Total Phenolic, Cinnamic Acids and Selected Microelements in Gluten Free Pasta Fortified with Banana

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The aim of this study is to obtain gluten free pasta fortified with 10-40% fresh banana and dried banana in absence and in presence of ascorbic acid. Also, the obtained products were studied in term of total phenolic, cinnamic acids and selected microelements (Fe, Cu, Zn, Mn, Ni) composition. The results showed that addition of 30-40% fresh or dried banana in gluten free pasta leads to increasing of bioactive compounds of products.

Keywords: gluten free pasta, polyphenols, cinnamic acids

Gluten-free products are intended for people with celiac disease and who have a permanent intolerance to gluten and are obtained from grain of which proteins are not gluten generators. Rice is a grain matrix used successfully both in celiac diet and in technology of obtaining pasta. Rice pasta however, presents a low macro and micronutrients necessary for the body development. Gluten free pasta contents less phosphorus, potassium, calcium, magnesium, iron and zinc as regular pasta made from wheat.

In obtaining of a functional and dietary product an important role plays the biologically active compounds in its composition. Grains are an important source of elements and chemical compounds with potential biological activity, such as phenolic compounds [16, 18]. Phenolics in cereals can be subdivided into acids derived from either benzoic acid or cinnamic acids (CA). The most commonly CA found in cereals have seven carbon atoms, a benzenic ring, a carboxylic group and one or more hydroxyl and/or methoxyl groups [10]. Ferulic, p-coumaric, caffeic and sinapic acids are the main CA [10,18]. Ferulic acid represents one of the most abundant CA in grains [3,6,26]. CA presents biological importance having antioxidant anti-inflammatory and anticancer properties. Also is involved in reducing the level cholesterol and triglycerides and implicitly the risk of cardiovascular disease [16].

The aim of fortification is to increase the nutritional value of product by supplying with nutrients or biological active compounds. The fortification of pasta with fruits is relatively unusual. Combining the effect of rice gluten-free pasta with banana is an opportunity to obtain a novel dietary food with nutraceutical high potential [14,20,21].

Nutraceutical properties of bananas have been reported in previous studies [5,7,22]. The high content in fibre, polyphenols and potassium recommends the bananas consumption in food diet [9,19]. The use of ascorbic acid as pre-treatment in pasta producing technology increase the biological value of product and prevents enzymatic browning, biochemical and microbial activities that occur during pasta production [4].

The purpose of this study is: i) to obtain three types of gluten-free pasta made of rice flour (RF) with addition of different proportions of dried fruits of banana (DB), fresh banana (FB) and fresh banana pre-treated with ascorbic acid (FBA), ii) to characterize the products obtained, in terms of polyphenols, cinnamic acids, macro and micronutrients content.

Experimental part

Materials and methods

Raw materials

Rice flour (RF) was obtained from Pirifan, Romania, dried banana from Poex Czech and fresh banana from Kaufland market. In case of obtaining pasta with ascorbic acid addition, acid was added previously to fresh bananas, which were maintained 30 minutes in acid medium before introducing in the manufacturing recipe.

Pasta formulation

Pasta was prepared with rice flour by adding different concentrations (10, 20, 30 and 40% w/w) of DB, FB and FBA. One egg and 10 mL water were added for each sample. The dough was manually formed and cut in a pasta machine (Pasta machine, Kitchen collection, WN16195-150, China). Obtained pasta were dried 24 h at room temperature.

Microelements determination

The determination of microelements was done by the flame atomic absorption spectroscopy method (AAS) with graphite furnace. 3 g samples were burned 6 h at 650°C in furnace (Nabertherm B150, Lilienthal, Germany). The ash was dissolved in HCl 20%. Standard solutions (ICP Multielement Standard solution IV CertiPUR) were purchased from Merck. Each value is the mean of three independent determinations.

Total phenolic content (TP) and cinnamic acids (CA) determination

Total phenolic content was determined using a modification method of Arranz, 2010 [6]. Briefly, 0.5 g pasta was extracted 1 h at room temperature with 20 mL methanol:water (50:50, v/v) and the *p*H was adjusted to 2 with acetic acid.. The samples were centrifuged 10 min at 450 rot/min. 0.5 mL supernatant was treated with 1.25 mL

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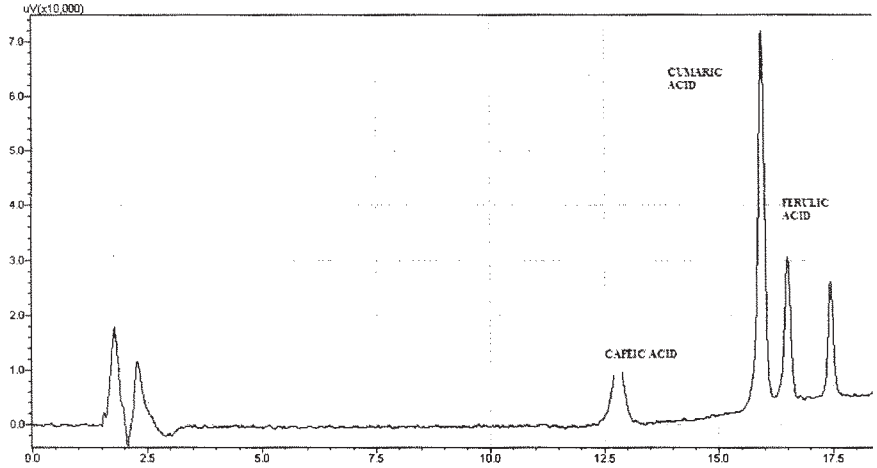

Fig. 1. HPLC chromatogram of cinammic acids (cafeic, ferulic, cumaric).

Samples	Cu[a]	Ni[a]	Mn[a]	Fe[a]	Zn[a]
RF	1.984±0.006	0.556±0.042	5.641±0.042	15.801±0.023	16.030±0.023
DB	1.623±0.005	0.529±0.015	12.314±0.021	20.539±0.012	11.032±0.041
10 % DB	0.848±0.037	0.434±0.013	3.852±0.027	8.426±0.015	8.448±0.062
20 % DB	1.506±0.013	0.405±0.006	5.734±0.015	17.153±0.046	15.056±0.055
30 % DB	2.172±0.014	0.345±0.030	8.313±0.022	23.930±0.022	18.293±0.175
40 % DB	2.663±0.018	0.355±0.046	10.640±0.022	18.045±0.023	15.560±0.386
10 % FB	1.906±0.152	0.383±0.022	5.639±0.063	14.562±0.289	14.887±0.132
20 % FB	1.652±0.135	0.253±0.116	6.205±0.225	14.414±0.208	16.286±0.112
30 % FB	2.053±0.092	0.432±0.041	6.888±0.125	13.096±0.140	15.770±0.284
40 % FB	1.678±0.024	0.456±0.037	6.443±0.323	10.170±0.116	15.346±0.186
10 % FBA	1.508±0.022	0.268±0.024	5.239±0.222	10.003±0.057	12.673±0.308
20 % FBA	1.455±0.023	0.109±0.052	2.613±0.256	10.159±0.153	11.611±0.175
30 % FBA	1.818±0.024	0.129±0.022	4.181±0.171	9.926±0.018	11.450±0.150
40 % FBA	1.888±0.055	0.131±0.018	3.896±0.497	13.735±0.192	11.486±0.104

[a]*means ± standard deviation (n=3).*

Table 1
MICROELEMENTS CONTENT (PPM) IN FORTIFIED GLUTEN FREE PASTA

Folin-Ciocalteu reagent diluted 1:10 with water. The sample was incubated 5 min at room temperature and 1 mL Na_2CO_3 60g/Lwas added. After 30 min of incubation at 50^{0}C the absorbance of samples were measured at 760 nm. Results were expressed as μg gallic acid equivalents per g sample (μg GAE/g). Linearity was obtained between 5–50 μg/mL.

The main CA in pasta (ferulic, caffeic and cumaric acids) was determined using high performance liquid chromatographic method (HPLC). LC-Shimadzu chromatograph equipped with SPD-10A UV detector, PERVAIL column 150 mm, internal diameter 4.6 mm was used. The chromatographic conditions were: mobile phases A: CH_3OH:CH_3COOH:H_2O (90:2:8, v/v), B: CH_3OH :CH_3COOH :H_2O (10:2:88, v/v), gradient program: 0 min. B 100%, 10 min B 85%, 15 min B 50%, 20 min B 30%, 25 min B 80%. The chromatogram of CA standard is presented in figure 1.

Results and discussions

Microelements content

In table 1 are presented the results obtained regarding microelements composition (Mn, Cu, Ni, Zn, Fe) of pasta with DB, FB and FBA.

Microelements have a fundamental role in the human diet. Celiac disease is often associated with mal absorption of the nutrients, vitamins and minerals in the gastro intestinal tract. In gluten free products the content of minerals varied considerably among the types of foods. Previous studies reported in gluten free pasta iron content 26 ppm, zinc 8 ppm and copper 4 ppm [25].

In our study the content of microelements in fortified pasta follows the sequence Fe >Zn>Mn>Cu>Ni.

Iron is important for the synthesis of hemoglobin and myoglobin and for the formation of iron-containing enzymes involved in electron transfer and oxidation-reductions [1]. Iron deficiency represents the most widespread and important micronutrient deficiency in humans [17]. Iron content in fortified pasta varies between 8.426-23.930 ppm, the highest content was detected in pasta with 30%DB. Pasta obtained with FBA in different proportions contain iron in lower amounts than pasta obtained with the FB addition without acid treatment, probably due to the reduction of ferric iron to ferrous iron and binding in soluble complexes [1]. Inclusion of ascorbic acid in recipe of gluten free pasta represents an efficient technological method to enhance the iron absorption, literature studies highlighting the role of acid in bioavailability of iron [1, 13].

Copper content of pasta varies between 0.848 to 2.663 ppm being lower compared with data reported in the literature for gluten-free pasta [25]. Maximum copper content (2.663 ppm) was registered in the sample with 40% DB addition. Higher copper content than control sample was registered also in samples with addition of 30% DB and 30% FB.

Manganese is a component of metal enzyme complexes and acts as an activator in reactions catalyzed by enzymes [12]. Manganese content of bananas (12.314 ppm) is higher than of rice flour (5.641 ppm). Fortification with 40% DB leads to double increase of the manganese content (10.64 ppm) compared with the control sample.

Nickel enters into the human body through primary food and drinking water. In terms of Ni content, our results indicate no significant differences between the values obtained for the control sample and sample with DB. Fortification pasta with fresh or dried banana does not influence nickel intake in the diet. Nickel content is between 0.109-0.556 ppm and is the microelement analyzed that is found in the lowest concentrations in banana pasta studied.

Samples	TP[a]	Caffeic Acid[a]	Cumaric acid[a]	Ferulic acid[a]
	μg/g	μg/g	μg/g	μg/g
RF	242.10±0.42	8.68±0.01	30.47±0.06	43.8±2.43
DB	244.00±1.41	2.15±0.03	10.85±0.04	14.79±0.43
10 % DB	196.95±0.07	6.79±0.01	7.28±0.05	13.66±1.53
20 % DB	204.45±0.35	7.52±0.01	13.28±0.33	22.34±0.57
30 % DB	213.80±0.56	6.11±0.06	17.20±0.12	30.41±0.52
40 % DB	227.80±0.40	6.19±0.01	12.57±0.33	28.44±0.48
10 % FB	306.86±0.11	14.33±0.35	21.76±0.87	24.83±0.85
20 % FB	329.23±0.25	10.03±0.35	25.40±0.62	37.43±0.66
30 % FB	365.23±0.25	8.46±0.40	14.80±0.80	23.56±0.81
40 % FB	367.40±0.35	10.30±1.4	10.76±0.45	31.40±0.34
10 % FBA	328.06±0.11	5.36±0.49	10.00±0.35	50.13±1.00
20 % FBA	408.83±0.06	14.70±0.65	8.70±0.36	52.73±0.64
30 % FBA	490.46±0.11	12.06±0.30	10.03±0.35	27.20±0.20
40 % FBA	509.13±0.11	9.86±0.41	13.30±0.36	22.63±0.47

[a]*means ± standard deviation (n=3).*

Table 2
TOTAL PHENOLICS (TP) and CINNAMIC ACIDS (CA) CONTENT (μg/g) IN FORTIFIED GLUTEN FREE PASTA

Zinc represents an essential metal entering into the composition of numerous metal enzymes. Whole cereals are good sources of zinc (20-78 ppm) [15], while in gluten-free products zinc content reported in the literature is lower (8 ppm) [25]. The zinc content in the samples analyzed varies between 8.448-18.293 ppm, the maximum values were registered in the case of the 30% DB addition. Fresh or dried bananas fortification leads to increased zinc intake of pasta, while acid treatment applied to fresh bananas induces a decrease in zinc content compared with the control sample.

TP and CA content

In table 2 are presented the results obtained regarding TP and CA (ferulic, cumaric and caffeic) of pasta with DB, FB and FBA.

TP content varies between 196.95-509.13 μg/g, the maximum values recorded being registered in the case of the ascorbic acid addition in the pretreatment of fresh bananas (328.06-509.13 μg/g), and the minimum values in the case of pasta with dried bananas (196.95-227.8 μg/g). TP content of pasta obtained from rice flour, determined in this study, was in agreement with previous published works and highlighting the TP content in various products derived from cereals between 14 and 543 μg/g depending of the nature of the extraction environment and analyzed matrix [2,11]. Verma, 2009 highlights a higher content in TP (1509.0-1306 mg/g) in different wheat varieties [26] and in oat based breakfast cereals, TP content ranged from 1506 to 1853 μgGAE/g [23]. In term of TP our results recorded in pasta fortified with DB are lower than the values recorded in pasta fortified with FB. The addition of banana in pasta induce an increase of TP content, the increase being significant when bananas are pretreated by adding ascorbic acid which also acts as antioxidants. Similar results regarding the increase of the TP in bananas treated with organic acids have been reported by Anyasi [4]. The way in that leads the hydrolysis is particularly important in CA recovering from cereals. Arranz, 2010 highlights the role of acid hydrolysis [6], while Verma, 2009 [26] highlights the importance of alkaline environment. Our results shown the increase of total polyphenol content in the case of ascorbic acid pre-treatment.

Regarding CA content the level of CA varies in order: ferulic>cumaric>caffeic. Ferulic acid is the most abundant cinnamic acid in cereals, representing up to 90% of total phenolic compounds [8].

CA is predominantly assigned in the coating and less in the grain endosperm. The literature studies reported a content of 11.5 μg/g ferulic acid in bran respectively 2.8 μg/g in wheat flour [6]. Our results highlight the high ferulic acid content in the control sample (43.8 μg/g) and lowest in DB (14.79 μg/g). In pasta samples with DB, ferulic acid varies between 13.66-30.41 μg/g, coumaric acid between 7.28-17.20 μg/g, and caffeic acid between 6.11-7.52 μg/g, the maximum values being recorded in the case of the 30% DB addition for coumaric and ferulic acid and to 20% DB addition of caffeic acid.

FB brings additional intake of CA. So, the caffeic acid content varies between 14.33-8.46 μg/g, coumaric acid between 10.76-25.40 μg/g, and ferulic acid between 24.83-37.43 μg/g. The pretreatment in acid medium of bananas does not lead to a significant change regarding the caffeic and coumaric acid content, instead there is an increase regarding ferulic acid content, which in the case of 20% FB addition increase up to 52.73μg/g.

Conclusions

Banana enriched gluten-free pasta with microelements, especially with iron and manganese, but also with iron and zinc. The addition of banana in gluten-free pasta, both in dry and fresh form, leads to an increase in iron content, the product proved to be a functional product intended for people suffering from iron deficiency anemia. The addition of FB or DB in pasta leads to manganese fortification of products, so manganese supplementation intake in gluten-free pasta products should be considered an important outcome of the study.

The addition of banana in pasta induce an increase of TP content, the increase being significant when bananas are pretreated by adding ascorbic acid which also acts as antioxidants. The maximum amount of ferulic and coumaric acid content was recorded in the case of 20% FB addition.

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