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A study on the importance of colour in pacharán

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Abstract Pacharán is a traditional drink of Navarra (Spain). This liqueur is an alcoholic drink which ranges from intense pink to red in colour and is based on sloe (*Prunus spinosa*, L.), essential oils of aniseed, and sugar. A sensory analysis was performed using samples from 21 different brands of commercial pacharán. Stepwise regression was employed to identify the physicochemical parameters responsible for the sensory attributes of colour, visual intensity of colour, and overall impression. The physicochemical variables which best predicted the sensorial attribute colour were colour intensity and titratable acidity. For the visual intensity of colour, key indicators were colour intensity, titratable acidity and hue, the last-mentioned variable having a negative effect. With respect to the overall impression, pH, ethanol content and colour intensity correlated to quality.

Key words Pacharán · Sensory analysis · Multivariate statistical analysis · Alcoholic beverage

Abbreviations *F* statistic (F of Fisher) = (student's t)² · *R*² Coefficient of determination · *MSE* Mean squared error · *P*_{corr.} partial correlation · *SQ*. (*ADJ.*) Adjusted R-squared · *SE* Standard error of the estimate · *MAE* Mean absolute error · *DurWat* Durbin-Watson-coefficient

Introduction

Pacharán is an alcoholic drink which is prepared by the maceration of sloes (*Prunus spinosa*, L.) in aqueous ethanol with subsequent addition of sugar and essential

oils of aniseed. The normal colour of pacharán is red or intense pink. Unfortunately, it has poor chromatic stability and the colour changes to orange or shades of yellow with time. The alcohol content of pacharán is about 25% vol. The attractive colour of this liqueur results from sloe pigments. Ramos and Macheix [1] found the following anthocyanins in fruit of the blackthorn: cyanidin-3-rutinoside (51%), cyanidin-3-glucoside (38.7%) and lesser quantities of peonidin-3-glucoside and peonidin-3-rutinoside. Similar results were obtained by Werner et al. [2]. Anthocyanins are compounds with poor stability, and some factors usually present during elaboration and storage of this drink that may provoke their degradation are higher temperatures, oxygen, light radiation, media pH, and prolonged storage [3,4]. Little research has been done on this liqueur [5]. Furthermore, the effects of physicochemical parameters on the sensorial characteristics of the commercial product have not been investigated.

Statistical multivariate methods of analysis are crucial tools for the comparison of sensorial and objective data. Galetto and Bednarezyk [6] used stepwise regression to relate the quality and intensity of flavour to the composition of onion oil. When they obtained the regression equation, they were surprised to find that the three compounds present in greatest concentrations, which were considered important contributors to the onion oil flavour in previous studies, did not appear in the equation. Upon detailed analysis of their results, they observed that some variables (compounds) were linearly dependent. When the number of variables is limited (by stepwise procedure), the probability that the variables included in the model will be linearly dependent decreases. More recently, Ferreira et al. [7] applied stepwise regression in order to correlate objective and sensorial data.

The present study was undertaken to determine the influence of physicochemical parameters on the sensorial attributes of colour, visual intensity of colour, and overall impression based on the evaluations of a group of selected tasters chosen from habitual consumers of

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this drink. This information would be applicable to routine quality control, which is essential in order to improve the current industrial processes.

Materials and methods

Materials. Twenty-one commercial brands of pacharán were used. This sampling represents more than 90% of the total industrial output. Commercial pacharán samples were stored at 5 °C and protected from light during the investigation.

Sensory panel. The tasting panel comprised 70 tasters (36 females, 34 males) chosen from habitual consumers of this drink. The ages of the panel members were 20–30 years old, 22 persons; 30–40 years old, 19 persons; 40–50 years old, 20 persons; and 50–55 years old, 9 persons.

Sensory tests. The sensory tests were carried out in a tasting hall which adheres to the rules of ISO 8589 (1988). Samples were served at the room temperature of the tasting hall (20 °C), and the existing relative humidity was 65%. White light with a luminosity of 360–380 lx was used.

Transparent cognac glasses, with a maximum capacity of 200 ml, were used and were filled with approximately 80 ml pacharán. To avoid interference from the different aromas and to avoid the risk of them saturating the atmosphere of the tasting room, the glasses were covered with a retractable and odourless film which the taster had to completely remove in order to analyse a sample and had then to re-cover the glass again after tasting. To neutralize flavours, the tasters were provided with saltless bread and water.

A scorecard was prepared for every sample that each taster evaluated. The tasters had to rate the three sensory attributes being researched on a discrete five point scale. The sensory attributes colour and overall impression were judged using a verbal scale of hedonistic ordering. The last sensorial attribute, visual intensity of colour, evaluated the intensity of the organoleptic property analysed. This was done using a discrete five-point scale in increasing order of acceptance or intensity.

Statistical design of the sensory analysis. Given the large number of samples analysed, an experimental design was employed using incomplete blocks [8]. In agreement with the incomplete block design chosen, each taster was presented with a block of three samples, each brand was judged by ten tasters, and no brand was tasted in combination with the same brand more than once. Samples were coded with random three-digit numbers and presented in a randomized order.

Analytical methods. According to the methods established by the European Economic Community and the Office International de la Vigne et du Vin the following characteristics were analysed for each brand of pacharán: (1) ethanol content, from densimetry of the distillate sample [9]; (2) pH, by direct potentiometric meas-

urement of the sample; (3) titratable acidity, from titration with standardised NaOH solution to pH 7 [9, 10]; (4) total sugar, from hydrolysis in acidic media followed by addition of an excess of alkaline cuprous solution and by determination of the resulting cupric ions by iodometry [11]; (5) colour intensity, from the sum of absorbances measured at 420 nm, 520 nm and 620 nm ($A_{420} + A_{520} + A_{620}$) [9]; and (6) hue, by the ratio of absorbances measured at 420 nm and 520 nm (A_{420}/A_{520}) [9].

A Crison model 2002 pH-meter was used to measure pH. For optical determinations, a UV-VIS spectrophotometer Shimadzu model UV-210 was used.

Statistical methods. The statistical methods employed belong to statistical multivariate analysis. A multiple analysis of variance was used taking two factors into consideration, taster and sample, in order to process the sensorial analysis data according to an incomplete block model [12]. In addition to the application of variance analysis to the sensory data, a stepwise multiple regression analysis was used to establish a statistical relationship between the sensory data and the analytical data. Application of these techniques was carried out with the help of Statgraphics software, version 7.1 (1993) and Statgraphics Plus, for Windows, version 1.4 (1995).

Results and discussion

A summary of the adjusted averages taken from the multiple analyses of variance carried out for each sensory attribute is shown in Table 1. A summary of the analytical results for the 21 commercial brands of pacharán is given in Table 2.

To determine which physicochemical parameters could significantly predict the sensorial qualifications assigned to the samples, a stepwise regression was done with respect to each sensorial attribute where the dependent variable was the sensorial variable, and potential independent variables were the six physicochemical

Table 1 Statistical summary of adjusted averages for sensorial evaluations

| Variable | Average | SD ^a | CV ^b | Minimum | Maximum |
|---------------------------------|---------|-----------------|-----------------|---------|---------|
| Colour ^c | 3.45 | 0.61 | 17.73 | 2.21 | 4.31 |
| Colour Intensity ^c | 3.29 | 0.70 | 21.40 | 2.05 | 4.48 |
| Overall Impression ^c | 3.13 | 0.33 | 10.56 | 2.13 | 3.85 |

^a Standard deviation

^b Coefficient of variation

^c On a scale of 1–5

Table 2 Statistical summary of physicochemical results

| Variable | Average | SD ^a | CV ^b | Minimum | Maximum |
|---------------------------------------|---------|-----------------|-----------------|---------|---------|
| Ethanol content (v/v) | 24.94 | 1.25 | 5.01 | 23.45 | 29.40 |
| Total sugar (g/l) | 138.45 | 25.12 | 18.15 | 101.04 | 207.20 |
| Titratable acidity (g/l) ^c | 2.58 | 0.82 | 32.00 | 1.49 | 4.04 |
| pH | 3.75 | 0.15 | 3.93 | 3.33 | 4.02 |
| Colour intensity | 1.39 | 0.42 | 30.18 | 0.52 | 2.10 |
| Hue | 1.63 | 0.38 | 23.45 | 0.95 | 2.33 |

^a Standard deviation

^b Coefficient of variation

^c Grams per litre of malic acid

Table 3 Stepwise selection for sensorial variable colour

| Selection: Forward R^2 : 0.532 | | | Adjusted: 0.507 MSE: 0.184 | | Step 1 df: 19 |
|-------------------------------------|-------------|-------------|----------------------------|-------------------|------------------|
| Variables in model | Coefficient | F -remove | Variables not in model | P_{corr} | F -enter |
| Colour intensity | 1.061 | 21.566 | pH | 0.039 | 0.027 |
| | | | Ethanol content | 0.024 | 0.010 |
| | | | Titrate acidity | 0.556 | 8.073 |
| | | | Hue | 0.448 | 4.516 |
| | | | Total sugar | 0.152 | 0.425 |

Table 4 Stepwise selection for sensorial variable colour

| Selection: Forward R^2 : 0.677 | | | Adjusted: 0.6407 MSE: 0.134 | | Step 2 df: 18 |
|-------------------------------------|-------------|-------------|-----------------------------|-------------------|------------------|
| Variables in model | Coefficient | F -remove | Variables not in model | P_{corr} | F -enter |
| Titrate acidity | 0.302 | 8.073 | pH | 0.003 | 0.000 |
| Colour intensity | 0.850 | 16.567 | Ethanol content | 0.141 | 0.345 |
| | | | Hue | 0.351 | 2.390 |
| | | | Total sugar | 0.216 | 0.830 |

Table 5 Model fitting results for sensorial variable colour

| Independent variable | Coefficient | SE | t -value | P |
|----------------------|-------------|-------|------------|-------|
| Constant | 1.486 | 0.330 | 4.498 | 0.000 |
| Titrate acidity | 0.302 | 0.106 | 2.841 | 0.011 |
| Colour intensity | 0.850 | 0.209 | 4.070 | 0.001 |

SQ. (ADJ.)=0.641 SE=0.366 MAE=0.282 DurWat=2.448

Table 6 Stepwise selection for sensorial variable visual colour intensity

| Selection: Forward R^2 : 0.716 | | | Adjusted: 0.701 MSE: 0.148 | | Step 1 df: 19 |
|-------------------------------------|-------------|-------------|----------------------------|-------------------|------------------|
| Variables in model | Coefficient | F -remove | Variables not in model | P_{corr} | F -enter |
| Colour intensity | 1.416 | 47.818 | pH | 0.018 | 0.006 |
| | | | Ethanol content | 0.396 | 3.344 |
| | | | Titrate acidity | 0.590 | 9.616 |
| | | | Hue | 0.544 | 7.582 |
| | | | Total sugar | 0.154 | 0.436 |

Table 7 Stepwise selection for sensorial variable visual colour intensity

| Selection: Forward R^2 : 0.815 | | | Adjusted: 0.794 MSE: 0.102 | | Step 2 df: 18 |
|-------------------------------------|-------------|-------------|----------------------------|-------------------|------------------|
| Variables in model | Coefficient | F -remove | Variables not in model | P_{corr} | F -enter |
| Titrate acidity | 0.287 | 9.616 | pH | 0.076 | 0.099 |
| Colour intensity | 1.215 | 44.680 | Ethanol content | 0.320 | 1.940 |
| | | | Hue | 0.474 | 4.914 |
| | | | Total sugar | 0.227 | 0.919 |

parameters analysed. The stepwise regression program used the F statistic as the criterion for adding ($F \geq 4$) or deleting ($F < 4$) an independent variable.

The stepwise regression was calculated adopting the sensorial attribute colour as the dependent variable. In the first step, intensity of colour, one of the six potential physicochemical variables, was incorporated and predicted 51% of the sensorial attribute (Table 3). In the second and last step (Table 4), the variable titrate-

ble acidity was introduced into the model, explaining an additional 13% of the variability in the sensorial attribute colour. The model's mathematical expression predicting 64% of the organoleptic attribute (Table 5) was the following:

Colour = 1.49 + 0.85 colour intensity + 0.30 titrate acidity

The results showed that samples with the greatest sum of absorbances at 420 nm, 520 nm, and 620 nm

Table 8 Stepwise selection for sensorial variable visual colour intensity

| Selection: Forward R^2 : 0.856 | | | Adjusted: 0.831 MSE: 0.084 | | Step 3 df : 17 | |
|-------------------------------------|-------------|-------------|----------------------------|-------------------|---------------------|--|
| Variables in model | Coefficient | F -remove | Variables not in model | P_{corr} | F -enter | |
| Titratable acidity | 0.227 | 6.657 | pH | 0.200 | 0.667 | |
| Colour intensity | 1.108 | 41.678 | Ethanol content | 0.336 | 2.036 | |
| Hue | -0.427 | 4.914 | Total sugar | 0.289 | 1.457 | |

Table 9 Model fitting results for sensorial variable visual colour intensity

| Independent variable | Coefficient | SE | t -value | P |
|----------------------|-------------|-------|------------|-------|
| Constant | 1.852 | 0.520 | 3.561 | 0.002 |
| Titratable acidity | 0.227 | 0.088 | 2.580 | 0.020 |
| Colour intensity | 1.108 | 0.172 | 6.456 | 0.000 |
| Hue | -0.427 | 0.192 | -2.217 | 0.041 |

SQ. (ADJ.)=0.831 SE=0.289 MAE=0.208 DurWat=3.086

wavelengths were regarded as the best by the tasters on the hedonistic scale with respect to colour intensity. Inclusion of the variable titratable acidity to complete the model can be explained by the chemical nature of the pacharán pigments, anthocyanins.

A stepwise regression analysis was calculated using as the dependent variable the sensorial attribute visual intensity of colour. The results of the first step appear in Table 6 and the physical variable colour intensity accounted for 70% of the variance in the organoleptic attribute. In the second step (Table 7), the variable titratable acidity was introduced into the model. The relationship between the sensorial variable visual intensity of colour and these two variables predicted 79% of the variation in this sensorial attribute. The last step incorporated the physical variable hue (Table 8). This im-

proved the stepwise regression model for the organoleptic variable visual intensity of colour allowing prediction of 83% of the variance in this sensorial attribute. The mathematical expression for the regression model was (Table 9):

Visual intensity of colour = 1.85 + 1.11 colour intensity + 0.23 titratable acidity - 0.43 hue

For colour intensity, the data demonstrate a strong linear relationship between analytical results and sensorial evaluation. The variable titratable acidity, which was included in the model in the second step, can be justified, again, by the chemical structure of anthocyanins. The variable hue changed the dependent sensorial variable (visual intensity of colour) in the opposite direction. Given the definition of hue (A_{420}/A_{520}), its value increases in proportion to the shift of the sample's maximum spectrophotometric absorbance from 520 nm to 420 nm wavelength. The tasters judged the samples with the highest measured hue values as having less visual intensity of colour.

Next, overall impression, a compound sensorial attribute, was studied. The physicochemical variable pH contributed most to the variability of overall impression explaining 24% of the variance (Table 10). In the second step, the objective variable ethanol content was incorporated (Table 11). These two variables, pH and ethanol content, predicted 45% of the overall impres-

Table 10 Stepwise selection for sensory variable overall impression

| Selection: Forward R^2 : 0.282 | | | Adjusted: 0.244 MSE: 0.083 | | Step 1 df : 19 | |
|-------------------------------------|-------------|-------------|----------------------------|-------------------|---------------------|--|
| Variables in model | Coefficient | F -remove | Variables not in model | P_{corr} | F -enter | |
| pH | 1.191 | 7.464 | Ethanol content | 0.553 | 7.908 | |
| | | | Titratable acidity | 0.258 | 1.285 | |
| | | | Colour intensity | 0.428 | 4.026 | |
| | | | Hue | 0.157 | 0.454 | |
| | | | Total sugar | 0.352 | 2.541 | |

Table 11 Stepwise selection for sensory variable overall impression

| Selection: Forward R^2 : 0.502 | | | Adjusted: 0.446 MSE: 0.061 | | Step 2 df : 18 | |
|-------------------------------------|-------------|-------------|----------------------------|-------------------|---------------------|--|
| Variables in model | Coefficient | F -remove | Variables not in model | P_{corr} | F -enter | |
| pH | 1.098 | 9.616 | Titratable acidity | 0.152 | 0.401 | |
| Ethanol content | 0.124 | 7.908 | Colour intensity | 0.477 | 5.017 | |
| | | | Hue | 0.109 | 0.204 | |
| | | | Total sugar | 0.267 | 1.301 | |

Table 12 Stepwise selection for sensory variable overall impression

| Selection: Forward R^2 : 0.615 | | | Adjusted: 0.547 MSE: 0.050 | | Step 3 df : 17 |
|-------------------------------------|-------------|-------------|----------------------------|-------------------|---------------------|
| Variables in model | Coefficient | F -remove | Variables not in model | P_{corr} | F -enter |
| pH | 1.024 | 9.053 | Titrateable acidity | 0.017 | 0.005 |
| Ethanol content | 0.120 | 8.897 | Hue | 0.082 | 0.108 |
| Colour intensity | 0.267 | 5.017 | Total sugar | 0.323 | 1.859 |

Table 13 Model fitting results for sensory variable overall impression

| Independent variable | Coefficient | SE | t -value | P |
|----------------------|-------------|-------|------------|-------|
| Constant | -4.066 | 1.547 | -2.629 | 0.018 |
| pH | 1.024 | 0.340 | 3.009 | 0.008 |
| Ethanol content | 0.120 | 0.040 | 2.983 | 0.008 |
| Colour intensity | 0.267 | 0.119 | 2.240 | 0.039 |

SQ. (ADJ.)=0.547 SE=0.223 MAE=0.148 DurWat=2.299

sion. The linear regression model was completed upon incorporation of the physicochemical variable colour intensity, which increased by 10% the predictive capability for variation in the sensorial attribute studied (Table 12). Thus, the results of the linear regression (Table 13) were:

Overall impression = $-4.10 + 1.02 \text{ pH} + 0.12 \text{ ethanol content} + 0.27 \text{ colour intensity}$

The pH is a factor that can be modified during the elaboration process. Also, the model shows that colour intensity plays a relevant part in the overall impression of the drink. Among the factors that affect colour intensity throughout the elaboration process of pacharán, are the quantity of sloes used per litre of pacharán produced, the maturity of the sloes, the state of the starting material (fresh, refrigerated, or frozen), the maceration technique (static or continuously agitated), the duration of maceration, and conditions of storage (inert atmosphere, temperature, and protection from light).

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