Extruded corn gruels containing linden flowers: quantitation of phenolic compounds and selected quality characteristics

DOI: 10.1515/chem-2015-0138
received December 31, 2014; accepted August 30, 2015.

Abstract: Extrusion-cooking of plant materials may enhance antioxidant activity and improve health benefits. Selected antioxidant polyphenols in extruded corn gruels enriched with different amounts of linden flowers were determined by LC-ESI-MS/MS and quality characteristics were determined.

Phenolic content increased with Tiliae inflorescentia addition and was not decreased by high-temperature extrusion. Linden flower incorporation into instant gruels should be limited to 10% to retain acceptable sensory properties.

Keywords: Tiliae inflorescentia, extrusion-cooking, corn gruels, polyphenols, LC-ESI-MS/MS analysis

1 Introduction

Extrusion-cooking has become a popular high temperature, short time processing method for vegetable raw materials in snacks, pasta, flat bread, instant gruels, baby foods, confectionery, modified starches and pet food [1]. Grits, gruels and instant cereals are basic carbohydrate sources in baby and infant diets. These products should be processed to improve their dispersibility and digestibility, since a 3-4 month-old baby’s pancreas has a limited ability to digest starch. Extrusion-cooking is much more efficient than traditional methods of infant cereals processing, e.g. drum or roll drying [2, 3].

Extrusion-cooking temperature, screw speed, moisture content, feed rate and residence time distribution are crucial for extrudate nutritional characteristics and antioxidant activity. The process changes texture, gelatinizes starch, cross-links proteins, and creates flavors [4]. It may inactivate antinutritional factors, denature undesirable enzymes or reduce lipid oxidation [5].

Extrusion-cooking may enhance food antioxidant activity and form resistant starch or insoluble fiber [6-8]. It retains more nutrition and active compounds than other thermal treatments, especially slow cooking or deep frying, but it is comparable to blanching, freezing or fermentation [9]. Analysis of extruded product extract showed higher antioxidant activity than in the raw materials; phenolics may be released [10-14].

Khanal et al. [15] reported the effects of extrusion-cooking on procyanidin monomers and dimers in grape seed and pomace. It appears to increase the level of low molecular weight bioactive compounds (procyanidins etc.) and biologically important monomers and dimers from polymer chains [16]. Extruded product enrichment with bioactive compounds is limited by secondary plant metabolites’ low thermal stability and their susceptibility to changes during processing [5,17].

Fruits and vegetables are the most popular components added to cereal extrudates, but some waste products or functional compound isolates may be used [8,13,18-20]. Linden flower (Tiliae inflorescentia) is one of the herbal supplements most often used. Its main constituents include flavonoids (quercetin glycosides, kaempferol
glycosides, tiliroside), phenolic acids, essential oils, phytosterols, organic acids, tannins, mucilage, minerals, niacin, and vitamin C [21-23]. Its pharmacological activity is in feverish colds, infectious diseases, and bronchitis, but it also has sedative and diuretic actions [24,25]. It is used as extracts or infusions (teas), but it may also be a pro-health component in infant or baby food.

Our aim was to determine selected polyphenols in extruded corn gruels enriched with different amounts of linden flower by LC-ESI-MS/MS and to evaluate their quality characteristics.

2 Experimental procedures

2.1 Chemicals

Analytical grade standards of gallic, protocatechuic, gentisic, 4-OH-benzoic, vanillic, caffeic, syringic, p-coumaric, ferulic, salicylic, veratric, synapic, 3-OH-cinnamic, and rosmarinic acids as well as rutin, hyperoside, isoquercetin, quercitrin, and apigenin-7-O-glucoside were purchased from Sigma–Aldrich Fine Chemicals (St. Louis, MO, USA). Tiliroside, kaempferol-3-rutinoside, astragalin were from Carl Roth (Karlsruhe, Germany). LC grade acetonitrile was purchased from Sigma–Aldrich Fine Chemicals (St. Louis, MO, USA), LC grade methanol and analytical grade ethanol were purchased from J.T. Baker (Phillipsburg, USA). LC grade water was prepared using a Millipore Direct-Q3 purification system (Bedford, MA, USA). The SPE columns were Bakerbond C18, 3 mL containing 500 mg end-capped (17.5% C) 40 µm reversed phase packing (J.T. Baker, Deventer, Netherlands; catalog No. 1218800017).

2.2 Plant Materials

*Tiliae inflorescentia* (series 096/2011) was purchased from “Kawon-Hurt” herbal industry (Gostyń, Poland). Corn grits was purchased in the local market (Vegetus, Poland).

2.3 Extrusion-cooking procedure

Blends of corn grits and ground linden flowers were prepared by mixing dry components in weight ratios of 100:0, 99:1, 97:3, 95:5, 90:10 and 80:20. The blended samples were conditioned to 15% moisture by spraying with water and mixing continuously for 10 minutes. Blends were processed in a TS-45 single screw extrusion-cooker (ZMCh Metalchem, Gliwice, Poland) with barrel length / screw diameter = 12, and screw compression ratio 3:1. The barrel temperatures were 120-135-140°C in the first zone, second zone, and forming die. The screw speed was 125 rpm and a 3 mm circular open die shaped the extrudate [29,30]. After cooling (extrudate moisture content was 6.0%) extrudates were ground in an iG5A laboratory grinder (TestChem, Poland) to less than 1 mm for instant gruels [3,29]. Samples were stored in polyethylene bags at room temperature.

2.4 Extraction procedure

Before extraction dry plant material was milled and sieved. Three 2 g portions were each extracted 3 times with 40 mL 80% aqueous ethanol in a Sonorex RK 100H ultrasonic bath (Bandelin Electronic, Germany) (20 kHz, 100 W) for 30 min at 60°C [26]. Extracts were filtered, combined and evaporated to dryness. Residues were dissolved in 10 mL of methanol.

2.5 Solid phase extraction (SPE)

Crude extracts were purified by SPE. 5 mL was passed through a previously conditioned Bakerbond C18 SPE column. Polyphenols were eluted with 5 mL 60% aqueous methanol followed by 10 mL of 30% aqueous methanol. The combined extracts were evaporated to dryness and dissolved in 10 mL of methanol in a volumetric flask. The procedure was repeated three times.

2.6 LC-ESI-MS/MS analysis

Analysis was performed using reversed-phase high-performance liquid chromatography with electrospray ionization mass spectrometry (LC-ESI-MS/MS). An Agilent 1200 HPLC system (Agilent Technologies, USA) equipped with a binary gradient solvent pump, degasser, autosampler and column oven connected to a 3200 QTRAP Mass spectrometer (AB Sciex, USA) was used.

Phenolic acid separations were slightly modified from the procedure of Nowacka et al. [27] They were carried out at 25°C on a Zorbax SB-C18 column (2.1 × 50 mm, 1.8-µm particles; Agilent Technologies, USA) with a mobile phase of 0.1% HCOOH in water (solvent A) and 0.1% HCOOH in methanol (solvent B), using 3 µL injections. The flow rate was 450 µL min⁻¹ and the gradient was: 0–0.8 min = 5%


Flavonoid glycoside separations were carried out at 25°C on an Eclipse XDB-C18 column (4.6 × 150 mm, 5-µm particles; Agilent Technologies, USA) with a mobile phase of 0.1% HCOOH in water (A) and 0.1% HCOOH in acetonitrile (B), using 5 µL injections. The flow rate was 400 µL min⁻¹ and the gradient was: 0–1 min = 18% B; 1.5–5.5 min = 20% B; 7–10 min = 25% B; 13–15 min = 60% B, 17–22 min = 18% B. The ESI operated in the negative-ion mode: capillary temperature 500°C, curtain gas 20 psi, nebulizer gas 50 psi, source voltage − 4500 V. Nitrogen was the curtain and collision gas.

For each compound the optimum multiple reaction mode (MRM) conditions were determined in the infusion mode. The data was acquired and processed using Analyst 1.5 software (AB Sciex, USA). Triplicate injections were made for each standard and sample. Analytes were identified by comparing retention time and m/z values obtained by MS and MS² with those of standards obtained under the same conditions (Tables 1 and 2).

### Table 1: LC-ESI-MS/MS phenolic acids results.

| Compound          | Peak no. | TR [min] | [M-H]- | Fragment ions | Collision energy [eV] |
|-------------------|----------|----------|--------|---------------|----------------------|
| Gallic acid       | 1        | 0.75     | 168.7  | 124.9         | 78.9                 |
|                   |          |          |        |                | - 14                 |
|                   |          |          |        |                | - 36                 |
| Protocatechuic acid| 2        | 1.73     | 152.9  | 107.8         | 80.9                 |
|                   |          |          |        |                | - 38                 |
|                   |          |          |        |                | - 26                 |
| Gentisic acid     | 3        | 2.73     | 152.8  | 107.9         | 81                    |
|                   |          |          |        |                | - 36                 |
|                   |          |          |        |                | - 30                 |
| 4-OH-benzoic acid | 4        | 3.40     | 136.8  | 92.9          | 123                   |
|                   |          |          |        |                | - 18                 |
|                   |          |          |        |                | - 12                 |
| Vanillic acid     | 5        | 4.72     | 166.8  | 107.9         | 128                   |
|                   |          |          |        |                | - 18                 |
|                   |          |          |        |                | - 12                 |
| Caffeic acid      | 6        | 4.92     | 178.7  | 134.9         | 88.9                 |
|                   |          |          |        |                | - 16                 |
|                   |          |          |        |                | - 46                 |
| Syringic acid     | 7        | 5.57     | 196.9  | 181.9         | 122.8                |
|                   |          |          |        |                | - 12                 |
|                   |          |          |        |                | - 24                 |
| p-Coumaric acid   | 8        | 6.01     | 162.7  | 119           | 93                    |
|                   |          |          |        |                | - 14                 |
|                   |          |          |        |                | - 44                 |
| Salicylic acid    | 9        | 6.20     | 136.8  | 93            | 75                    |
|                   |          |          |        |                | - 16                 |
|                   |          |          |        |                | - 48                 |
| Ferulic acid      | 10       | 6.28     | 192.8  | 177.9         | 133.9                |
|                   |          |          |        |                | - 12                 |
|                   |          |          |        |                | - 16                 |
| Synapic acid      | 11       | 6.33     | 222.8  | 148.9         | 121                   |
|                   |          |          |        |                | - 20                 |
|                   |          |          |        |                | - 36                 |
| Rosmarinic acid   | 12       | 6.60     | 358.7  | 160.8         | 132.6                |
|                   |          |          |        |                | - 20                 |
|                   |          |          |        |                | - 30                 |

### Table 2: LC-ESI-MS/MS flavonoid glycosides results.

| Compound           | Peak no. | Tₘ [min] | [M-H]- | Fragment ions | Collision energy [eV] |
|--------------------|----------|----------|--------|---------------|----------------------|
| Rutin              | 1        | 9.62     | 608.7  | 299.6         | - 46                 |
|                    |          |          |        |                | - 38                 |
|                    |          |          |        |                | - 28                 |
| Hyperoside         | 2        | 11.40    | 462.7  | 299.7         | - 28                 |
|                    |          |          |        |                | - 24                 |
| Isoquercetin       | 3        | 11.65    | 462.7  | 299.7         | - 30                 |
|                    |          |          |        |                | - 27                 |
| Kaemperol-3-rutinoside | 4    | 12.41    | 592.7  | 284.8         | - 38                 |
|                    |          |          |        |                | - 22                 |
| Astragalin         | 5        | 14.03    | 466.8  | 254.8         | - 40                 |
|                    |          |          |        |                | - 54                 |
| Quercitrin         | 6        | 14.32    | 466.8  | 299.7         | - 30                 |
|                    |          |          |        |                | - 27                 |
| Apigenin-7-glucoside | 7    | 14.32    | 430.7  | 267.7         | - 38                 |
|                    |          |          |        |                | - 16.9               |
| Tiliroside         | 8        | 17.50    | 592.8  | 284.8         | - 30                 |
|                    |          |          |        |                | - 25.4               |

B; 2–3 min = 20% B; 5.5–8 min = 85% B; 9.5–12 min = 5% B. The ESI operated in the negative ion mode: capillary temperature 600°C, curtain gas 25 psi, nebulizer gas 60 psi, source voltage − 4500 V. Nitrogen was the curtain and collision gas.
2.7 Physical properties

Extrudate expansion, which varies with processing and composition, is an important quality factor and should be as great as possible. The radial expansion index is the ratio of extrudate to die diameter [30]. Ten replicate measurements were done for each recipe. The water absorption index (WAI) is the ratio of gel to dry sample. It was determined as described previously [31] with some modification. Ground extrudates (0.7 g) were suspended in 7 mL room temperature water in plastic tubes and mixed. After gentle stirring for 10 min the tubes were closed and centrifuged for 10 min at 12500 x g in a T24 centrifuge (VEB MLW MEDIZINETECHNIK, Leipzig, Germany) at ambient temperature (21°C). WAI was the ratio of gel remaining after supernatant removal to the weight of original dry solids. The supernatant was dried in an air oven at 105°C to constant weight. The water solubility index (WSI) is the percentage of dry matter recovered after the supernatant is evaporated from the WAI determination. WAI and WSI determinations were replicated in triplicate.

The dry gruel color was tested using a Lovibond CAM-System 500 Colour and Appearance Measurements System (The Tintometer Ltd., UK). 20 replicate measurements were performed for each sample. CIE-Lab scale was used to evaluate \( L^* \) for lightness, \( a^* \) for (+)redness(-)greenness and \( b^* \) for (+)yellowness(-)blueness [32]. Background color values were: \( L^* = 94.0, a^* = 2.7 \) and \( b^* = -0.4 \). Parameters for reference corn gruels were: \( L^* = 93.42, a^* = -3.94, b^* = 24.43 \). The color change index \( \Delta E \) was calculated following Carrini et al. [33].

For sensory tests gruels were prepared by mixing with 45°C water (20:80 gruel:water) and served. Sensory characteristics include the taste, color, flavor, consistency, and overall quality. A 15-member semi-trained panel judged gruels on a 5-point scale (1 = weak, 5 = very good). Acceptability was evaluated on a 9-point hedonic scale.

Table 3: LC-MS/MS polyphenol analytical parameters.

| Compound                  | LOD  | LOQ  |\( R^2 \) | Linearity range | Recovery | Regression equation         |
|---------------------------|------|------|----------|-----------------|----------|-----------------------------|
| Gallic acid               | 0.050| 0.100| 0.9985   | 0.05–10.00      | 93.7     | \( y = 312 x - 1.59e+004 \) |
| Protocatechuic acid       | 0.010| 0.020| 0.9995   | 0.05–25.00      | 98.2     | \( y = 48.5 x + 9.41e+003 \) |
| Gentisic acid             | 0.008| 0.015| 0.9997   | 0.025–25.00     | 102.3    | \( y = 409 x - 3.16e+004 \) |
| 4-OH-benzoic acid         | 0.040| 0.080| 0.9992   | 0.05–5.00       | 95.3     | \( y = 597 x + 2.1e+004 \)  |
| Vanillic acid             | 0.050| 0.100| 0.9992   | 0.1–50.00       | 93.2     | \( y = 73.1 x + 3.67e+003 \) |
| Caffeic acid              | 0.040| 0.060| 0.9985   | 0.05–1.00       | 94.5     | \( y = 1.39e+003 x + 3.28e+004 \) |
| Syringic acid             | 0.050| 0.100| 0.9994   | 0.1–50.00       | 93.3     | \( y = 1.39e+003 x + 3.28e+004 \) |
| p-Coumaric acid           | 0.050| 0.100| 0.9988   | 0.125–2.50      | 95.4     | \( y = 794 x + 8.47e+004 \)  |
| Salicylic acid            | 0.020| 0.050| 0.9991   | 0.05–1.00       | 94.4     | \( y = 3.23e+003 x + 2.83e+005 \) |
| Ferulic acid              | 0.010| 0.025| 0.9966   | 0.05–5.00       | 93.1     | \( y = 380 x + 2.01e+004 \)  |
| Synapic acid              | 0.010| 0.025| 0.9980   | 0.025–5.00      | 93.3     | \( y = 119 x - 226 \)       |
| Rosmarinic acid           | 0.010| 0.020| 0.9996   | 0.025–12.50     | 94.8     | \( y = 284 x - 1.65e+003 \)  |
| Rutin                     | 0.005| 0.010| 0.9983   | 0.02–2.5        | 98.5     | \( y = 280x - 8.49e+003 \)   |
| Hyperoside                | 0.010| 0.020| 0.9987   | 0.05–2.5        | 95.1     | \( y = 354x - 185 \)        |
| Isoquercetin              | 0.008| 0.020| 0.9991   | 0.05–2.5        | 101.9    | \( y = 353x - 498 \)        |
| Kaempferol-3-rutinoside   | 0.001| 0.003| 0.9975   | 0.05–2.5        | 99.1     | \( y = 639x - 1.11e+004 \)  |
| Astragaline               | 0.002| 0.004| 0.9992   | 0.01–2.5        | 93.1     | \( y = 935x + 1.15e+004 \)  |
| Quercetin                 | 0.002| 0.004| 0.9994   | 0.05–2.5        | 101.8    | \( y = 574x + 98.4 \)       |
| Apigenin-7-glucoside      | 0.0005| 0.001| 0.9992    | 0.005–1.00      | 95.3     | \( y = 3.02e+003x + 1.4e+004 \) |
| Tiliroside                | 0.0005| 0.001| 0.9972    | 0.005–1.00      | 92.9     | \( y = 782x - 7.28e+003 \)  |
Extruded corn gruels containing linden flowers

Table 4: Polyphenols content (n = 3).

| Compound                     | Corn gruel | Linden inflorescence | Yield ± SD[^a^][^b^] [µg g[^1^] of dry weight] |
|------------------------------|------------|----------------------|-----------------------------------------------|
| Gallic acid                  | -          | 68.10 ± 0.78         | 3.22 ± 0.02                                   |
| Protocatechuic acid          | -          | 373.67 ± 2.89        | 12.83 ± 0.03                                  |
| Genticis acid                | -          | 6.60 ± 0.01          | 0.90 ± 0.01                                   |
| 4-OH-benzoic acid           | BQL[^b^]   | 19.13 ± 0.09         | 0.53 ± 0.00                                   |
| Vanillic acid                | -          | 5.68 ± 0.06          | BQL                                           |
| Caffeic acid                 | -          | 2.54 ± 0.01          | BQL                                           |
| Syringic acid                | -          | 0.28 ± 0.00          | BQL                                           |
| p-Coumaric acid             | 1.21 ± 0.01| 11.06 ± 0.45         | 2.89 ± 0.13                                   |
| Salicylic acid              | 0.51 ± 0.02| 4.80 ± 0.09          | 0.57 ± 0.02                                   |
| Ferulic acid                | 0.43 ± 0.01| 4.57 ± 0.12          | 0.57 ± 0.03                                   |
| Synaptic acid               | BQL        | 0.72 ± 0.06          | -                                             |
| Rosmarinic acid             | -          | 1.13 ± 0.08          | -                                             |
| Rutin                       | 5.60 ± 0.00| 166.00 ± 3.00        | 7.50 ± 0.10                                   |
| Hyperoside                  | -          | 62.90 ± 0.10         | BQL                                           |
| Isoquercetin                | 0.30 ± 0.00| 1256.72 ± 28.90      | 3.11 ± 0.40                                   |
| Kaempferol-3-rutinoside     | 0.20 ± 0.00| 63.90 ± 0.60         | 3.32 ± 0.00                                   |
| Astragalin                  | 0.20 ± 0.00| 1083.34 ± 11.50      | 29.60 ± 0.10                                  |
| Quercetin                   | -          | 448.32 ± 1.50        | 11.73 ± 0.20                                  |
| Apigenin-7-glucoside        | 0.10 ± 0.00| 0.80 ± 0.00          | 0.21 ± 0.00                                   |
| Tiliroside                  | -          | 499.33 ± 4.70        | 6.70 ± 0.11                                   |

[^a^] SD - standard deviation (n=3), [^b^] BQL - peak detected, concentration lower than the LOQ but higher than the LOD

where: 1=dislike extremely, 9=like extremely. Gruels were deemed acceptable if their mean acceptability scores were above 5 [34].

3 Results and discussion

3.1 Determination of polyphenols content

Our objective was the qualitative and quantitative analysis (LC-ESI-MS/MS) of phenolic extracts of corn gruels containing linden flower. Ultrasound assisted extraction [26] followed by SPE was precise and accurate (Tables 2 and 3). Ethanol, 80% aqueous ethanol, methanol, and 80% aqueous methanol were extractants; 80% aqueous ethanol gave higher yields of all the polyphenols because of their relatively polar nature.

Precision was evaluated by intra-day and inter-day tests. Intra-day experiments were performed by replicate analysis of six aliquots of the same sample within one day. Inter-day tests were carried out on three consecutive working days in the same way as intra-day experiments. Three peak area measurements for each component were carried out. The standard deviations are in good agreement with the requirements for a developed method (Table 4). Good linearity was obtained for all compounds. The correlation coefficients for all calibration curves were \( R^2 > 0.9972 \). Example chromatograms are shown in Figs. 1 and 2.

Recovery studies were performed to assess accuracy. Crude extracts were spiked with standard solution (three concentration levels) and SPE and analysis were carried out as for real samples. The experiment was repeated three times. Recoveries ranged from 92.9% (tiliroside) to 102.3% (gentisic acid), demonstrating the method’s accuracy.
Phenolic content increased with the addition of linden flower (Table 4). In gruels without linden addition only ten phenolic compounds were identified. These were 4-OH-benzoic, p-coumaric, salicylic, ferulic, and synapic acids as well as rutin, isoquercetin, kaempferol-3-rutinoside, astragalin, and apigenin-7-glucoside. In *Tiliae inflorescentia* extract twenty polyphenols were found. The additional ones were gallic, protocatechuic, vanillic, caffeic, syringic, gentisic, rosmarinic acids along with hyperoside, quercetrin, and tiliroside. In gruel with 5% and 10% linden addition eighteen phenolic compounds were identified, and nineteen were found in gruel with 20% *Tilia*.

Most polyphenols increased proportionally to the linden addition, but some phenolic acids (e.g. p-cumaric and ferulic acids) did not increase significantly with additional flower. This may be due to limited solubility of these acids in the extractant or acid content variation in the linden.

Extrusion process conditions preserve the antioxidant compounds; high-temperature extrusion-cooking does not deactivate polyphenols in raw *Tilia inflorescentia*. This agrees with Özer and coworkers [35] who found that extrusion-cooking had no effect on total phenolic content in extrudates containing chickpea, corn, oat, carrot and hazelnut.

### 3.2 Physical properties of enriched snacks

Radial expansion indices are in Table 5. Increased linden decreased expansion ($R^2 = 0.954$). The difference between reference corn and extrudates with the highest linden addition was 30.8%, which may reflect increased fiber in the products.

WAI measures granule or starch water absorption after swelling in excess water. WSI is the free polysaccharide or polysaccharide released after water addition [8,31]. The WAI decreased significantly as additive increased ($R^2 = 0.9715$), attributed to decreasing starch content with increasing linden and less water absorption by starch. WAI (Table 5) ranged from 5.51 g g$^{-1}$ for corn gruels to 4.65 g g$^{-1}$ for extrudates containing the most linden. Replacement of starchy raw materials by vegetables, fruits, or high-fiber additives reduces the starch undergoing swelling and gelatinization during processing so WAI is usually much lower with more additives and can be temperature-dependent [36]. Testing barley-tomato pomace extrudates, Altan and coworkers [37] reported that WAI decreases from 7.03 to 6.10 g g$^{-1}$ with increasing temperature and pomace level.

WAI is often used as an indicator of starch degradation. It depends mostly on starch granule disruption, amylose and amylopectin depolymerization, starch gelatinization and the consequent starch solubilization generated in the extruder by pressure, heating, shearing and residence time [1,8,38]. WSI results (Table 5) showed decreased solubility with linden enrichment (from 15.32% for corn extrudates to 7.86% for the highest additive level). Increasing additives increases fiber content and decreases starch, reducing solubility.

Linden addition decreased *L* values ($R^2 = 0.953$, Table 5). Green-red balance varied from -3.94 for a sample without additives to -2.66 for 10% and 0.28 for 20% linden; the product became more red with increasing additive. The nature of the linden used may be key to the redness
Extruded corn gruels containing linden flowers

and yellowness improvements with increasing additive
\( R^2 = 0.9133 \) and \( 0.9765 \). \( b^* \) increased from 24.43 for control
gruels to 30.87 for extrudates with 20% linden. Yellowness
was observed in all samples because carotenoids are
present in both corn grits and linden.

Color, flavor, taste and consistency characteristics
are presented in Table 6. The best colors were for corn
snacks and gruels with 1% additive; increasing linden
lowered the color results (\( R^2 = 0.9607 \)). The panelists
noted that linden flower addition darkened and gave a red
tint to gruels, confirmed by instrumental measurements
(Table 5). Flavor and taste notes also decreased with
increased linden content (\( R^2 = 0.9722 \) and 0.9896), because
of the distinctive linden odor and taste. Good sensory
properties were found with linden addition limited to
5%, with overall quality notes 3.86–3.12. More additive
significantly lowered the sensory notes to 2.45 and 2.01 for
extrudates with 10 and 20% linden. These high proportions
also lowered gruel acceptability (\( R^2 = 0.9716 \) (Table 6) due
to the darker color, intense flavor and distinctive linden
taste. Acceptability results were below 6.0 for those with
10% and 20% linden.

4 Conclusions
High-temperature extrusion-cooking did not decrease the
polyphenolics present in both raw materials. Linden herb
enriched instant gruels demonstrate the incorporation of
nutritionally functional components into food products
by extrusion-cooking. 10 and 20% linden incorporation
lowered extrudate expansion, reduced WAI and WSI
values and considerably lowered instant gruel acceptance
due to intense herbal taste and flavor. Linden in instant
gruels should be below 10% to improve nutritional
characteristics and retain acceptable sensory properties.

Acknowledgment: This work used equipment purchased
by the project “The equipment of innovative laboratories
doing research on new medicines used in the therapy

\[
\begin{array}{cccccccc}
\text{Additive} & \text{Expansion ratio} & \text{Water absorption} & \text{Water solubility} & \text{Lightness} & \text{Redness-greenness balance} & \text{Yellowness-blueness balance} & \text{Color change index} \\
\text{amount} & [-] & \text{index WAI} & \text{index WSI} & L^* & a^* & b^* & \Delta E \\
[\%] & & [g g^{-1}] & [\%] & & & & \\
0 & 6.00 \pm 0.12 & 5.51 \pm 0.11 & 15.32 \pm 0.15 & 93.42 \pm 0.49 & -3.94 \pm 0.79 & 24.43 \pm 2.89 & \text{ref} \\
1 & 5.77 \pm 0.21 & 5.49 \pm 0.15 & 14.84 \pm 0.09 & 92.62 \pm 0.47 & -3.99 \pm 0.62 & 21.10 \pm 2.45 & 3.42 \\
3 & 5.15 \pm 0.20 & 5.35 \pm 0.08 & 14.34 \pm 0.13 & 92.42 \pm 0.56 & -3.38 \pm 0.54 & 21.96 \pm 2.56 & 2.72 \\
5 & 4.88 \pm 0.10 & 5.21 \pm 0.12 & 13.89 \pm 0.22 & 92.30 \pm 0.69 & -3.53 \pm 0.72 & 23.74 \pm 2.22 & 1.38 \\
10 & 2.55 \pm 0.86 & 5.10 \pm 0.07 & 12.09 \pm 0.67 & 88.96 \pm 2.60 & -2.66 \pm 0.95 & 26.51 \pm 3.56 & 5.08 \\
20 & 1.85 \pm 0.95 & 4.65 \pm 0.01 & 7.86 \pm 0.11 & 83.64 \pm 3.65 & 0.28 \pm 1.18 & 30.87 \pm 3.37 & 12.45 \\
\text{R}^2 & 0.9540 & 0.9715 & 0.9605 & 0.9537 & 0.9133 & 0.9765 & 0.9664 \\
\text{Regression equation} & y = -0.164x^2 + 0.272x + 5.903 & y = -0.036x^2 + 0.093x + 5.441 & y = -0.428x^2 + 1.685x + 13.659 & y = -0.627x^2 + 2.680x + 90.7 & y = 0.285x^2 - 1.286x - 2.699 & y = 0.823x^2 - 4.326x + 27.429 & y = 1.512x^2 - 10.061x + 18.022 \\
\end{array}
\]

\[
\begin{array}{cccccccc}
\text{Added linden} & \text{Color}^a & \text{Flavor}^a & \text{Taste}^a & \text{Consistency}^a & \text{Overall quality}^a & \text{Acceptability}^b \\
[\%] & & & & & & & \\
0 & 4.05 \pm 0.89 & 3.60 \pm 1.43 & 3.70 \pm 1.34 & 4.10 \pm 1.21 & 3.86 & 7.85 \pm 2.37 \\
1 & 4.20 \pm 0.89 & 3.50 \pm 1.24 & 3.15 \pm 1.27 & 4.20 \pm 0.95 & 3.76 & 7.15 \pm 2.28 \\
3 & 3.40 \pm 1.10 & 2.70 \pm 1.08 & 2.65 \pm 0.88 & 3.75 \pm 0.91 & 3.12 & 6.17 \pm 1.84 \\
5 & 2.95 \pm 0.89 & 2.20 \pm 0.83 & 2.50 \pm 0.95 & 3.40 \pm 0.94 & 2.76 & 6.15 \pm 1.63 \\
10 & 2.65 \pm 1.55 & 1.85 \pm 1.34 & 2.10 \pm 1.35 & 3.10 \pm 1.50 & 2.45 & 5.45 \pm 2.55 \\
20 & 1.85 \pm 2.30 & 1.50 \pm 1.96 & 1.85 \pm 2.25 & 2.85 \pm 1.85 & 2.01 & 4.85 \pm 1.72 \\
\text{R}^2 & 0.9607 & 0.9722 & 0.9896 & 0.9578 & 0.9810 & 0.9716 \\
\text{Regression equation} & y = -0.049x^2 - 0.116x - 0.009x^2 - 0.524x & y = 0.003x^2 - 0.596x & y = -0.020x^2 - 0.139x & y = -0.006x^2 & y = 0.028x^2 & y = 0.028x^2 \\
\end{array}
\]

*a sensory profile in 5-point scale, \( b^* \) acceptability in 9-point hedonic scale

Table 5: Selected properties of corn gruels enriched with linden flower.

Table 6: Sensory assessment and acceptence results for corn gruels enriched with linden flower.
of civilization and neoplastic diseases” within the Operational Program Development of Eastern Poland 2007-2013, Priority Axis I Modern Economy, Operations I.3 Innovation Promotion.

References

[1] Mościcki L., Wójtowicz A., Raw materials in production of extrudates, In: Mościcki, L. (Ed.), Extrusion-cooking techniques. Applications, theory and sustainability, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany, 2011.

[2] Fernandez-Artigas P., Garcia-Villanova B., Guerra-Hernandez E., Blockage of available lysine at different stages of infant cereal production, J. Sci. Food Agric., 1999, 79, 851-854.

[3] Wójtowicz A., Ocena wybranych cech jakościowych ekstrudowanych zbożowych kaszek błyskawicznych, Żywność. Nauka. Technologia. Jakość, 2007, 4(53), 46-54, (in Polish).

[4] Faraj A., Vasanthan T., Hoover R., The effect of extrusion cooking on resistant starch formation in waxy and regular barley flours, Food Res. Int., 2004, 37, 517-523.

[5] Singh S., Gamlath S., Wakeling L., Nutritional aspects of food extrusion: a review, Int. J. Food Sci. Technol., 2007, 42, 916-929.

[6] Larrea M.A., Chang Y.K., Bustos F.M., Effect of some operational extrusion parameters on the constituents of orange pulp, Food Chem., 2005, 89, 301-308.

[7] Zhang M., Bai X., Zhang Z., Extrusion process improves the functionality of soluble dietary fiber in oat bran, J. Cereal Sci., 2011, 54, 98-103.

[8] Stojcska V., Ainsworth P., Plunkett A., Ibanoğlu S., The advantage of using extrusion processing for increasing dietary fibre level in gluten-free products, Food Chem., 2010, 121, 156–164.

[9] Nicoli M.C., Anese M., Parpinel M., Influence of the antioxidant properties of fruit and vegetables, Trends Food Sci. Technol., 1999, 10, 94-100.

[10] Zieściński H., Kozłowska H., Lewczuk B., Bioactive compounds in the cereal grains before and after hydrothermal processing, Innovative Food Sci. Emerg. Technol., 2002, 1, 159-169.

[11] Moro-Rochin S., Gutiérrez-Uribe J.A., Serna-Saldívar S.O., Sánchez-Peña P., Reyes-Moreno C., Milán-Carrillo J., Phenolic content and antioxidant activity of tortillas produced from pigmented maize processed by conventional nixtamalization or extrusion cooking, J. Cereal Sci., 2010, 52, 502-508.

[12] Zieliński H., Kozłowska H., Phenolic content and antioxidant activity of total phenolics in selected cereal grains and their different morphological fractions, J. Agric. Food Chem., 2000, 48, 2008-2016.

[13] Choi S.W., Lee S.K., Kim E.O., Oh J.H., Yoon K.S., Parris N., et al., Antioxidant and antimelanogenic activities of polyamine conjugates from corn bran and related hydroxyccinnamic acids, J. Agric. Food Chem., 2007, 55, 3920-3925.

[14] Wang Y.Y., Ryu G.H., Physicochemical and antioxidant properties of extruded corn grits with corn fiber by CO2 injection extrusion process, J. Cereal Sci., 2013, 58, 110-116.

[15] Khanal R.C., Howard L.R., Prior R.L., Procyanidin content of grape seed and pomace, and total anthocyanin content of grape pomace as affected by extrusion processing, J. Food Sci., 2009, 74(6), H174-182.

[16] Khanal R.C., Howard L.R., Brownmiller C.R., Prior R.L., Influence of extrusion processing on procyanidin composition and total anthocyanin contents of blueberry pomace, J. Food Sci., 2009, 74, H52–58.

[17] Camire M.E., Camire A.L., Krumhaw K., Chemical and nutritional changes in foods during extrusion, Critical Rev. Food Sci. Nutr., 1990, 29, 35-57.

[18] Brennan C., Cleary L., The potential use of cereal (1-3,1-4)-β-D-glucans as functional food ingredients, J. Cereal Sci., 2005, 42, 1–13.

[19] Charalampopoulos D., Wang R., Pandiella S.S., Webb C., Application of cereals and cereal components in functional foods: a review, Int. J. Food Microbiol., 2002, 79, 131–141.

[20] Sangwan V, Tomar S.X., Singh R.R.B., Singh A.K., Ali B., Galactooligosaccharides: novel components of designer foods, J. Food Sci., 2011, 76(4), R103-111.

[21] Sroka Z., Belz J., Antioxidant activity of hydrolyzed and non-hydrolyzed extracts of the inflorescence of linden (Tilia inflorescentia), Adv. Clin. Exp. Med., 2009, 18, 329-335.

[22] Toker G., Aslam M., Zesilada E., Memisolu M., Ito S., Comparative evaluation of the flavonoid content in official Tiliae flos and Turkish lime species for quality assessment, J. Pharm. Biomed. Anal., 2001, 26, 111-121.

[23] Wawrzyniak E., Leszczenie ziołami. Kompendium fitoterapii, Instytut Wydawniczy Związków Zawodowych, Warszawa, 1992, (in Polish).

[24] Rumińska A., Ożarowski A., Leksykon roślin leczniczych, PWRI, Warszawa, 1990, (in Polish).

[25] Toker, G., Küpell, E., Memisoglu, M., Yesilada, E., Flavonoids with antinociceptive and anti-inflammatory activities from the leaves of Tilia argentea (Silver linden). J. Ethnopharmacol. 2005, 95, 393-397.

[26] Oniszczuk A., Podgórski R., Oniszczuk T., Żukiewicz-Sobczak W., Nowak R., Waksmundzka-Hajnos M., Extraction methods for determination of phenolic compounds from Equisetum arvense L. herb., Ind. Crops Prod., 2014, 25, 1166-1171.

[27] Nowacka N., Nowak R., Drozd M., Olech M., Los R, Malm A., Analysis of phenolic constituents, antiradical and antimicrobial activity of edible mushrooms growing wild in Poland, LWT - Food Sci. Technol., 2014, 59, 689-694.

[28] Bittová M., Krejzová E., Roblová V, Kubáň P, Kubáň V., Monitoring of HPLC profiles of selected polyphenolic compounds in sea buckthorn (Hippophae rhamnoides L.) plant parts during annual growth cycle and estimation of their antioxidant potential, Cent. Eur. J. Chem., 2014, 12(11), 1152-1161.

[29] Wójtowicz A., Influence of raw materials wetting and extrusion-cooking process conditions on selected properties of instant cereal grits, Acta Agrophysica, 2008, 11, 2, 545-556 (in Polish, abstract in English).

[30] Wójtowicz A., Kolas A., Mościcki L., The influence of buckwheat addition on physical properties, texture and sensory characteristic of extruded corn snacks, Polish J. Food Nutr. Sci., 2013, 63, 239–244.

[31] Wójtowicz A., Mościcki L., Influence of legume type and addition level on quality characteristics, texture and microstructure of enriched precooked pasta, LWT - Food Sci. Technol., 2014, 59, 1175–1185.
[32] Farris S., Piergiovanni L., Optimization of manufacture of almond paste cookies using response surface methodology, J. Food Eng., 2009, 32, 64- 87.

[33] Carini E., Vittadini E., Curti E., Antoniazzi F., Viazzani P., Effect of different mixers on physicochemical properties and water status of extruded and laminated fresh pasta, Food Chem., 2010, 122, 462–469.

[34] Bustos M.C., Perez G.T., León A.E., Sensory and nutritional attributes of fibre-enriched pasta, LWT - Food Sci. Technol., 2011, 44, 1429-1434.

[35] Özer E.A., Herken E.N., Güzel S., Ainsworth P., Ibanoglu S., Effect of extrusion process on the antioxidant activity and total phenolics in a nutritious snack food, Int. J. Food Sci. Technol., 2006, 41, 289-293.

[36] Nyombaire G., Siddiq M., Dolan K.D., Physico-chemical and sensory quality of extruded light red kidney bean (Phaseolus vulgaris L.) porridge, LWT - Food Sci. Technol., 2011, 44, 1597–1602.

[37] Altan A., Mc Carthy K., Maskan M., Evaluation of snack foods from barley–tomato pomace blends by extrusion processing, J. Food Eng., 2008, 84, 231–242.

[38] Ondo S.E., Singkhornart S., Ryu, G.H., Effects of die temperature, alkalized cocoa powder content and CO2 gas injection on physical properties of extruded cornmeal, J. Food Eng., 2013, 117, 173–182.