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### Influence of Wine Chemical Compounds on the Foaming Properties of Sparkling Wines

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Additional information is available at the end of the chapter

http://dx.doi.org/10.5772/intechopen.70859

#### **Abstract**

The foam of a sparkling wine is a key parameter of its quality, and the main characteristic differentiating sparkling wines from the so-called still wines. Both foam formation and duration are directly related to the chemical composition of sparkling wines. This chapter reviews the most recent studies made to determine the influence of chemical compounds on the foamability and foam stability of sparkling wines. Foam properties of sparkling wines are ruled by a large number of molecules, but some compounds seem to be more relevant than others to explain their behavior. The content of total amino acids, polysaccharides, anthocyanins, coumaric acid, and isorhamnetin showed high correlation values with foam quality parameters. The alcohol content and the concentration of acid polysaccharides, proanthocyanidins and free SO<sub>2</sub> are the factors which most negatively affect foam quality. A recent study, by means of prediction models, has concluded that the different forms of malvidin show the highest influence on the foamability parameters in rosé sparkling wines, followed by amino acid compounds, while foam stability model was only predicted by polysaccharides rich in arabinose and galactose. These research findings provide industry with a better understanding of the compositional factors influencing the foam quality of sparkling wines.

**Keywords:** sparkling wine, foaming properties, quality, chemical composition, predictive models

#### 1. Introduction

Nowadays the economic impact of sparkling wine shows a fast growth in the world wine trade because of its high added value. According to the report published in the year 2014 by the



International Organization of Vine and Wine [1], sparkling wine production increased by 40% in the last decade and by 7% compared to global wine production.

Sparkling wines are obtained after a second fermentation of a base wine that can be carried out in closed bottles or in hermetically sealed tanks. High quality sparkling wines, such as Champagne wines in France, Cava wines in Spain or Talento in Italy, are fermented in closed bottles following the traditional method, and they remain in contact with the yeast lees in a bottle. The first fermentation transforms grape must into base wine. The essence of the traditional method is the second fermentation, which takes place in the bottle and increases the alcohol content and internal bottle pressure (up to 5–7 atmospheres). After this second alcoholic fermentation, the wine is aged on yeast lees for at least 9 months (EC Regulation N° 606/2009) [2]. Autolysis of the yeast occurs during this prolonged contact and involves hydrolytic enzymes that act to release cytoplasmic (peptides, fatty acids, nucleotides, amino acids) and cell wall (mannoproteins) compounds into the wine. This aging on yeast lees leads to significant changes in wine composition and the organoleptic and foam properties of the wine are modified [3].

In sparkling wines the level of dissolved carbon dioxide (CO<sub>2</sub>) found in the liquid phase is indeed a parameter of paramount importance. CO<sub>2</sub> is responsible for the visually appealing, and very much sought-after repetitive bubbling process (the so-called effervescence). In fact, foam is the characteristic that differentiates sparkling wines from still wines, being the first sensory attribute that tasters and consumers perceive and that determines the final quality of sparkling wines [4]. Moreover, dissolved CO<sub>2</sub> is also responsible for the very characteristic tingling sensation in aroma and mouthfeel sensations [5]. During carbonated beverage tasting, dissolved CO<sub>2</sub> acts on both trigeminal receptors [6], and gustatory receptors, via the conversion of dissolved CO<sub>2</sub> to carbonic acid [7], in addition to the tactile stimulation of mechanoreceptors in the oral cavity (through bursting bubbles). Moreover, a link has been evidenced between carbonation and the release of some aroma compounds in carbonated waters [8].

The formation of foam, its stability and the size of the bubbles in sparkling wines are directly related to the surface tension. This can be defined as the force per unit area that maintains the bond between the molecules at the surface of the liquid. The presence of surfactants reduces the surface tension of the liquid and allows to the formation and persistence of bubbles. Secondary fermentation in sparkling wines leads to the formation of carbon dioxide, which increases the pressure inside the bottle and causes the gas to dissolve in the liquid. When the bottle is opened, the difference between the pressure in the bottle and that of the atmosphere causes the dissolved gas to spontaneously leave the liquid. Once the pressure on the surface of the liquid has been equalized with the atmospheric pressure, bubbles continue to form inside the liquid [9].

Currently, the quality of sparkling wine is linked to the formation and persistence of foam. Quality foam can be defined as one that causes a slow release of CO<sub>2</sub>, in ring shapes from the depths of the liquid, with small bubbles that contribute to the formation of a crown over the surface of the wine, covering it completely, and with bubbles two or three rows deep [10]. Foam duration is directly related to bubble stability, and stability is itself dependent on the

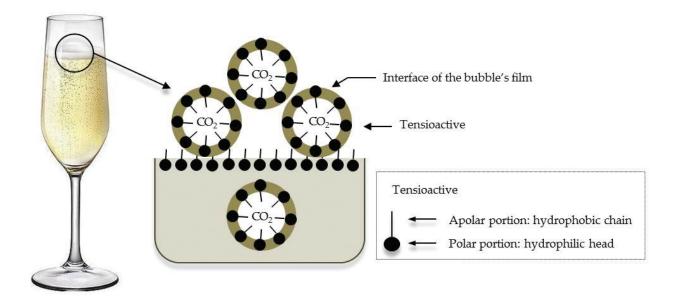


Figure 1. Carbon dioxide/liquid interphase of the bubble's film. Adapted from Ref. [11].

composition of the film that supports it [11]. In sparkling wines, bubbles consist of gas surrounded by a film of wine constituents. These tensioactive components and other substances afford viscosity to the film, giving texture to the bubble (**Figure 1**) [4]. In fact, it was established that foaming properties depend on compounds that decrease surface tension and increase the viscosity of the film between the bubbles. This factor contributes to foam stabilization and renders the bubbles more resistant to coalescence [12, 13].

In brief, foam formation and persistence is directly dependent upon its chemical composition, and the synergistic interaction among numerous foam active compounds which, due to aggregation or complex formation, may modify their surface-active properties. For this reason, and in order to ascertain which compounds affect foam quality, it is necessary to evaluate as many compounds as possible. In this sense, several scientific studies have been carried out in an attempt to determine the wine compounds that could play a role in the foam properties of sparkling wines. Many of these studies carried out in model solutions and in base and sparkling wines, are summarized in the reviews made by several authors [11, 14]. The present chapter increases the knowledge on this topic and reviews the latest studies made to determine the influence of proteins, peptides, amino acids, polysaccharides, phenolic compounds, lipids, organic acids and others on the foamability and foam stability of sparkling wines.

#### 2. Measuring of foaming properties of sparkling wines

Most of the studies published in the literature on sparkling wine foam quality are aimed at establishing the effect of the chemical composition of grape juices, base wines and sparkling

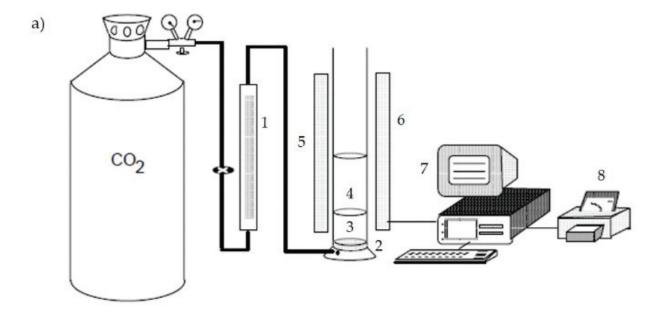
wines on their foaming properties. In order to correlate the foaming properties with the physical and chemical characteristics of sparkling wines, much effort has been made to find instrumental techniques that can be used to obtain a quantifiable value for foam quality, and consequently to be able to compare sparkling wines. Among them, methods based on measuring the kinetics of CO<sub>2</sub> discharging, gas sparging methods, and image analysis methods are some of the most often employed [15].

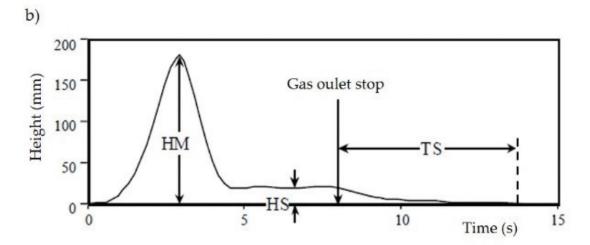
An automated equipment, called "Mosalux" was designed to measure the foaming properties of wines [16]. This apparatus was adapted from that described by Rudin [17] and allows measurement of the increase with time of the height of a wine foam column submitted to a definite effervescence [16]. In fact, this is an objective and normalized method based on the interruption of a beam of ultra red light by the foam produced after the injection of CO<sub>2</sub> into the wine. Three parameters can be measured.

- HM: maximum height reached by the foam after carbon dioxide injection through the glass frit, expressed in mm; this could represent the foam-ability, the wine's ability to foam.
- HS: foam stability height during carbon dioxide injection, expressed in mm; this could represent the foam stability, the wine's ability to produce stable foam or persistence of foam collar.
- TS: foam stability time, until all bubbles collapse, when CO<sub>2</sub> injection is interrupted, expressed in s; this could represent the foam stability time, once effervescence has decreased.

**Figure 2** shows the description of the "Mosalux" equipment and an example of the plot generated during a foam measurement.

The "Mosalux" equipment has been the most widely used since 1990 and in addition to research laboratories. It is probably the most used instrumental system in sparkling wine cellars for foam characterization. Moreover, a good relationship has been established between the foaming properties obtained by using "Mosalux" and foam sensory analysis [18]. The "Mosalux" apparatus has also been used to determine other parameters such as the expansion of foam E, the Bickerman coefficient  $\Sigma$  [19] (lifetime of a bubble in dynamic conditions, when formation and destruction of bubbles are balanced), and the lifetime of foam LF [20]. When comparing the different foam parameters (HM, HS, TS, E, LF, and  $\Sigma$ ) obtained by the gas sparging method, it was concluded that the best parameters to characterize the foam capacities of wines were HM,  $\Sigma$ , and TS [21]. Other variation of this system uses an ultrasound emitter-detector and a waveguide to detect foam fluctuations [22, 23] to obtain Hpeak (maximum height reached by the foam after air injection through a glass frit). Hpeak has been related to the wine's ability for foaming and Hplato (foam height stability during air injection) has been related to the average bubble lifetime. Correlation between the results obtained with this technique and sensory analysis has also been established [24].





**Figure 2.** (a) Diagram of the "Mosalux" equipment. (1) Flowmeter, (2) test tube, (3) wine, (4) foam, (5) infrared emitter, (6) infrared receiver, (7) personal computer, (8) printer; (b) example of a foam profile of a sparkling wine.

#### 3. Impact of wine macromolecules on the sparkling wine foam quality

**Table 1** includes a summary of the compounds that have been related to foam properties in the different scientific studies published, making reference to the type of sample used: model wine, grape juice, base wine, sparkling wine or isolated foam.

**Table 2** shows the correlations (r) at significance level (p < 0.05) between parameters that determine foam properties (HM, HS, TS, Peak H and Plateau H) and the chemical composition of grape juices, base wines and sparkling wines.

Compounds	Type of sample	Results	References
Proteins	Model wine	Increase foam	[67]
	Model wine	Increase foam height	[38]
	BW <sup>a</sup>	Increase foam height	[16]
	Separated foam	Increase foam	[34, 35]
	Model wine and BW <sup>a</sup>	Increase foam stability	[20]
	BW <sup>a</sup>	Increase foam height and foam stability	[39]
	BW <sup>a</sup> and SW <sup>a</sup>	Reduce foam height and increase foam stability	[29]
	$BW^a$	Increase foam height and reduce foam stability	[25]
	SW <sup>a</sup>	Increase foam height and foam stability	[40]
	Grape juice	Increase foam height	[12]
	$BW^a$	Increase foam height and reduce foam stability	[26]
	SW <sup>a</sup>	Increase foam height, foam stability height and decrease foam stability time	[41]
	Grape juice and BW <sup>a</sup>	Increase foam height	[42]
	BW <sup>a</sup> and SW <sup>a</sup>	Increase foam height and foam height stability	[22]
	BW <sup>a</sup> and SW <sup>a</sup>	Increase foam height	[43]
	SW <sup>a</sup>	Increase foam height	[44]
	$BW^a$	Increase foam height	[45]
	SW <sup>a</sup>	Increase foam height stability	[24]
	$BW^a$	Increase foam height and foam stability	[46]
	SW <sup>a</sup>	Increase maximum height, foam height stability and effervescence	[23]
	$BW^a$	Increase foam stability	[70]
	BW <sup>a</sup> and SW <sup>a</sup>	Increase foam height and foam stability height	[47]
	SW <sup>a</sup>	Increase foam height and foam stability height	[48]
	BW <sup>a</sup> and SW <sup>a</sup>	Increase foam height and foam stability height	[27]
	Model wine	Cooperative effects between mannoproteins and the proteins of grape origin to improve foamability	[33]
	BW <sup>a</sup> and SW <sup>a</sup>	Increase foam height	[49]
	$BW^a$	Increase foam height	[50]
Peptides	BW <sup>a</sup> and SW <sup>a</sup>	No influence on foam height and foam height stability	[22]
	SWa	Improve foam height stability	[24]
Amino acids	$BW^a$	Decrease foam stability time	[25]
	SW <sup>a</sup>	Proline and glutamine increase foam height and foam stability height Decrease foam stability time	[41]
	BW <sup>a</sup> and SW <sup>a</sup>	Increase foam height and foam height stability	[22]
	$SW^a$	Increase maximum height, foam height stability and effervescence	[23]
	SW <sup>a</sup>	Increase foam height and foam stability height	[28]

Compounds	Type of sample	Results	References	
Polysaccharides	Model wine	Increase foam stability	[38]	
	Separated foam	Increase foam	[34]	
	BW <sup>a</sup> and SW <sup>a</sup>	Xylose in polysaccharides increase foam stability	[29]	
	$BW^a$	Increase foam height	[25]	
	SW <sup>a</sup>	Increase foam height and stability time	[40]	
	BW <sup>a</sup>	Total polysaccharides increase foam height and reduce foam stability time  Acid and neutral polysaccharides increase foam height	[26]	
	Grape juice and BW <sup>a</sup>	Total and neutral polysaccharides increase foam height	[42]	
	BW <sup>a</sup> and SW <sup>a</sup>	Increase foam height and foam height stability	[22]	
	BW <sup>a</sup> and SW <sup>a</sup>	Polysaccharides (Mr of 62,000–48,000, 13,000–11,000, and 3000 to 2000) increase foam height, and the Mr. 3000–2000 polysaccharide reduce foam stability	[43]	
	SW <sup>a</sup>	Total and acid polysaccharides decrease foam stability time	[66]	
	BW <sup>a</sup>	Reduce foam height	[45]	
	SW <sup>a</sup>	Mannoproteins increase maximum height, foam height stability and effervescence	[23]	
	Model wine and SW <sup>a</sup>	Increase foam height and foam height stability	[30]	
	Model wine	Increase foam stability	[56]	
	Model wine	Mannoproteins with low content of protein (5%) increase foam stability. Arabinogalactans and hydrophobic low molecular weight fraction (<1 kDa) increase foamability.	[32]	
	SW <sup>a</sup>	Mannoproteins, arabinogalactans and pectic polysaccharides (HMW) increase foam height, foam stability height and foam stability time	[31]	
	Model wine	Mannoproteins increase foamability	[33]	
	SW <sup>a</sup>	Mannoproteins and PRAG increase foam stability time	[28]	
	BW <sup>a</sup> and SW <sup>a</sup>	High molecular weight polysaccharides decrease foam height	[49]	
	BW <sup>a</sup>	Increase foam stability time	[50]	
Polyphenols	Model wine	(+)-catechin increase foamability and foam stability	[61]	
	SW <sup>a</sup>	Increase foam height and reduce foam stability	[40]	
	Grape juice	Total polyphenol increase foam height Nonflavonoid phenol increase foam height Flavonoid phenol increase foam height	[12]	
	$BW^a$	Non flavonoids phenols decrease foam stability time	[26]	
	Grape juice and BW <sup>a</sup>	Total polyphenols, ortodiphenols, flavonoids and nonflavonoids reduce foam stability time	[42]	
	BW <sup>a</sup>	Reduce foam height		
	SW <sup>a</sup>	Anthocyanins increase foam height and foam stability height Proanthocyanidins decrease foam height and foam stability height	[28]	
	$BW^a$	Increase foam stability time	[50]	

Compounds	Type of sample	Results	References
Lipids	BW <sup>a</sup>	C8 and C10 increase collar height and reduce stability foam	[16]
	Model wine and BW <sup>a</sup>	Lipids are only foam active compounds at low alcohol concentration	[64]
	BW <sup>a</sup> and SW <sup>a</sup>	Linoleic acid increase foam stability Palmitic acid increase foam height	[29]
	BW <sup>a</sup> and separated foam	C8, C10, and C12 reduce foam height. Ethyl esters of hexanoic, octanoic, and decanoic acids increase foam height.	[65]
	SW <sup>a</sup>	Monoacylglycerols of palmitic and stearic acids and glycerylethylene glycol fatty acid derivatives increase the promotion and stabilization of foam	[31]
Organic acids	Model wine and BW <sup>a</sup>	Tartaric acid increase foam	[20]
	BW <sup>a</sup> and SW <sup>a</sup>	Tartaric acid increase foam height	[29]
	BW <sup>a</sup>	Malic acid increase foam height Titratable acidity increase foam height Lactic acid decrease foam height Citric and galacturonic acid reduce foam stability time pH reduce foam stability time	[25]
	SW <sup>a</sup>	Malic acid increase foam height and reduce stability foam	
	Grape juice	pH increase foam height Total acidity decrease foam height	[40]
	SW <sup>a</sup>	Galacturonic acid decrease foam stability time	[12]
	BW <sup>a</sup>	Titratable acidity, malic acid increase foam height and reduce foam stability time  Lactic acid reduce foam height and increase foam stability time  Citric acid and galacturonic acid reduce foam stability time	[41]
	$BW^a$	Malic acid increase foam height	[26]
	SW <sup>a</sup>	Tartaric acid increase foam height pH decrease foam height Lactic acid decrease foam stability time	[45]
	BW <sup>a</sup> and SW <sup>a</sup>	Gluconic acid reduce foam height	[49]
Others	Separated foam	Iron increase foam	[34]
	Model wine and BW <sup>a</sup>	Glycerol increase foam	[20]
	BW <sup>a</sup> and SW <sup>a</sup>	Glucose increase foam height Total content of SO <sub>2</sub> reduce foam stability y-butyrolactone increase foam stability	[29]
	BW <sup>a</sup>	Acetaldehyde, ethyl acetate, diacetaldehyde and isoamylic alcohols reduce foam stability time Alcohol content increase foam height and foam stability height Glucose increase foam height and fructose reduce foam height	[25]
	Grape juice	Fructose, glucose and methanol increase foam height Free sulfur dioxide decrease foam height Soluble solid concentration and maturity index increase foam height	[12]
	BW <sup>a</sup>	Alcohol content increase foam height Turbidity increase foam height and reduce foam stability time	[26]

Compounds	Type of sample	Results	References
		Free sulfur dioxide increase foam height and reduce foam stability time Conductivity increase foam height and reduce foam stability time	
	SW <sup>a</sup>	Residual sugars and ethanolamine increase foam height and foam stability height Ethyl acetate decrease foam stability time	[41]
	SW <sup>a</sup>	Botrytis cinerea infection decrease foamability	[44]
	BW <sup>a</sup>	Alcohol concentration and total SO <sub>2</sub> reduce foam height	[45]
	SW <sup>a</sup>	Ethanol, volatile acidity and total $SO_2$ reduce foam height Volatile acidity and total $SO_2$ reduce foam stability time	[66]
	$BW^a$	Lysozyme have a protective effect on foaming properties	[71]
	Model wine	Botrytis cinerea protease activity decrease wine foaming properties	[69]
	$BW^a$	Botrytis cinerea infection decrease foamability and foam stability	[70]
	Model wine	Glycerol and glycerol plus ethyloctanoate increase foam height and foam stability time	[32]
	BW <sup>a</sup> and SW <sup>a</sup>	Ethanol content reduce foam height	[49]

Table 1. Compounds related to foam properties in sparkling wines.

<sup>a</sup>BW: base wines; SW: sparkling wines.

In the majority of the works shown in **Tables 1** and **2**, the chemical compounds have been related to the foam physical parameters obtained by the "Mosalux" device [12, 16, 25–28] or other variations of this method [20, 22–24, 29–33]. All studies have shown that the foam properties of sparkling wines mainly depend on the qualitative composition and quantitative content of surface active substances. The relation found between the foaming properties and the different wine macromolecules is detailed below.

#### 3.1. Proteins

Despite of the low concentration of proteins in sparkling wines (ranging from 4 to 16 mg/L) [14], previous works have shown that these compounds are largely involved in the foaming properties of sparkling wines due to their surfactant properties. Surfactant agents are inferred to stabilize foams by settling at the bubble's edge, with the hydrophobic side interacting with the gas phase and the hydrophilic side interacting with the aqueous liquid phase [34]. The behavior of proteins in the foam depends on their hydrophobicity, solubility (dependent on the isoelectric point and the pH of the wine), and molecular weight [35, 36]. The net charge of macromolecules depends on the pH [37]. The isoelectric point of the wine proteins is between 3.5 and 4.5 [35] and between 4.6 and 5.0 [29]. At the wine pH, 2.9, its proteins would be positively charged and could migrate to the wine/air interphase and to stabilize foam [20]. However, characterization of foaming proteins have showed that foam formation is dependent on protein hydrophobicity but not on their molecular weight or isoelectric point [34].

Proteins	Compounds	Type of sample	НМ	HS	TS	Peak H	Plateau H	References
SVW	Proteins	BW <sup>a</sup>	0.32		-0.51			[25]
BW   0.58		Grape juice	0.91					[12]
Maino acids		$SW^a$				0.62	0.49	[22]
Marino acids		BW <sup>a</sup>	0.31					[45]
Amino acids         SWa         0.85         0.63         SWB         28           Acid amino acids         SWa         0.85         0.63         SWB         28           Acid amino acids         SWa         0.85         0.68         SWB         28           Acid amino acids         SWa         0.85         0.68         SWB         28           Basic amino acids         SWa         0.66         0.64         0.48         28           Basic amino acids         SWa         0.66         0.64         0.48         28           Basic amino acids         SWa         0.66         0.64         0.48         228           Basic amino acids         SWa         0.66         0.64         0.48         228           Aspartic acid         SWa         0.66         0.62         0.67         1221           Bywa         SWa         0.46         0.71         1221           Glutamic acid         BWa         0.77         0.50         0.66         0.71         1221           Glutamic acid         BWa         0.77         0.54         0.66         0.71         1221           Serine         BWa         0.77         0.54         0.56 <td></td> <td>BW<sup>a</sup> and SW<sup>a</sup></td> <td>0.58</td> <td></td> <td></td> <td></td> <td></td> <td>[49]</td>		BW <sup>a</sup> and SW <sup>a</sup>	0.58					[49]
Amino acids         SWa         0.85         0.63         1         28         29         28         29         28         29         28         29         28         29         28         29         28         29         29         28         29         29         29         29         29         29		BW <sup>a</sup> and SW <sup>a</sup>	0.44					[43]
Total amino acids         SW"         0.85         0.62         0.75         0.82         0.82         0.82         0.83		Grape juice	0.75					[42]
Acid amino acids         SW"         0.82         0.85         0.68         128           Neutral amino acids         SW"         0.85         0.68         128           Basic amino acids         SW"         0.75         0.62         128           Total biogenic amines         SW"         0.66         0.64         0.48         128           Aspartic acid         SW"         0.86         0.63         122         0.67         122           Hydroxyproline         BW"         """"""""""""""""""""""""""""""""""""	Amino acids							
Neutral amino acids         SW*         0.85         0.68         128           Basic amino acids         SW*         0.75         0.62         228           Total biogenic amines         SW*         0.66         0.64         0.48         28           Aspartic acid         SW*         0.86         0.63         20.52         0.67         122           Hydroxyproline         BW*         -0.39         -0.39         25         28           Glutamic acid         BW*         -0.46         -0.50         25         28           Glutamic acid         BW*         -0.50         0.66         0.71         122         28           Serine         BW*         0.77         0.54         0.46         0.71         122         28           Serine         BW*         0.77         0.54         0.46         0.71         122         25         28           Serine         BW*         0.62         0.59         0.58         0.66         0.68         122         25         28         28         28         28         28         28         28         28         28         28         28         28         28         28         28 <td< td=""><td>Total amino acids</td><td>SW<sup>a</sup></td><td>0.85</td><td>0.63</td><td></td><td></td><td></td><td>[28]</td></td<>	Total amino acids	SW <sup>a</sup>	0.85	0.63				[28]
Basic amino acids   SW <sup>a</sup>   0.75   0.62	Acid amino acids	SW <sup>a</sup>	0.82	0.58				[28]
Total biogenic amines       SW <sup>a</sup> 0.66       0.64       0.48       1.28       1.28         Aspartic acid       SW <sup>a</sup> 0.86       0.63       0.52       0.67       122         Hydroxyproline       BW <sup>a</sup> 0.86       0.63       -0.39       1.28       1.28         Hydroxyproline       BW <sup>a</sup> 0.46       -0.50       1.28       1.28         Glutamic acid       BW <sup>a</sup> 0.67       0.50       0.60       0.71       122         Sw <sup>a</sup> 0.77       0.54       0.46       0.71       122         Swan       0.79       0.54       0.46       0.71       122         Swan       0.62       0.59       0.58       1.28       1.28         Asparagine       BW <sup>a</sup> 0.62       0.59       0.58       1.28       1.28         Glycine       SW <sup>a</sup> 0.69       0.59       0.58       1.29       1.28       1.28         Glycine       SW <sup>a</sup> 0.88       0.66       0.35       1.22       1.28       1.28       1.28       1.28       1.28       1.28       1.28       1.28       1.28       1.28       1.28       1.28       1.28       1.28       1.28	Neutral amino acids	SW <sup>a</sup>	0.85	0.68				[28]
Aspartic acid SWa 0.86 0.63	Basic amino acids	SW <sup>a</sup>	0.75	0.62				[28]
Swa	Total biogenic amines	SW <sup>a</sup>	0.66	0.64	0.48			[28]
Flydroxyproline   Flydroxypr	Aspartic acid	SW <sup>a</sup>				0.52	0.67	[22]
SW <sup>a</sup>   0.46		SW <sup>a</sup>	0.86	0.63				[28]
Sumana   S	Hydroxyproline	BW <sup>a</sup>			-0.39			[25]
SWa       0.66       0.71       [22]         Serine       SWa       0.77       0.54       0.46       0.71       [22]         Serine       BWa       0.77       0.54       0.46       0.71       [22]         Swa       0.62       0.59       0.58       28]       [28]         Asparagine       BWa       0.62       0.59       0.58       28]       [25]         Swa       0.79       0.68       0.45       0.41       0.57       [22]         Swa       0.88       0.66       0.35       [28]       [25]         Glutamine       Bwa       0.37       0.36       28       [25]         Swa       0.88       0.66       0.35       28       [25]         Histidine       Swa       0.42       0.50       0.48       [22]         Threonine       Swa       0.56       0.42       0.50       0.48       [22]         Poline       Bwa       0.56       0.42       0.58       0.69       [25]		SW <sup>a</sup>	0.46					[28]
Serine       SWa       0.77       0.54       0.46       [28]         Serine       BWa       -0.425       [25]         SWa       0.62       0.59       0.56       0.68       [22]         Asparagine       BWa       -0.39       0.58       [25]         Swa       0.79       0.68       0.41       0.57       [22]         Swa       0.79       0.68       0.41       0.57       [22]         Swa       0.88       0.66       0.35       [28]         Glutamine       Bwa       0.37       -0.36       [25]         Swa       0.41       0.57       [22]         Swa       0.37       -0.36       [25]         Histidine       Swa       0.42       0.42       [28]         Histidine       Swa       0.56       0.42       0.50       0.48       [22]         Threonine       Swa       0.56       0.42       0.58       0.69       [25]	Glutamic acid	$BW^a$			-0.50			[25]
Serine       BWa       -0.425       [25]         SWa       0.62       0.59       0.56       0.68       [22]         Asparagine       BWa       0.62       0.59       0.58       [25]         Swa       0.79       0.68       0.41       0.57       [22]         Glycine       Bwa       0.79       0.68       0.45       [25]         Swa       0.88       0.66       0.35       [25]         Glutamine       Bwa       0.37       -0.36       [25]         Swa       0.37       -0.36       [25]         Swa       0.42       0.53       [22]         Histidine       Swa       0.56       0.42       0.50       0.48       [22]         Threonine       Swa       0.56       0.42       0.58       0.69       [25]		SW <sup>a</sup>				0.66	0.71	[22]
SWa		SW <sup>a</sup>	0.77	0.54	0.46			[28]
SWa	Serine	$BW^a$			-0.425			[25]
Asparagine BW <sup>a</sup> -0.38 [25]  SW <sup>a</sup> 0.79 0.68 0.45 [28]  Glycine BW <sup>a</sup> 0.88 0.66 0.35 [28]  Glutamine BW <sup>a</sup> 0.37 -0.36 [25]  SW <sup>a</sup> 0.41 0.57 [22]  SW <sup>a</sup> 0.88 0.66 0.35 [28]  Glutamine BW <sup>a</sup> 0.37 -0.36 [25]  SW <sup>a</sup> 0.50 0.42 [28]  Histidine SW <sup>a</sup> 0.56 0.42 [28]  Proline BW <sup>a</sup> 0.34 0.58 0.69 [25]		SW <sup>a</sup>				0.56	0.68	[22]
SWa		SW <sup>a</sup>	0.62	0.59	0.58			[28]
SWa 0.79 0.68 0.45 [28]  BWa -0.39 0.41 0.57 [22]  SWa 0.88 0.66 0.35 [28]  Glutamine BWa 0.37 -0.36 [25]  SWa 0.88 0.66 0.35 [25]  SWa 0.88 0.66 0.35 [25]  Histidine SWa 0.42 [28]  Threonine SWa 0.56 0.42 [28]  Proline BWa 0.34 0.58 0.69 [25]	Asparagine	BW <sup>a</sup>			-0.38			[25]
Glycine       BWa       -0.39       [25]         SWa       0.41       0.57       [22]         SWa       0.88       0.66       0.35       [28]         Glutamine       BWa       0.37       -0.36       [25]         SWa       0.53       [22]         SWa       0.42       [28]         Histidine       SWa       0.56       0.42       [28]         Proline       BWa       0.34       0.58       0.69       [25]		SW <sup>a</sup>				0.41	0.57	[22]
SWa       0.41       0.57       [22]         SWa       0.88       0.66       0.35       [28]         Glutamine       BWa       0.37       -0.36       [25]         SWa       0.53       [22]         SWa       0.42       [28]         Histidine       SWa       0.56       0.42       0.50       0.48       [22]         Threonine       SWa       0.56       0.42       [28]       [28]         Proline       BWa       0.34       0.58       0.69       [25]		SW <sup>a</sup>	0.79	0.68	0.45			[28]
SWa 0.88 0.66 0.35 [28]  Glutamine BWa 0.37 -0.36 [25]  SWa 0.42 [28]  Histidine SWa 0.42 [28]  Threonine SWa 0.56 0.42 [28]  Proline BWa 0.34 0.58 0.69 [25]	Glycine	BW <sup>a</sup>			-0.39			[25]
Glutamine BWa 0.37 -0.36 [25] SWa 0.42 [28] Histidine SWa 0.56 0.42 [28] Proline BWa 0.37 -0.36 [25]		SW <sup>a</sup>				0.41	0.57	[22]
SWa       0.53       [22]         SWa       0.42       [28]         Histidine       SWa       0.50       0.48       [22]         Threonine       SWa       0.56       0.42       [28]         Proline       BWa       0.34       0.58       0.69       [25]		SW <sup>a</sup>	0.88	0.66	0.35			[28]
SWa     0.42     [28]       Histidine     SWa     0.50     0.48     [22]       Threonine     SWa     0.56     0.42     [28]       Proline     BWa     0.34     0.58     0.69     [25]	Glutamine	BW <sup>a</sup>	0.37		-0.36			[25]
Histidine SW <sup>a</sup> 0.50 0.48 [22] Threonine SW <sup>a</sup> 0.56 0.42 [28] Proline BW <sup>a</sup> 0.34 0.58 0.69 [25]		$SW^a$					0.53	[22]
Threonine SW <sup>a</sup> 0.56 0.42 [28] Proline BW <sup>a</sup> 0.34 0.58 0.69 [25]		SW <sup>a</sup>			0.42			[28]
Proline BW <sup>a</sup> 0.34 0.58 0.69 [25]	Histidine	$SW^a$				0.50	0.48	[22]
	Threonine	SW <sup>a</sup>	0.56	0.42				[28]
$SW^a$ [22]	Proline	$BW^a$		0.34		0.58	0.69	[25]
		SW <sup>a</sup>						[22]

Compounds	Type of sample	HM	HS	TS	Peak H	Plateau H	References
	SW <sup>a</sup>	0.82	0.60	0.34			[28]
Histamine	SW <sup>a</sup>	0.39	0.42	0.43			[28]
GABA	$BW^a$			-0.38			[25]
	SW <sup>a</sup>				0.52	0.60	[22]
	SW <sup>a</sup>	0.77	0.52				[28]
Arginine	BW <sup>a</sup>			-0.36			[25]
	SW <sup>a</sup>				0.50	0.62	[22]
	SW <sup>a</sup>	0.83	0.65				[28]
lpha alanine	SW <sup>a</sup>				0.53	0.63	[22]
	$BW^a$			-0.37			[25]
	SW <sup>a</sup>	0.83	0.65	0.39			[28]
B alanine	SW <sup>a</sup>	0.92	0.55				[28]
Tyrosine	$BW^a$			-0.53			[25]
	SW <sup>a</sup>				0.49	0.63	[22]
	SW <sup>a</sup>	0.81	0.60				[28]
Valine	$BW^a$			-0.50			[25]
	$SW^a$				0.52	0.67	[22]
Methionine	$BW^a$			-0.34			[25]
	$SW^a$				0.51	0.63	[22]
	SW <sup>a</sup>	0.89	0.58				[28]
Cysteine	SW <sup>a</sup>	0.79	0.49				[28]
Isoleucine	$BW^a$						[25]
	SW <sup>a</sup>	0.67	0.64	0.47			[28]
Leucine	$BW^a$			-0.34			[25]
	SW <sup>a</sup>				0.51	0.64	[22]
	SW <sup>a</sup>	0.42	0.55	0.55			[28]
Phenylalanine	BW <sup>a</sup>			-0.29			[25]
	SW <sup>a</sup>				0.42	0.62	[22]
	SW <sup>a</sup>	0.84	0.62	0.36			[28]
Ornithine	$BW^a$			-0.31			[25]
	SW <sup>a</sup>	0.79	0.64				[28]
Tryptophan	$BW^a$			-0.37			[25]
	SW <sup>a</sup>	0.85	0.59				[28]
Lysine	$BW^a$			-0.36			[25]
	SW <sup>a</sup>					0.52	[22]
	$SW^a$	0.66	0.61				[28]

Compounds	Type of sample	HM	HS	TS	Peak H	Plateau H	References
Spermidine	SW <sup>a</sup>	0.72	0.41				[28]
Tyramine	SW <sup>a</sup>			0.35			[28]
Putrescine	SW <sup>a</sup>	0.51	0.59	0.43			[28]
Cadaverine	SW <sup>a</sup>	-0.35					[28]
Phenylethylamine	SW <sup>a</sup>		0.60				[28]
Isoamylamine	SW <sup>a</sup>	-0.55					[28]
Polysaccharides							
Total polysaccharides	Grape juice	0.55					[42]
	BW <sup>a</sup>	0.40					[42]
	SW <sup>a</sup>				0.80	0.68	[22]
	SW <sup>a</sup>			0.64			[28]
Polysaccharides from yeasts	SW <sup>a</sup>			0.53			[28]
Polysaccharides from grapes	SW <sup>a</sup>			0.68			[28]
Neutral polysaccharides	Grape juice	0.65					[42]
	BW <sup>a</sup>	0.46					[42]
	SW <sup>a</sup>				0.82	0.71	[22]
Acid polysaccharides	BW <sup>a</sup>	-0.76					[45]
High molecular weight polysaccharides	BW <sup>a</sup> and SW <sup>a</sup>	-0.65					[49]
Polysaccharides Molecular Mass 62,000–48,000	BW <sup>a</sup> and SW <sup>a</sup>	0.51					[43]
Polysaccharides Molecular Mass 13,000–11,000	BW <sup>a</sup> and SW <sup>a</sup>	0.46					[43]
Polysaccharides Molecular Mass 3000–2000	BW <sup>a</sup> and SW <sup>a</sup>	0.32					[43]
Mannoproteins	SW <sup>a</sup>			0.47			[28]
Polysaccharides rich in arabinose and galactose	SW <sup>a</sup>			0.72			[28]
Homogalacturonans	SW <sup>a</sup>			0.58			[28]
Glucans	SW <sup>a</sup>			0.40			[28]
Polyphenols							
Absorbance 520 (nm)	$BW^a$			-0.35			[25]
Absorbance 280 (nm)	Grape juice	0.92					[12]
	$BW^a$			-0.63			[42]
Total polyphenol	Grape juice	0.76					[12]
	$BW^a$			-0.60			[42]
	$BW^a$	-0.45					[45]
Total proanthocyanidins	SW <sup>a</sup>	-0.73					[28]

Compounds	Type of sample	HM	HS	TS	Peak H	Plateau H	References
Nonflavonoid phenol	Grape juice	0.59					[12]
	$BW^a$			-0.33			[42]
Total flavan-3-ols	$SW^a$	0.50		0.42			[28]
Flavonoid phenol	Grape juice	0.52					[12]
	BW <sup>a</sup>			-0.64			[42]
Ortodiphenols	BW <sup>a</sup>			-0.49			[42]
Total monomeric anthocyanins	SW <sup>a</sup>	0.96	0.80				[28]
Non-acylated anthocyanins	SW <sup>a</sup>	0.97	0.81				[28]
Acetyl-glucoside anthocyanins	SW <sup>a</sup>	0.94	0.75				[28]
Coumaryl-glucoside anthocyanins	SW <sup>a</sup>	0.88	0.67				[28]
delphinidin-3-glucoside	$SW^a$	0.94	0.71				[28]
cyanidin-3-glucoside	SW <sup>a</sup>	0.84	0.60				[28]
petunidin-3-glucoside	SW <sup>a</sup>	0.95	0.73				[28]
peonidin-3-glucoside	SW <sup>a</sup>	0.87	0.65				[28]
malvidin-3-glucoside	SW <sup>a</sup>	0.98	0.85				[28]
delphinidin-3-(6-acetyl)-glucoside	SW <sup>a</sup>	0.91	0.67				[28]
cyanidin-3-(6-acetyl)-glucoside	SW <sup>a</sup>	0.89	0.62				[28]
petunidin-3-(6-acetyl)-glucoside	$SW^a$	0.92	0.69				[28]
peonidin-3-(6-acetyl)-glucoside	SW <sup>a</sup>	0.89	0.65				[28]
malvidin-3-(6-acetyl)-glucoside	$SW^a$	0.89	0.92				[28]
delphinidin-3-(6-p-coumaryl)-glucoside	SW <sup>a</sup>	0.76	0.52				[28]
cyanidin-3-(6-p-coumaryl)-glucoside	SW <sup>a</sup>	0.92	0.68				[28]
petunidin-3-(6- <i>p</i> -coumaryl)-glucoside	$SW^a$	0.78	0.55				[28]
peonidin-3-(6-p-coumaryl)-glucoside	$SW^a$	0.91	0.67				[28]
malvidin-3-(6-p-coumaryl)-glucoside	SW <sup>a</sup>	0.94	0.76				[28]
cis-caftaric	SW <sup>a</sup>	-0.65					[28]
trans-fertaric	SW <sup>a</sup>	0.35					[28]
coumaric acid	$SW^a$	0.77	0.37				[28]
ferulic acid	SW <sup>a</sup>	-0.39		-0.41			[28]
gallic acid	SW <sup>a</sup>	0.62					[28]
(+)-catechin	$SW^a$	0.50		0.42			[28]
quercetin-3-rutinoside	$SW^a$	-0.43					[28]
myricetin	$SW^a$		0.36				[28]
quercetin	SW <sup>a</sup>	0.58					[28]
kaempferol	SW <sup>a</sup>			0.53			[28]
isorhamnetin	SW <sup>a</sup>	0.84					[28]

Compounds	Type of sample	HM	HS	TS	Peak H	Plateau H	References
Lipids							
C8 (n = 28)	BW <sup>a</sup> and separated foam	-0.43					[65]
C10 (n = 28)	BW <sup>a</sup> and separated foam	-0.66					[65]
C12 (n = 28)	BW <sup>a</sup> and separated foam	-0.57					[65]
Ethyl hexanoate (n) 28	BW <sup>a</sup> and separated foam	0.65					[65]
Ethyl octanoate (n) 28	BW <sup>a</sup> and separated foam	0.86					[65]
Ethyl decanoate (n) 28	BW <sup>a</sup> and separated foam	0.90					[65]
Organic acids							
Titratable acidity	BW <sup>a</sup>	0.46					[25]
	Grape juice	-0.59					[12]
pH	BW <sup>a</sup>			-0.32			[25]
	Grape juice	0.71					[12]
Citric acid	$BW^a$			-0.38			[25]
Galacturonic acid	BW <sup>a</sup>			-0.42			[25]
Malic acid	BW <sup>a</sup>	0.46					[25]
	BW <sup>a</sup>	0.40					[45]
Lactic acid	BW <sup>a</sup>	-0.43					[25]
Gluconic acid	BW <sup>a</sup> and SW <sup>a</sup>	-0.36					[49]
Others							
Alcohol content	BW <sup>a</sup>	0.47	0.46				[25]
	BW <sup>a</sup>	-0.47					[45]
	BW <sup>a</sup> and SW <sup>a</sup>	-0.92					[49]
Glucose	BW <sup>a</sup>	-0.31					[25]
	Grape juice	0.58					[12]
Fructose	$BW^a$	0.56	0.32				[25]
	Grape juice	0.73					[12]
Ethanolamine	$BW^a$		0.31				[25]
Acetaldehide	$BW^a$			-0.35			[25]
Ethyl acetate	BW <sup>a</sup>			-0.51			[25]
Diacetaldehyde	BW <sup>a</sup>			-0.36			[25]
Isoamylic alcohols	$BW^a$			-0.43			[25]
•							=

Compounds	Type of sample	HM HS TS	Peak H Plateau H References
Maturity index	Grape juice	0.78	[12]
Soluble solid concentration	Grape juice	0.75	[12]
Methanol	Grape juice	0.80	[12]
Free sulfur dioxide	Grape juice	-0.65	[12]
Total sulfur dioxide	BW <sup>a</sup>	-0.68	[45]
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**Table 2.** Correlation coefficients (r) at significance levels (p < 0.05) between parameters that determine foam properties (HM, HS, TS, Peak H and Plateau H) and the chemical composition of grape juices, base wines and sparkling wines.

Proteins have been the most studied compounds in relation to wine foamability. Most studies indicate a positive influence of protein content on foam height in grape juices, base wines and sparkling wines [16, 20, 22–27, 38–50] (**Tables 1** and **2**). Some of this studies showed positive correlations between proteins and parameter HM [12, 25, 42, 43, 45, 49], Peak H, and Plateau H [22]. The highest correlations between proteins and foamability parameters were observed in juices of white grapes (r > 0.75) [12, 42]. Correlation between proteins and foamability parameters was lower in base wines and sparkling wines [22, 25, 43, 45, 49] (**Table 2**). The work conducted in Spanish sparkling wines was an exception to this because authors observed a negative relation between proteins and foam height [29].

The correlations between proteins and foam stability have shown contradictory results. Therefore, some proteins have been described as good foam formers but poor stabilizers, while others are poor foam formers but good stabilizers [13, 20, 25, 26, 29, 39, 41]. Inverse relationship between HM and TS [16, 25, 26] could justify that proteins may be active agents on foamability but may not sustain a foam collar for a long time.

The influence of specific proteins on foam quality has also been studied in several research papers. Grape invertase is one of the most abundant protein present in wine (from 9 to 14% of the total protein content of a Chardonnay wine) [51]. This grape protein possesses a pI close to the pH of wine and a high hydrophobicity, potentially conferring good surface properties on this protein [51]. Significant decreases in the invertase content in base wines have been shown to correlate with decreases in foam height and foam stability [46]. Other grape proteins, such as thaumatin-like proteins and chinases, did not contribute alone to the formation and stabilization of foam; however, when synergistically acting with mannoproteins, foam height was found to be maximized [33]. On the other hand, the release of proteins from the yeast cells prior to autolysis has also been shown to contribute to foam height and foam stability height in sparkling wines [23, 24, 47].

#### 3.2. Peptides

<sup>a</sup>BW: base wines; SW: sparkling wines.

The hydrophobicity of peptides may be related to the quality of sparkling wine foam [52, 53]. Proteins and peptides with molecular weight within 24–60 kDa, even in low concentrations,

provide for the foam formation in base wine [13, 31, 47] since they form adsorption layers with high mechanical strength and, as a result, increase the stability of the sparkling wine foam. In fact, a positive correlation has been reported between polypeptide molecular mass, hydrophobicity and foam stabilizing activity in beer [54, 55]. Although no correlations have been found between peptides and foam properties of sparkling wines [22], bentonite added to the tirage solution produced a reduction in both protein and peptide contents and thereby negatively affected foaming properties [24] (**Table 1**).

#### 3.3. Amino acids

In addition to proteins and peptides, some authors agree in considering amino acids as foaming agents. At wine pH, amino acids carry a net positive charge, so they are surfactant with hydrophilic and hydrophobic groups. This property causes amino acids to be retained in the air/liquid interface, and thus reduces the wine surface tension, improving the sparkling wine ability to foam [28].

Moreno-Arribas et al. [22] showed positive correlations between free amino acids and white sparkling wine foamability (**Tables 1** and **2**). The authors observed that maximum height (Peak H) was significantly correlated with most of the amino-acids, although coefficients of over 0.60 were only found for glutamic acid (r = 0.66). Moreover, Plateau H (associated to bubble lifetime) was highly correlated with glutamic acid (r = 0.71), serine (r = 0.68), valine (r = 0.67) and proline (r = 0.69). Lower positive correlations were found by Andrés-Lacueva et al. [25] in white base wines between glutamine and proline and foamability parameters.

Other study conducted by our research group in white and rosé sparkling wine showed the highest positive correlations between total amino acids and foam height (r = 0.85) and total amino acids and foam stability height (r = 0.63) [28] (**Table 2**). Biogenic amines showed the same behavior as amino acids, although lower correlation values were observed [28] (**Table 2**). When comparing the different amino acids analyzed, glycine,  $\beta$ -alanine, and methionine had the highest correlation with foam height (r > 0.88) [28] (**Table 2**). In general, amino acids with non-polar side chains showed higher values of correlation than amino acids with polar side chains. At wine pH, amino acids are protonated and they act as cationic surfactants according to the hydrophobicity of their side chains. Their amphiphilic character could cause amino acids to become concentrated at the liquid–gas interfaces, improving the sparkling wine foamability [28].

Negative correlations have been observed between amino acids and foam stability time in base wines [25] (**Tables 1** and **2**). However, conflicting results have been published on the influence of amino acid on foam stability of sparkling wines. It has shown that lower levels of amino acids favors a greater stability time of foam [41]; while other authors did not found any influence of these compounds on the foam stability time [28].

It was confirmed that the autolytic capacity of yeast was important for the quality of sparkling wines [23]. The use of a mutant having accelerated autolysis showed that the second fermentation of wines with this mutant improved the foaming properties versus a control strain due to

higher increase in both nitrogen compounds (proteins, peptides and amino acids) and polysaccharides [23].

#### 3.4. Polysaccharides

Contradictory results have been published on the effect of polysaccharides on foam quality. Girbau Sola et al. [45] showed a negative influence of acid polysaccharides on foam height in base wines (r = -076). The same authors showed that polysaccharides were negatively correlated with foam stability but positively with the average bubble lifetime or Bikerman's coefficient [45]. Similarly, polysaccharides with a molecular weight higher than 180 kDa have also shown a negative influence on foam height (r = -0.65), although these authors associated the negative contribution with the presence of  $\beta$ -glucans secreted by *Botrytis cinerea* and stated that other polysaccharides probably would not have a negative effect [49] (**Tables 1** and **2**).

In contrast with the results described above, most studies point to a positive influence of total polysaccharides on both foamability [22, 25, 26, 40, 42] and foam stability [28, 29, 50, 56] (**Table 1**). The relation of the molecular weight of polysaccharides and the foaming properties of wines has also been studied. Polysaccharides of molecular mass of 62 to 48 kDa; 13 to 11 kDa; and 3 to 2 kDa have been demonstrated to be active agents on foamability, and polysaccharides with molecular mass of 3 to 2 kDa might be a foam stability agent, since they were correlated with the Bikerman coefficient [43].

Among polysaccharides, glycoproteins like mannoproteins released by yeast during fermentation and autolysis, have been described as the major compounds affecting foaming properties [13, 23, 30, 33]. The hydrophobic nature of glycoproteins explains why they are better foam stabilizers and foam producers than non-glycosylated proteins. Glycoproteins present a protein moiety with hydrophobic and hydrophilic domains and sugar moieties, which are hydrophilic and they could interact with surface-active materials and be absorbed at the gas/liquid interface. The hydrophilic glycans are located at the liquid layer, among the bubbles, corresponding to the oxidic zone of the protein. Hence, when the layer surrounding the bubbles becomes thinner, the viscosity increases and drainage of the liquid is delayed. The hydrophobic polypeptides increase the surface tension of the bubbles, resulting in more stable foam [13]. In this sense, the literature has tried to explain the influence of mannoproteins on foaming properties. Mannoproteins also influence the viscosity of the bubble wall and reduces the drainage of the liquid [34]. Foaming may be due to their interactions with proteins [36] and their surface properties and capacity to reorientation quickly at the liquid/gas interface in the bubble when the foam is formed [20]. In fact, the proteinaceous fraction of mannoproteins is able to bind to the liquid/air interface and interact with other compounds by means of electrostatic or hydrophobic forces, hydrogen bonds, or covalent linkages [13]. These interactions could lead to the formation of a strong viscoelastic film that could be highly resistant to tension and able to withstand the film's thickness [13], preventing coalescence of bubbles and leading to more stable foams. As a matter of fact the presence of both glycocompounds and protein material deriving from macromolecular fractions of different molecular weights in the adsorption layer of the foam of sparkling wines has been reported [56], and the presence of aggregated materials involving yeast glycoproteins and other unidentified wine components has also been indicated as contributing to the foam stability of sparkling wines [57, 58]. In this sense, reconstitution experiments performed by adding in a model solution different molecular fractions isolated from wine indicated that a synergistic effect in foamability and foam stability exists between high and low molecular weight wine compounds [31]. The fraction most responsible for foam stability was mainly influenced by mannoproteins with low content of protein (5%) and the foamability by arabinogalactans and a hydrophobic low molecular weight fraction (< 1 kDa) [32].

The specific contribution of the different families of wine polysaccharides to the wine foaming properties has been recently studied by our research group [28]. Mannoproteins, glucans, polysaccharides rich in arabinose and galactose, rhamnogalacturonans type II, and homogalacturonans did not show any influence on the foamability of sparkling wines. On the contrary, positive influence was found between foam stability time and all wine polysaccharides, with the exception of rhamnogalacturonans type II. Surprisingly, polysaccharides rich in arabinose and galactose showed higher positive correlations on foam stability (r = 0.72) than mannoproteins (r = 0.47) [28] (Table 2).

#### 3.5. Polyphenols

It is widely known that polyphenols are highly reactive compounds. Some authors have tried to establish a correlation between them and the quality of foam in grape juices, base wines and sparkling wines. Polyphenols can interact with proteins and polysaccharides [36, 37], mainly the low molecular weight polyphenols [59], which participate in the hydration layer of the proteins [60]. Moreover, the formation of hydrogen bonds between the hydroxyl groups of the phenolic compounds and the polar head groups of proteins can be particularly relevant for the interaction with the air/liquid interface of the bubble film [61, 62]. These formed compounds could adsorb at the interface and form a stabilizing film around bubbles, which could promote foam formation [28].

Most of the studies carried out to correlate the influence of phenols on foam quality of sparkling wines have shown contradictory results [12, 26, 28, 40, 42, 45, 50, 61] (**Tables 1** and **2**). In fact, total phenolics did not shown correlation with any foam instrumental property in sparkling wines [28], but they showed a negative correlation with foam height in base wines (r = -0.45) [45], and a high positive correlation with foam height in grape juices (r = 0.76) [12]. Moreover, most of studies refer to global measurements of phenolic compounds, which could lead to inaccurate results difficult to understand. A recent study of our group has analyzed the relation of individual phenolics with foam parameters in white and rosé sparkling wines, which could be critical for their production [28].

The study concluded that each phenolic compound exhibits different behavior patterns on foam instrumental properties (**Table 2**). Non acylated, acetyl glucoside and coumaryl glucoside anthocyanins showed the highest positive correlations with foamability, with values

ranging from 0.67 to 0.97, but these compounds did not show any effect on the foam stability time. Authors attributed this effect to the interaction of anthocyanins with wine proteins through hydrophobic interactions and hydrogen bonds. Attachment of a long aliphatic chain could confer interesting surfactant behavior on flavylium cations. Therefore, the product formed could be retained in the liquid/air interface, resulting in a reduction of the interfacial tension and an increase in the foamability. On the other hand, total proanthocyanidins showed high negative correlation with sparkling wine ability to foam (r = -0.73). Since proteins play an important role on the foamability of sparkling wines, the negative correlation of proanthocyanidins with foam height could be due to the precipitation of wine proteins by tannins. *Cis*-caftaric was the hidroxicinamic acid most negatively correlated with foam height (r = -0.65), while coumaric acid showed the most positive effect (r = 0.77) and isorhamnetin was the flavonol with a major influence on foam height (r = 0.84).

#### 3.6. Lipids

Some authors describe that lipids can accumulate in the foam, reducing surface tension and stabilizing it [63]. However, the researches made in wines to establish the possible relationships among lipid content, fatty acids, and foam behavior have produced contradictory findings (Table 1). The addition of octanoic and decanoic fatty acids to wines had a negative effect on the foam stability time, but it positively influenced foam collar height [16]. However, the addition of a lipid mixture to wine did not affect their foam, but when the ethanol concentration was reduced, authors observed an adverse effect on bubble lifetime [64]. They concluded that linolenic acid and palmitic acid were, respectively, the best indicators of foam stability and foam height in base wines and sparkling wines respectively, both having a positive influence [29].

Moreover, it was studied the influence of fatty acids (free and bound as ethyl esters) on wine foaming in different white wines and separated foam (Tables 1 and 2). The free fatty acids C8, C10, and C12 were negatively correlated with foam height with values ranging from 0.43 to 0.66, whereas the ethyl esters of hexanoic, octanoic, and decanoic acids were positively related with values ranging from 0.65 to 0.90. These authors found that the value of foam height was directly proportional to the ratio of esterified to non-esterified fatty acids. So, the higher the coefficient, the greater the foamability; thus, it appeared that it was the esterified forms of fatty acids that increased foam height [65]. It was also shown that monoacylglycerols of palmitic and stearic acids and glycerylethylene glycol fatty acid derivatives were surface active compounds preferentially partitioned by the sparkling wine foam rather than the liquid phase, allowing the inference of their role as key components in the promotion and stabilization of sparkling wine foam [31].

#### 3.7. Organic acids

With regards to organic acids (**Tables 1** and **2**), López-Barajas et al. [12] observed low negative correlations between titratable acidity and foamability in grape juices of white varieties (r = -0.58). However, other studies showed that tartaric acid, titratable acidity and pH

increased foam height in grape juices, base and sparkling wines [12, 20, 25, 26, 29, 66]. In fact, pH and foamability in grape juices were highly correlated (r = 0.71) [12], while titratable acidity exhibited lower influence on foam height (r = 0.46) and foam stability time (r = -0.32) in white base wines [25]. In the same way, it was observed that acidity had a marked effect on foam since it modified protein solubility; if the juice acidity was low, protein hydrophobicity would be high, the surface activity could be increased, and then juice would have a higher foamability [35].

Different authors agree in pointing to malic acid as an enhancer of the foam height in base wines and sparkling wines [25, 26, 40, 45], but also stated that malic acid reduces foam stability time [26, 40]. On the contrary, lactic acid exerted the opposite effect on foam height [25, 26]. Malic acid and lactic acid showed low negative correlations with foam height [25, 45], which could indicate that malolactic fermentation is not recommended as a way to maximize foamability in sparkling wines. Moreover, conflicting results have been published on the influence of lactic acid on foam stability time. Some authors have observed a positive influence of lactic acid on foam stability in base wines [26], while others showed the opposite effect in sparkling wines [66]. Other acids such as citric and galacturonic acid reduced foam stability time in base and sparkling wines [25, 26, 41]. Moreover, the presence of gluconic acid due to *Botrytis cinerea* was shown to negatively affect wine foamability (r = -0.36) [49].

#### 3.8. Others

Several authors agree that sulfur dioxide negatively affect the foaming qualities of wines [12, 26, 29, 45, 66] due to SO<sub>2</sub> is a denaturing agent of proteins [16]. In fact, negative correlations have been obtained between free and total sulfur dioxide and foam height in grape juices and base wines [12, 45].

There is some controversy about the effect of ethanol content on foaming quality. Some authors consider that ethanol has beneficial effects on foam [25, 26] while others assign it negative contribution [45, 49, 66]. The negative effect of ethanol on foam seems to be dependent on its content [67]. This could be explained by the ethanol modification of the solvent properties, the interactions between the protein and the solvent, and the structure of the adsorption layer [68]. When the alcohol content is low, other surfactants can be more active and thus more easily adsorbed at the interface, stabilizing the foam formed [20, 64]. In this sense, higher alcohol content was reported to decrease foamability [16]; however, this effect could be counteracted by other compounds produced in the second fermentation. In this regard, juices with a maturation index [ratio between soluble solids (°Brix) and titratable acidity (grams of tartaric acid per litter of juice) ranging from 4 to 5.5 had high foamability [12]. In fact, it was observed a high positive correlation between foam height and maturation index (r = 0.78) [12]. Subsequently, these results were confirmed, showing that maturation indexes for foamability and stability above 5.5 provided the wine with a less optimal alcoholic content for the formation of foam than wine produced from grapes with a maturation index within the stated range [45].

Glycerol is known to contribute to the viscosity of the wines. Due to its tensoactive properties, glycerol has shown a positive influence on foamability in sparkling wines [20, 32]. On the other hand, iron [34] and residual sugars [25, 29, 41] have been related with an improvement of foamability in sparkling wines.

The effect of *Botrytis cinerea* on the foaming characteristics of sparkling wines has also been studied [44, 69, 70]. In these works, it was concluded that this infection can cause a drastic reduction in foamability, since it uses up the proteins in the medium.

Diverse studies have been published about the influence of stabilization treatments, either using clarifiers or filtrations, on the foam quality of wines [20, 24, 41, 46, 47, 71–74]. In all cases, the foams were negatively affected by these treatments, and this was directly correlated with a decrease in the protein concentration. On the contrary, lysozyme additions made to the musts and wines before and after bentonite or charcoal treatments seem to have a protective effect on the wine proteins, and thereby an increase in foamability [71].

Research conducted suggest that many compounds influence foam capacity of sparkling wines (**Tables 1** and **2**); however, the most influencing compounds on the foaming properties have proved to be total amino acids, polysaccharides, anthocyanins, coumaric acid and isorhamnetin, all of them showing correlation coefficients higher than 0.75 (**Table 2**). On the contrary, the alcohol content and the concentration of acid polysaccharides, proanthocyanidins and free SO<sub>2</sub> are the factors which most negatively affect foam quality (**Table 2**).

#### 4. Prediction of foaming properties

In view of the results shown in **Tables 1** and **2**, it can be concluded that foamability and foam stability is a complicated issue. In fact, the foaming capacity of wines depends on a complex equilibrium among all the compounds that favor its formation and stability and those that do not. There is not one compound or group of compounds that is responsible for making and keeping good quality foam. Instead, foam quality depends on a synergistic relationship between many different compounds that when acting together result in the foaming properties.

Foam behavior results from the synergistic interaction between the different foam active compounds which, due to aggregation or complex formation, may modify their surface-active properties. Thus, foaming properties not only are due to the presence or absence of a specific group of compounds but also are influenced by the net balance of the number and type of compounds ranging among different chemical structures. For this reason, and in order to ascertain which compounds have a major influence on the foam quality of sparkling wines, it is necessary to evaluate as many compounds together as possible, and to study the combined effect of all them. In this sense, statistical tools of multiple linear regression [12, 22, 26, 28, 75] and partial least squares regression analysis [29] has been used by several authors in an attempt to predict the foam properties of sparkling wines, and find out the chemical compound that provided the best predictive model of the foam properties.

Most of the studies include in the models all the variables that are usually analyzed in the wineries, and try to predict values for foamability, foam stability and Bickerman coefficient  $\Sigma$  [12, 26, 75]. Results of these researches have shown a great influence of proteins,  $SO_2$ , absorbance at 280 nm, glycerol and maturation index. Moreover, stepwise analysis showed that the foam height and Bickerman coefficient of sulphited grape juices could be predicted with a probability higher than 89.97% by the following polynomial equations (Eq. (1) and (2)) [12]:

$$HM = -126.80 + 1.04$$
Combined  $SO_2 + 16.85$ OD280 + 1.07Proteins - 44.40Glycerol (1)

$$\sum = 4.76 + 1.68 Maturation index - 5.48 Tartaric acid + 0.34 Glucose$$
 (2)

Other study conducted by Pueyo et al. [29] applied PLS regression to predict foam height and foam stability in base wines and sparkling wines using 73 chemical variables analyzed. Tartaric acid, glucose, total palmitoleic acid and protein content were the most influent variables in the prediction of foam height in base wines. However, total contents of oleic, palmitic, and stearic acids, and the content of 1-hexanol were the most important variables for predicting foam height in sparkling wines. With regards to foam stability, the variables with high predictive relevance in base wines were the total content of linolenic and undecanoic acids and the free content of undecanoic acid, while the total content of SO<sub>2</sub>, the isobutanol, the total acidity, and proteins were the variables with high predictive relevance.

Moreno-Arribas et al. [22] observed that neutral polysaccharides, protein nitrogen and phenylalanine displayed high positive contribution to the prediction of maximum foam height (Peak H), and height at which the foam stabilizes in sparkling wines (Plateau H). The fitted final models, which presented the following adjusted equations (Eq. (3) and (4)), explained 76% of Peak H variation and 70% of the variation of Plateau H.

Peak 
$$H = 194.31 + 0.37$$
Neutral polysaccharides  $+ 59.68$ Protein nitrogen (3)

Plateau 
$$H = 180.45 + 0.17$$
Neutral polysaccharides  $+ 3.80$ Phenylanine (4)

A recent work carried out in our group in 2015 used multiple linear regression analysis in white and rosé sparkling wines differentiating models which anthocyanins were included. It was concluded that the different forms of malvidin had the highest influence on the foam height and foam stability height parameters, followed by amino acid compounds ((Eq. (5) to (8)), while foam stability model was only predicted by polysaccharides from grapes, concretely by polysaccharides rich in arabinose and galactose ((Eq. (9) and (10)) [28].

HM (rosé sparkling wines) = 
$$84.882 + 0.065$$
Total amino acids  $+ 5.242$ Non-acylated anthocyanins  $- 0.477$ Total proanthocyanidins ( $R^2 = 90.2\%$ )

HM (white sparkling wines) =  $66.997 + 0.206$ Total amino acids ( $R^2 = 73.3\%$ ) (6)

HS (rosé sparkling wines) =  $9.730 + 0.331$ Basic amino acids  $+ 2.492$ Acetyl  $-$  glucoside anthocyanins  $+ 0.995$ Total biogenic amines  $+ 0.013$ Neutral amino acids ( $R^2 = 97.4\%$ )

$$HS \left( white \ sparkling \ wines \right) = 13.258 + 2.906 Total \ biogenic \ amines \left( R^2 = 19.2\% \right) \qquad (8)$$

$$TS \big( ros\'e \ sparkling \ wines \big) = -22.277 + 0.489 Polysaccharides \ from \ grapes \big( R^2 = 46.7\% \big) \quad (9)$$

$$TS(white sparkling wines) = -7.348 + 0.359 Polysaccharides from grapes(R2 = 33.9%) (10)$$

#### 5. Conclusions

In conclusion, this work shows that the foam properties of sparkling wines are ruled by a large number of molecules that act in a synergistic way. Nevertheless, some compounds seem to be more relevant than others to explain their foam properties.

Although contradictory results have sometimes been obtained, a high correlation ( $\geq$  0.75) has been found in the literature between the foam properties of sparkling wines and the content of total amino acids, polysaccharides, anthocyanins, coumaric acid and isorhamnetin. On the contrary, the alcohol content and the concentration of acid polysaccharides, proanthocyanidins and free SO<sub>2</sub> are the factors which most negatively affect foam quality.

A recent study, by means of prediction models, has also concluded that the different forms of malvidin shows the highest influence on the foam height and foam stability height parameters, followed by amino acid compounds, while foam stability model was only predicted by polysaccharides from grapes, concretely by polysaccharides rich in arabinose and galactose.

These research findings provide industry with a better understanding of the compositional factors influencing the foam quality of sparkling wines.

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