

REGULAR ARTICLE

Linear programming formulation of a dairy drink made of cocoa, coffee and orange by-products

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ABSTRACT

The agricultural industry generates large amounts of residues, commonly considered as waste. By-products from industrial processing of cacao, coffee and orange were used to formulate a dairy drink. The enriched dairy product was elaborated using a 10% aqueous extract of cocoa bean shells, coffee silverskin and orange peel. A design of mixtures of extreme vertices was applied to test the proportions of the ingredients of the aqueous extract. Sensorial characteristics like taste, odor, color and appearance were evaluated by a semi-trained testing panel applying the method of multiple comparisons, comparing the test formulations with a commercial drink of coffee and cocoa. The test formulations that were rated similar to the reference drink were selected to improve their total polyphenol content (TPC) applying a mathematical process of linear optimization. This approach indicated an optimal formulation containing 74 % cocoa bean shells, 24.50% coffee silverskin and 1.50% orange peel. This formulation gave TPC values of 5.74 ± 0.41 Gallic Acid Equivalent (GAE) mg/g, $82.20 \pm 0.08\%$ antioxidant activity by the diphenylpicrylhydrazyl (DPPH) assay and 114.78 mg/l caffeine content. The results demonstrate the feasibility to produce a drink enriched in antioxidant compounds retaining good sensorial attributes using industrial by products.

Keywords: Optimization; Formulation; Sensory evaluation; Mixture design

INTRODUCTION

Industrial production, including the agricultural industry, generates significant amounts of residues and by-products (Chanakya and Alwis, 2004). Cocoa bean industry dispose tons of cocoa bean shell as waste every year (Arlorio et al., 2005). However, this residue can provide a ready source of inexpensive polyphenols (Redgwell et al., 2003). The presence of flavonoids in extract of cocoa bean shell have been identified (Azizah et al., 1999) and *in vitro* research have demonstrated that flavonoids prevent low-density lipoprotein oxidation (Morel et al., 1996). Coffee silverskin is one of the main residues of coffee production and can cause serious environmental problems to soil (Nabais et al., 2008). Nevertheless, current investigations has proposed coffee silverskin as a good source of nutrient due to its antioxidant activity (Borrelli et al., 2004). Orange juice is one of the most consumed beverages today (Martin et al., 2010), the generation of orange waste is estimated

between 15 to 25 million tons per year (Marín et al., 2007) in which citrus peel is the major constituent, representing 44% of the weight fruit mass (Widmer et al., 2010). The extraction of phenolic compounds from orange peel to use them as antioxidant in foods have been demonstrated (Huang et al., 2009).

Recent research has proposed the use of residues and by products for the formulation of food products (Ribeiro et al., 2014). Main attention has been focused in the use of coffee skin and Martinez- Saez et al. (2014) proposed the development of an antioxidant beverage that could low fat. In addition, experiments have shown that antioxidant activity can be enhanced when a blend of different antioxidant sources is realized (Awe et al., 2013) resulting in better functional qualities of the product. For example, Huang et al. (2009) demonstrated that addition of orange peel extract into black tea resulted in better anti-obesity effect than black tea or orange peel extract alone.

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Linear programming is an important tool that is aimed to maximize or minimized a linear function taking account linear equality and/or inequality constraints. Most of the linear programming models have been used in diet optimization, based on the impact of cost and nutrition as constraints (Moraes et al., 2012). However, some research have demonstrated the importance of considering the palatability of the product as a constraint (Darmon et al., 2006). On this background, we have used the sensorial evaluation to define the constraint of a programming model to optimize a drink formulation in dependence of the polyphenol content of cocoa bean shells, coffee silver skin and orange peel.

MATERIALS AND METHODS

Extract preparation

Fresh samples of cocoa bean shells, coffee silverskin and orange peel were dried individually at 60°C in an oven with air circulation during 16 h. The dried residues were mixed according to the formulations obtained from the experimental design; a 10% aqueous extract was prepared by boiling the mixture at 100°C for 5 min. Higher levels of aqueous extract provided too much astringency to the infusion, resulting in a unpleasant taste. The preparations were allowed to sediment for 5 min at room temperature and the solids were separated by filtration.

Experimental design

An experimental design was obtained applying the equation 1:

$$Y_i = \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_{12} X_1 X_2 + \beta_{13} X_1 X_3 + \beta_{23} X_2 X_3 + \beta_{ij} X_{ij}^2 \dots \quad (1)$$

Here, Y_i is the result; the beta symbols (β) represent the coefficients to be adjusted by regression analysis; X_1, X_{12}, X_{ij}^2 are the lineal, interaction and quadratic effect of the components respectively, in which X_1 represent the cocoa bean shells, X_2 represent coffee silverskin and X_3 represent orange peel. The experiments were performed according to the following restrictions:

$$74.00\% \leq X_1 \leq 100\% \quad (2)$$

$$00.00\% \leq X_2 \leq 24.50\% \quad (3)$$

$$00.00\% \leq X_3 \leq 1.50\% \quad (4)$$

The restrictions of the model were defined based on previous experiments where the combination of those components displayed a pleasing flavor. Due to the restrictions applied, the simplex region was sub divided into a new region in which were included the possible mixture

combinations as described by Silveira and Leite (2010). In this case, the design of extreme vertices was applied to the experiments with mixtures.

Dairy drink preparation

Preliminary experimental work was realized in order to define the composition of the drink through trial and error assay. The final acceptable formula was mixing the aqueous extract from by products to skim milk (37%), sugar (5.87%), stabilizers and preservatives (0.13%) and pasteurized at 71.7°C for 15 seconds, followed by fast cooling at 4°C for storage and later evaluation.

Sensorial evaluation

The sensorial panel was composed of 30 semi-trained participants who were asked to evaluate taste, odor, color and appearance of the samples. Sensorial evaluations were done applying the test of multiple comparisons (ABNT, 1995). Samples were coded with random numbers of 4 digits and compared to a standard labeled as 'R', a cold commercial drink of mocha coffee with characteristic similar to the drink we aimed to design. Panelists compared each coded sample with the reference sample and graded them using a sensorial scale of 9 points (Table 1).

The data was analyzed applying a variance analysis and Dunnett method for multiple comparisons (Dunnett, 1955).

Total polyphenol content and DPPH assay

Total polyphenol content (TPC) was determined by the Folin-Ciocalteu method and the polyphenol activity was expressed as Gallic Acid Equivalent (GAE) (Lachman et al., 1998). Briefly, 250 µl sample were mixed with 250 µl Folin-Ciocalteu's reagent (Sigma-Aldrich). Na_2CO_3 20% (750 µl) was added after 5 min and the mixture allowed to proceed for 2 h; absorbance was measured at 765 nm. The antioxidant activity (AA %) of each component was determined by the free DPPH assay with some modifications. The reaction mixture consisted of 0.5 ml sample, 3 ml absolute ethanol and 0.3 ml of a 0.5 mM DPPH in ethanol. Absorbance was measured at 517 nm

Table 1: Sensorial evaluation and scale of rating scores (ABNT, 1995)

Rating score	Equivalent rate
1	Extremely inferior to R
2	Markedly inferior to R
3	Moderately inferior to R
4	Slightly inferior to R
5	Equal to R
6	Slightly superior to R
7	Moderately superior to R
8	Markedly superior to R
9	Extremely superior to R

after 30 min incubation. Concentration was determined applying the following equation:

$$\% \text{ inhibition} = \frac{\text{control} - \text{test}}{\text{control}} \times 100 \quad (5)$$

Caffeine analysis by HPLC

The assay for caffeine determination was adapted from the method described by Amaro et al., 2008. A Perkin Elmer 200 instrument was used for high pressure liquid chromatography (HPLC), equipped with UV-VIS detector and a C18 column 250 x 4.20 mm with a solid phase of 5 μm. The mobile phase used was a 40:60 mix HPLC-grade methanol-water, with a flow rate of 1ml/min, 5 min ejection time and detection at 254 nm. Injection volume for samples and standards was 10 μl.

Optimization

A lineal programming model was developed with the aim to maximize the total polyphenol content in the formulations, limiting this approach to those formulations that scored similar to the reference in the sensorial evaluation. The target objective function was:

$$\text{Maximize } Z = \sum_{j=1}^n c_j x_j \quad (6)$$

$$\text{Subject to } b_j \leq x_j \leq u_j, \quad j=1, \dots, n$$

$$x_j \geq 0,$$

Where Z is the total polyphenol content (TPC) expressed as GAE mg/g in the sample, c_j is the TPC (GAE mg/g)

Table 2: Total polyphenol content in components

Variable	Ingredient	Total polyphenol content (mg GAE/g)
X ₁	Cocoa bean shell	4.55
X ₂	Coffee silver skin	6.63
X ₃	Orange peel	27.81

Table 3: Summary of the sensorial evaluation^a

Run	Factors ^b (%)			Mean acceptance ratings ^c			
	X ₁	X ₂	X ₃	Taste	Odor	Color	Appearance
1	100,00	0	0	6,03±1,52	6,73±1,44*	6,77±1,41*	6,97±1,25*
2	75,50	24,50	0,00	4,90±2,07	6,47±1,76*	7,00±1,34*	6,93±1,60*
3	98,50	0,00	1,50	4,97±1,38	6,40±1,54*	6,30±1,42	6,43±1,43*
4	74,00	24,50	1,50	6,73±1,57*	6,37±1,71*	7,03±1,50*	6,73±1,74*
5	93,50	6,13	0,38	5,80±1,61	6,93±1,34*	6,77±1,19*	6,77±1,33*
6	81,25	18,38	0,38	6,47±1,50*	7,00±1,34*	7,67±1,06*	7,83±1,12*
7	92,75	6,13	1,13	6,03±1,52	6,97±1,43*	7,57±1,30*	7,67±1,24*
8	80,50	18,38	1,13	7,23±1,17*	7,17±1,51*	7,67±1,22*	7,87±1,31*
9	87,75	12,25	0,00	5,87±2,03	7,13±1,63*	7,77±1,25*	7,87±1,17*
10	99,25	0,00	0,75	6,00±1,91	7,00±1,44*	7,67±1,18*	7,80±1,10*
11	74,75	24,50	0,75	6,67±1,24*	7,27±1,55*	7,33±1,35*	7,23±1,10*
12	86,25	12,25	1,50	5,87±1,55	6,50±1,59*	6,63±1,72*	6,93±1,46*
13	87,00	12,25	0,75	5,37±1,27	6,30±1,73*	6,13±1,50	6,43±1,56*

^aScores are based on a 9-point scale with 1, extremely inferior to R; 5, no difference; and 9, extremely better than R, ^bFactors were: X₁: Cocoa bean shell, X₂: Coffee silverskin, X₃: Orange peel, ^cMean values are not significantly different from R, ^dcold commercial drink of mocha coffee (p<0.05)

measured in ingredient j and x_j is the proportion of ingredient j used in the formulation; b_j and u_j are the minimum and maximum percentage of ingredient j that can be used in the formulation, respectively.

RESULTS AND DISCUSSION

TPC was measured in cocoa bean shells, coffee silverskin and orange peel with the aim to establish the objective function. As shown in Table 2, orange peel had the highest TPC, and was in accordance with the value (23.3 mg GAE/g) reported by Khan et al. (2010).

The major polyphenols present in orange peel are flavanone glycosides, polymethoxylated flavone aglycons, flavone glycosides and C-glycosylated flavones (Sawalha et al., 2009) and health benefit such as anti-inflammatory, anti-carcinogenic, anti-viral, antioxidant, anti-thrombogenic and anti-atherogenic properties has been reported it (Middleton et al., 2000; Whitman et al., 2005; Lai et al., 2007; Li et al., 2009). TPC reported for coffee silverskin was higher than the value found in the literature 0.17 mg EGA/g sample (Jiménez-Zamora et al., 2015). Phenolic compounds present in coffee silverskin are similar to the phenolic in coffee brews, and chlorogenic acid is the main polyphenols present (Bresciani et al., 2014). Higher values of TPC were observed in the samples of cocoa bean shells compared to the values (2,56 GAE mg/g) reported by Bruna et al. (2009).

Thirteen formulations were obtained from the design of extreme vertices mixtures (Table 3). The average values for each formulation in each sensorial variable were as shown in Table 3. Taste was rated from 4.90 (Run 2) to 7.23 (Run 8); odor was rated from 6.30 (Run 13) to 7.27 (Run 11); color was rated from 6.13 (Run 13) to 7.77 (Run 9) and

appearance was rated from 6.43 (Run 3 y 13) to 7.87 (Run 8 y 9). The results show that most of formulations were rated as slightly or moderately superior to the reference drink in the variables odor, color and appearance. However, only the formulations 2, 3 and 13 were rated as ‘similar to R’ regarding taste. The formulations 1, 5, 7, 9, 10 y 12 were rated as ‘slightly superior to R’ while the formulations 4, 6, 8 and 11 were rated as ‘moderately superior to R’.

Because the differences for all 4 sensorial variables were statistically different from the reference R, the formulations 4, 6, 8 and 11 were selected to define the constraints for the analysis of lineal optimization. The objective function equation and the constraints are presented in Table 4. The model was solved using Solver, Microsoft Excel 2010.

The model indicated an optimal formulation of: 74% cocoa bean shells, 24.50% coffee silver skin, and 1.50% orange peel. The predicted TPC for the proposed model was 5.41 mg GAE/g sample, while the observed value was 5.74 ± 0.41 mg GAE/g sample. TPC, antioxidant activity and caffeine content was calculated for the optimal formulation and higher polyphenol, antioxidant activity ($82.20 \pm 0.08\%$) and caffeine (114.78 ± 2.83 mg/l) content than the reference ‘R’ was found (Table 5). Chlorogenic acid present in coffee silverskin may interact with the caffeine and both contribute on fat reduction (Martinez-Saez et al., 2014). Orange peel extract, caffeine and polyphenols present in coffee and cocoa by product extract may exhibit a synergistically effect on anti-obesity (Huang et al., 2009). Furthermore, the levels of caffeine found in the formulation could have positive effects in the improvement on neuromuscular coordination and cognitive function and

elevation of mood (Glade, 2010). However, antagonistic interactions may occurs among the caffeine and conjugated linoleic acid present in the milk because of the pro-oxidant properties of caffeine (Anesini et al., 2012).

Several investigations have indicated that adding milk to tea or cocoa products cause negative effect because of an interaction between polyphenols and milk protein reduce the antioxidant activity (Arts et al., 2002 and Niseteo et al., 2012) and cause bioavailability loss (Serafini et al., 1996). However, milk was added into the formulation to lower the astringency cause by the addition of coffee silverskin. A low loss in nutritional quality was obtained considering that only a small part of proteins can interact with the polyphenols present in the matrix (Gallo et al., 2013). Additionally, the addition of milk and sugar may stabilize the antioxidant activity of the beverage (Vasundhara et al., 2008)

CONCLUSIONS

An optimal formulation was obtained by lineal optimization, containing cacao by- products at 74%, coffee silver skin at 24.5% and orange peel at 1.50%. This formulation had 5.74 ± 0.41 GAE mg/g for TPC levels, antioxidant activity by elimination of radicals DPPH $82.20 \pm 0.08\%$ and 114.78 mg/l caffeine, demonstrating the feasibility to prepare a dairy drink with acceptable sensorial traits and rich in antioxidant compounds. This values represent a positive predictor for the acceptance of the product in the market. In addition, this model can be used to reformulate the product according to the variation in polyphenol content of raw materials, which are expected to fluctuate since they are generated as residues from the agricultural industry.

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Author contributions

M. Q. and A.B. were responsible of the conception and design of the experiment. G. F. and K.S. were in charge of the acquisition of data. M.Q. analyzed, interpreted the data and prepared the manuscript. P. M. did the critical revision.

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Table 4: Objective function and constraints in the modeling

Objective function	Subjected to
Maximize $Z=4,55X_1+6,63X_2+27,81X_3$	$X_1+X_2+X_3=100$
	$74.00 \leq X_1 \leq 81.25$
	$18.38 \leq X_2 \leq 24.50$
	$0.75 \leq X_3 \leq 1.50$
	$X_1, X_2, X_3 \geq 0$

Table 5: Total polyphenols and antioxidant activity

Parameter	Optimized formulation $X_1=74.00\%$, $X_2=24.50\%$ $X_3=1.50\%$	Reference “R”	P value
Predicted total polyphenols value (GAE mg/g sample)	5.41	-	-
Observed total polyphenols value (GAE mg/g sample)	5.74 ± 0.41^a	3.93 ± 0.84^b	0.028
Antioxidant activity (%)	82.20 ± 0.08^a	55.54 ± 0.03^b	<0.001
Caffeine (mg/l)	114.78 ± 2.83^a	47.44 ± 1.49^b	<0.001

Mean values in the same row not followed by the same letter are significantly different ($p < 0.05$)

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