RESEARCHES REGARDING THE SUPERIOR VALORISATION OF BY-PRODUCTS FROM THE WINERY INDUSTRY, AND THE OBTAINING OF BAKERY PRODUCTS WITH FUNCTIONAL PROPERTIES

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Abstract. *The paper presents in summary the great potential of the wine industry in Romania, as a supplier of by-products with special biochemical characteristics. From all of the by-products known, the most notable are the epicarp and grape seeds, which can be used directly in the bakery industry, and due to the high content of fiber, antioxidants and unsaturated fatty acids, represent a high functional potential. The undertaken studies aimed to introduce in the technological flow an optimal quantity of grape seed powder (GSP), respectively grape epicarp powder (GEP), in order to maximize the functional effect, and the sensory characteristics. For this purpose, the nutritional and rheological profile of mixtures of wheat flour and semi-degreased grape seeds and grape epicarp were first realized. Subsequently, the bakery products with additions of grape epicarp in a proportion of 5, 10, 12, 15% and respectively semi-degreased grape seeds in proportion of 3, 5, 7, 9% were made on an industrial technological flow. The obtained bakery products were analyzed from physical and sensorial point of view, the conclusions showing that the maximum percentage of by-products use is 12% for grape epicarp, and 7% for semi-degreased grape seeds respectively.*

Keywords: functional bakery products, grape seeds and epicarp

1. Introduction

1.1. The concept of functional food product

In the current socio-economic context, human nutrition leads to chronic imbalances characteristic of modern man, which is why healthy eating will become in the near future an important therapeutic means for maintaining or even regaining health. Nutritional improvements for a healthy diet have the effect of reducing the health costs that are today extremely expensive for chronic diseases caused mainly by unhealthy eating and sedentary lifestyle [10].

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With the growing population and food security needs, either the re-formulation of existing food products or the development of new foods will be targeted.

Research in this area covers a wide range of topics, such as: the need for primary prevention of chronic diseases caused by non-sanogenic diets; development of nutritional intervention programs; innovation in the field of functional ingredients and bioactive compounds with high potential; new methods for encapsulating valuable bioactive compounds; design and development of innovative products; personalized nutrition; various aspects of food safety and quality.[1], [9], [11-14]

Therefore, the creation of a food with a nutritional profile as complete as possible, to meet the specific requirements of the consumer (related to age, health, type of daily activities), is a constant goal of current research in nutrition. In Europe, functional food enjoys a special interest, the topic being addressed by the 47 projects funded on this topic, in which 513 institutions participated in the FP5, FP6, FP7 competitions with 150 million euros [15].

Within this work, the potential of new bakery products developing by adding in wheat flour by-products from the winery industry with high content of bioactive compounds, such as grape seeds and grape epicarp.

1.2. The concept of functional food product

In the case of Romania, the annual consumption of bread per capita is about 90 kg, compared to the European average of 50 kg and 93% of Romanians consume bread daily (Ministry of Health, 2011). These data demonstrate the importance of bread in the Romanian diet. A recent study found that 83% of consumers prefer white bread, followed by black bread (25%) and homemade bread (23%) [8].

In her work, Apostol L., [1], has studied the increase in the nutritional value of bakery products using two different sources of nutrients, namely Jerusalem artichoke (*Helianthus tuberosus L*) and hemp seeds (*Cannabis sativa L*) partially degreased, a waste resulting from the technological process of obtaining cold-pressed oil. The experimental results on the chemical composition of Jerusalem artichoke tubers revealed that, of the total constituent substances, about 63% is the inulin content. The inulin-rich content of this ingredient used in experimental research confirms that Jerusalem artichoke tubers have functional potential. Also, the mineral content is high, namely : potassium, calcium and magnesium.

Hemp seed flour has in its composition, in appreciable quantities, substances with high functional potential, such as fibers, minerals and last but not least essential fatty acids, with an optimal ratio of ω-6 / ω-3 of 3: 1 [1].

From the point of view of the functional potential of both *Jerusalem artichoke* and partially defatted hemp seeds, the experimental results revealed that the terms "rich in fiber", a source of calcium, potassium, magnesium and zinc can be issued, providing more than 15% of the recommended daily dose per 100 g of product. All these indications may be preceded by the term "naturally".

Fortified wheat flour with different percentages of Jerusalem artichoke (5%, 10%, 15% and 20%) and partially defatted hemp (5%, 10%, 15% and 20%) and a mixture of the two ingredients (5% Jerusalem artichoke + 6%, 10% and 15% partially defatted hemp seeds) was analyzed from a compositional point of view and the influence of these ingredients on the nutritional composition and rheological properties of wheat flour was studied [1].

The conclusions of the study show that the sample of bread with the addition of 5% Jerusalem artichoke and 6% partially defatted hemp seeds has the highest coefficient of acceptability of the participants in the sensory analysis [1].

In the doctoral thesis (Popa A., 2013) has developed a new, functional food product with the potential to be widely consumed daily, as is the case with white bread reformulated by adding oat derivatives (oatmeal and oat bran) as functional ingredients. The raw materials studied for their use in the development of new bakery products, with functional potential, were: *Solomon* oats and its derivatives, sifted oatmeal and oat bran, as well as mixtures of wheat-oat flour (flour content or oat bran in proportions of 20, 40, 60, 80 and 100%), and all experimental results were compared with white wheat flour 550 [10].

In order to establish the technology of obtaining breads with the addition of oats, as a functional ingredient, baking tests were performed, as well as comparative physico-chemical and sensory analyzes.

Research has led to the optimization of mixtures of wheat flour and oat derivatives to obtain bakery products with nutritional mentions of: "iron source", "magnesium source", "magnesium rich" and "zinc source" with a positive sensory impact from the consumer.

In its article, Bhattarai S, [2], carried out a study on improving the functional properties of bakery products, by adding buckwheat flour and green tea. Products with the addition of buckwheat flour in proportions of 20%, 30%, 40% and 50% and 1%, 3% and 5% green tea were made, which were compared with a control sample of wheat flour. The products were assessed sensorial based on 5 parameters: core color, shell color, taste, smell and overall appearance. The optimal variant identified by the test team was the one with content of 40% buckwheat and 3% green tea. In this variant, the lipid content was 2.93 ± 0.31%, similar to rye bread specialties, in which the value of this parameter is approx. 2.6%.

The fiber content was 2.12 ± 0.16%, similar to that of rye bread containing approx. 2.36% fiber. The protein content was 16.56 ± 1.12%, significantly higher than that of wheat flour products, due to the appreciable intake of protein from buckwheat flour [2].

The humidity of the optimized product was 27.17%, significantly lower than the average humidity of wheat flour products with the value of approx. 33.8% (Bhattarai S, et al., 2012), given that the sensory testing team did not specify significant differences in texture in the analyzed products. As the lipid content in the product developed (2.93 ± 0.31%) was higher than in the control sample (1.9%), the effects of satiety and persistence of taste were more intense. The protein content was 16.56%, significantly higher than the normal protein content of white flour bread (6-10%) [2].

The authors found that the shelf life of the product increased by approx. 3 days, compared to white flour bread kept in similar conditions, a phenomenon attributed to the antifungal activity of catechin EGCG in green tea [2].

Other ingredients used to make functional bakery products are: extracts of *Pleurotus Ostreatus (1-3)(1-6)*ß-Glucan (Frioui M. et al., 2017), mangosteen fruit flour *Garcinia Mangostana* (Ibrahim U.K., et al., 2018), chia seeds flour (Kurek M.A., 2019), etc. [3], [4], [5], [6], [7].

2. Materials and research methodology

2.1. Materials

Grape epicarp flour used in the experimental research was a by-product obtained during manufacture of red *Vitis vinifera* from Romania, and was furnished by a local wine-making factory. Grape skins were collected after the grapes were crushed and the juice was obtained. Fresh samples were manually sieved to separate skin fraction from the seeds. Skin fractions were dried and grounded. The level of degradation of the components of this material may be considered low because all the steps were performed at low temperature.

The grape seed flour used in the experimental research was supplied by the Romanian company SC 2E PROD SRL, Alexandria, Teleorman. After the mechanical extraction of grape oil, the partially degreased seeds were dried and crushed.

The first wheat flour used in the study was 480 type (ash, d.m. – 0.48%) and was provided by Titan S.A. (Bucharest, Romania). Four types of mixtures of 480 type wheat flour and different proportions of defatted grape seeds flour were obtained, in the following ratios: 97:3, 95:5, 93:7 and 91:9 (w/w).

The second wheat flour used in the study was 550 type (ash, d.m. – 0.55%) and was provided by M.P. Băneasa-Moară S.A. Bucuresti. Three types of mixtures of 550 type wheat flour and different proportions of grape epicarp flour were obtained, in the following ratios: 95:5, 90:10, 88:12 and 85:15 (w/w).

2.2. Research methodology

Physico-chemical indicators of the samples were determined using the following methods:

- Method of determining humidity (SR ISO 712:2009);
- Method of determining acidity (SR 90:2007);
- Method of determining the total ash content (SR ISO 2171:2009);
- Method of determining the total fat content, Soxhlet (SR 90:2007);
- Method of determining the crude protein content (SR ISO 20483:2007);
- Method of determining the crude fiber content AOAC 991.43;
- Method of determining the fatty acid content by gas chromatography;
- Method of determining the mineral content.

The rheological characteristics of the doughs obtained were determined using the Mixolab apparatus, the Chopin + protocol. It uses the standardized protocol ICC No. 173 for a complete characterization of the rheological behavior of the flour (protein network, starch and enzymatic activity) and produces a simple graph of interpretation of the results. The device measures in real time the torque (expressed in Nm) produced by the passage of the dough between the two mixing arms, and studies rheological and enzymatic parameters. The operating parameters of the device for the analysis of the rheological behavior of the dough are the following: tank temperature 30°C, mixing speed 80 min^{-1}, heating speed 2°C / min, the total time of an analysis being 45 minutes. C1, C2, C3, C4, C5 are specific points on the rheological diagram, and TC1, TC2, TC3, TC4, TC5 are their correspondent time (min). C1 it is used to determine water absorption; C2 measures protein weakening as a function of mechanical work and temperature; C3 measures starch gelatinization; C4 measures hot gel stability; C5 measures starch retro-gradation in the cooling phase.

3. Results and discussions

3.1. Mixtures of wheat flour and grape seeds flour

The results obtained for mixtures of wheat flour and grape seed flour (97:3, 95:5, 93:7 and 91:9) are presented in table 1 (protein, ash, total fat and crude fiber) and table 2 (mineral content).

Table 1. Components of wheat flour and its mixtures with grape seed flour

	Samples				
	P0 (100:0)	P1 (97:3)	P2 (95:5)	P3 (93:7)	P4 (91:9)
Protein	10.50 ± 0.10	10.63 ± 0.15	10.72 ± 0.13	10.81 ± 0.19	10.9 ± 0.14
Ash	0.48 ± 0.01	0.56 ± 0.03	0.61 ± 0.04	0.66 ± 0.04	0.71 ± 0.02
Total fat	0.90 ± 0.05	1.05 ± 0.05	1.15 ± 0.05	1.25 ± 0.03	1.35 ± 0.05
Crude fiber	0.69 ± 0.10	3.6 ± 0.18	7.3 ± 0.28	10.1 ± 0.34	14.3 ± 086

Table 2. Mineral content of wheat flour and of its mixtures with grape seed flour

Sample	Mineral content (mg mineral/100 g sample)				
	Ca	Mg	K	Cu	Fe
P0 (100:0)	43.8 ± 0.59	47.7 ± 0.55	187 ± 0.75	0.78 ± 0.09	1.1 ± 0.22
P1 (97:3)	54.66 ± 0.40	58.20 ± 0.33	192.20 ± 0.93	1.49 ± 0.09	1.29 ± 0.21
P2 (95:5)	61.90 ± 0.10	65.21 ± 0.56	195.66 ± 0.34	1.68 ± 0.11	1.58 ± 0.22
P3 (93:7)	69.15 ± 0.74	72.21 ± 0.68	199.13 ± 1.10	2.34 ± 0.20	1.84 ± 0.37
P4 (91:9)	74.32 ± 0.13	79.02 ± 0.63	207.12 ± 1.13	2.97 ± 0.13	2.02 ± 0.54

It can be observed that the flour mixes has a high content of Ca, Mg, Cu and Fe, and fibers.

Table 3. Rheological behavior of mixture of grape seed flour and wheat flour

Parameter	Abbreviation	P0 (100:0)	P1 (97:3)	P2 (95:5)	P3 (93:7)	P4 (91:9)
Water absorption (%)	CH	58.2	58.0	56.7	56.9	57,0
Stability (min)	ST	8.50	9.10	8.88	9.48	9,83
Amplitude (Nm)	A	0.100	0.104	0.081	0.078	0,105
Maximum consistency during:						
– phase 1 (Nm)	C1	1.143	1,065	1,111	1,081	1,068
	TC1	1.20	1.22	1.12	1.35	1,05
– phase 2 (Nm)	C2	0.461	0.469	0.486	0.428	0,416
	TC2	16.62	16.68	16.40	16.63	17,00
– phase 3 (Nm)	C3	2.041	2.030	2.106	2.129	2,091
	TC3	24.53	24.43	24.08	23.17	23,62
– phase 4 (Nm)	C4	1.553	1.479	1.458	1.360	1,429
	TC4	30.95	30.67	29.95	30.63	28,75
– phase 5 (Nm)	C5	3.131	2.977	3.009	3.033	3,032
	TC5	45.02	42.00	45.02	45.02	45,02

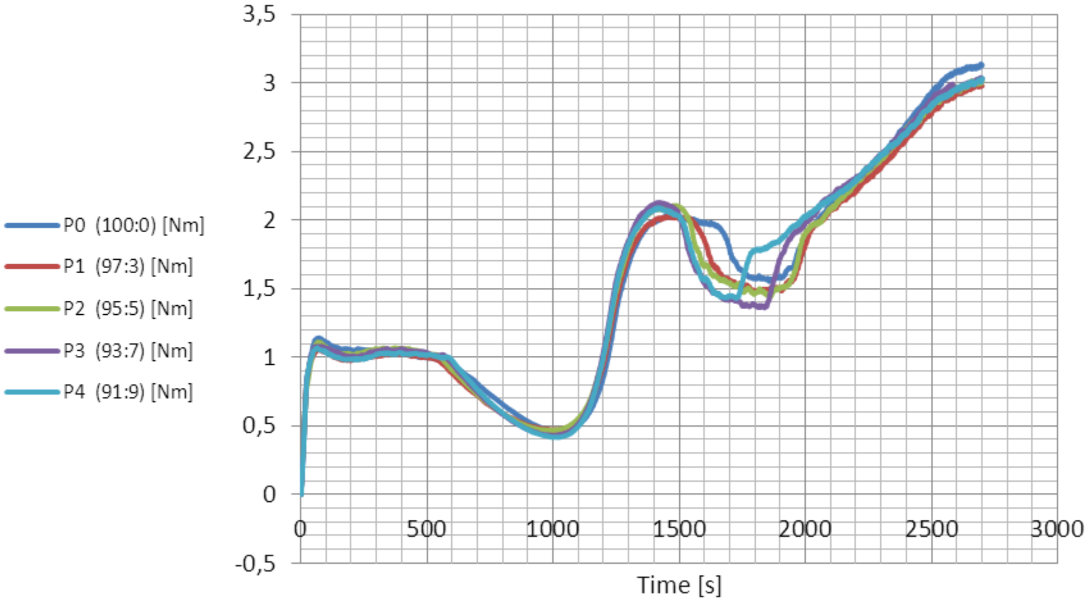

Fig. 1. Mixolab curves for grape seed and wheat flour and their mixtures

In table 3 are presented the main rheological parameters acquired by Mixolab equipment. A significant different behavior can be observed during enzymatic retro-gradation for the probes P2, P3, P4.

3.2. Mixtures of wheat flour and grape epicarp flour

The results obtained for the case of mixtures of wheat flour and epicarp flour (95: 5, 90:10, 88:12, and 85:15) are presented in table 4 (protein, ash, total fat and crude fiber) and table 5 (mineral content).

Table 4. Components of wheat flour and its mixtures with grape epicarp flour

Composition % d.m.	Samples				
	P0 (100:0)	P5 (95:5)	P6 (90:10)	P7 (88:12)	P8 (85:15)
Protein	13.2 ± 0.24	13.3 ± 0.25	13.40 ± 0.25	13,47 ± 0.23	13.50 ± 0.21
Ash	0.55 ± 0.01	0.85 ± 0.02	1.25 ± 0.02	1.39 ± 0.01	1.63 ± 0.03
Total Fat	1.04 ± 0.07	1.25 ± 0.06	1.49 ± 0.07	1.58 ± 0.04	1.71±0.07
Crude Fiber	1.9 ± 0.12	2.49 ± 0.35	3.05 ± 0.38	3.34 ± 0.44	3.63 ± 0.56

In table 6 are presented the main rheological parameters aquired by Mixolab equipment.

Table 5. Mineral content of wheat flour and of its mixtures with grape seed flour

Sample	Mineral content (mg mineral/100 g sample)				
	Ca	Mg	K	Cu	Fe
P0 (100:0)	44.9 ± 0.61	48.7 ± 0.53	189 ± 0.76	0.87 ± 0.19	1.6 ± 0.24
P5 (95:5)	66.5 ± 0.63	50.0 ± 0.55	301.8 ± 0.87	1.38 ± 0.10	1.67 ± 0.25
6 (90:10)	89.1 ± 0.79	52.2± 0.57	416.1 ± 0.99	1.97 ± 0.19	2.21 ± 0.28
P7 (88:12)	103.4 ± 0.66	53.1± 0.52	478.2 ± 0.89	2.08 ± 0.20	2.46 ± 0.27
P8 (85:15)	111.3 ± 0.89	54.5 ± 0.59	531.2 ± 1.01	2.54 ± 0.22	2.76 ± 0.30

Table 6. Influence of grape epicarp flour added to wheat flour in different proportions on mixolab characteristics (rheological behavior)

Parameter	Abbreviation	P0 (100:0)	P5 (95:5)	P6 (90:10)	P7 (88:12)	P78 (85:15)
Water absorption (%)	CH	56.0	56.5	57.2	57.6	57.8
Stability (min)	ST	10.07	10.28	10.73	11.14	12.23
Amplitude (Nm)	A	0.103	0.093	0.095	0.109	0.117
	Maximum consistency during:					
– phase 1 (Nm)	C1	1.10	1,111	1,099	1.098	1,097
	TC1	5.55	6.37	8.68	9.77	10.45
– phase 2 (Nm)	C2	0.454	0.469	0.486	0.528	0.667
	TC2	16.95	16.68	17.28	17.65	17.72
– phase 3 (Nm)	C3	2.327	2.432	2.491	2.487	2.490
	TC3	24.53	24.43	24.08	23.08	23.17
– phase 4 (Nm)	C4	2.216	2.258	2.296	2.269	2.275
	TC4	27.58	26.78	26.37	26.14	26.01
– phase 5 (Nm)	C5	3.664	3.607	3.221	3.106	3.008
	TC5	45.02	45.02	45.2	45.2	45.02

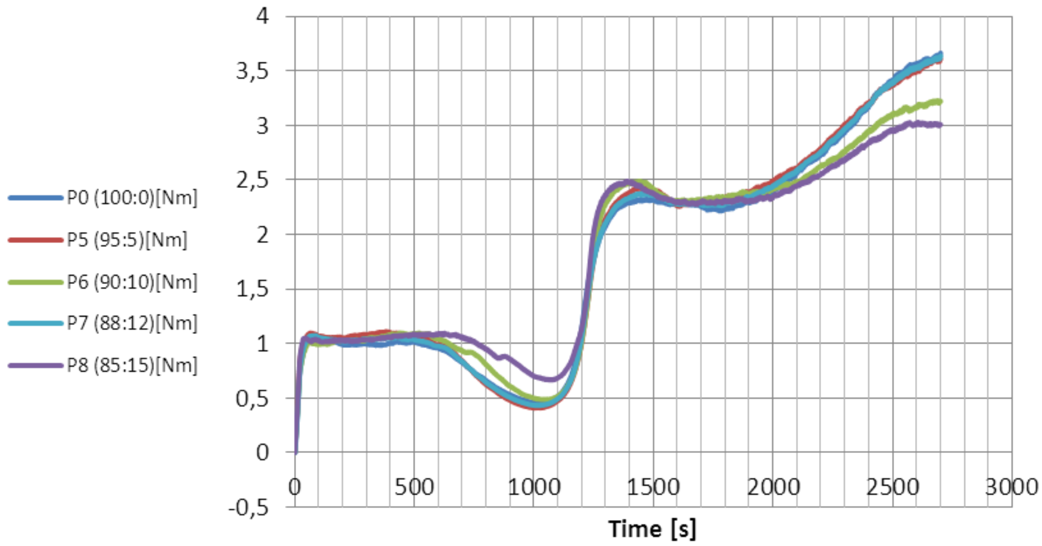

Fig. 2. Mixolab curves for grapes epicarp flour and wheat flour mixtures

From figure 2 can be observed that the samples with 12% and 15% of grape epicarp are characterized by a final consistency significant reduced.

3.3. Discussions

Following the analysis of the results of the experimental researches, a series of assessments are made regarding the increase of the nutritional value with the increase of the content of added by-products, respectively the rheological behavior of the doughs formed with the obtained flour mixtures [5-7].

It was thus found that the addition of grape seed flour or grape epicarp slightly increases the value of the protein content in the mixture. At the same time, the amount of fiber in the mixture increases by over 225% in the case of the addition of grape seed flour (7% addition), and by about 90% in the case of the addition of grape epicarp (15% addition).

The calcium content increases by 57%, and the magnesium content by 51% in the case of the addition of grape seed flour (7% addition).

In the case of the addition of grape epicarp flour (15% addition), the calcium content increases by 154%, and the potassium content by 184%.

The rheological studies performed show a slight reduction (by about 10%) of the viscosity of the dough in the dough formation phase and a similar increase of the stability period. The gelling phase of starch provides higher viscosities with the increase of epicarp and grape seed addition.

The addition of grape seed flour produces a sudden decrease in the torque resistant immediately after the maximum point reached in the gelatinization phase of starch, which indicates a rapid hydrolysis of it. The sample with 15% of grape epicarp is characterized by a final consistency of the products reduced by 20%, which excludes it as a potential variant for the formation of bakery products.

Analyzing the limits imposed by the dough processing technology, it is observed that the maximum limits for the additions studied are 7% grape seed flour, respectively 12% grape epicarp flour.

Conclusions

(1) Fortification of bakery products by adding food by-products is a large research topic, with favorable results, on the one hand on increasing their nutritional value and on the other hand contributes to the implementation of the concept of circular economy by superior capitalization of bio-resources in Romania [9], [5-8].

(2) The research carried out in the paper highlights the potential of increasing the content of fibers and minerals through the addition of grape seed flour and grape epicarp flour, as well as the limits imposed by the rheological conditions necessary for the formation and technological processing of the dough [6], [10].

(3) Thus, the results of the physico-chemical and rheological analyzes performed present as possible the variants of additions of 7% grape seed flour, respectively 12% grape epicarp flour.

(4) Future research directions envisage the addition of various additives (gluten, enzymes) in order to improve the baking properties of flour mixtures with high degrees of replacement with by-products from the winemaking industry, respectively grape seeds and epicarp [7].

(5) An important aspect of enriching the nutritional value of food products is the choice of vector foods, of those foods consumed by the entire population, homogeneous and stable, which can be processed and obtained under standardized conditions [1], [3], [7], [10].

(6) Functional food innovation is not a linear, single-actor process, but the result of a collective effort by a variety of actors such as food companies, universities, intermediate research institutes, authorities, consumers and support infrastructure, including investors and consulting firms. Cooperation between

food producers will become increasingly important, for example in the distribution of research risks and costs.

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