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Innovative shrimp products: physico-chemical and nutritional characterisation

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Abstract

This paper had three major objectives. The first was to obtain an innovative ready-to-eat food product, using shrimp as a basic raw material, namely: appetizer cream, in two variants: one with baked red peppers and the second with green olives, using raw and auxiliary materials from the Romanian market. Second objective was to characterize the finished products obtained from the point of view of the total polyphenols and certain mineral elements content (K, Ca, Mg, Fe, P, Mn, Cu, Cd, Zn, Pb, Cr, Ni), as well as in terms of antioxidant activity, compared to the raw materials used. The third objective was to determine the proximate composition and energy value of the two variants of shrimp appetizer cream. From the raw and auxiliary materials used to obtain the two varieties of shrimp appetizer cream, the richest content of total polyphenols was found in black pepper (23.18 ± 0.56 mg acig gallic/g), followed by roasted capsicum pepper (13.89 ± 0.42 mg gallic acid /g) and green olives (12.40 ± 0.38 mg gallic acid /g). Shrimp had a total polyphenol content of 2.08±0.10 mg acid galic/g. Regarding the finished products, the highest content of total polyphenols was recorded for the appetizer cream variant with shrimp and baked red peppers: 6.93 ± 0.28 mg gallic acid /g, which also had the strongest antioxidant activity: 18.74±0.70 mg Trolox/g. Among the heavy metals analyzed, Cd was not identified in either the raw materials or the finished products. Pb was present in shrimp in a higher concentration (0,833±0.029 ppm) than the maximum limit provided by law. All other raw materials and finished products had concentrations of heavy metals below the maximum limits provided by law. The two varieties of appetizer with shrimp cream were very similar both in terms of proximate composition and energy value. Varianta de cremă aperitiv cu creveți și ardei capia copt a avut o valoare energetică puțin mai mică (229.70 kcal/100g) față de variantă cu măsline verzi (233.33 kcal/100g).

Keywords: shrimp, appetizer, polyphenols, antioxidant activity, mineral elements

1. Introduction

Shrimp are some of the most delicious seafood and are part of the traditional cuisine of many nations. Their popularity has created a demand for these products worldwide. Given the limited supply of wild catches, shrimp farming has been launched in many countries to meet growing demand [1]. Shrimps are a large group of crustaceans that vary in size, from microscopic sizes to about 35 cm long. They are widely distributed, occurring in marine and brackish waters and also in freshwaters from the equator to the polar regions.

Most species of shrimp are marine, and about a quarter of the species described are found in freshwater [2].

From a nutritional point of view, shrimp are especially valuable. They are an extremely good source of protein and are low in fat and calories, making them a healthy choice for consumers. In addition, shrimp meat contains unsaturated fatty acids, such as eicosapentaenoic acid (EPA) and docosahexaenoic acid (DHA), which are essential in the human diet [3,4].

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Also, shrimp are a good source of vitamin B12, selenium and astaxanthin - a carotenoid compound with important antioxidant action. Fresh and cleaned shrimp can be served either cooked or uncooked with sauces. Because their flavor is neutral, shrimp form a natural additive in salads, pasta, curry, soups and fried foods. The average protein content of fresh shrimp is 19.4 g / 100 g and contributes 87% of the total energy [5]. The lipid levels analyzed in shrimp were around 1.15 g/100 g. No other meat dish can claim such a low level of lipids as fresh shrimp. The lipid composition of shrimp comprises 65-70% phospholipids, 15-20% cholesterol and 10-20% total acyl glycerols. The predominance of phospholipids in shrimp lipids indicates the rich nutritional quality, these being an integral part of the cell membrane and transport lipoproteins. In addition, 32% of shrimp lipids are composed of polyunsaturated fatty acids (PUFA), a term commonly associated with high-quality seafood. For this purpose, approximately 64% are ω-3 PUFAs and the remaining 33% are ω-6 PUFAs, which results in a ω-3/ω-6 PUFA ratio around 1.9, which indicates great health benefits [6]. Astaxanthin has been found to be a powerful natural antioxidant, exceeding ten times the antioxidant activity of β-carotene and 500 times higher than that of α-tocopherol. The level of astaxanthin in wild shrimp has been reported to vary between 740 and 1400 µg / 100 g, which again supports the argument for their inclusion in the daily diet. The human diet requires minerals such as calcium, phosphorus, magnesium, potassium and sodium in large quantities and therefore they are called macro-minerals. A quantity of 100 g of shrimp provides> 100 mg of calcium,> 300 mg of phosphorus and> 40 µg of selenium. Among the many functions, minerals help regulate fluid balance, enzyme production and bone health. Consumption of shrimp (100 g/day) would provide about ten vitamins and ten minerals. Shrimp contain important vitamins such as vitamin A (180 IU), vitamin D (2 IU) and vitamin E (1.32 µg), vitamin B12 (1.11 µg) and vitamin B3 (1.77 mg) [5].

Fresh shrimp are extremely perishable, so they appear on the markets mainly in the form of raw-frozen or cooked products. In addition to the fresh and cooked product, a ready-to-eat (RTE) product would be more convenient for the consumer. Current market trends reflect a rapidly growing demand for convenient ready-to-eat and ready-to-cook products [4].

The aim of this paper was, first of all, to obtain an innovative food product that meets several conditions: to be ready-to-eat, to use shrimp as a basic raw material, to be tasty, nutritious and with high protective qualities on the human body. Thus, we chose to obtain a shrimp-based appetizer cream, in two variants: one with baked red peppers and the second with green olives. Another aim of the paper was to determine the total polyphenol content, antioxidant activity and content of certain mineral elements of the two products, compared to the raw and auxiliary materials, as well as to calculate the proximate composition and energy value of the two finished products.

2.Material and methods

2.1.Obtaining the shrimp-based appetizer creams

Two assortments of appetizer cream based on shrimp were obtained, using raw and auxiliary materials on the Romanian market, in the quantities presented in Table 1.

Figure 1. Recipes used to obtain the two varieties of shrimp cream

Raw/auxiliary material	**Shrimp appetizer cream with baked red peppers (C1)**	**Shrimp appetizer cream with green olives (C2)**
Shrimp (frozen *Litopanaeus Vannamei*) (g)	200	200
Baked red peppers (frozen, *Max* variety) (g)	75	-
Green olives (g)	-	75
Onion (g)	50	50
Olive oil (g)	80	80
Lemon juice (g)	28	28
Black pepper (g)	2	2
Garlic (g)	3	3
Salt (g)	3	-

The shrimp and baked red peppers were thawed and washed well, the onion and garlic were subjected to the cleaning, washing and chopping steps and then all the raw and auxiliary materials were weighed according to the recipes from Table 1. The shrimp were blanched for 2 minutes in boiled water, the onion and garlic were cooked for 2 minutes in 20 ml of olive oil, and then all the ingredients corresponding to each recipe were mixed in a blender, until a pasta with a fine consistency. The appetizer creams thus obtained were placed in jars with an airtight lid and were sterilized at 130 ° C for 2 hours. After cooling, the jars were labeled and stored at a temperature of 18-20 ° C and a maximum humidity of 70%.

2.2.Determination of total polyphenol content, antioxidant activity, proximal composition and energy value

Determination of total polyphenols content (by the Folin-Ciocâlteu method) and of the antioxidant activity (by the CUPRAC assay) both for the raw and auxiliary materials, as well as for the appetizer creams obtained, the same way of working described by Dumbrava *et al*., (2016) [7] was used. All analytical determinations were performed in triplicate. The results were expressed as a mean and standard deviation (mean ± SD). The proximate composition and energy value of the two shrimp appetizer creams were determined by calculation, using "USDA Food Compozition Databases" [8].

2.3.Determination of the mineral elements content by atomic absorption spectrophotometry

Both the raw materials used and the finished products obtained were subjected to the analysis of the content of various mineral elements:

The method is based on the measurement, by atomic absorption spectrometry, of the mineral elements concentration in the acid extract obtained from the ash of the food sample. The analytical process comprises two stages: dry mineralization and dosing, by atomic absorption spectroscopy, respectively by flame emission spectroscopy (in the case of K) [9,10]. The determinations of mineral elements were performed according to the standard SR EN 14082: 2003 [11].

2.2.1. Reagents: concentrated hydrochloric acid (density 1.19, concentration 37%) (Merck, Germany), concentrated nitric acid (minimum 65%) (Merck, Germany), 30% hydrogen peroxide (Merck, Germany), heavy metal standard solutions 1000 mg / l (Merck, Germany).

2.2.2.Apparatus: Atomic absorption spectrophotometer type Varian Spectra AA 220; Sartorius LP 220 S analytical balance (10^{-3} g accuracy); Nabertherm LE2 / 11 calcination furnace; Friocell III-BMT thermoregulatory oven.

2.2.3. Sample processing and mineralization: The sample under analysis was processed accordingly (chopping, grinding, grinding, homogenizing) so as to obtain a uniform and homogeneous mass. A quantity of 3.00 g of sample was weighed in a porcelain crucible and pre-calcined in a flame until no more smoke escapes from the crucible. After pre-calcining in the flame, the crucible was placed in a thermoregulatory furnace. Its temperature was gradually raised to 500 ± 100 °C, where a convenient time for completion of calcination was maintained (10-16 hours). The resulting ash must be uniform in color (white or gray) and contain no carbon black spots. After the ash was ready, the crucible was allowed to cool in the calcination oven with the oven door open. After cooling, the crucible was placed on an asbestos plate and waited for its complete cooling to add 5 ml of 6 mol/l hydrochloric acid. The acid evaporated on the sand bath. The residue was dissolved in an exact volume (10 ml to 30 ml) of 0.1 mol / l nitric acid. The control sample was treated in the same way as the analysis samples.

2.2.4. Spectrophotometric determination: Before the proper determination, with approx. 30 minutes, the appliance was switched on, the cathode lamp corresponding to the first element to be determined was actuated, the operational parameters were adjusted (wavelength, sensitivity, etc.), the compressor was switched on and the flow rate of acetylene and air was adjusted, the flame was lit, the height of the burner was adjusted - all according to the operating instructions that came with the appliance. During the adjustment of the functional parameters, deionized water was continuously aspirated and its zero point was adjusted. At least 3 standard working solutions were aspirated in turn, the absorption for each was measured and recorded, thus establishing the standard curve. The sample solution was then aspirated, absorbance recorded and concentration calculated. From the same solution of the sample the other elements were further determined under the same conditions, using standard solutions and specific cathode lamps.

2.2.4. Calculation and expression of results: The following mineral elements were determined for each sample: K, Ca, Mg, Fe, P, Mn, Cu, Cd, Zn, Pb, Cr, Ni. The final content of the determined mineral element (C) is calculated using the relation:

C (mg/kg or ppm) = a x f /m

where:

f **-** dilution factor,
a **-** the content of the element read by the device in mg / l
m - sample mass taken into operation.
For each sample the determinations were performed in triplicate, and the results expressed as mean ± standard error.

3.Results and discussion

3.1. Analysis of total polyphenol content

Determination of total polyphenols content for the two variants of shrimp appetizer creams (C1 and C2) and for the raw and auxiliary materials, by the Folin-Ciocâlteu method led to the results presented in Figure 1.

Analyzing the data from Figure 1. we can see that among the raw and auxiliary materials used to obtain the two varieties of shrimp cream, C1 and C2, the richest content of total polyphenols was found in black pepper (23.18 ± 0.56 mg gallic acig/g), followed by baked red peppers (13.89 ± 0.42 mg gallic acid/g) and green olives (12.40 ± 0.38 mg gallic acid/g). It is also found that in the case of shrimps, a rather high content of total polyphenols (2.08 ± 0.10 mg gallic acid/g) was determined, higher than in the case of onions (1.82 ± 0.08 mg gallic acid/g) and garlic (1.34 ± 0.05 mg gallic acid/g). Andrade and Ferreira [11] determined the concentration of total polyphenols in black pepper using different extraction methods and found values between 14 ± 4 mg gallic acid/g and 268 ± 13 mg gallic acid/g, the values obtained in this work being within this range. In the case of green olives, depending on their degree of maturity, Aprile et al. [12], found concentrations of total polyphenols between 14.0 and 29.68 mg gallic acid/g dry mass.

Of the two finished products obtained, the highest total polyphenol content was recorded in the case of appetizer cream with baked red pepper and shrimp (C1): 6.93 ± 0.28 mg gallic acid/g,

3.2. Antioxidant activity analysis

The antioxidant activity of the two varieties of shrimp appetizer cream and of the raw and auxiliary materials, determined by the CUPRAC method, is presented in Figure 2.

From the analysis of the experimental data it is noted that the baked red peppers had the strongest antioxidant activity (20.16 ± 0.82 mg Trolox/g), followed by black pepper (16.28 ± 0.72 mg Trolox/g) and green olives (12.84 ± 0.76 mg Trolox/g). Lemon juice and garlic had very close values of antioxidant activity (10.75 ± 0.41 mg Trolx/g, respectively 10.47 ± 0.78 mg Trolox/g). The shrimp used had a good antioxidant activity (8.84 ± 0.30 mg Trolox/g), even higher than that related to onion (7.84 ± 0.28 mg Trolox/g). Álvarez-Parrilla *et al*., [13] reported, for different types of peppers in Mexico, an antioxidant activity ranging from 7.16 mg Trolox/g to 13.85 mg Trolox/g. Andrade and Ferreira [11] found for black pepper, depending on the type of extraction method used, values of antioxidant activity in the range: 10.25 mg Trolox/g and 54 mg Trolox/g. Regarding olives, Gouvinhas *et al*., [14], for olives of different origins and in different stages of ripening, found values of antioxidant activity between 12.82 mg Trolox/g and 81.95 mg Trolox/g, the minimum values being for green olives and growing with their degree of ripeness. Both finished product variants had a very good antioxidant activity, with similar values, appetizer cream with shrimp and baked red pepper showing a slightly higher antioxidant activity (18.74 ± 0.70 mg Trolox/g) than appetizer cream with shrimp and green olives (17.42 ± 0.80 mg Trolox/g).

3.3. Mineral elements analysis

The results on the content of mineral elements in the samples of raw materials and finished products, determined by atomic absorption spectrophotometry, are presented in Table 2.

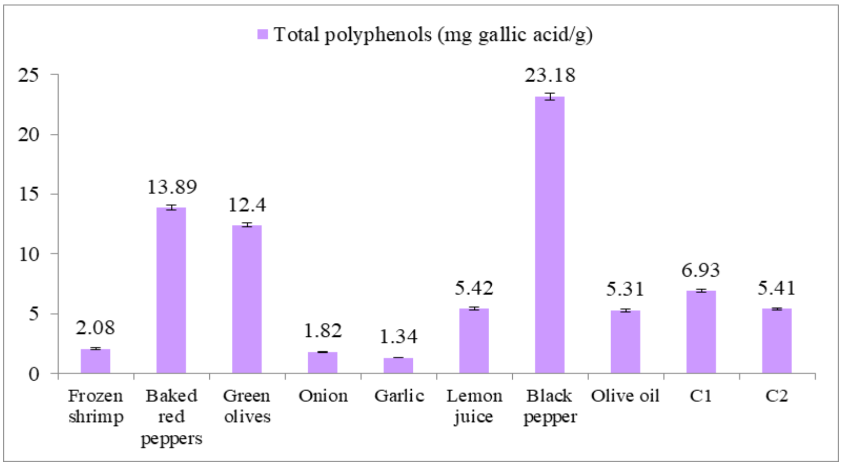

Figure 1.Total polyphenols content of shrimp appetizer cream assortments (C1 and C2) and of raw and auxiliary materials

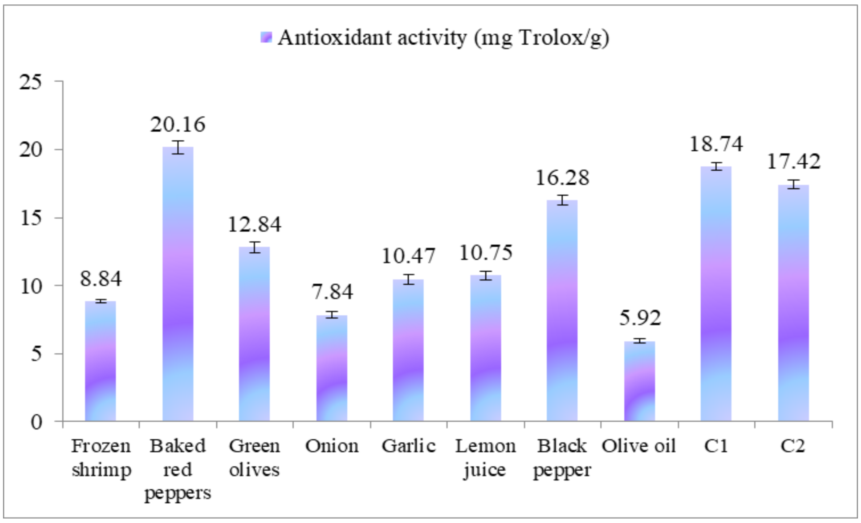

Figure 2. Antioxidant activity of the two variants of shrimp appetizer cream (C1 and C2) and of raw and auxiliary materials

Table 2. Mineral content of raw materials and finished products (ppm)

Sample / Mineral element	Raw materials			Finished products	
	Baked red peppers	**Green olives**	**Shrimp**	**C1**	**C2**
Cu	3.689±0,156	2,598±0,067	6,630±0,215	3,103±0,095	0,520±0,024
Cd	-	-	-	-	-
Cr	0.650±0,028	0.587±0.026	0.713±0,024	0.604±0,014	0.372±0,007
Ni	0.289±0,008	0.739±0,010	1.445±0,068	0.488±0,012	0.971±0,021
Pb	0.435±0,100	0.144±0,005	0.833±0,029	0.471±0,011	0.355±0,012
Zn	10.766±0,484	1.491±0,036	14.510±0,500	5.342±0,218	2.252±0,053
Fe	15.628±0,348	8.098±0,218	41.648±1,323	6.737±0,229	3.432±0,053
Mn	-	-	3.392±0.102	-	-
Ca	309±5,292	1669±36.346	545±6.245	612±8.000	674±17.436
Mg	48±1.732	111±2..340	181±2.645	106±3.605	142±2.645
K	765±14.106	501±8,888	1317±13,228	809±14,731	646±13,114
P	1559±23.643	458±15.874	692±12.124	732±20.297	201±6.082

From Table 2 it is observed that among the heavy metals analyzed, Cd was not identified neither in the raw materials nor in the finished products. Regarding Cu and Zn, we note that these two heavy metals are below the maximum limits provided by law, both in raw materials and in finished products [15]. The highest Cu and Zn content in the raw materials was found in shrimp (6,630 ± 0.215 ppm and 14.510 ± 0.500 ppm, respectively), followed by baked red peppers (3.689 ± 0.156 ppm and 10.766 ± 0.484 ppm, respectively). Of the two shrimp creams obtained, the C1 variant had the highest content of Cu and Zn (3,103 ± 0.095 ppm, respectively 5.342 ± 0.218 ppm). With regard to lead (Pb), shrimp had a concentration of this heavy metal above the legal limit (0.833 ± 0.029 ppm, the maximum limit being 0.500 ppm [15]), all other raw materials and finished products having appropriate concentrations of of this heavy metal. Nickel, this special microelement, involved in preserving the integrity of cell membranes, is present in the highest amount in shrimp (1,445 ± 0.068 ppm), followed by green olives (0.739 ± 0.010 ppm), and among the finished products, C2 appetize cream (with olives green) had the highest content (0.971 ± 0.021 ppm). Iron, an essential metal for the body, is best represented in shrimp (41,648 ± 1,323 ppm), followed by baked red peppers (15,628 ± 0.348 ppm), and among the finished products, the C1 variant (6,737 ± 0.229 ppm). Manganese, this important microelement for the body, was found only in shrimp (3,392 ± 0.102 ppm), in other raw materials and in finished products not being detected.

Among the macroelements, calcium was in the highest concentration in green olives (1669 ± 36,346 ppm), respectively in C2 appetizer cream (674 ± 17,436 ppm), and magnesium was best represented in shrimp (181,000 ± 0.504 ppm) followed of green olives (111,000 ± 1,024 ppm), respectively in C2 appetizer cream (142,000 ± 0.800 ppm). The highest potassium content was also determined in shrimp (1317 ± 13,228 ppm) followed by baked red pepper (765 ± 14,106 ppm), respectively in C1 appetizer cream (809 ± 14,731 ppm). Regarding phosphorus, it was best represented in baked capsicum pepper (1559 ± 23,643 ppm) and in C1 appetizer cream (732 ± 20,297 ppm).

3.4. Analysis of the proximate composition and energy value

Table 3. shows the results for the approximate composition and energy value obtained by calculation for each of the two varieties of shrimp appetizer cream.

Table 3. Nutritional and energy values of the two shrimp appetizer cream variants (relative to 100g)

C1	C2
Proximate composition	**Proximate composition**
Proteins (g): 9.52	Proteins (g): 9.59
Total lipids (g): 20.63	Total lipids (g): 21.23
- saturated fatty acids (g): 1.95	- saturated fatty acids (g): 2.05
Cholesterol (mg): 73.01	Cholesterol (mg): 73.52
Total carbohydrates (g): 3.17	Total carbohydrates (g): 2.74
-sugars (g): 1.38	-sugars (g): 0.75
- dietary fiber (g): 0.66	- dietary fiber (g): 0.91
Salt (mg): 322.00	Salt (mg): 321.46
Energy value: 229.70 kcal	**Energy value:** 233.33 kcal

The two varieties of appetizer cream with shrimp are very similar both in terms of composition and energy value. The C1 spread cream variant had a slightly lower energy value (229.70 kcal/100g) compared to the C2 variant (233.33 kcal/100g). The protein content was almost identical for the two finished products (9.52 g/100g for C1 and 9.59 g/100g for C2). Total lipids and saturated fatty acids were found in slightly higher amounts in cream appetizer with shrimp and green olives (21.23 g/100g, respectively 2.05 g/100g compared to 20.63 g/100g, respectively 1.95 g/100g for the product C1), but the total carbohydrates and sugars were in higher concentration in the C1 appetizer cream version (3.17 g/100g, respectively 1.38 g/100g compared to 2.74 g/100g, respectively 0.75 g/100g for the green olive product variant - C2). We note that in both products lipids (unsaturated) predominate, these coming mainly from the used olive oil and shrimp and ensuring the creamy, spreadable structure of the products, but also the protein content is quite high.

4. Conclusions

1. An innovative, ready-to-eat shrimp-based food product was obtained: 'shrimp appetizer cream', in two variants: one with baked red peppers (C1) and the second with green olives (C2), using raw and auxiliary materials from the Romanian market and a simple obtaining technology.

2. Among the raw and auxiliary materials, the highest content of total polyphenols was in black pepper, followed by baked red peppers and green olives. Shrimp had a fairly high content of total polyphenols, being higher than that of onions and garlic. The experimental results obtained were within the limits found in the literature data. Of the two finished products obtained, the version C1 had a higher concentration of total polyphenols than the version C2.
3. Among the raw and auxiliary materials used, the highest antioxidant activity had the baked red peppers, followed by black pepper and green olives, and the finished product variant C1 presented the best antioxidant activity.
4. The determination of a number of 12 mineral elements (Cu, Cd, Cr, Ni, Pb, Zn, Fe, Mn, Ca, Mg, K, P) from the raw materials and finished products showed that all the heavy metals determined were below the limits provided by law, with one exception: shrimp lead that has exceeded the legal limit. Also, among the raw materials analyzed, shrimps were the richest in the following mineral elements: Cu, Cr, Ni, Zn, Fe, Mg, and the fint product variant C1 was the most concentrated in: Cu, Cr, Pb , Zn, Fe, K and P of the two products obtained, while the C2 variant was richer in Ni, Ca and Mg.

Compliance with Ethics Requirements. Authors declare that they respect the journal's ethics requirements. Authors declare that they have no conflict of interest and all procedures involving human or animal subjects (if exist) respect the specific regulation and standards.

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