain) and four dextrans (BioChemika; 12, 25, 50 and 80 kDa) purchased from Fluka (St. Louis, MO, USA). The polysaccharides were quantified according to the peak area for each fraction using the external standard method with pectin and dextran commercial standards (Sigma–Aldrich, Saint Louis, MO, USA) in a range between 0 and 2 g/L ($r2 > 0.99$).

8. Determination of proteins by HRSEC-DAD

The samples were processed and analysed using the methodology described by Canals *et al*. (1998). Fifteen mL of each sample were concentrated in triplicate following a two steps dialysis in tubes with a molecular weight cutoff of 3.5 kDa (Spectrum Laboratories Inc., Rancho Dominguez, CA, USA). The first step lasted 48h with 0.3 M ammonium

acetate ≥ 98.0 % (Sigma–Aldrich (Madrid, Spain)) solution with a rate of 1:10 (sample:solution) and constant agitation. The second step was carried out with water for another 48h. The dialyzed samples were subsequently lyophilised and preserved at −20 °C.

The soluble fractions were analysed by high-resolution size-exclusion chromatography (HRSEC) in order to determine the molecular distribution and quantify the proteins obtained from the samples37. The lyophilized samples were resuspended in 0.6 µL of ammonium acetate solution (300 mM) and centrifuged (12,000 g for 5 min). The supernatant was filtered through 0.22 µm acetate cellulose filters (Merck Millipore, Darmstadt, Germany) and then 100 µL of supernatant was injected into the chromatographic system. The analyses were carried out in HPLC Agilent 1200 Series system (Agilent Technologies Inc., Santa Clara, USA) equipped with a G1311A quaternary pump, a G1316A column oven, a G1329A autosampler (Agilent Technologies, Santa Clara, CA, USA) and with a diode array detector (G1315D - DAD) to monitor output at 230 and 320 nm. Separation was carried out at 20 °C using an S 165 Shodex gel permeation HPLC column 210 (OHpak 166 SB-803 HQ, 300 mm × 8 mm i.d.; Showa Denko, Tokyo, Japan). The mobile phase consisted of an aqueous solution of 300 mmol/L ammonium acetate applied at a constant flow of 0.6 mL/min for 70 min. The proteins were quantified according to the peak area for each fraction using the external standard method with bovine serum albumin (Sigma–Aldrich, Madrid, Spain) in a range between 0 and 1 mg/mL (r2 > 0.99).

9. Sensory analysis

All sensory analyses were performed in the tasting room of the Faculty of Oenology of Tarragona (University Rovira i Virgili), which was designed in accordance with UNE 87004.197 (AENOR, 2010). Tasting was carried out using ISO official tasting glasses (ISO-3591, 1997). All the samples were tasted by 10 trained panelists. This panel was made up of seven males and three females aged between 22 and 60. For each sample, tasters were required to evaluate the intensity of six sensory attributes (Colour, Balance Reduction/Oxidation, CO_2 integration, Structure, Acidity and Global quality) on a scale of 1 to 10 (1 = 'slight intensity', 10 = 'maximum intensity'). In the case of Balance Reduction/Oxidation the scale goes from the presence of evident reduction notes (1) to high oxidation notes (10). The intensity level of each descriptor was then expressed as the mean value of all the judges. No more descriptors were used so as not to over complicate the tasting. A sensory training session was held beforehand so that the panelists could agree on the criteria for each of the different sensory attributes. Samples were served randomly to avoid the influence of the tasting order.

TABLE 1. Influence of cation exchange treatment on pH.

Percentage of treated grape juice in the blend	Grape juice	Base wine	Sparkling wine 11 months	Sparkling wine 20 months
Control	3.21 ± 0.01 F b	3.13 ± 0.02 F a	3.17 ± 0.02 D a	3.15 ± 0.01 C a
5 %	3.15 ± 0.01 EF b	3.06 ± 0.06 E a	3.09 ± 0.03 C a	3.11 ± 0.01 C a
10 %	3.13 ± 0.01 E b	3.06 ± 0.00 E a	3.05 ± 0.01 C a	3.05 ± 0.04 BC a
15 %	3.05 ± 0.04 D a	3.02 ± 0.00 DE a	3.06 ± 0.03 C a	2.98 ± 0.09 AB a
20 %	3.03 ± 0.02 CD a	2.97 ± 0.03 CD a	3.05 ± 0.07 C a	2.95 ± 0.06 AB a
25 %	2.98 ± 0.03 C a	2.94 ± 0.01 BC a	2.97 ± 0.00 B a	2.94 ± 0.03 AB a
35 %	2.90 ± 0.06 B a	2.87 ± 0.01 B a	2.91 ± 0.01 A a	2.90 ± 0.02 A a
45 %	2.77 ± 0.02 A a	2.81 ± 0.02 A a	2.88 ± 0.02 A b	2.87 ± 0.02 A b

Results are expressed as mean ± standard deviation of three replicates. Different letters in a row indicate the existence of statistical difference ($p < 0.05$). First row (capital letters) indicates the influence the percentage of cation exchange treated grape juice in the blend. Second row (lowercase letters) indicates the influence of the elaboration process.

10. Statistical analysis

The data shown are the arithmetic means of triplicates with the standard deviation for each parameter. Two-way ANOVA and Tukey comparison tests were carried out using the XLSTAT software (Addinsoft, Paris, France).

RESULTS AND DISCUSSION

1. Influence of cationic exchange treatment on the general composition of grape juice, base wine and sparkling wine

Table 1 shows the effect of the treatment with the cationic exchange column on the pH.

The initial pH value of the grape juice was 3.21 ± 0.01. This value can be considered as very common for Macabeo grape juice harvested for sparkling wine production in the region. This value decreased significantly in the base wine and sparkling wines of 11 and 20 months of aging. This small decrease in pH can be associated with the crystallisation of potassium hydrogen tartrate caused by the presence of ethanol. When potassium hydrogen tartrate crystallises, a proportion of hydrogen tartrate anion is removed from the tartaric acid equilibrium causing a displacement towards the release of protons (Devatine *et al*., 2002).

This table also shows that the cationic exchange treatment clearly reduces the pH. In general, the higher the proportion of treated grape juice the lower the pH, and this tendency was observed in all the samples: grape juices, base wines and both sparkling wines. It was also observed that the pH of the base wines was in general lower than in its corresponding grape juices; however, the differences was only significant for the control, and 5 and 10 % of treatment. This decrease in pH after alcoholic fermentation occurs, because the presence of ethanol reduces the solubility of potassium acid tartrate, and when this salt precipitates, it shifts the equilibrium of tartaric acid towards the release of protons. The lack of significance when the percentage of treatment was higher than 10 % could be because the removal of potassium caused by the cationic exchange treatment progressively diminishes the crystallisation of potassium hydrogen tartrate.

Table 2 shows the influence of the cationic exchange treatment on the titratable acidity (TA) of the different grape juice blends and their corresponding base and sparkling wines.

TABLE 2. Influence of cation exchange treatment on titratable acidity

Percentage of treated grape juice in the blend	Titratable acidity (g of tartaric acid/L)			
	Grape juice	Base wine	Sparkling wine 11 months	Sparkling wine 20 months
Control	5.70 ± 0.02 A c	5.53 ± 0.04 A b	5.05 ± 0.11 A a	4.61 ± 0.34 A a
5 %	5.93 ± 0.15 AB a	5.76 ± 0.02 B a	5.57 ± 0.15 B a	5.58 ± 0.25 B a
10 %	5.93 ± 0.15 AB a	6.02 ± 0.06 C a	5.95 ± 0.14 BC a	6.10 ± 0.21 BC a
15 %	6.00 ± 0.24 AB a	6.20 ± 0.05 C a	6.10 ± 0.12 C a	6.15 ± 0.27 BC a
20 %	6.23 ± 0.15 BC a	6.49 ± 0.04 D a	6.35 ± 0.10 CD a	6.34 ± 0.19 C a
25 %	6.38 ± 0.15 CD a	6.74 ± 0.05 E a	6.55 ± 0.18 D a	6.48 ± 0.23 C a
35 %	6.68 ± 0.15 DE a	7.30 ± 0.05 F b	7.16 ± 0.16 E b	7.20 ± 0.20 D b
45 %	6.98 ± 0.15 E a	7.92 ± 0.17 G b	7.61 ± 0.19 F b	7.69 ± 0.27 D b

Results are expressed as mean ± standard deviation of three replicates. Different letters in a row indicate the existence of statistical difference ($p < 0.05$). First row (capital letters) indicates the influence the percentage of cation exchange treated grape juice in the blend. Second row (lowercase letters) indicates the influence of the elaboration process.

TABLE 3. Influence of cation exchange treatment on ethanol and residual sugars.

Percentage of treated grape juice in the blend	Base wine								Sparkling wine (11 months)							
	Ethanol (% v/v)				Residual sugars (g/L)				Ethanol (% v/v)				Residual sugars (g/L)			
Control	10.85	±	0.05	B	0.88	±	0.40	A	12.32	±	0.06	C	0.26	±	0.03	A
5 %	10.83	±	0.07	B	0.78	±	0.29	A	12.29	±	0.08	BC	0.23	±	0.04	A
10 %	10.84	±	0.01	B	0.97	±	0.09	AB	12.32	±	0.01	C	0.30	±	0.02	AB
15 %	10.80	±	0.07	B	0.99	±	0.25	AB	12.27	±	0.07	BC	0.36	±	0.02	B
20 %	10.79	±	0.03	B	0.90	±	0.13	A	12.26	±	0.03	BC	0.29	±	0.02	AB
25 %	10.74	±	0.05	AB	1.13	±	0.42	AB	12.21	±	0.06	AB	0.39	±	0.06	B
35 %	10.66	±	0.02	A	1.44	±	0.35	BC	12.15	±	0.02	A	0.60	±	0.03	C
45 %	10.66	±	0.02	A	1.78	±	0.32	C	12.15	±	0.02	A	0.69	±	0.04	C

Results are expressed as mean ± standard deviation of three replicates. Different letters in a row indicate the existence of statistical difference ($p < 0.05$). First row (capital letters) indicates the influence the percentage of cation exchange treated grape juice in the blend. Second row (lowercase letters) indicates the influence of the elaboration process.

TABLE 4. Influence of cation exchange treatment on potassium concentration of base wine.

Percentage of treated grape juice in the blend	[Potassium] (mg/L)			
Control	412.79	±	21.15	D
5 %	349.74	±	12.94	C
10 %	279.07	±	6.16	B
15 %	243.99	±	9.81	AB
20 %	236.10	±	9.71	A
25 %	234.58	±	3.24	A
35 %	233.58	±	11.86	A
45 %	223.14	±	7.93	A

Results are expressed as mean ± standard deviation of three replicates. Different letters in a row indicate the existence of statistical difference ($p < 0.05$).

The TA value of the control grape juice was 5.70 ± 0.02 g of tartaric acid/L, which is a very common value for Macabeo grape juice used for Cava production. In this case, a decrease in the TA of the control base and sparkling wines was observed with respect to the control grape juice. This reduction in TA in the control samples may be related to the development of malolactic fermentation, as discussed later, and also to the previously described crystallisation of potassium hydrogen tartrate caused by the presence of ethanol in wines, which matches very well with the observed pH decrease. However, this behaviour was dampened and even inverted as the proportion of treated grape juice was increased in the final blend. In any case, the cationic exchange treatment exerted a significant effect on the TA of the grape juices since the higher the proportion of treated grape juice in the blend, the higher the TA. This effect was maintained in the base and sparkling wines.

Table 3 shows the ethanol content and residual sugars of the different base and sparkling wines of 11 months of aging.

As expected, the ethanol content of the sparkling wines was on average 1.47 % higher than in the base wines. This increase matches a normal sugar/ethanol transformation yield of the sugar added in the tirage liquor (22 g/L of sucrose) for the second fermentation.

In general, no large differences were found in the ethanol content or in the residual sugars as a function of the proportion of the treated grape juice included in the blend. However, it seems that when the pH was very low, the yeasts had some difficulties in finishing the first and second fermentations completely since the ethanol content was slightly lower and the residual sugar concentration slightly higher. In any case, these differences were so small that they have very little practical and technical relevance.

Table 4 shows the potassium concentration of the base wines.

As expected, the potassium concentration decreased progressively as the proportion of treated grape juice in the blend increased. It should be noted that the proportion of potassium extracted decreases with a steep slope to eventually reach almost asymptotic behaviour as the proportion of treated must increases. In any case. these data confirm the effectiveness of cationic exchange treatment for removing this cation from wines.

The main acids were analysed to better understand the influence of the cationic exchange treatment on the wine acidic composition (Table 5).

Tartaric acid concentration increased progressively as the proportion of treated grape juice in the blend increased.

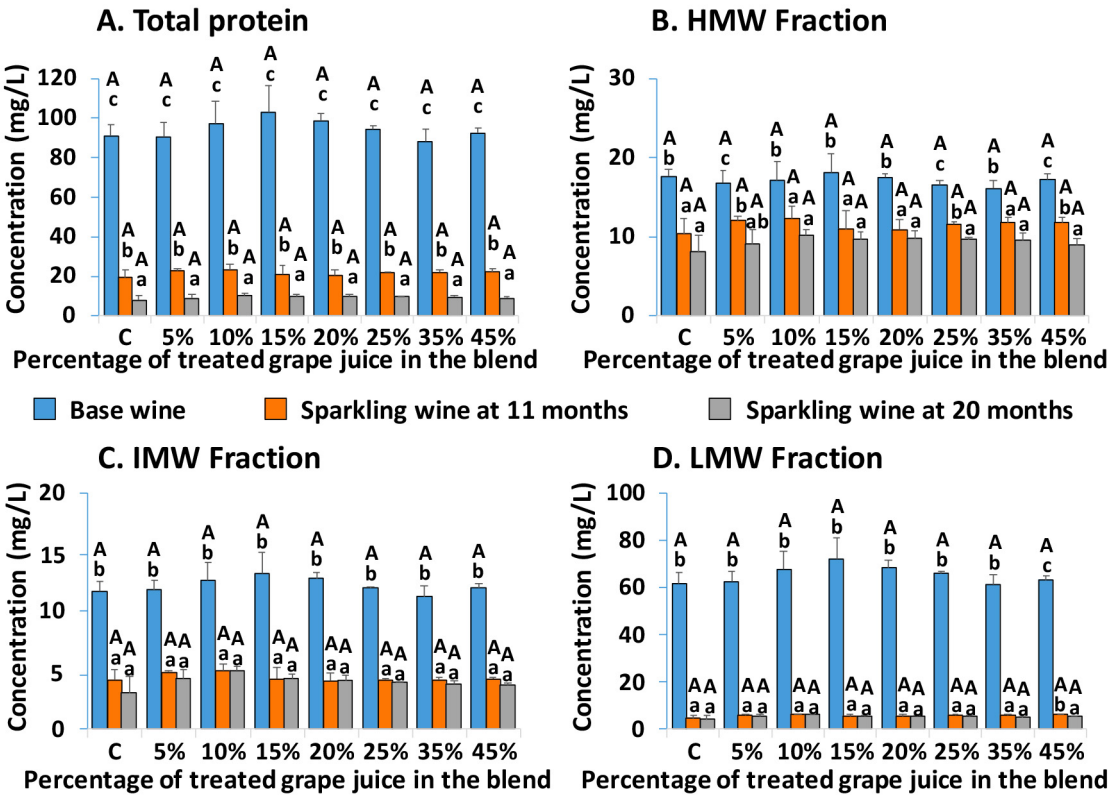

FIGURE 2. Protein composition.

All data are expressed as the arithmetic mean of 3 replicates ± standard deviation. C: Control wine. HMW: high molecular weight fraction (MW > 80 kDa); IMW: intermediate molecular weight fraction (80 kDa > MW > 60 kDa); LMW: low molecular weight fraction (MW < 60 kDa); Different capital letters indicate statistically significant differences ($p < 0.05$) between the samples as a function of the percentage of cation exchange treated grape juice in the blend. Different lowercase letters indicate statistically significant differences ($p < 0.05$) between the different steps of the elaboration process.

TABLE 5. Influence of cation exchange treatment on acidic composition of base wines

Percentage of treated grape juice in the blend	Tartaric acid (g/L)			L-Malic acid (g/L)			L-Lactic acid (g/L)			Acetic acid (g/L)			Succinic acid (g/L)			Citric acid (g/L)			Σ acids (mEq/L)		
Control	2.55	± 0.08	A	0.03	± 0.00	A	0.42	± 0.01	B	0.24	± 0.02	A	0.68	± 0.05	A	0.02	± 0.01	A	54.75	± 2.25	A
5 %	2.93	± 0.12	B	0.67	± 0.00	B	0.01	± 0.00	A	0.26	± 0.04	AB	0.44	± 0.06	A	0.12	± 0.02	B	62.73	± 3.26	B
10 %	3.18	± 0.14	BC	0.67	± 0.01	B	0.00	± 0.00	A	0.26	± 0.02	AB	0.49	± 0.01	A	0.13	± 0.02	B	67.16	± 2.58	C
15 %	3.36	± 0.10	CD	0.68	± 0.01	B	0.00	± 0.02	A	0.26	± 0.02	AB	0.50	± 0.01	A	0.10	± 0.05	B	69.29	± 2.63	C
20 %	3.65	± 0.13	D	0.68	± 0.02	B	0.02	± 0.02	A	0.24	± 0.01	AB	0.46	± 0.11	A	0.14	± 0.02	B	73.08	± 4.14	D
25 %	3.60	± 0.09	D	0.69	± 0.02	B	0.01	± 0.01	A	0.26	± 0.01	AB	0.53	± 0.01	A	0.14	± 0.01	B	73.84	± 2.02	D
35 %	4.24	± 0.08	E	0.69	± 0.01	B	0.01	± 0.01	A	0.27	± 0.01	B	0.42	± 0.17	A	0.15	± 0.00	B	80.80	± 3.62	E
45 %	4.61	± 0.13	E	0.68	± 0.02	B	0.00	± 0.00	A	0.31	± 0.03	C	0.55	± 0.10	A	0.14	± 0.01	B	88.18	± 3.85	F

Results are expressed as mean ± standard deviation of three replicates. Different letters in a row indicate the existence of statistical difference ($p < 0.05$).

The explanation for this behaviour is very simple. Briefly, the elimination by crystallisation of tartaric acid in the form of potassium hydrogen tartrate in the wine decreased as the potassium concentration of the medium became lower. This is the main reason why the tartaric acid concentration and the titratable acidity increase when the proportion of treated grape juice is increased in the final blend. These results are in agreement with other previous studies (Ibeas *et al*., 2015; Cristina Lasanta *et al*., 2013; Walker *et al*., 2004).

It should also be noted that the concentrations of the L-malic and citric acids of the control wine were almost zero and that L-lactic acid was present in a quantifiable concentration (0.42 g/L). In contrast, all the other wines maintained similar concentrations of L-malic and citric acids (around 0.68 and 0.13 g/L respectively) and the L-lactic acid concentration was negligible. It seems, therefore, that the control wine was the only one that performed malolactic fermentation, although all the base wines were equally sulfited as soon as alcoholic fermentation was completed. This different behaviour was probably a result of the higher pH favouring the development of lactic acid bacteria and also reducing the antiseptic effectiveness of the sulfur dioxide (Liu and Gallander, 1983). These data demonstrate that a relatively high pH carries an increased risk of unwanted malolactic fermentation taking place, and that therefore the use of cation exchange is also helpful in preventing it. A significant increase in acetic acid concentration was observed in the base wines in which the proportion of treated grape juice was very high, probably because their very low pH induced higher stress in the yeasts. In any case, this increase in acetic acid did not affect the final quality. Finally, no significant differences in the succinic acid concentration were found.

2. Influence of cationic exchange treatment on the protein fraction of base and sparkling wines

Figure 2 shows the protein concentration of the different base wines and their corresponding sparkling wines at 11 and 20 months. As expected, the total protein concentration decreased drastically between the base wines and sparkling wines. This decrease was mainly due to the lower and intermediate molecular weight (LMW and IMW) fractions, whereas the high molecular weight (HMW) was less affected. This protein reduction between base and sparkling wines has been reported previously and has been mainly attributed to the deproteinising effect of the riddling agent bentonite (Martínez-Rodriguez and Polo, 2003; Vanrell *et al*., 2006).

Almost all wine proteins have a positive electric charge at wine pH since their isoelectric point is higher than the pH of the medium. Therefore, it is reasonable to assume that cation exchange resins can retain part of these proteins. However, according to our results, cationic exchange does not seem to remove them since neither the concentration of the total protein nor any of its molecular weight fractions are affected by the treatment. This is a very interesting result, because proteins have been described as being foam enhancers and stabilisers (Cilindre *et al*., 2007; Maujean *et al*., 1990; Medina-Trujillo *et al.*, 2017).

3. Influence of cationic exchange treatment on the polysaccharide fraction of base and sparkling wines

Figure 3 shows the total polysaccharide concentration of the base wines and their corresponding sparkling wines at 11 and 20 months of aging time.

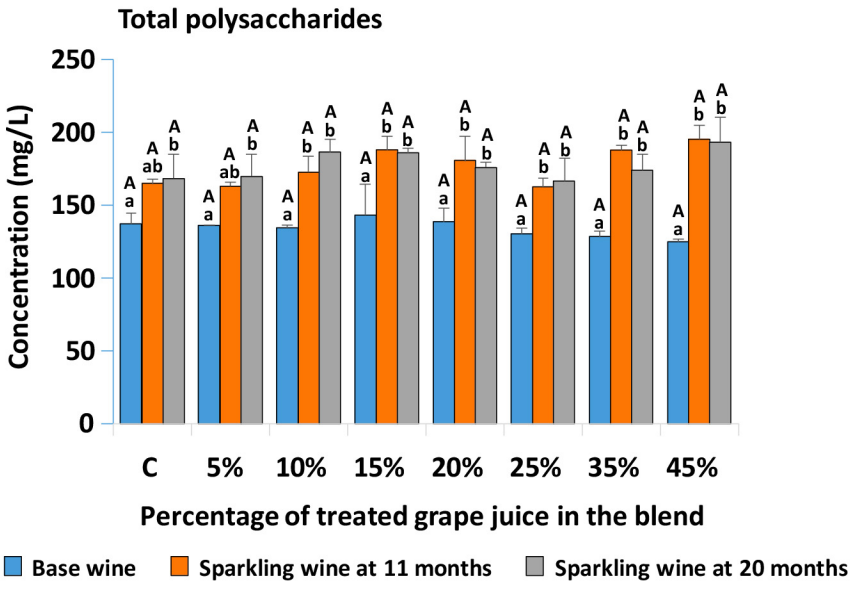

FIGURE 3. Polysaccharide composition.

All data are expressed as the arithmetic mean of 3 replicates ± standard deviation. C: Control wine. Different capital letters indicate statistically significant differences ($p < 0.05$) between the samples in function of the percentage of cation exchange treated grape juice in the blend. Different lowercase letters indicate statistically significant differences ($p < 0.05$) between the different steps of the elaboration process.

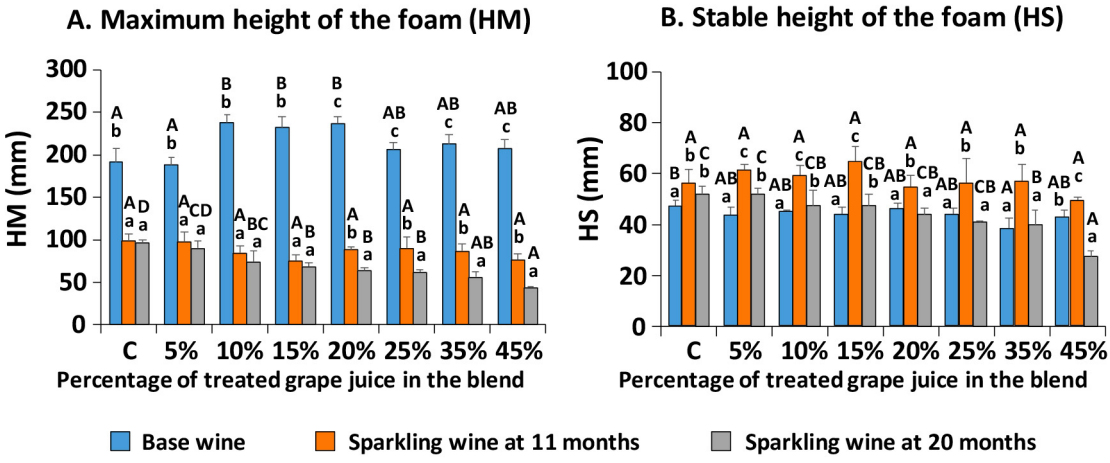

FIGURE 4. Foam parameters.

All data are expressed as the arithmetic mean of 3 replicates ± standard deviation. C: Control wine. Different capital letters indicate statistically significant differences ($p < 0.05$) between the samples as a function of the percentage of cation exchange treated grape juice in the blend. Different lowercase letters indicate statistically significant differences ($p < 0.05$) between the different steps of the elaboration process.

In this case, a small but significant increase was observed in the total concentration of the polysaccharides of the sparkling wines compared to their corresponding base wines. This higher polysaccharide content of sparkling wines can be attributed to the release of mannoproteins and polysaccharides from yeast autolysis during the second fermentation and subsequent aging time in contact with the lees (Kemp *et al*., 2019; Martí-Raga *et al*., 2016; Martínez-Lapuente *et al*., 2013). In contrast, treatment by cationic exchange did not affect the polysaccharide concentration since no significant differences were observed between the control base wine and the blends with different proportions of treated grape juice. Similar results were obtained for the sparkling wines. Moreover, no differences were observed in any of the different molecular weight polysaccharide fractions (data not shown).

4. Influence of cationic exchange treatment on the foaming properties of base and sparkling wines

Figure 4A shows the maximum height of the foam (HM) of the base wines and their corresponding sparkling wines of 11 and 20 months of aging.

In all cases, the HM of sparkling wines was significantly lower than in the corresponding base wines. No significant differences in HM were detected between sparkling wines aged 11 and 20 months when the percentage of grape juice treated in the blend was less than 20 %. However, when the proportion of treated grape juice was higher, a significant decrease in HM was observed in older sparkling wines. It therefore seems that high percentages of cationic exchange treatment can negatively affect the foamability of sparkling wines over time. This observed decrease in HM after the second fermentation has been described elsewhere and has two probable causes. First, the second fermentation increases ethanol content, which is negative for foam (Dussaud *et al*., 1994), and second, the use of bentonite as a riddling agent removes surface active agents like proteins (Dambrouck *et al*., 2005; Martínez-Rodriguez and Polo, 2003; Vanrell *et al*., 2006). In fact, our results confirm a drastic reduction in protein concentration in sparkling wines with respect to the base wines (Figure 2).

Figure 2B shows the stable height of the foam (HS) of base wines and sparkling wines of 11 and 20 months of aging. In general, a significant increase in HS was observed in the sparkling wines of 11 months of aging with respect to their corresponding base wines. Other authors have described the HS of sparkling wines to be usually lower than in their corresponding base wines (Martí-Raga *et al*., 2016; Martínez-García *et al*., 2017; Vanrell *et al*., 2006). Nevertheless, similar or even increased values of HS after the second fermentation have also been reported (Cilindre *et al*., 2010; Esteruelas *et al*., 2015b).

Only slight differences were detected in the foam parameters of the base wines and sparkling wines at 11 months of aging as a function of the percentage of treated grape juice included in the blend. However, the sparkling wines of 20 months showed a clear decreasing trend in both parameters, HM and HS, as the percentage of the treated grape juice included in the blend increased. This data therefore indicate that the cationic exchange treatment of the grape juice does not affect the foaming properties of the base wine and young sparkling wines, but that it can negatively affect the foaming characteristics of older sparkling wines, especially when the proportion of treated grape juice is higher.

5. Influence of cationic exchange treatment on the sensory attributes of sparkling wines

Figure 5 shows in a radar chart the results obtained from the sensory analysis with the sparkling wine samples aged for 20 months.

The results showed that the only sensory attribute in which the trained panel found clear differences was the acidity,

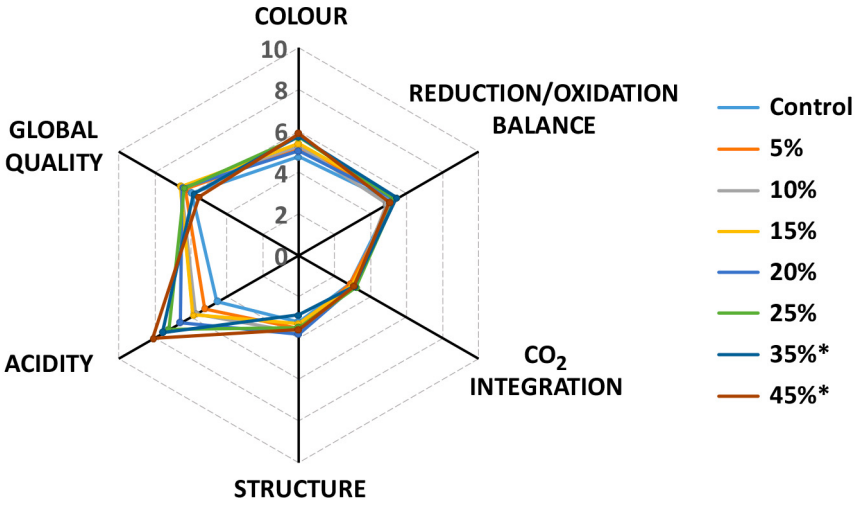

FIGURE 5. Influence of cationic exchange treatment on the sensory perception of sparkling wines after 20 months of aging.

All data are the arithmetical average corresponding to the results of 10 tasters. The asterisk (*) indicates that the panel considered the acidity as excessive.

with no differences detected in any of the other descriptors. The panel detected a clear increase in acidity of the sparkling wines as the proportion of cation exchange treatment increased. The panel also considered that the sparkling wine gained in freshness when the proportion of the treated grape juice in the blend was not too high. However, the acidity of the sparkling wines with a very high proportion of treated grape juice was considered excessive. The fact that the panel did not find any differences in the other sensory attributes indicates that the cation exchange treatment of the grape juice does not exert a negative sensory effect on the final sparkling wines.

CONCLUSIONS

The cation exchange treatment of the grape juice made it possible to increase the titratable acidity and reduce the pH of the base wines and their corresponding sparkling wines. This effect is clearly associated with the reduction of potassium levels. Its effect on other chemical parameters, such as ethanol content, residual sugars, L-malic acid, L-lactic acid, succinic acid, citric acid and acetic acids, can be considered as negligible. Moreover, no significant effects were observed on the concentration of any of the protein or polysaccharide fractions. Cationic exchange treatment of the grape juice did not negatively affect the foaming properties of the base wine or young sparkling wines; however, it caused a decrease in foamability and persistence of the foam in older sparkling wines, especially when the proportion of treated grape juice was higher.

A trained panel only found that the acidity of the sparkling wines was greater as the percentage of cationic exchanged treated grape juice increased. The higher acidity was perceived as positive when percentage of treated grape juice in the blend was relatively low, because the sparkling wines gained freshness. However, the sparkling wines with the higher percentages of treatment were considered as too acidic.

It can therefore be concluded that applying cationic exchange treatment to the grape juice is a very useful tool for reducing the pH of sparkling wines and increasing their freshness; however, the fact that excessive treatment can damage the acidity balance and negatively affect the quality of the sparkling wine should be taken into account.

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