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Influence of Fatty Acids on Foaming Properties of Cider

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Seventy-seven ciders from four consecutive harvests, which were produced at industrial scale by cider-makers from the region of Asturias (northern Spain), were analyzed to evaluate their foam capacity. The Bikerman method for the evaluation of foaming characteristics was adapted to ciders. In foaming, there are two parameters, foam formation and foam stability, which are found to be related to each other. To determine the relationship between fatty acid content and foaming properties of cider, the multivariate analysis technique of canonical correlation analysis was applied. Foam stability is positively related to the content of caprylic acid. Foam height is positively related to linolenic, pentadecanoic, and palmitic acid and negatively related to stearic and linoleic acid.

KEYWORDS: Fatty acids; cider; foam properties; canonical correlation analysis

INTRODUCTION

Cider is a popular beverage in Asturias (Spain), as well as in other countries of Europe and North America, and represents one of the most important economic sources of that region after animal productions such as milk and meat. Therefore, in recent years abundant research (*1*−*3*) has been addressed to improve cider quality and to establish a denomination of origin for Asturian cider.

As is well-known, consumers judge the sparkling beverages not only by their taste and flavor but also by their foaming characteristics. In this sense, cider has some sensory foaming properties different from those of sparkling wines or beers. In fact, excessive and nonconsistent lacing and/or high foam stability cause a decrease in sensory assessment. For this reason, foam behavior is one of the most important quality characteristics of cider. Consequently, knowledge of foam active substances is important to cider-makers.

Studies carried out on fermented beverages such as beer or sparkling wines showed a relationship between chemical composition and foaming properties (*4*−*6*). For a long time, proteins (*5*, *7*, *8*) were considered to be the most important foam active compounds, but some studies have revealed that there are other compounds such as polysaccharides, iron, and copper which play an important role in the foam behavior in sparkling wines (*9*, *10*), beer (*11*), or sparkling base wines (*6*). Few papers report that fatty acids have an influence in foam formation and stability depending on their molecular weight. Maujean et al. (*12*) found a correlation between caprylic and capric acid and the foaming properties of still wines. Pueyo et al. (*5*) found a relationship between the total content of linolenic acid and the foam stability in wines and between the total content of palmitic acid and foam height in sparkling wines. Moreover, the higher fatty acids, such as linoleic and oleic acid, may be involved in the foam inhibition phenomenon (*13*). Therefore, the relationship between fatty acids and foaming properties might be of certain interest, because these compounds could modify the foam properties of cider. However, we have not found any precedents, in published research, on the foaming properties of cider and its fatty acid profile.

The use of fatty acid profiles allowed us to differentiate ciders made from apples harvested in the Asturias region from those made from apples harvested outside the region (*2*). At the same time, there are also differences in apple varieties on the basis of their profile of fatty acids (*3*). Because the level of fatty acids in cider is determined by several factors such as apple mixture, harvest, and the action of yeasts during the fermentation process, all of these factors should be taken into account in order to control the foaming properties of cider.

This study reports the possible relationship between the fatty acid composition of cider and its foaming characteristics. To this purpose, we have determined the fatty acid profile and foaming properties of 77 ciders. The foaming capacity of these ciders was measured with a device especially designed for this research. Multivariate analysis technique was applied to determine the relationship between both groups of variables.

MATERIALS AND METHODS

Samples and Chemicals. Seventy-seven samples of cider were frozen (−20 °C) and later analyzed. All reagents, standards, and solutions were of analytical grade.

Analytical Procedures. Fatty acids were analyzed by GC according to the method previously developed by the authors (*2*), using a column of acidified polyethylene glycol and a flame ionization detector. Concentrations of fatty acid were calculated by the internal standard method and expressed in milligrams per liter referred to cider.

Foaming Characteristics. Analytical grade CO_2 from a cylinder passed through a glass frit (10 μm pore size) fitted in the bottom of a

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Table 1. Mean Values and RSD of Fatty Acid Content in Cider ($n = 77$)

fatty acid	mean, mg/L ± RSD
caproic (C6:0)	3.3 ± 1.7
caprylic (C8:0)	3.2 ± 1.9
capric (C10:0)	3.5 ± 1.5
lauric (C12:0)	0.5 ± 0.2
myristic (C14:0)	0.3 ± 0.2
pentadecanoic (C15:0)	0.04 ± 0.03
palmitic (C16:0)	1.4 ± 0.6
palmitoleic (C16:1)	0.12 ± 0.09
stearic (C18:0)	0.3 ± 0.2
oleic (C18:1)	0.2 ± 0.2
linoleic (C18:2)	0.3 ± 0.3
linolenic (C18:3)	0.12 ± 0.08

graduated glass tube (0.985 cm i.d.). A flow rate of 30 mL/min was selected. Two parameters were measured: MH, the maximum height reached by the foam after carbon dioxide injection through the glass frit, expressed in millimeters, representing the ability of cider to foam; and FS, the time of foam stability, until all bubbles collapse, when carbon dioxide injection is interrupted, expressed in seconds. Samples were analyzed in triplicate. Ten milliliters of sample, previously degassed and filtered, was poured into the tube, and all measurements were carried out at room temperature. Before each measurement, the column was washed with 95% ethanol, Milli-Q water, and the sample to be analyzed, and air was passed through the fritted plate.

Statistical Analysis. Statgraphics Plus 4.0 was used to carry out the statistical data analysis. Correlation analysis was performed between the two foam parameters (MH and FS) of the 77 ciders and between the parameters MH and FS and the 11 fatty acids analyzed. One-way ANOVA considering as qualitative independent variable harvest and as quantitative dependent variables MH and FS was carried out. Canonical correlation analysis was used to establish the linear relationship between fatty acid composition and foaming characteristics.

RESULTS AND DISCUSSION

Fatty Acid Composition. Fatty acids were identified and quantified as methyl esters. Quantitative information was obtained using the internal standard method. An individual internal standard curve was generated for each fatty acid due to differences in response factors. Two internal standards were used: nonanoic (C9:0) and heptadecanoic acid (C17:0). The major fatty acids found were caproic, caprylic, capric, and palmitic. Saturated acids predominate over unsaturated ones. The statistics of method were described by the authors in a previous paper (*2*). **Table 1** reports the mean values of fatty acids for 77 ciders from four consecutive harvests.

Foaming Characteristics. The foam parameters (MH and FS), which were determined three times for each bottle, had average relative standard deviations <14 and 9%, respectively.

There was high variation between the values of MH and FS in cider. The values of the foam height ranged from 30.2 to 137.8 mm, whereas FS ranged from 8.0 to 35.0 s.

A positive linear correlation ($r = 0.72$, $p < 0.01$) (**Figure 1**) was observed between foam height and foam stability at the 99% confidence level, which indicates a moderately significant strong relationship between variables. It had also been observed in sparkling wines by Andrés-Lacueva et al. (*6*). Therefore, ciders with high MH would have a persistent collar, and they are stable over time.

On the other hand, significant differences ($p < 0.05$) between the foam height ($p = 0.001$) and the foam stability ($p = 0.0001$) values due to harvest factor were observed when one-way analysis of variance (ANOVA) was applied.

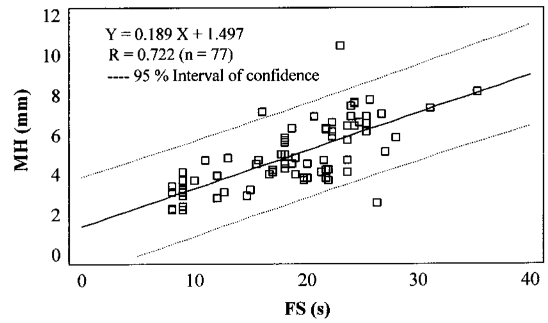

Figure 1. Relationship between foam height and foam stability of all ciders ($n = 77$).

Table 2. Correlation Coefficients and Significance Levels between Foam Parameters and Fatty Acids

	HM		TS	
fatty acid	*r*	*p*	*r*	*p*
caproic	0.242	0.034	0.413	0.0002
caprylic	0.278	0.014	0.433	0.0001
capric	−0.308	0.006	−0.214	0.062
lauric	−0.196	0.087	−0.154	0.181
myristic	−0.125	0.278	−0.207	0.071
pentadecanoic	−0.330	0.003	−0.503	0.0001
palmitic	−0.241	0.035	−0.408	0.0001
palmitoleic	−0.376	0.001	−0.528	0.0001
stearic	−0.315	0.005	−0.431	0.0001
oleic	−0.316	0.005	−0.440	0.0001
linoleic	−0.030	0.797	−0.163	0.156
linolenic	0.222	0.053	0.276	0.015

Correlation Analysis. This analysis provides a preliminary view of the relationships between the fatty acid composition and foaming characteristics. Correlation ranges from −1 to +1 and measures the strength of the linear relationship between variables. A positive correlation suggests that two variables fluctuate in the same direction, whereas a negative correlation suggests that two variables fluctuate in the opposite direction; *p* values below 0.05 indicate a statistically significant correlation at the 95% confidence level.

Table 2 shows the correlation coefficients of the variables corresponding to foaming characteristics, MH and FS, and those corresponding to the fatty acid composition of the ciders studied together with the significance level (*p*). It can be observed that foam height and stability are significantly related to most of the fatty acids. Positive coefficients were found for caproic, caprylic, and linolenic acid. That is to say, ciders with a greater amount of these compounds should have higher and more stable foam. On the other hand, high levels of pentadecanoic, palmitic, palmitoleic, stearic, and oleic acid in cider should indicate the lowest values of MH and FS. It is important to note that these coefficients show only the sign of the correlation between fatty acids and foam properties.

Canonical Correlation Analysis (CCA). The purpose of CCA is to summarize or explain the relationship between two sets of variables by isolating a small number of linear combinations from each set of variables that have the highest possible correlation between the sets.

Table 3 shows the results of the application of canonical correlation to the data of fatty acid composition and foaming properties. Two canonical variables were calculated in each group. The first canonical variable relates mostly to caprylic acid (0.706) for the first group and to foam stability in the other group. The second canonical variable relates best to linolenic (0.835), pentadecanoic (0.798), palmitic (0.754), stearic (−0.740),

Table 3. Correlations of the Two Canonical Variables (VC1 and VC2) with the Original Variables

	VC1	VC2
Fatty Acids		
caprylic	0.706	–0.384
pentadecanoic	–0.415	0.798
palmitic	–0.525	0.754
stearic	0.401	–0.740
linoleic	–0.273	–0.703
linolenic	0.233	0.835
Foaming Properties		
MH	–0.401	1.073
FS	1.030	0.360

and linoleic acid (−0.703) in the first group and to foam height in the second group. Caprylic acid has a positive correlation with foam stability, whereas linolenic, pentadecanoic, and palmitic acid are the fatty acids that best define the foam height. Pueyo et al. (*5*) found the same relationship between palmitic acid and foam height in sparkling wines. Stearic and linoleic acid have a negative relationship with foam formation. Studies carried out in other beverages (*13*) showed that fatty acids such as linoleic and oleic acid can inhibit the foam formation at concentrations >0.1 μg/mL, probably as a consequence of a spreading effect that causes a local thinning of the film and finally its breakage.

Conclusions. The MH and FS parameters in cider are related to each other. We found a linear relationship between foam height and foam stability. Foaming properties were affected by harvest.

We have found that caprylic acid best defines the foam stability in cider. The relationship between both variables is positive. That is to say, ciders with this fatty acid in the lipidic fraction will form more stable foam than ciders with lower concentration of the same acid. The fatty acids that best define the foam height were linolenic, pentadecanoic, palmitic, stearic, and linoleic acid; the relationship between them is positive in the case of linolenic, pentadecanoic, and palmitic acid but negative in the case of stearic and linoleic acid.

In this research we study the relationship between fatty acids and foaming properties, but attention should be drawn to the fact that foam is a very complex phenomenon, which depends on the equilibrium of many compounds rather than on any absolute value. Moreover, the composition of cider could be modified by different variables (harvest, apple mixture, etc). For this reason, the study of chemical composition in order to identify the compounds responsible for foaming properties is currently under investigation.

LITERATURE CITED

(1) Mangas, J. J.; Moreno, J.; Rodríguez, R.; Picinelli, A.; Suárez, B. Analysis of Polysaccharides in Cider: Their Effect on Sensory Foaming Properties. *J. Agric. Food Chem.* **1999**, *47*, 152−156.

(2) Blanco-Gomis, D.; Mangas Alonso, J. J.; Margolles Cabrales, I.; Arias Abrodo, P. Gas Chromatographic Analysis of Total Fatty Acids in Cider. *J. Agric. Food Chem.* **2001**, *49*, 1260−1263.

(3) Blanco-Gomis, D.; Mangas Alonso, J. J.; Margolles Cabrales, I.; Arias Abrodo, P. Characterization of Cider Apples on the Basis of Their Fatty Acid Profiles. *J. Agric. Food Chem.* **2002**, *50*, 1097−1100.

(4) Brissonnet, F.; Maujean, A. Identification of Some Foam-Active Compounds in Champagne Base Wines. *Am. J. Enol. Vitic.* **1991**, *42* (2), 97−102.

(5) Pueyo, E.; Martín-Álvarez, P. J.; Polo, M. C. Relationship between foam characteristics and chemical composition in wines and cavas (sparkling wines). *Am. J. Enol. Vitic.* **1995**, *46*, 518−524.

(6) Andrés-Lacueva, C.; López-Tamames, E.; Lamuela-Raventós, R. M.; Buxaderas, S.; Torre-Boronat, M. C. Characteristics of sparkling base wines affecting foam behavior. *J. Agric. Food Chem.* **1996**, *44*, 989−995.

(7) Malvy, J.; Robillard, B.; Duteurtre, B. Influence des Protéines sur le Comportement de la Mousse des Vins de Champagne. *Sci. Aliments* **1994**, *14*, 87−98.

(8) Bikerman, J. J. The unit of foaminess. *Trans. Faraday Soc.* **1938**, *34*, 634−638.

(9) Moreno-Arribas, V.; Pueyo, E.; Nieto, F. J.; Martín-Álvarez, P. J.; Polo, M. C. Influence of Polysaccharides and the Nitrogen Compounds on Foaming Properties of Sparkling Wines. *Food Chem.* **2000**, *70*, 309−317.

(10) Dussaud, A.; Robillard, B.; Carles, B.; Duteurtre, B.; Vignes-Adler, M. Exogenous Lipids and Ethanol Influences on the Foam Behavior of Sparkling Base Wines. *J. Food Sci*. **1994**, *59*, 148−167.

(11) Bamforth, C. W. The foaming properties of beer. *J. Inst. Brew.* **1985**, *91*, 370−380.

(12) Maujean, A.; Poinsaut, P.; Dantan, H.; Brissonnet, F.; Cossiez, E. Étude de la tenue et de la qualité de mousse des vins effervescents. II. Mise au point d'une technique de mesure de la mousabilité de la tenue et de la stabilité de la mousse des vins effervescents. *Bull. O.I.V.* **1990**, *711*−*712*, 405−427.

(13) MacLeod, A. M. Beer. In *Alcoholic Beverages*; Rose, A. H., Ed.; Academic Press: London, U.K., 1977.

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