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EFFECT OF THE EXPANDING PROCESS ON THE CONTENT OF PHENOLIC COMPOUNDS IN EXPANDED GRAINS

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K e y w o r d: millet grains, expanded grains, bioactive compounds, phenolic compounds.

A b s t r a c t

The aim of the study was to determine to what extent the process of expansion affects the interaction of phenolic compounds with other dry matter components such as starch, cellulose, fiber and protein.

As a research material millet grains and popping were used. The content of total phenolic compounds and contents of free and liberated from the ester and glycosidic bonds phenolic acids were determined. The content of phenolic compounds was analysed spectrophotometrically. To induce a characteristic color reaction a Folin-Ciocalteu reagent was used. The measurement was performed at a wavelength of 720 nm to the blank sample. Results were expressed as D-catechin.

The content of phenolic compounds, extracted with 80% methanol was 157.97 mg/100g dry matter for millet grain and 129.45 mg/100 g dry matter for popping.

WPŁYW PROCESU EKSPANDOWANIA NA ZAWARTOŚĆ ZWIĄZKÓW FENOLOWYCH W POPPINGU

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S ł o w a k l u c z o w e: ziarna prosa, popping, substancje biologicznie aktywne, związki fenolowe.

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Abstrakt

Celem pracy było ustalenie, w jakim stopniu proces ekspandowania wpływa na interakcję związków fenolowych z innymi składnikami suchej masy np. skrobią, celulozą, błonnikiem i białkiem.

Materiałem badawczym było ziarno prosa oraz popping. Oznaczono zawartość związków fenolowych ogółem, zawartość wolnych i uwolnionych z połączeń estrowych i glikozydowych fenolokwasów. Zawartość związków fenolowych oznaczono spektrofotometrycznie. Do wywołania charakterystycznej reakcji barwnej stosowano odczynnik Folina-Ciocalteu. Pomiar wykonano przy długości fali 720 nm wobec próby odczynnikowej. Wyniki podano w przeliczeniu na D-katechinę.

Zawartość związków fenolowych, wyodrębnionych 80% metanolem, wynosiła w ziarnie prosa 157,97 mg/100 g s.m., a w poppingu 129,45 mg/100g s.m.

Introduction

The terms „natural phytocompounds" or „bioactive plant compounds" apply to chemical substances which occur in plants and are potentially bioactive, for example, as antioxidants (TROSZYŃSKA, CISKA 2002, ZIELIŃSKIET al. 2012, IZADI et al. 2012). Bioactive compounds differ in terms of their physical and chemical properties and can be classified into hydrophilic ones (phenols, vitamin C, glucosinolates), which protect the aqueous environment of cytosol, and hydrophobic ones (tocopherols, carotenoids, phytosterols), which protect cellular membranes and lipoproteins from the destructive action of free radicals (KOPCEWICZ, LEWAKA 2002).

Cereal grain contains considerable amounts of bioactive compounds (polyphenols, tocopherols and phytosterols), which are strong antioxidants (PETERSON et al. 2001, WOLOCH et al. 2007, CZAPSKI, GORECKA 2014). Moreover, they protect grain from internal and external threats. They stimulate the growth of microflora, the feeding of insects and rodents and heal damaged parts of plants (KOPCEWICZ, LEWAKA 2002). The properties of bioactive substances depend mainly on their chemical structure. Bioactive compounds of plant origin include phenols, terpenoids, carotenoids, glucosinolates, alkaloids, capsaicinoids, betalains, allyl compounds, polyacetylenes and polysaccharides. Phenolic compounds are among the most common bioactive substances. Consumed with other ingredients of food, these compounds contribute to improvement of human health and play an important role in disease prevention. For example, they reduce the risk of a number of diseases, such as cancers, heart diseases or diet-related diseases (GRAJEK 2007, CZAPSKI, GORECKA 2014). Cereals and farinaceous products are among the most frequently consumed foods. They contain a range of phenolic compounds, which are a good source of natural antioxidants.

Millet is a cereal, which is rich in phenolic compounds. It is not very popular and often overlooked, but is a valuable material for the production of functional foods. It is one of the oldest crops and it used to be one of the main

cereals (CZERWIŃSKA 2010). Millet grain is mainly used to produce millet groats, but recently it has also been used to produce flakes and expanded grain (popping). Grain changes its physical and chemical properties during the process of expanding, for example, its volume increases many times (TYBURCY 2000). ZIELIŃSKI et al. (2012) report that processing grain can result in changes in polyphenol content, which include an increase in the content of phenolic acids.

The available literature contains a number of reports, which indicate the possibility of the formation of strong chemical bonds between phenolic compounds and components of dry matter, mainly proteins and polysaccharides (CHANDRA, SEKARA, SHAHIDI 2010).

Therefore, the hypothetical question arises: to what extent can the thermal energy of the expanding process cause interaction between the components mentioned above? In order to answer this question, the aim of this study was to evaluate the changes, which take place in phenolic compounds of millet grain during the production process of expanded grain. It involved examination of how the process of expanding affects interactions of phenolic compounds with other components of dry matter, such as starch and protein.

Material and methodology

Millet grains and expanded millet grains (popping) were used as the study material. The expanding process was conducted on a prototype device at Przedsiębiorstwo Produkcyjno-Handlowo-Usługowe „Szarłat" s.c. in Łomża. Grains containing 9–12% of moisture were heated at 280°C for a few seconds. The experimental part was conducted in three independent replications and the samples of the expanded grains were further analysed.

In order to verify the hypothesis put forward in this study and to achieve the study objective, its scope was restricted to determination of the total content of phenolic compounds, occurring both in free forms and as bound by ester and glycoside bonds in millet grain and expanded millet grain.

The material was prepared for the experiment by grinding and degreasing by the Soxhlet method, as per the Polish Standard (PN-ISO 6492:2005).

Phenols were isolated from the prepared material and were subsequently analysed by the method described by ZADERNOWSKI (1987).

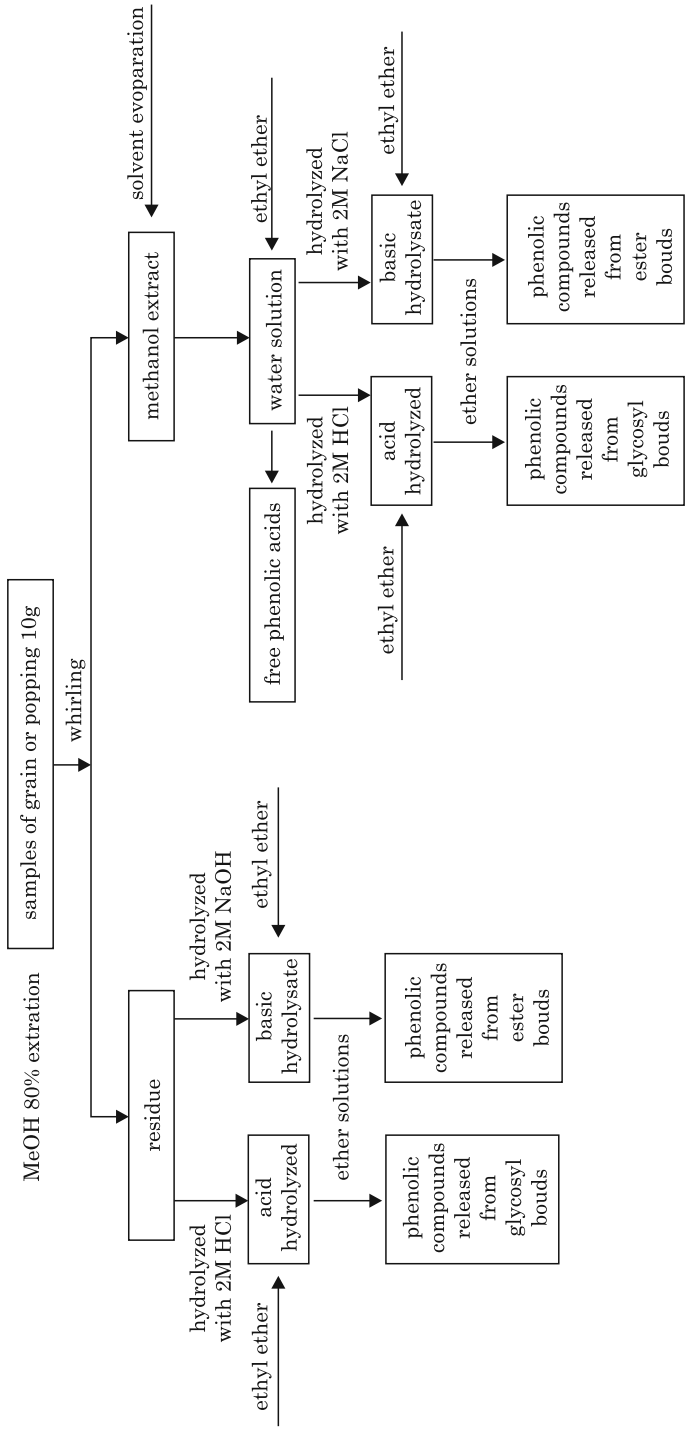

Fig. 1. A diagram of the extraction and isolation of phenolic compounds

Isolation of low-molecular phenolic compounds from grains and expanded grains

A 10 g sample was taken from the ground study material, to which 50 cm^3 of 1% solution of HCl in 80% MeOH was added and the whole sample was shaken in a shaker for 20 minutes.

The extraction was conducted twice more; each time 50 cm^3 of a 1% solution of HCl in 80% methanol was used and the whole sample was shaken in a shaker for 15 minutes. The extracts were filtered and then condensed on an R210 rotary vacuum evaporator (Buchi Labortechnik AG, Postfach, Switzerland) until the solvent had evaporated completely. The condensed extract obtained in this manner was dissolved in methanol or water at pH 2, transferred to a 50 cm volumetric flask and made up to volume. The extract dissolved in methanol was used to assay the total amount of phenolic compounds. The extraction residue was dried and kept for further analyses.

Isolation of free low-molecular phenolic compounds (FLPC) from a mixture of the organic compounds extracted with methanol from millet grains and expanded millet grains

The extract isolated from ground millet grains and expanded grains, which is a mixture of low-molecular organic compounds, was dissolved in water at pH 2. Phenolic compounds were extracted from the prepared mixture with ethyl ether by continuous liquid-liquid extraction for 24 hours. Subsequently, ether was evaporated and the condensed sample was transferred to a 10 mL volumetric flask and rinsed out with 80% methanol. Free low-molecular phenolic compounds were assayed in the prepared samples by the colorimetric method. The FLPC extraction residue was subjected to alkaline and acidic hydrolysis in order to isolate phenolic compounds bound by ester and glycoside bonds with other low-molecular organic compounds soluble in 80% methanol.

Isolation of phenolic compounds bound by the ester bond with other low-molecular organic compounds, isolated with methanol from millet grains and expanded grains

The ether extraction residue was evaporated to dryness in a stream of nitrogen and the sample was then dissolved in 50 cm^3 of 2M NaOH and stirred with an electromagnetic agitator for 4 hours. After that time, the sample was acidified to pH 2 and the phenolic compounds released from esters were

extracted with ethyl ether by continuous liquid-liquid extraction. Subsequently, ether was evaporated and the condensed sample was transferred to a 10 mL volumetric flask and rinsed out with 80% methanol. The amount of released compounds was determined by the spectrophotometric method using the Folin-Ciocalteu reagent.

Isolation of phenolic compounds bound by the glycosidic bond with other low-molecular organic compounds, isolated with methanol from millet grains and expanded grains

The ether extraction residue was evaporated to dryness in a stream of nitrogen and subsequently dissolved in 50 cm^3 of 2M HCl and hydrolyzed for 1 hour by heating it up on a boiling water bath under a reflux condenser. After that time, the sample was acidified to pH 2 and free phenolic compounds were extracted with ethyl ether by continuous liquid-liquid extraction. Subsequently, ether was evaporated and the condensed sample was transferred to a 10 mL volumetric flask and rinsed out with 80% methanol.

The amount of the phenolic compounds released from glycosides was determined by the spectrophotometric method using the Folin-Ciocalteu reagent.

Isolation of phenolic compounds released from esters which are present in extraction residue of millet grain and expanded grain

2 g portions of the methanol extraction residue were weighed after the residue was dried and homogenized. Subsequently, 50 cm^3 of 2M NaOH was added and the whole sample was stirred with an electromagnetic agitator for 4 hours. After that time, the sample was acidified to pH 2 and free phenolic compounds were extracted with ethyl ether by continuous liquid-liquid extraction. Subsequently, ether was evaporated and the condensed sample was transferred to a 10 mL volumetric flask and rinsed out with 80% methanol.

The amount of phenolic compounds released from esters was determined by the spectrophotometric method using the Folin-Ciocalteu reagent.

Isolation of phenolic compounds released from glycosides which are present in extraction residue of millet grain and expanded grain

The extraction residue was dried and 2 g portions of it were weighed. Subsequently, 50 cm^3 of 2M HCl was added and the whole sample was

hydrolyzed for 1 hour, heating it up in a boiling water bath under a reflux condenser. After that time, the sample was acidified to pH 2 and free phenolic compounds were isolated with ethyl ether by continuous liquid-liquid extraction. Subsequently, ether was evaporated, then condensed sample was transferred to a 10 mL volumetric flask and rinsed out with 80% methanol. The amount of phenolic compounds released from the glycosides was determined by the spectrophotometric method using the Folin-Ciocalteau reagent.

Plotting a calibration curve 100 mg of D-catechin was dissolved in methanol and the volume was made up to 100 cm^3. The stock solution was used to make dilutions from 1 to 10, containing 0.01 to 1.0 mg of D-catechin, respectively. 0.25 cm^3 of the solution was sampled from each diluted solution and the following were added in sequence: 0.25 cm^3 of the Folin-Ciocalteu reagent and 0.5 cm^3 of sodium carbonate solution; the whole sample was made up with distilled water to the volume of 5 cm^3. After 30 minutes, the absorbance was read out at the wavelength of 720 nm against a blank sample.

Phenolic compounds assay in the sample before and after hydrolysis

The amount of phenolic compounds released from glycosides was determined by spectrophotometry, using the Folin-Ciocalteu reagent, by the method described in AOAC (Association of the Official Analytical Chemists 1974).

0.5 mL of the extract, 0.25 mL of Folin-Ciocalteu reagent (diluted at 1:1 v/v with distilled water, prepared several minutes before), 0.5 mL of sodium carbonate and 3.75 mL of distilled water were sampled to a centrifuge tube. After all the components were added, the samples were mixed, capped with a stopper and left for 25 minutes. After that time, they were centrifuged at 12,000 rpm in an Eppendorf centrifuge. Subsequently, absorbance was measured at the wavelength of 720 nm against a blank sample (0.25 mL of Folin-Ciocalteu reagent, 0.5 mL of sodium carbonate and 4.25 mL of distilled water were sampled to a centrifuge tube). The content of phenolic compounds was converted to the content of D-catechin and is given as the number of mg per 100 g dry matter of millet grain.

Discussion of results

An analysis of increased reactivity of phenolic compounds compared to other components of dry matter, caused by increased energy potential during industrial processing, should take into account the chemical diversity of this

group of organic compounds. Phenolic compounds are a very large group of organic substances which perform diverse, non-nutritional, functions in the body. After they are consumed with food, the majority of phenolic compounds retain their bioactive properties and positively affect the function of the human body.

Literature reports have described the anti-oxidative properties of phenolic compounds which occur in grain, grains (IZADI et al. 2012, ZIELIŃSKI et al. 2012, KIM et al. 2010, TROSZYŃSKA, CISKA 2002), fruit and vegetables (GRAJEK 2007, CZAPSKI, GÓRECKA 2014,) and their inhibitory effect on enzyme activity (KUBICKA, JĘDRYCHOWSKI 2001, KOPCEWICZ, LEWAKA 2002). CHOI et al. (2007) showed methanol extracts of sorghum, rice, millet and barley contain high concentrations of polyphenolic compounds and, consequently, high anti-oxidative activity. KOPCEWICZ, LEWAKA (2002) reported that phenolic compounds in plants and crops perform the function of enzymatic activity inhibitors. On the other hand, KUBICKA, JĘDRYCHOWSKI (2001) claim that phenolic compounds extracted from pumpkin with an enzyme do not have an inhibitory effect on the enzyme activity. In their opinion, the lipoxygenase activity depends on the chemical composition of extraction solutions.

Phenolic acids, derivatives of cinnamic and benzoic acids, are the main group of phenolic compounds. Free phenolic acids are present in small amounts in plants and their presence usually results from the fact that they have not been transformed into bound forms during physiological processes. Phenolic acids usually occur in a bound form in different parts of plants, including grain and grain, as components of low- or high-molecular weight polyphenolic compounds. For example, various forms of depsides are low-molecular polyphenols. High-molecular polyphenols include lignin procyanidins, hydrolyzing tannins, flavonoids, with which phenolic acids form conjugates bound by ester or glycoside bonds. GAWLIK-DZIKI (2004) reports that some derivatives of cinnamic acid are commonly present in esters with carboxylic acids or glucose, while derivatives of benzoic acid usually occur as glycosides. Derivatives of cinnamic acid occur as free compounds, as a depside or as glycosides. Chlorogenic acid, which occurs in grain, in oily seeds and in coffee, is an example of a depside. It is formed by binding caffeic acid with quinic acid. Another example is ellagic acid, a dimer of gallic acid, whose molecules are bound at the second position by a C-C bond and by two symmetric ester bonds between the carboxylic group of one acid and the hydroxyl group of the other, forming a system of four condensed rings (BOCK et al. 1981). Esters of synapinic acid and choline, or sinapine, is a compound which typically occurs in the *Brassicaceae* family plants (ZADERNOWSKI 1987). Most depsides occur in bound forms, for example, they are parts of hydrolyzing tannins and form complexes with proteins and polysaccharides.

Apart from the structures described above, phenolic acids bind with lipids, sterols, polysaccharides, peptides.

Due to the high diversity of their chemical structure and mutual relationships, as well as their ability to interact with other organic compounds, such as sugars, proteins and lipids, phenolic compounds are difficult to isolate and assess physicochemically, for example, in terms of their antioxidative or inhibitory properties.

Therefore, an analytical procedure was applied to extract phenolic compounds in this study whose detailed description is provided in the methodology part of the paper. Phenolic compounds are usually extracted with methanol or acetone (SHAHIDI, NACZK 2006). Methanol is an organic polar solvent, which is effective in the extraction of low-molecular polyphenols, such as phenolic acids, depsides, flavonoids, glycosides and esters of phenolic acids with monosaccharides, fatty acids and sterols. Acetone is used to extract procyanines, catechins, tannins and polyphenols, typical of grain shells. In this study, phenolic acids were extracted from millet grain and expanded grain with 80% methanol acidified with 1% HCl. A similar extraction solvent has been used by other researchers. It must be borne in mind that extraction of phenolic compounds is frequently incomplete, with only free phenolic acids and their conjugates as low-molecular esters and glycosides being isolated. This is because some phenolic acids occur in plants as cellular walls polymers, e.g. pectin, protein, fiber, polysaccharides.

One such example is ferrulic acid, which forms esters and glycosides present in the cellular walls of cereals. Most of the ferrulic acid and p-coumaric acid present in cereals is bound with arabinoxylans (SHAHIDI, NACZK 2006). Therefore, it seems justified to conduct pre-hydrolysis and to cleave the bonds between phenolic compounds and the protein or polysaccharide matrix. ZADERNOWSKI (1987), ROSS et al. (2009), GARCIA-SALAS et al. (2010), WATSON (2014) propose conducting alkaline hydrolysis with 2 M NaOH, followed by acidic hydrolysis with 2 M HCl. Both of these methods of hydrolysis have been applied in this study.

Fig. 2 shows the total amount of phenolic compounds found in four samples of millet grain and in two samples of expanded grain. The amount comprises low-molecular forms of phenolic compounds soluble in 80% methanol; these include mainly free phenolic acids and their conjugates as well as free forms of other polyphenols. It does not include phenolic acids bound with cellular wall polymers because these are compounds with high reactivity and affinity, bound by strong chemical bonds, which cannot be broken by methanol. Easy formation of complexes of phenolic acids with flavonoids, structural molecules of plant cells (proteins, lignins, cellulose) and other acids (e.g. maleic and tartaric acid) determines the diversity of compounds in the group and their solubility in methanol and acetone.

The mean total content of phenolic compounds is listed in table 1; the values were converted to the content of catechin and expressed in mg/100 g of sample. The total content of phenolic compounds in the samples of millet grains under analysis ranged from 134.68 to 178.83 mg/100 g (mean 157.97 ± 19.08 mg/100 g) and from 122.08 to 136.82 mg/100 g (mean 129.45 ± 10.42 mg/100 g) in samples of expanded grains. Similar amounts of phenolic compounds were found in millet grains by ZHANG et al. (2014)

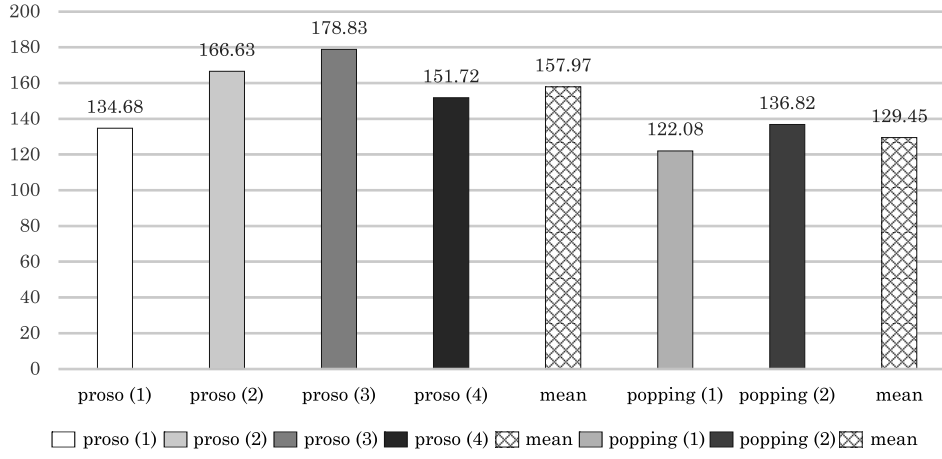

Fig. 2. The total content of free phenolic compounds (soluble in 80% methanol), expressed in mg per 100 g of millet grains and expanded grains

Table 1
Mean content of phenolic compounds, expressed in mg per 100 g of millet grains and expanded grains

	Total phenolic compounds [mg/100 g]	Free phenolic acids [mg/100 g]	Free phenolic acids and other forms of phenolic compounds released by hydrolysis of methanol extract and breaking:		Phenolic acids and other forms of phenolic compounds released by hydrolysis of millet grains extract residue and breaking:	
			ester bonds	glycoside bonds	ester bonds	glycoside bonds
Millet grains	157.97±19.08	110.98±10.15	13.25±1.15	25.74±0.89	90.27±8.31	78.94±8.01
Expanded grains	129.45±10.42	98.99±5.19	11.83±1.06	17.62±1.36	92.87±1.51	116.68±12.64

ZHANG et al. (2014) report that the content of free polyphenols ranged from 27.48 to 151.14 mg of gallic acid equivalent / 100 g of dry weight of a sample.

An analysis of the total content of phenolic compounds showed that expansion resulted in an 18% reduction of the content of free low-molecular

phenolic compounds in samples of expanded grains. Some phenolic compounds were probably not isolated from expanded grains by extraction with methanol because of their secondary, strong bonding with components of dry matter of expanded grains. Such bonds are too strong to be broken by extraction of grains and expanded grains with methanol. Bound phenolic compounds were also present in millet grains, but their content was much smaller than in expanded grains.

According to ZHANG et al. (2014) the amount of phenolic compounds which occur in a bound form in millet grain ranged from 55.95 to 305.81 mg of gallic acid equivalent per 100 g of dry matter. The contents of bound phenolic compounds and of total phenolic compounds were 62.08% and 67.05%, respectively (ZHANG et al. 2014). The interaction of free polyphenols, mainly phenolic acids, with other substances, may result from supplying large amounts of energy to the system during the expanding process, but it may also be caused by changes in the ring structure in aromatic polyphenol rings.

Low-molecular phenolic compounds isolated from millet grain or expanded grain with methanol include mainly free phenolic acids, their depsides and conjugates with flavonoids or glycosides, which are formed by binding phenolic acids with other polyphenols or mono- and disaccharides, inositol. The content of free phenolic acids in millet grain was 110.98 ± 10.15 mg/100 g of sample and it was lower by 11.99 mg/100 g in expanded grain. This demonstrates that during the expanding process, part of the free phenolic acids or their conjugates can form stable complexes with polymers present in dry matter, for example, with proteins, lignins and cellulose.

The solution obtained after free phenolic acids were isolated was hydrolyzed in both alkaline and acidic environments. Both the methods of hydrolysis are not fully selective and both ester and glycoside bonds can be broken simultaneously. For example, both glycoside bonds and weak ester bonds can be broken in an acidic environment. This increases the amount of polyphenols released and disturbs the total balance of phenolic compounds.

Alkaline hydrolysis produced 13.25 ± 1.15 mg of phenolic compounds released from esters/100 g of millet grains and 11.83 ± 1.06 mg/100 g (Fig. 3.) of expanded grain. Many more phenolic acids were isolated by acidic hydrolysis: 25.74 ± 0.89 mg/100 g of millet grain and 17.62 ± 1.36 mg/100 g of expanded grain. The phenolic compounds isolated from millet grain and expanded grain by extraction with methanol were a mixture of free phenolic acids and other species into which phenolic acids were incorporated. More phenolic acids in these compounds were bound in the form of glycosides than as esters.

Very interesting findings were obtained in an assay of phenolic acids in the residue after extraction of low-molecular phenolic compounds with methanol. Phenolic acids were isolated from the extraction residue during alkaline and

acidic hydrolysis by breaking ester and glycoside bonds. Mainly complexes of phenolic acids with cellular wall polymers (proteins, polysaccharides) were broken. The amount of phenolic acids released from esters in the samples under analysis varied slightly and was 90.27 ± 8.31 mg/100 g of millet grain and 92.87 ± 1.51 mg/100 g (Fig. 4.) of expanded grain. Significant differences were observed in terms of the amount of phenolic acids released from glycoside compounds. Expanded grain contained 116.68 mg of free phenolic acids/100 g, which was considerably more than in millet grain (78.94 mg/100 g). This shows that the content of bound phenolic compounds was higher than that of free forms. This also indicates that the process of expanding may result in some phenolic compounds forming stable complexes with other components of dry matter, e.g. cellular wall polymers. MAILLARD and BERSET (1995) claim that these compounds perform various functions, e.g. they act as antioxidants.

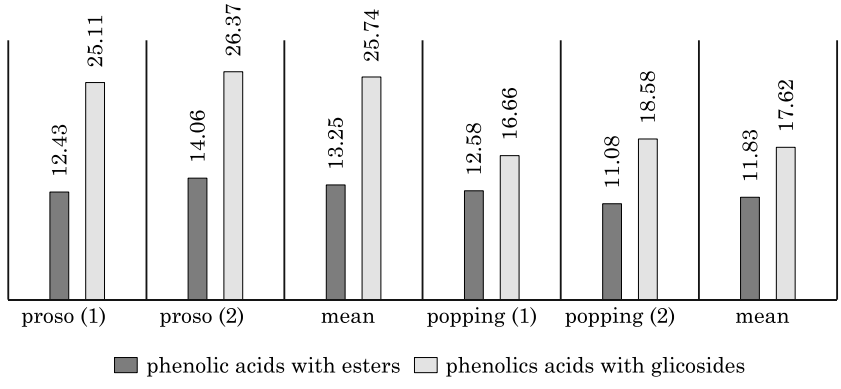

Fig. 3. Content of phenolic acids released from esters and glycosides, expressed in mg per 100 g of millet grains and expanded grains

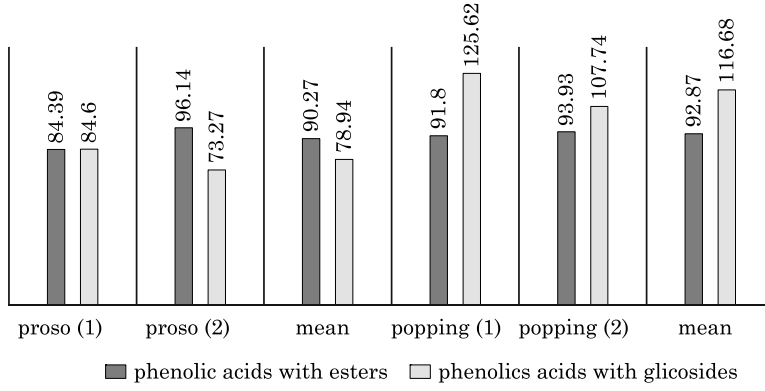

Fig. 4. Content of phenolic acids bound with components of extraction residue, released from esters and glycosides, expressed in mg per 100 g of millet grains and expanded grains

Summary and conclusions

The total phenolic compounds content was higher in millet grains than in expanded millet grains. This means that some of the phenolic compounds were bound during the expanding process. The polyphenol content was probably affected by the high temperature of the expanding process.

Phenolic acids bound in esters were isolated in alkaline hydrolysis. The content of free phenolic acids was higher in millet grains than in expanded millet grains.

Phenolic acids bound in glycosides were released in acidic hydrolysis. The amount of free phenolic acids was higher in millet grains than in expanded millet grains.

It may be claimed that more phenolic acids forms conjugate with carbohydrates (glycosides) than with proteins (esters).

The general conclusion can be drawn on the basis of the study that the thermal energy supplied during the millet grain expanding process increases the amount of phenolic compounds bound with other components of dry matter of expanded grain. This may make protein in expanded grain less digestible.

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