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Physicochemical Changes and Sensory Characterization of a Balsamic Vinegar Dressing at Different °Brix

Jorge Chirife · Marina Sansiñena · Mara V. Galmarini · Maria Clara Zamora

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Abstract A balsamic vinegar dressing was developed by concentrating commercial balsamic vinegar (wine vinegar + grape juice) by evaporation under controlled conditions; evaporation increased the content of glucose + fructose that was naturally present in the balsamic vinegar leading to high Brix values. The water activity (a_w) and viscosity of the balsamic dressing at various °Brix were measured and modeled using previously reported equations for the behavior of fructose/glucose, which showed a good fit. A quantitative descriptive analysis was performed and samples were grouped in three clusters corresponding to low (31.1–51.2), intermediate (64.0–67.5), and high (71.8–76.0) °Brix. Samples of highest °Brix were associated with sweetness, caramel flavor, visual viscosity, and reduced sourness and acetic aroma, attributes which differentiated these samples from the control and which are considered desirable for a dressing to be used with cold meats, cheeses, and desserts.

Keywords Balsamic vinegar · Dressing · Water activity · Acetic acid · Sensory analysis · Sugars

J. Chirife · M. Sansiñena · M. V. Galmarini · M. C. Zamora (✉)
Facultad de Ciencias Agrarias,
Pontificia Universidad Católica Argentina,
Cap. Gral. Ramón Freire 183,
CP1429 Buenos Aires, Argentina
e-mail: zamoramariacl@gmail.com

M. V. Galmarini · M. C. Zamora
Consejo Nacional de Investigaciones
Científicas y Técnicas (CONICET),
Buenos Aires, Argentina

Introduction

Industrial or commercial balsamic vinegars consist of vinegar, grape juice, caramel coloring, or other flavors and are aged for a few months. In some restaurants, industrial balsamic vinegar is reduced down to a syrupy consistency and served on various kinds of salads or cold meats; usually the balsamic vinegar in a small saucepan is added with sugar, simmered, and reduced by two thirds of its original volume. However, since this process is not standardized, the evaporation yields random sugar concentrations (°Brix); in addition, sucrose is usually added which modifies the flavor of the final reduction (Plessi et al. 2006; Saiz-Abajo et al. 2004).

The objective of the present study was to produce a concentrated balsamic dressing from industrial vinegar under controlled evaporation conditions (without adding sucrose) until high different Brix values were reached. For the resulting dressings, physicochemical properties such as water activity (a_w), viscosity, and titratable acidity were measured. In addition, sensory evaluation of the different °Brix dressings was conducted. Our study intended to describe the conditions for the development of a commercial concentrated vinegar dressing which may be used by consumers at home.

Materials and Methods

Sample Preparation

One national commercial balsamic vinegar consisting of wine vinegar, grape juice, caramel color, and sulfur dioxide (31 °Brix, pH 3.2, and 5% acidity) was purchased in a nationwide supermarket chain during November–December

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2008. Balsamic vinegar was evaporated in a heating mantle (93–95 °C, with stirring) to increase its soluble solid concentration (as measured with a refractometer) to different Brix values (in the range 50 to 77 °Brix); no other ingredients were added. The heating time was determined based on Brix values, with different heating times (maximum 2.30 h) being used to reach the desired Brix values. Preparation of dressing was duplicated.

Viscosity and sensory evaluations were performed on replicates; therefore, slight variations on the Brix values were observed in different replicates.

Physicochemical Determinations

Water Activity (a_w)

Water activity was measured using a dew point/chilled mirror water activity meter, "Aqualab" Series 3TE with temperature control (Decagon Devices, Pullman, WA, USA). The a_w meter was first calibrated with saturated salt solutions (Resnik et al. 1984; Resnik and Chirife 1988). Measurements were conducted at 25±0.2 °C and the average of three measurements was reported.

°Brix

Samples of concentrated balsamic vinegar were tempered at 25 °C over a constant temperature plate and °Brix were measured using hand refractometers (Model N-2 and Model N-3E, Atago, Japan). Measurements were made in duplicate.

pH

The pH of samples were measured using a glass electrode (Hanna Instruments, Portugal) calibrated with buffer solutions of pH 4.0 and 7.0. Measurements were made in duplicate.

Titratable Acidity

Titratable acidity was evaluated by titration with 0.1 N sodium hydroxide using phenolphtalein as indicator; the results were expressed as acetic acid content. Measurements were made in duplicate.

Viscosity

Viscosity was measured using a rotating viscometer (Brookfield LVDV-I+; Brookfield Engineering Laboratories, Inc., Middleboro, MA, USA). Measurements were made at different rotational speeds to cover the whole viscosity range. A small sample adapter with SC4-34 spindle and the UL/Y adapter with UL spindle were used to cover the whole viscosity range. Viscosity was determined at 15, 25, and 35 °C by placing the sample chamber in a water jacket connected to a constant temperature bath. Measurements were done in duplicate at increasing shear rates; values less than 10% torque were discarded because of the amplified errors in the readings.

Sensory Evaluation

Nine assessors (eight females and one male, 20–60 years old), staff members of Facultad de Ciencias Agrarias, Pontificia Universidad Católica Argentina, were trained (4 h) in visual viscosity, acetic aroma, sourness, sweetness, caramel and wine flavor, pungency and astringency, as well as in the use of unstructured scales. For this purpose, the panel was provided with aroma and flavor references. During two testing sessions (2 h long each), assessors were asked to rank the samples to be analyzed according to perceived intensity of each attribute (ASTM 1977). In this way, the sample (or samples) which represented the maximum and/or minimum intensity for each attribute was obtained, finally establishing the limits of the scale by consensus. Quantitative descriptive analysis (Stone and Sidel 1993) was performed using a 10-cm unstructured scale taking into account the extremes previously obtained for each attribute during the training period.

Testing took place in individual booths kept at 22±2 °C, under daylight (6,500 K). Five milliliters of samples were placed in sealed 35-ml glass flasks identified with random three-digit codes and evaluated in duplicate. Six samples were evaluated in each session (two sessions; approximately 1 h each).

Viscosity was visually determined based on previous work reported by Zamora (1994). Acetic aroma was determined by sniffing of the headspace while sourness, sweetness, pungency, astringency, and caramel and wine flavor were orally evaluated. Samples were swallowed to evaluate pungency in throat and mineral water was provided for oral rinsing.

Statistical Analysis

Analysis of variance (ANOVA) was performed to detect differences among samples (General Linear Model command in SPSS v. 13.0; SPSS Inc. Chicago, IL, USA). The variability of each descriptor was analyzed by considering assessor as a random factor, because the assessor's panel is a random sample from a larger population, and sample and replication as fixed factors because the levels under study are the only levels of interest. Multiple means comparisons were analyzed using the Student–Neuman–Keuls test at $p<0.05$. Correlation among sensory descrip-

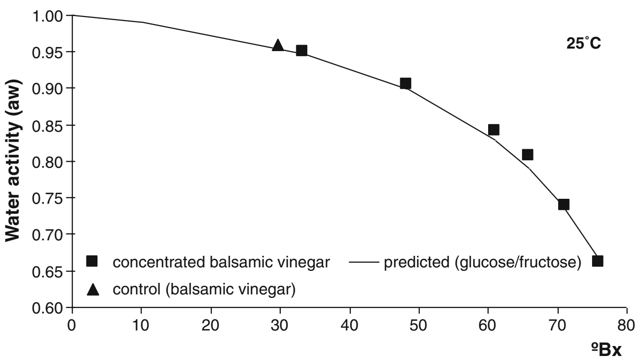

Fig. 1 Comparison of measured a_w data in concentrated balsamic vinegar with predicted curve for fructose/glucose solutions (Eq. 1)

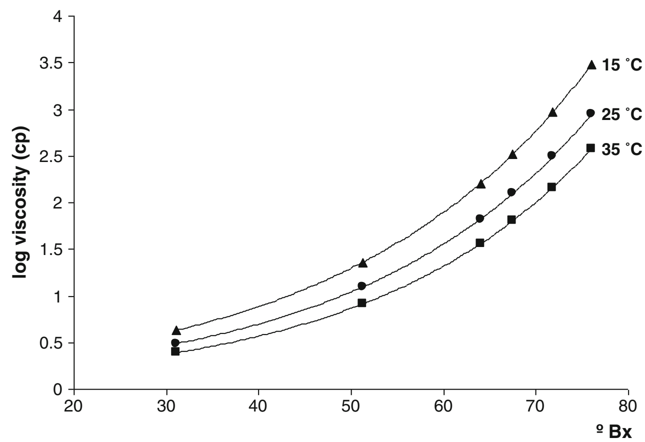

Fig. 2 Viscosity of concentrated balsamic vinegar solution at 15, 25, and 35 °C as a function of Brix values. *Solid lines* were predicted using Eqs. (3), (4), and (5)

tors and instrumental determinations was analyzed by Pearson's correlation (SPSS v.13.0. partial least-squares regression; PLS); relationship between instrumental (X variables, regressors = predicting) and sensory data (Y variables, regressands = predicted, independent in the context of regression analysis) were analyzed by Infostat v. 2007 (Universidad Nacional de Córdoba, Argentina). Finally, cluster analysis was performed by K-Means command in SPSS v. 13.0.

Results and Discussion

Water Activity (a_w)

Water activity of balsamic vinegar concentrated up to 76.0 °Brix is shown in Fig. 1; error bars cannot be observed because the errors in our a_w measurement are estimated to be ±0.004 and this will overlap with the size of the (black square) symbols. Increasing °Brix resulted in a noticeable reduction in water activity. The 76.0 °Brix value is close to the lowest a_w (0.62) permitting microbial growth (Christian 1963), thus consisting in an effective hurdle for inhibition of osmophilic yeast and mold growth.

The fructose + glucose content of grape juice is approximately 91% on dry matter basis, and fructose alone is 52%; thus, the ratio of fructose/glucose is 1.3 (USDA). Therefore, the lowering of a_w in concentrated balsamic vinegar (Fig. 1) is likely to be due to fructose and glucose since they are the main constituents of grape juice (USDA) present in balsamic vinegar. The prediction of water activity of glucose/fructose may be adequately described by Norrish's equation (Chirife et al. 1982),

$$a_w = X_w \cdot \exp\left(-2.25 \cdot X_2^2\right) \quad (1)$$

where X_w is the molar fraction of water, X_2 is the molar fraction of solute, and constant 2.25 is valid for both sugars, fructose or glucose (Chirife et al. 1982; Chirife et al. 2006; Baeza et al. 2009). This is equivalent to saying that the water activity of fructose or glucose solutions of same concentrations is identical. Figure 1 also compares the measured data of water activity in concentrated

Table 1 Viscosities of concentrated balsamic vinegar at 15, 25, and 35 °C

Viscosity (cp)			
°Bx	15°C	25°C	35°C
31.3	4.4	3.2	2.5
50.8	19.8	12.3	8.3
61.0	65.6	35.5	20.0
67.3	224.4	111.0	59.9
72.1	898.1	349.5	145.7
77.0	4,705.5	1,472.6	552.4

Table 2 °Brix values, titratable acidity, and pH of samples subjected to sensory analysis

Sample	°Bx	Titratable acidity (g acetic acid/100ml)	pH
1[a]	31.1	4.8	3.2
2[b]	51.2	5.5	3.3
3[b]	64.0	5.3	3.3
4[b]	67.5	5.2	3.3
5[b]	71.8	3.7	3.4
6[b]	76.0	2.9	3.4

[a] Control, commercial balsamic vinegar

[b] Subjected to evaporation/concentration at 93–95 °C

Table 3 *F* values of samples for evaluated sensory attributes

Attribute	ANOVA *F* value			
	Replicate (R)	Sample (S)	Assessor (A)	Interaction S × A
Acetic aroma	0.142	124.8**	0.515	1.245
Sourness	0.369	355.4**	3.870	0.860
Sweetness	0.007	859.9**	0.836	0.765
Visual viscosity	0.030	528.2**	1.482	1.800
Pungency	0.557	95.5**	3.117*	2.100*
Astringency	0.395	38.9**	2.172	1.447
Caramel flavor	2.690	272.9**	2.370	0.927
Wine flavor	0.042	30.9**	1.181	2.215*

*$p<0.05$; **$p<0.001$

balsamic vinegar with the curve predicted by Eq. (1) (full line). The agreement between experimental and predicted values confirms that fructose and glucose (from grape juice) are the main determinants of the reduction of water activity.

Viscosity

Concentrated balsamic vinegar samples exhibited a Newtonian behavior and their viscosities at 15, 25, and 35 °C are shown in Table 1; each determination of viscosity is the average of two replicates and the individual values did not differ in more than 5%. Increasing Brix values from 31.3 (control) to 77.0 resulted in a dramatic increase in viscosity from 3.2 cp to 1472.6 cp a 25 °C.

The viscosity of concentrated balsamic vinegar was fitted to °Brix using the following equations (Eqs. 2 to 4);

$$\log \mu = 0.194 e^{0.038^{\circ}\mathrm{Bx}} \qquad \text{at } 15^{\circ}\mathrm{C} \qquad r^2 = 0.9962 \tag{2}$$

$$\log \mu = 0.141 e^{0.040^{\circ}\mathrm{Bx}} \qquad \text{at } 25^{\circ}\mathrm{C} \qquad r^2 = 0.9984 \tag{3}$$

$$\log \mu = 0.106 e^{0.042^{\circ}\mathrm{Bx}} \qquad \text{at } 35^{\circ}\mathrm{C} \qquad r^2 = 0.9982 \tag{4}$$

Figure 2 shows measured and predicted (Eqs. 2 to 4) viscosity values at 15, 25, and 35 °C.

Acidity

The °Brix, titratable acidity, and pH of samples concentrated at 93–95 °C and subjected to sensory evaluation are shown in Table 2. All determinations are the average of duplicate values, which did not differ in more than 3–4%.

The pH increased from 3.2 (control sample) to 3.4 for the sample of 76.0 °Bx.

Titratable acidity (i.e., total acidity) of each concentrated sample is the sum of retained volatile acid (i.e., acetic acid) plus non-volatile acids originally present in the wine vinegar and grape juice. As shown in Table 2, up to 67.5% °Bx total acidity of samples remained more or less the same; however, a significant decrease is observed at the higher Brix values (71.8–76.0). The interpretation of the results in terms of loss of acetic acid is complex due to the fact that total acidity is not expressed on a constant basis because water content of samples continuously decreases during evaporation; also during concentration, water evaporates and also should some acetic acid. For equilibrium evaporation of a volatile liquid, it can be derived for the volatile (other than water) retention:

$$\mathrm{AR} = (\mathrm{WR})^{\alpha} \tag{5}$$

where AR and WR are the fraction of the initial amounts of volatile (acetic acid in this case) and water, respectively, at

Table 4 Mean scores and standard error deviation of sensory attributes for each sample

	Sample 1[a]	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6
Acetic aroma	9.75 ±0.36a	9.02±0.41b	8.62±0.31c	7.57±0.69d	7.04±0.59e	6.15±0.22f
Sourness	9.86±0.24a	8.47±0.71b	7.51±1.00c	5.99±0.86d	3.95±0.43e	2.70±0.14f
Sweetness	1.43±0.17a	2.35±0.39b	3.44±0.44c	4.33±0.39d	5.27±0.29e	6.04±0.08f
Visual viscosity	1.30±0.18a	2.62±0.50b	4.79±0.80c	6.36±0.60d	7.90±0.55e	9.16±0.13f
Pungency	6.20±0.22a	5.53±0.66b	4.81±0.70c	3.60±0.65d	3.20±0.75d	2.22±0.84f
Astringency	5.27±1.10a	4.74±0.99ab	4.35±0.87b	4.25±0.95b	3.24±0.87c	2.03±0.75d
Caramel flavor	1.52±0.65a	2.48±0.94b	4.40±0.86c	6.26±1.10d	7.20±1.02e	8.58±1.22f
Wine flavor	5.73±0.61a	4.77±0.84b	4.76±0.66b	4.12±1.00b	3.16±1.04c	1.92±0.90d

Different lowercase letters represent significant differences ($p<0.05$) among samples according to Student–Neuman–Keuls test

[a] Physicochemical characteristics of samples 1 to 6 are described in Table 2

any moment in the evaporation process (Coumans et al. 1994) and α is the relative volatility of acetic acid with respect to water. The relative volatility $\alpha_{aa\ w}$ of acetic acid with respect to water (w) is defined as:

$$\alpha_{aa\ w} = P^{o}{}_{aa} \cdot \chi_{aa} / P^{o}{}_{w} \cdot \chi_{w} \quad (6)$$

where χ_{aa} is the thermodynamic activity coefficient of acetic acid in the mixture, χ_{w} is the thermodynamic activity coefficient of water, and $P^{o}{}_{aa}$ and $P^{o}{}_{w}$ are the saturated vapor pressures of the pure components (acetic acid and water) at evaporation temperature. Bomben et al. (1973) reported that the relative volatility of acetic acid in water at infinite dilution is 0.73 and calculated that in water at 100 °C the retention of acetic acid was 31% after evaporation of 80% of the water. This means that more acetic acid than water was retained. However, attempting calculation for present situation is complicated because we are not in the presence of an "infinite dilution" but with a 5% solution of acetic acid. Also, it is well known that the activity coefficient of organic volatiles (i.e., acetic acid) may be strongly affected by the presence of dissolved sugars (fructose + glucose in this case) (Bomben et al. 1973), and during concentration of balsamic vinegar the total sugar concentration increases progressively.

Sensory Evaluation

The ANOVA of mixed model for attribute scores is summarized in Table 3. The source of variation was determined to be samples (p<0.001), except for pungency and wine flavor where the assessor (p<0.05) and sample × assessor interactions (p<0.05) were the source of variation. Assessors, replications, and sample × assessor interactions were non-significant for every other attribute, suggesting that panel performance was consistent.

The average values for every evaluated attribute are presented in Table 4. As observed, practically all samples were different in every attribute except for astringency where samples 1 and 2 and also 2, 3, and 4 did not show significant differences among them; the same thing happened with wine flavor among samples 2, 3, and 4. The two most different samples were 1 and 6; the larger variations were observed for visual viscosity (Δ=7.86; where Δ is obtained by subtracting to the mean values for sample 6 the ones for sample 1 for the given attribute), sourness (Δ=7.16), and caramel flavor (Δ=7.06). Assessors perceived a noticeable decrease in sourness rather than an increase in sweetness, likely because differences in perceived sourness are related to a sour–sweet interaction. Although sweet and sour tastes are perceived by their own unique pathways, their

Table 5 Correlation among sensory attributes and instrumental measurements

	Acetic aroma	Sourness	Sweetness	Visual viscosity	Pungency	Astringency	Caramel flavor	Wine flavor	°Bx	Titr. acidity
Acetic aroma										
Sourness	0.993***									
Sweetness	−0.991***	−0.992***								
Visual viscosity	−0.987***	−0.988***	0.999***							
Pungency	0.997***	0.987***	−0.993***	−0.993***						
Astringency	0.953***	0.964**	−0.941**	−0.933**	0.936**					
Caramel flavor	−0.989***	−0.984***	0996***	0.998***	−0.997***	−0.925**				
Wine flavor	0.976***	0.979**	−0.956**	−0.946**	0.959**	0.989***	-0.942**			
°Bx	−0.908*	−0.903*	0.942**	0.940**	−0.919**	−0.829*	0.930**	−0.855*		
Titr. acidity	0.781	0.816*	−0.751	−0.746	0.752	0.887*	−0.740	0.851*	−0.514	
Inst. visc.	−0.995***	−0.995***	0.996***	0.993***	−0.993***	−0.962**	0.990***	−0.976**	0.931**	−0.776

*p<0.05; **p<0.01; ***p<0.001

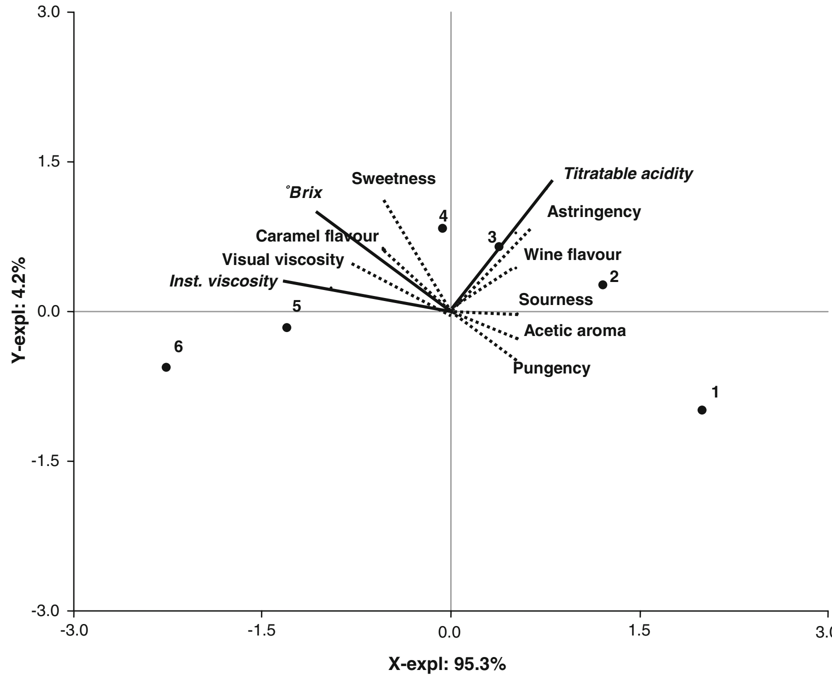

Fig. 3 Partial least-squares regression (PLS2) factors for sensory attributes and instrumental determinations. *Solid line* corresponds to instrumental measurements and *dotted line* to sensory data

perceived intensities are different when both are present in a mixture. In general, sourness is suppressed by sweeteners with a very stable pattern and the amount of sourness suppressed depends on both components' levels (Galmarini et al. 2008). Mixture suppression is a phenomenon whereby the perceived intensity of two tastes in a mixture is less than if they were unmixed, at the same concentration (Schifferstein and Fritjers 1991; Lawless and Heymann 1998).

Table 5 shows Pearson's correlations among sensory attributes and instrumental measurements. Sourness–sweetness interaction can be observed in Table 5 which shows a negative correlation ($p<0.001$) between these two attributes. This table also shows that all attributes—with the exception of titratable acidity—are highly correlated among them. Sensory viscosity was very well correlated with the instrumental determination ($p<0.001$). Moreover, visual viscosity also correlated very well with sweetness, caramel flavor, and °Brix. Figure 3 shows the partial least-squares regression factors for sensory attributes and instrumental determinations.

According to the sensory descriptive analysis, samples were grouped into three clusters corresponding to low (31.1–51.2), intermediate (65.0–67.5), and high (71.8–76.0) °Brix. Samples of highest °Brix were associated with increased sweetness, caramel flavor, visual viscosity, and reduced sourness and acetic aroma, all of which are desirable in the dressing studied here.

Conclusions

A balsamic vinegar dressing was developed concentrating commercial balsamic vinegar (wine vinegar + grape juice) by evaporation under controlled conditions until different Brix values were obtained. At the highest °Brix, the increasing sugar (fructose + glucose from grape juice) concentration was associated with a dramatic increase in product viscosity and a concomitant reduction of titratable acidity (likely due to some acetic acid evaporation) leading to a product with a balanced sweet/sour taste.

According to the sensory descriptive analysis, samples were grouped into three clusters corresponding to low (31.1–51.2), intermediate (64.0–67.5), and high (71.8–76.0) °Brix values. The samples of highest °Brix were associated with sweetness, caramel flavor, visual viscosity, and also a reduced sourness and acetic aroma, attributes which are desirable for a dressing.

The increased Brix values led to a significant reduction in water activity resulting in a product with reduced risk of osmophilic yeast/mold growth.

The selection of °Brix may be used to modify the flavor profile (sour/sweetness balance) of the product as well as its viscosity.

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