

Rossana V. C. Cardoso<sup>1</sup>, Ângela Fernandes<sup>1,\*</sup>, José Pinela<sup>1</sup>, Maria Inês Dias<sup>1</sup>, Carla Pereira<sup>1</sup>, Tânia C. S. P. Pires<sup>1</sup>, Márcio Carochó<sup>1</sup>, Esteban Fernández Vasallo<sup>2</sup>, Isabel C. F. R. Ferreira<sup>1</sup> and Lillian Barros<sup>1</sup>

<sup>1</sup> Centro de Investigação de Montanha (CIMO), Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5300-253 Bragança, Portugal

<sup>2</sup> Molendum Ingredient, Calle de la Milana S/N, Coreses, 49530 Zamora, Spain

afeitor@ipb.pt

## INTRODUCTION

Cereal grains are rich in phytochemicals and nutrients, such as phenolic acids, flavonoids, carbohydrates, dietary fibers, proteins, and tocopherols, among other constituents, which have a vital role in preventing cardiovascular and digestive system diseases, overweight and obesity, inflammation, type 2 diabetes, and some types of cancer. The food industry has focused on the production of functional foods based on different types of cereals, due to the growing consumer's demand for healthier foods. For this purpose, both cereals and their constituents offer unlimited potential and are an excellent raw material for the production of functional foods and functional ingredients, in particular for the design of novel food products based on cereals or their by-products. With the growing world population and given the limited resources our planet can provide, it is essential to produce enough food to meet the growing demands and needs of the human population and also to ensure food security. However, with restricted arable land, the agri-food industry by-products should become recycled within the food chain and, thus, be valorized as a sustainable source of food and food ingredients, also promoting the circular economy. This study was performed to provide a detailed nutritional and chemical characterization of cereal by-products, namely wheat, maize, and rye bran and/or germ, currently produced in large quantities by food ingredients industrial groups, but which have low or no commercial value.

## METHODOLOGY

The proximate composition was evaluated by AOAC official procedures, free sugars and tocopherols were determined using liquid chromatography coupled to a refraction index (HPLC-RI) and fluorescence (HPLC-FL) detectors, respectively. Fatty acids were determined by gas chromatography coupled to a flame ionization detector (GC-FID), organic acids by ultra-fast liquid chromatography coupled to a diode detector (UPLC-DAD)

## RESULTS

Carbohydrates (including sucrose) were the major nutritional constituents (56.35–78.12 g/100 g dw), followed by proteins (11.2–30.0 g/100 g dw). The higher energy value (432.3 kcal/100 g dw) was presented by the wheat germ and also presented the highest citric acid content (0.857 g/100 g dw), the most abundant organic acid detected. Sucrose was the most abundant in all cereal by-products, reaching 10.4 g/100 g dw in wheat germ, 3.84 g/100 g dw in the maize bran-germ mixture and approximately 2.9 g/100 g dw in the bran samples. Unsaturated fatty acids predominated in all samples given the high content of linoleic (53.9–57.1%) and oleic (13.4–29.0%) acids. Wheat germ had the highest levels of tocopherols (22.8 mg/100 g dw).

Table 1. Proximate composition and energy value of the cereal by-products.

	Wheat germ	Maize bran-germ	Rye bran	Wheat bran
Fat (g/100 g dw)	9.64±0.1 <sup>d</sup>	8.08±0.01 <sup>c</sup>	3.9±0.1 <sup>a</sup>	5.05±0.02 <sup>b</sup>
Proteins (g/100 g dw)	30.0±0.1 <sup>d</sup>	11.2±0.2 <sup>a</sup>	15.3±0.1 <sup>b</sup>	16.4±0.1 <sup>c</sup>
Ash (g/100 g dw)	3.97±0.05 <sup>d</sup>	2.66±0.04 <sup>a</sup>	3.54±0.04 <sup>c</sup>	3.12±0.04 <sup>b</sup>
Carbohydrates (g/100 g dw)	56.35±0.02 <sup>a</sup>	78.12±0.04 <sup>d</sup>	77.2±0.1 <sup>c</sup>	75.42±0.01 <sup>b</sup>
Energy (kcal/100 g dw)	432.3±0.1 <sup>d</sup>	429.8±0.2 <sup>c</sup>	405.4±0.1 <sup>a</sup>	412.8±0.1 <sup>b</sup>

In each line, different letters indicate significant differences ( $p < 0.05$ ) between samples. The number of significant figures of each mean value was conditioned by the standard deviation, which was rounded to one significant figure. dw - dry weight.

Table 2. Composition in sugars and organic acids of the cereal by-products.

	Wheat germ	Maize bran-germ	Rye bran	Wheat bran
Free sugars (g/100 g dw)				
Fructose	nd	0.15±0.02	nd	nd
Glucose	0.18±0.01 <sup>c</sup>	0.16±0.01 <sup>b</sup>	nd	0.14±0.01 <sup>a</sup>
Sucrose	10.4±0.1 <sup>c</sup>	3.84±0.01 <sup>b</sup>	2.92±0.03 <sup>a</sup>	2.9±0.1 <sup>a</sup>
Trehalose	0.25±0.01	nd	nd	nd
Raffinose	4.65±0.03 <sup>d</sup>	0.4±0.1 <sup>a</sup>	0.59±0.01 <sup>b</sup>	1.69±0.01 <sup>c</sup>
Total of free sugars	15.2±0.1 <sup>d</sup>	4.4±0.1 <sup>b</sup>	3.51±0.02 <sup>a</sup>	4.7±0.1 <sup>c</sup>
Organic acid (g/100 g dw)				
Oxalic acid	0.090±0.001 <sup>c</sup>	0.105±0.001 <sup>d</sup>	0.0471±0.0001 <sup>a</sup>	0.0593±0.0001 <sup>b</sup>
Malic acid	nd	nd	tr	tr
Ascorbic acid	tr	tr	nd	nd
Shikimic acid	nd	nd	nd	tr
Citric acid	0.857±0.002 <sup>d</sup>	0.204±0.001 <sup>a</sup>	0.424±0.001 <sup>b</sup>	0.539±0.001 <sup>c</sup>
Fumaric acid	tr	tr	tr	tr
Total of organic acids	0.946±0.002 <sup>d</sup>	0.309±0.001 <sup>a</sup>	0.471±0.001 <sup>b</sup>	0.598±0.001 <sup>c</sup>

In each line, different letters indicate significant differences ( $p < 0.05$ ) between samples. The number of significant figures of each mean value was conditioned by the standard deviation, which was rounded to one significant figure. dw - dry weight; nd - not detected; tr - traces (below LOQ - Limit of Quantification).

Table 3. Composition in fatty acids and tocopherols of the cereal by-products.

	Wheat germ	Maize bran-germ	Rye bran	Wheat bran
Fatty acids (relative %)				
C14:0	0.12±0.01 <sup>a</sup>	nd	0.14±0.01 <sup>b</sup>	0.126±0.001 <sup>a</sup>
C15:0	0.073±0.003 <sup>a</sup>	nd	0.15±0.01 <sup>c</sup>	0.104±0.001 <sup>b</sup>
C16:0	18.02±0.02 <sup>c</sup>	10.6±0.3 <sup>a</sup>	15.59±0.04 <sup>b</sup>	18.3±0.2 <sup>c</sup>
C16:1	0.17±0.02 <sup>b</sup>	0.101±0.004 <sup>a</sup>	0.27±0.02 <sup>d</sup>	0.20±0.01 <sup>c</sup>
C18:0	0.86±0.01 <sup>a</sup>	2.955±0.001 <sup>c</sup>	1.3±0.1 <sup>b</sup>	1.32±0.01 <sup>b</sup>
C18:1n9c	13.4±0.1 <sup>a</sup>	29.0±0.1 <sup>d</sup>	17.31±0.04 <sup>c</sup>	16.07±0.04 <sup>b</sup>
C18:2n6c	57.1±0.1 <sup>d</sup>	54.8±0.2 <sup>b</sup>	53.9±0.1 <sup>a</sup>	56.3±0.2 <sup>c</sup>
C18:3n3	8.0±0.1 <sup>c</sup>	1.04±0.01 <sup>a</sup>	8.6±0.1 <sup>d</sup>	5.17±0.05 <sup>b</sup>
C20:0	0.205±0.001 <sup>a</sup>	0.48±0.01 <sup>b</sup>	nd	0.24±0.01 <sup>a</sup>
C20:1	1.35±0.03 <sup>c</sup>	0.168±0.005 <sup>a</sup>	1.456±0.003 <sup>d</sup>	1.0±0.1 <sup>b</sup>
C22:0	0.25±0.02 <sup>a</sup>	0.36±0.03 <sup>b</sup>	0.42±0.01 <sup>c</sup>	0.41±0.01 <sup>c</sup>
C20:5n3	0.30±0.02 <sup>a</sup>	nd	0.47±0.01 <sup>c</sup>	0.40±0.02 <sup>b</sup>
C24:0	0.20±0.01 <sup>a</sup>	0.46±0.01 <sup>c</sup>	0.49±0.03 <sup>d</sup>	0.29±0.01 <sup>b</sup>
SFAs	19.73±0.02 <sup>c</sup>	14.9±0.3 <sup>a</sup>	18.1±0.1 <sup>b</sup>	20.8±0.2 <sup>d</sup>
MUFAs	14.9±0.1 <sup>a</sup>	29.2±0.1 <sup>d</sup>	19.03±0.02 <sup>c</sup>	17.3±0.1 <sup>b</sup>
PUFAs	65.4±0.1 <sup>d</sup>	55.9±0.2 <sup>a</sup>	62.9±0.1 <sup>c</sup>	61.9±0.3 <sup>b</sup>
Tocopherols (mg/100 g dw)				
α-Tocopherol	13.46±0.01 <sup>d</sup>	3.38±0.02 <sup>a</sup>	4.1±0.1 <sup>b</sup>	5.23±0.04 <sup>c</sup>
β-Tocopherol	9.27±0.04 <sup>d</sup>	0.12±0.03 <sup>a</sup>	1.27±0.01 <sup>b</sup>	2.99±0.01 <sup>c</sup>
γ-Tocopherol	nd	1.61±0.03 <sup>b</sup>	nd	0.140±0.001 <sup>a</sup>
δ-Tocopherol	0.046±0.001	nd	nd	nd
Total of tocopherols	22.8±0.1 <sup>d</sup>	5.10±0.02 <sup>a</sup>	5.4±0.1 <sup>b</sup>	8.35±0.04 <sup>c</sup>

In each line, different letters indicate significant differences ( $p < 0.05$ ) between samples. The number of significant figures of each mean value was conditioned by the standard deviation, which was rounded to one significant figure. SFA - saturated fatty acids; MUFA - monounsaturated fatty acids; PUFA - polyunsaturated fatty acids; dw - dry weight; nd - not detected.

## CONCLUSION

These milling by-products can have value-added potential in the food market as a low-cost material for the development of nutrient-rich ingredients and bioactive compounds. Wheat germ, maize bran-germ mixture, rye bran, and wheat bran could be directed to human nutrition as a sustainable way to promote the development of novel and functional foods, the bioresource-use efficiency, and the circular bioeconomy in this so important food sector.

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