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DRYING OF THE AQUEOUS EXTRACT OF ACORN *QUERCUS ROBUR* IN A SPOUT-FLUID BED

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Abstract: The results of the chemical investigations of variously treated acorn samples are presented in this paper with the aim of obtaining data on the amount of nutritious components and biologically active substances. The *Quercus robur* acorn, which belongs to the *Fagaceae* family, was investigated in a raw, thermally treated form and as an extract that was subsequently dried in a dryer with a fluidized bed. The obtained results regarding the content of tannin, nitrogen containing compounds, macro- and microelements indicate that acorn maintains its functional characteristics after the investigated treatments.

Key words: acorn, tannins, functional food, drying, thermal treatment, spout-fluidized bed.

Introduction

The use of acorn in human diet has been registered in written documents since the end of the nineteenth century in Serbia (Pelagić, 1893), with recommendations about its application and benefitial action. The preparation of drinks based on thermally treated acorn (dry roasting) was especially recommended for children. There are data in the current literature on the antioxidative action of some acorn components (Lee, Jeang and Man–Jinoh, 1992; Chiou, 1989).

Acorn has a high moisture content and for longer storage the moisture content must be reduced to below 10-15 mass. %. Acorn may be used as an additive to dough, for the preparation of bread. When roasted and chopped

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(*Qurcus semen tostum* or *Glandes Quercus tostea*), it is administered as an astringent and antidiarrhoeals (Gorunović and Lukić, 2001). Beside biologically nutritious components, acorn also possesses biologically active substances that enable the utilization of acorn in the preparation of functional food (Lee, Jeang and Man-Jinoh, 1992; Chiou, 1989; Rakić, 2000; Rakić, Maletić, Perunović and Svrzić, 2004).

The term functional food was first presented in Japan in the nineteen eighties. The Institute of Medicine's Food and Nutrition Board defined this term as "any food or food ingredient that might provide a health benefit beyond the traditional nutrients it contains" (Claire and Hesler, 1998; Ferrari, 2000; Ferrari and Torres, 2003). Some previous results on the thermal treatment of acorn indicated that the ethanolic extracts of thermally treated acorn have increased protective properties in regard to lipids than native samples (Rakić, Maletić, Perunović and Svrzić, 2004).

Materials and Method

Materials: The representative sample used in this investigation was the *Quercus robur* acorn which belongs to the *Fagaceae* family. The fruit was collected in October 2004. Healthy, ripe nuts that had fallen to the ground, wihout mechanical or other damage, were collected in the park Zemun in Belgrade. Regarding the high moisture content (more than 30 mass. %), the samples were first dried in an oven at 50 °C for 20 hours to ensure safe storage.

Thermal treatment: The thermal treatment consisted of "dry roasting" the samples, previously crushed in a mortar, at 200 °C for 15 minutes. After roasting the sample was ground in a laboratory mill .

Extraction : The aqueous acorn extract was obtained after thermal treatment and milling in a Buehler MLU202 laboratory mill (Switzerland) in a 2-litre glass round bottom vessel equipped with a reflux condenser for 30 minutes after the sample started boiling. Distilled water was used as the solvent.

Drying of the solution in a dryer with a fluidized bed : The liquid extract was dried in a dryer with a fluidized bed, the scheme of which is presented in Fig.1. Air at room temperature was utilized to form the fluidized layer: fluid density ρ_f =1.204 kg/m^3, heat capacity C_{pf} = 1.00 kJ/kg^{o}C, fluid viscosity μ_f = 1.78x10^{-5}Pas, air humidity x = 0.011-0.013 kg H_2O/kg air. Polyethylene particles were used as the column packing (particle diameter d_p = 3.2 mm, particle density ρ_p = 940 kg/m^3, air velocity at minimum fluidization U_{mF} = 0.78 m/s, terminal air velocity U_t= 8.7 m/s, voidage ε = 0.35, sphericity ϕ = 0.87).

The central part of the experimental unit was a column of 250 mm diameter and 1.5 m height, which had a perforated conical bottom at an angle of 45 ^{o}. A tube (pipe) of 65 mm diameter and 600 mm length was positioned in the column axis 5 cm from the bottom of the column. The air for the formation of the fluidized bed was introduced by a jet and annular outlet.

The jet outlet, internal diameter 50 mm, was positioned axially at the bottom of the column, while the annular connector was set laterally on the bottom of the column in the zone below the perforated cone. Air was transported to the column by 2.2 kW ventilators, independently for the jet and annular flow.

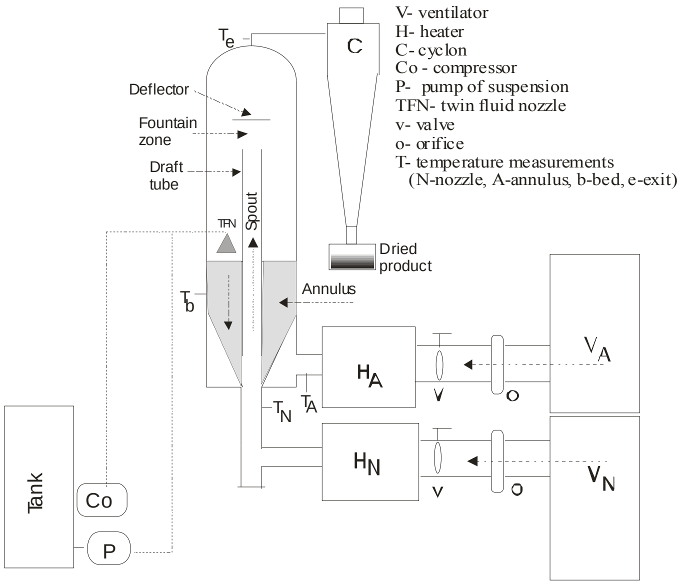

Fig. 1. - Scheme of a dryer with a fluidized bed

The airflow rate was measured by standard orifice plates and regulated by flaps positioned on the pipelines just in front of the heat exchangers.

A highly efficient cyclone was used at the column outlet to collect the powder during extract drying. The air was heated by sets of heaters, 11.2 kW each, independently for each flow. The capacity of the utilized experimental unit was 10 l/h of evaporated water. The drying of the acorn suspension in a fluidized bed with a central tube (pipe) was performed in such a manner that the bed was previously heated to the temperature of the bed required to dry the suspension.

By spraying the liquid phase at the top of the annulus, each particle of the bed was covered with a thin film of suspension. The liquid film dried due to the existence of the central tube (pipe) and the directed movement of the particles in the annulus of the bed. Additional drying of the film on the particle surface and its transformation into a solid coating occurs by transporting the particles of inert packing with the coated extract film through the tube (pipe) upwards in the flow of hot air. Upon exiting the central tube (pipe) and hitting the deflector positioned over the tube (pipe), the solid coating crumbles and falls off the particle packing, which again drops to the top of the annulus and continues to circulate downward through the annulus. The formed powder, carried by the airflow, is separated from the air and collected at the bottom of the cyclone.

The drying parameters were the following: mass air flow on the jet flow 100 kg/h at 140 °C, mass air flow on the annular flow 150 kg/h at 120 °C, while the bed temperature was maintained at 70 °C.

Physical and chemical characteristics: The acorn samples were characterized physically by determining the number of nuts in 1 kg, the mass of 1000 nuts and the ratio of the shell and the nut (Stilinić, 1985.). The chemical analysis consisted of determining the moisture content (at 105°C to constant mass) and the protein content according to Kjeldahl by applying a semi-micro procedure using a "Tecator-Kjeltec System 1002" apparatus. The ash content was determined at 800°C to constant mass (Kaludjerski and Filipović, 1998). The tannin content was determined spectrophotometrically with phosphorus tungstic acid according to the method of the Yugoslav Pharmacopoeia (Ph. Jug. 5, Vol.1 and 3, 2001). A JENWAY B6105 U.V./ Vis Spectrophotometer was used at the wavelength 715 nm.

Determination of the macro-and micro elements : Various methods were used to determine the macro- and microelements. The plant samples were dried and milled to a powder. Preparatory chemical analysis was performed by the method of "dry burning" at 500-550 °C (Jones and Case, 1990), after which the samples were transferred to an acidic solution (HCl). Phosphorus was determined from this solution (2.50 g/100 ml) colorimetrically by the vanadate-molybdate method. Potassium was determined from the same solution by a flame photometer. The AAS method was applied to determine Fe and Cu from the same solution (Jakovljević and Blagojević, 1998). The content of the microelements was determined using a Varian 1200 AA atomic absorption spectrometer.

Data and statistical analysis :The obtained experimental data were processed using mathematical-statistical methods (SAS Institute Inc., *JMP*^{R} 1995). The relative dependence between investigated traits were defined. The obtained coefficients (correlation and determination) were tested by t-test for the risk level of 5% and 1%.

Results and Discussion

The investigations encompassed the following samples: native *Quercus robur* acorn$^{(1)}$, thermally treated (dry roasting) $^{(2)}$ and dried suspension of water acorn extract obtained by drying in a fluidized bed$^{(3)}$. The basic characteristics of the investigated samples are presented in table 1.

T a b. 1. - Sensory characteristics of the analysed samples

	Treatment	Look
Sample 1	Dried and milled nut	Light brown powder
Sample 2	Thermal treated nut at 200^0C – 20 min	Dark brown powder
Sample 3	Dried suspension of water acorn extract	Brown powder

The physical characteristics of the starting material are important for several reasons, foremost the nut collecting procedure, including the mechanical separation of the shell from the nut, drying and crushing or milling. The basic physical properties of the collected acorn nuts are presented in table 2.

T a b. 2. - Physical characteristics of oak acorn, *Quercus robur*

Run	1	2	3	4	5
Length (cm)	3.53	3.68	3.57	3.67	3.58
Width (cm)	2.14	2.09	2.15	2.17	2.28
Number of bead in 1.kg	137.49	139.32	139.19	138.51	139.52
Mass of 1000 bead (kg)	7.31	7.40	7.37	7.11	7.55
Crust (%)	13.57	13.85	14.21	14.41	14.22
Nub (%)	86.43	86.15	85.79	85.59	85.78
Shape	peaked cylindrical	peaked cylindrical	peaked oval	peaked oval	peake d oval

The acorn (*Quercus robur)* was extended-ovally or cylindrically shaped, pointy at the tip, light brown colored with darker longitudinal stripes, smooth and shiny. Based on the mass of 1000 nuts and their number in one kilogram, as well as their length and width, the acorn nuts did not significantly differ externally. The differences were minimal, mostly in nut size and the obtained values were in agreement with the data of other authors (C h i o u , 1989; J o v a n o v i ć, 1985). The samples were subjected to critical temperature conditions that led to more expressed hydrolytic reactions, the degradation of existing and the formation of new compounds within a broader research program of studying the changes in chemical composition of acorn subjected to thermal treatment (dry roasting), hydrothermal treatment (preparation of aqueous extract), as well as solvent drying (fluidized dryer). The changes in the content of the nitrogen-containing and tannin fractions were of particular interest. The results of the changes in the chemical composition during the denoted procedures of *Quercus robur* acorn treatment are presented in table 3.

T a b. 3. – Content of moisture, ash and protein in oak acorn, *Quercus robur*

	Moisture (%)	Ash (%)	Protein (%)
Sample 1	7.95	2.17	4.22
Sample 2	1.88	3.25	4.67
Sample 3	3.85	8.33	14.18

The moisture content of the investigated samples was found to lie in the allowed limits. To ensure safer and longer storage, the acorn samples were dried immediately upon collection and the moisture content was lowered to 7.89%, sample 1. This value lies within the limits that enable safe storage. The thermally treated acorn samples, sample 2, had acceptable values within the limits for safe storage, under the applied experimental conditions. It is significant that the dry aqueous extract, sample 3, was not too hydrophilic and that the moisture content 3.7% was lower than the limiting values required for its stability.

Tannins are complex, polyphenolic, non-nitrogen-containing, non-toxic compounds with a harsh flavour. Tannins are mostly amorphous compounds that are soluble, especially in boiling water (C h i o u, 1989). The characteristic of tannin is to chemically react with proteins and form insoluble complexes. The harsh flavour originates from the bonding of tannin with proteins and mucopolysaccharides in the mouth (K o v a č e v i ć, 2000). Fig. 2 shows the tannin contents in the investigated samples 1,2 and 3 of *Quercus robur* acorn.

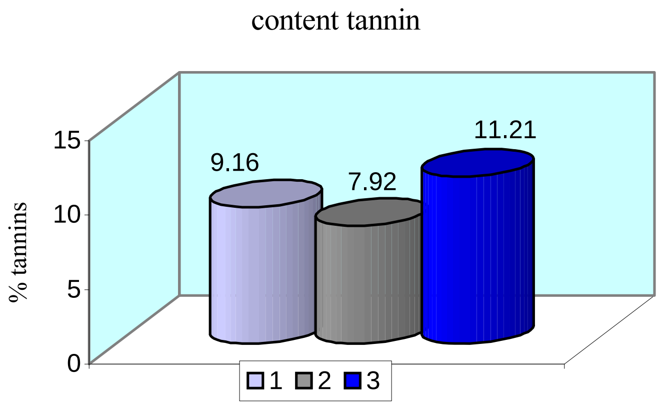

Fig. 2. -The content of tannin in acorn for samples 1, 2 and 3

The results indicate that acorn is a raw material rich in tannins. Thermal treatment leads to a decrease in the tannin concentration, while extract drying yields a somewhat higher content compared to the starting sample, due to concentration effects and the short drying time. The mean value of the total tannins content, calculated in regard to dry matter, was somewhat increased in comparison to previous results for *Quercus cerris* (R a k i ć, M a l e t i ć, P e r u n o v i ć and S v r z i ć, 2004). Tannins are extracted by hot water and therefore their content in dried extract is higher than in native core.

In the human body phosphorus is involved in maintaining the normal hydrogen ion concentration, i.e. the acid-base equilibrium in the body, while potassium is a physiologically very important element that affects the values of the intra- and extracellular osmotic pressure, the bioelectricity of cell membranes and the enzymatic degradation of carbohydrates. Potassium deficiency in the human body causes weakening of the musculature and may also lead to paralysis (Savićević, Djordjević, Gec, Kocijančić, Milošević, Milošević et al. 1983). Fig. 3 shows the contents of P and K in the investigated acorn samples and the products obtained by “dry roasting” and by drying the extract in a fluidized bed.

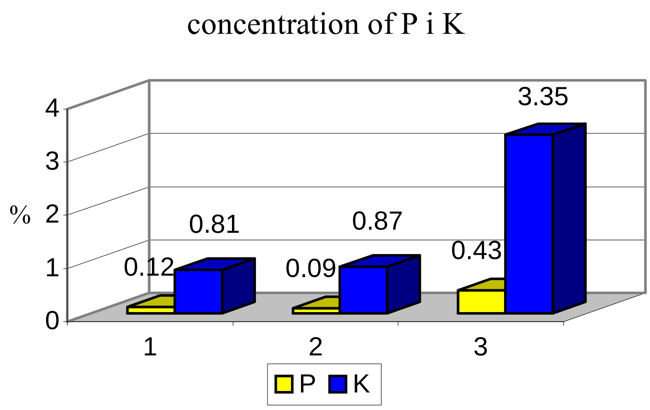

Fig. 3.- The dependence of the concentration of P and K on the thermal treatment of *Quercus robur* acorn

The difference in the P content in native and thermally treated acorn is insignificant. The procedure of aqueous extraction and solution drying gives a product that contains approximately 4 times greater concentration of P in the product compared to the concentration in the raw material, which confirmed the positive aspects of this procedure.

Potassium is much more present in acorn than phosphorus. Thermal treatment did not relevantly influence the potassium concentration. Aqueous extraction and solution drying increased the concentration about 6 times, which was also important for this procedure of obtaining the final product.

The role of oligoelements or trace elements in the human body is biocatalytical, so they have also been called inorganic vitamins. Fe is a constitutive part of hemoglobin and myoglobin, while so-called functional Fe is found deposited in the liver, spleen and bone marrow (Ferrari and Torres, 2003). The role of Cu is indispensible in the synthesis of hemoglobin and for the utilization of Fe by hematogenic organs. It is considered that Cu has a catalytic role in the bonding of Fe to globin and a significant role in the formation of erythrocytes (Leung, 1998, Gutteridge, 1995). The Fe and Cu contents obtained by analyzing samples 1,2 and 3 are presented in Fig. 4.

The concentration of Fe in native and thermally treated samples is considerable. Dry roasting considerably increased the concentration compared to the raw sample, which was not the case for the final product obtained upon extract drying in which the concentration decreased to almost half the value. The thermal treatment of acorn did not relevantly affect the Cu content, while the Cu content in the final product increased in the extract drying procedure.

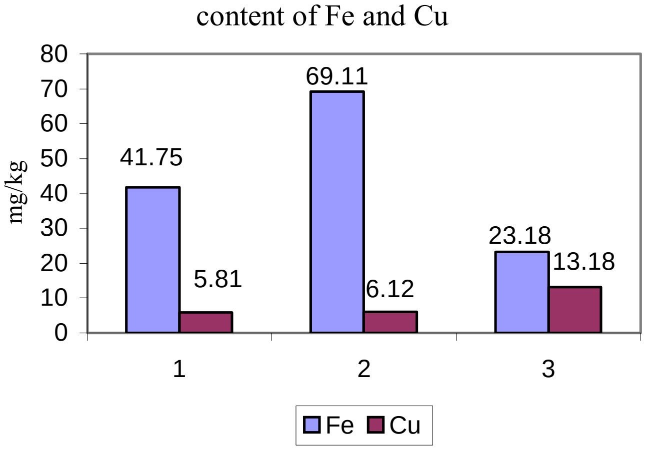

Fig. 4.- The content of Fe and Cu in samples 1,2 and 3, of Q*uercus robur* acorn

Conclusion

Oak acorn *Quercus robur* is characterized by its variety of nutritional, energetic and functional-protecting materials. Dry aqueous extract of thermally treated oak acorn seeds contains: 11.21% tannins, 14.18% proteins, 8.33% crude ash, 3.35% K, 0.43% P, 23.18 mg/kg Fe and 13.18mg/kg Cu. The application of thermal and hydrothermal treatments, as well as the procedure of drying the aqueous extract, showed significant results regarding the concentrating of components that have functional properties. Increased contents were evident in the case of proteins, total mineral matter, macroelements (phosphorus and potassium), as well as microelements such as iron and copper, with the comment that further research must explain the cause of the iron concentration decrease in the case of liquid extract drying.

Acorn is a raw material that has not yet been commercialized. As a cheap and available plant material, it presents a potential source of biologically active components, the application of which is possible in the food, pharmaceutical and other industries.

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SUŠENJE VODENOG EKSTRAKTA HRASTOVOG ŽIRA *QUERCUS ROBUR* U SUŠIONIKU SA FONTANSKO-FLUIDIZOVANOM SLOJEM

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R e z i m e

U ovom radu su predstavljeni rezultati hemijskih ispitivanja različito tretiranih uzoraka hrastovog žira, u cilju dobijanja podataka o količini hranljivih komponenti i supstanci sa biološki aktivnim dejstvom. Ispitivan je žir *Quercus robur*, koji pripada familiji *Fagaceae*, u sirovom, termički tretiranom obliku i ekstraktu koji je naknadno sušen u sušioniku sa fontansko-fluidizovanim slojem. Dobijeni rezultati u pogledu sadržaja, tanina, azotnih jedinjenja, makro i mikroelemenata pokazuju da hrastov žir, nakon ispitivanih tretmana, zadržava svoje funkcionalne karakteristike.

Hemijski sastav nativnog hrastovog žira kao i proizvodi dobijeni opisanim postupcima u ovom radu, ukazuje na prihvatljivost ove sirovine sa aspekta njegove primene u ljudskoj ishrani. Hrastov žir *Quercus robur* se odlikuje raznovrsnošću hranljivih, energetskihe i funkcionalno-zaštitnih materija. Postupkom termičkog i hidrotermičkog tretmana kao i postupkom sušenja vodenog ekstrakta postižu se značajni rezultati u pogledu koncentrisanja materija koje imaju funkcionalna svojstva. Povećanje sadržaja je evidentno kod proteina, ukupnih mineralnih materija, makroelemenata (fosfor i kalijum), kao i mikroelemenata (gvoždje i bakar) s tim što se u u budućim istraživanjima mora definisati razlog pada koncentracije gvoždja pri sušenju tečnog ekstrakta.

Hrastov žir je sirovina koja nije komercijalizovana, a kao jeftin i lako dostupan biljni materijal, predstavlja potencijalni izvor biološki aktivnih komponenti, čija je primena moguća u prehrambenoj , farmaceutskoj i drugim industrijama.

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