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Physicochemical Properties of Flour and Starch Obtained from Various Quinoa Varieties

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Abstract: Currently, there is a growing interest in traditional country products, particularly those with proven health benefits. The aim of this study was to describe the chemical composition and properties of flours and starches obtained from various quinoa. The examined quinoa quinoa starches contained 7-18 times less protein and 10-25 times less lipid compared to flours. The content of amylose in the starches ranged from 15.9 to 18.5%. Flour and starch samples were also analysed for their thermal properties (DSC), pasting profile (RVA) and the content of free radicals. The Ecuadorian quinoa starches had a much higher onset (51.9-53.6°C) and peak temperature (59.3-62.1°C) than the ones from Bolivian varieties (respectively 48.5-51.6°C i 56.9-59.6°C). All the quinoa starches were susceptible to the formation of free radicals (1.05-2.06 $\times 10^{19}$ spins/g) irrespective of their geographical origin. The properties of the others flours and starches isolated from quinoa were influenced by the geographical origin and variety of quinoa.

Keywords: quinoa, starch, electron paramagnetic resonance EPR, rheology, retrogradation

1. Introduction

Starch is a non-toxic, biodegradable plant polysaccharide. Owing to its interesting natural properties (as well as in the form of modified starch), it is used not only as a valuable textural and sensory component in food but also finds applications in many other (non-food) industrial sectors (Copeland et al., 2009; Garcia et al., 2020; Apriyanto et al., 2022).

Starch grains contain not only carbohydrates (amylose and amylopectin) but also water, proteins, lipids, and minerals, which influence the nutritional, physical, and chemical characteristics of both the starch itself and the food products containing it. Quinoa is classified as a pseudocereal, which means it is not a true grain, but due to its properties and high starch content it can be utilised in the food industry in a similar role (FAO, 2011). The proportions of all starch components depend on its botanical origin, hence it is important to search for other starch sources besides the most common ones (such as corn, rice, sorghum, and potato starch) – including those more challenging to cultivate and less efficient, e.g. spelt and pumpkin starch (Rożnowski et al., 2015; Przetaczek-Rożnowska, 2017; Przetaczek-Rożnowska et al., 2018).

There is a growing interest in traditional country products and local dietary components, especially those with proven health benefits (Chacon et al., 2023; Roy and Kumar, 2023; Rożnowski et al., 2015). Therefore, food producers and technologists are focused on food products that not only provide essential nutrients but also effectively support pharmacological therapies in treating lifestyle-related diseases, such as digestive disorders, obesity, and cardiovascular ailments (Navruz-Varli and Sanlier, 2016). Thanks to its valuable components, quinoa is one of the products likely to play a significant role in the European diet in the near future.

Quinua (Chenopodium quinoa Willd.) has been cultivated in the Andean region for several thousand years, being one of the main highly nutritious compound food for farmers (Angeli et al., 2020). The Spanish conquest of South America initiated the process of marginalising quinoa and replacing it with barley and wheat. However, the global opening up of the European and US markets in the second half of the 20^{th} century marked the beginning of a quinoa cultivation renaissance and, interestingly, expansion. The main producers of quinoa are Peru and Bolivia, accounting for 90% of the world's production, followed by the United States (6%). European countries have a smaller share – approximately 0.3% (FAO, 2011).

Quinoa has low water requirements, which makes it stand out as a potential alternative for arid areas worldwide. Additionally, it can be grown in various soil types with sandy to loamy texture and also under a wide pH range. The capacity of this plant to produce in saline areas with low fertility allows its cultivation in areas unsuitable for other crops, and its tolerance to frost before flowering is a valuable capacity for cold climates (FAO, CIRAD 2015).

With a carbohydrate content ranging from 49% (Angeli et al., 2020) to 74% (Wright et al., 2002), quinoa seeds are strong alternatives to potatoes and maize in starch production. Additionally, the plant is a rich source of lysine, methionine, and cysteine amino acids, which occur in much lower amounts in other plants (FAO, 2011; Jancurova et al., 2009). It is believed that no other plant has such a well-balanced composition of amino acids (FAO, CIRAD, 2015). Quinoa grain containing 6% of fibre supports digestion and contains three times more iron than wheat and five times more than rice. Almost half of its total fatty acid content is in the form of linoleic acid, with unsaturated fatty acids accounting for about 80% (FAO, 2011).

The benefits of using quinoa seeds result from their low glucose and fructose content, as well as the absence of gluten, which allows for the use of isolated starch in the production of food for diabetics and individuals suffering from celiac disease. In comparison to other grains, quinoa exhibits antioxidant properties due to the presence of flavonoids (Mu et al., 2023).

The use of quinoa in traditional Andean medicine has been known since ancient times. Preparations based on quinoa are used for treating bleeding, angina, liver diseases, cystitis, healing broken bones, applying to wounds and bruises, treating dandruff, and as a good hair tonic or even as a laxative (FAO, 2011). The implementation of quinoa-based compounds against cancerous tissue (FAO, CIRAD, 2015; Navruz-Varli and Sanlier, 2016), as well as the study of the process of free radicals formation, will contribute to the reduction of cancer-related diseases.

Despite the advantages of quinoa, its use in the European food industry remains limited, and research on the physical and chemical properties of its starch is not widespread (FAO, CIRAD, 2015; Pycia et al., 2019). Therefore, the aim of this study was to determine selected functional properties of flour and starch obtained from quinoa seeds imported from South American countries and to analyse their free radicals.

2. Research Material

2.1. Materials

The study material included flours obtained from the seeds of three varieties of quinoa (white, red, and black) originating from two producer nations (Bolivia and Ecuador). The seeds of each quinoa variety were ground with a GM 200 knife mill (Retsch, Germany) and subsequently sieved through a Retsch AS 200 vibratory sieve shaker (200 µm mesh). These quinoa flours as samples were used for analyses. One portion of each flour was subjected to physical and chemical analyses, whereas the other portion was used for starch isolation.

2.2. Starch Isolation

Starch was isolated according to the Narpinder et al. method (2004), with the authors' own modification. Distilled water (500 mL) was added to 1 kg of quinoa flour and the resulting dough was rinsed in a vessel with distilled water. The slurry was screened through a nylon cloth (100 mesh). During the rinsing process, the dough was kneaded continuously to make sure the texture was not grainy. The obtained starch milk was stirred (2600 × g) for 15 minutes (Rotina 420, Hettich, Germany). The supernatant was decanted and the layer of impurities from above the sediment was removed. A new portion of starch milk was added and the whole sample was stirred again. The cycle was repeated three times.

The starch was then collected and dried at room temperature until it reached an air-dry state. The obtained polymer was ground using an RM 200 mortar grinder (Retsch, Germany) and subsequently sieved through an AS 200 vibratory sieve shaker (Retsch, Germany) mesh size of 125 µm.

3. Research Methods

3.1. Analysis of the Chemical Components of Quinoa Flours and Starches

The total protein content was determined with the Kjeldahl method (PN-A-04018) using the conversion factor of N×5.70 in samples earlier subjected to wet mineralisation in a B-426 digestion unit and distillation in a B-324 distillation unit (Büchi Labortechnik, Switzerland).

The lipid content was determined with the Soxhlet method (PN-EN ISO 3947). Extractions were conducted for two hours with petroleum ether as the solvent in a B-811 extraction system (Büchi Labortechnik, Switzerland).

The content of amylose was determined with the Morrison and Laignelet method (1983), and absorbance was measured using a V-630 UV/VIS spectrophotometer (Jasco, Japan).

3.2. Thermal Treatment and EPR Measurements of Free Radicals

Free radicals were measured using an ELEXSYS–500 EPR spectrometer (Bruker, Germany) operating in a band of X (9.2 GHz) at a modulation frequency of 100 kHz. The measurements were conducted at room temperature and also at liquid nitrogen temperature (77 K) with a modulation amplitude of 0.3 mT and microwave power of 0.01–30 mW. The number of spins was determined by means of the comparative method using a standard of $VOSO_4 \times 5\ H_2O$ diluted with non-magnetisable K_2SO_4 with the number of spins being 5×10^{19} per 1 gram (Dyrek et al., 1994; Lozos et al., 1974).

3.3. Determination of the Water Binding Capacity of Quinoa Flour and Starch and Its Solubility in Water

The flour and starch water binding capacity and solubility in water were determined according to the Leach et al. method (1953) with the authors' own modification. The flour and starch samples (1.0 g db with 70 g deionised water) were continuously stirred in a water bath at temperatures of 25 ± 0.5°C, 40 ± 0.5°C or 60 ± 0.5°C for 30 minutes. After heating, they were cooled to 25°C in a water bath at 25 ± 0.5°C. Each suspension was centrifuged at 3000 × g for 15 minutes; 20 mL of each supernatant were heated at 40°C for 12 hours in glass pans, after which the pans were heated in an air-forced oven Venticell (BMT, Czech) at 130°C for 1 hour until constant weight.

Solubility in water (S) of flour and starch was calculated according to the following formula:

$$S = \frac{8\,000 \cdot DS}{20 \cdot S_{db}},$$

where DS is the total mass of the dried supernatant, S_{db} is flour or starch weight on dry matter basis.

The sediment was weighed and the obtained data were used to calculate the water binding capacity (WBC) of flour or starch according to the formula:

$$WBC = \frac{\mathrm{S_w} - \mathrm{S_{db}}}{\mathrm{S_{db}}},$$

where S_w is sediment weight, S_{db} is flour or starch weight on dry matter basis weight.

3.4. Pasting Properties of Quinoa Starch

The pasting properties were determined in a Tecmaster Rapid Visco Analyser (Perten Instruments) on the basis of a modified method of Wani et al. (2014). The water suspensions of starch (10% db) were equilibrated at 50°C for 1 minute at a speed of 960 rpm, then heated to 95°C and held for 20 minutes at that temperature, before cooling to 50°C and then holding at 50°C for 10 minutes. The heating and cooling rates were 4.5°C/min. Except for rapid stirring at 960 rpm for the first minute to disperse the sample, a constant paddle rotational speed of 160 rpm was used throughout analyses. Pasting temperature (PT), peak viscosity (PV), trough viscosity (TV), final viscosity at 50°C (FV), calculated breakdown viscosity (BD = PV – TV) and setback viscosity (SB = FV – TV) were calculated from the obtained viscograms.

3.5. Thermodynamic Characteristics of Starch Gelatinisation and Retrogradation

The thermal characteristics of starch gelatinisation was determined using a differential scanning calorimeter (DSC 204 F1 Phoenix, Netzsch, Germany) (Rożnowski et. al, 2021). Starch samples (3.5 mg) and water (10.5 mg) were inserted into pans, sealed hermetically, and stored at room temperature for 24 hours. They were then heated in the calorimeter to a temperature ranging from 20 to 120°C at a rate of 10°C/min with an empty calorimetry pan used as a reference. The onset temperature (To_1), peak temperature (Tp_1), and endset temperature (Te_1), along with the enthalpy (ΔH_1) and the peak height index (PHI_1) were calculated from the $\Delta H_1/(Tp_1 - To_1)$ ratio and were estimated on the basis of the gelatinisation thermograms.

After analysis, the pans with samples were cooled and stored in a laboratory incubator Climacell (BMT, Czech) at 4°C for seven days, after which the thermodynamic measurements were repeated. The enthalpy (ΔH_2), onset temperature (To_2), peak temperature (Tp_2), and endset temperature (Te_2) were determined. The transition temperature range of the melting of recrystallised amylopectin (ΔT_2), and the peak height index (PHI_2) and the retrogradation ratio $R = \Delta H_2/\Delta H_1 \times 100\%$ were calculated.

3.6. Statistical Analysis

All the analyses were conducted at least triplicate which provided the basis for one-way analysis of variance. The obtained results were verified with an HSD Tukey test (α = 0.05) using Statistica 13.0 software to identify homogeneous groups. The coefficients of Pearson linear correlations between the selected determined parameters were also calculated (α = 0.05).

4. Results and Discussion

The physical properties of flour and starch are vital indicators of quality and technological applicability. These properties are related to the non-carbohydrate components: protein, amylose, and fat. The protein content in quinoa seeds was between 11.1 and 12.1% (Table 1). These values were comparable with the literature data concerning various kinds of quinoa, and reported its level at 9-22% (Valencia--Chamorro, 2003; Nowak et al., 2016; Barakat et al., 2017; Angeli et al., 2020). This is a considerably higher protein content than that found in popular cereals, such as corn (5.4-6.7) and rice (5.9-8.3%) (USDA, 2023). The quinoa flours examined in this study did not differ significantly in protein content depending on seed origin and variety (Table 1).

Table 1. Content of components of quinoa flour and the number of radicals
Tabela 1. Skład mąki komosowej oraz liczba wolnych rodników

Sample/Próbka		Protein/Białko [%]	Fat/Tłuszcz [%]	Radicals/Rodniki [spins/g sample]
Bolivian flour/ Mąka boliwijska	W	11.79^{ab}	8.25^{a}	$1.09 \times 10^{19\,b}$
	R	11.38^{bc}	6.16^{c}	$1.06 \times 10^{19\,b}$
	B	12.05^{a}	6.19^{c}	$1.10 \times 10^{19\,b}$
Ecuadorian flour/ Mąka ekwadorska	W	11.26^{bc}	7.43^{ab}	$1.13 \times 10^{19\,b}$
	R	11.06^{c}	7.00^{bc}	$1.05 \times 10^{19\,b}$
	B	11.37^{bc}	7.34^{ab}	$1.13 \times 10^{19\,b}$

Values denoted in the columns by the same letters are not statistically significantly different (α = 0.05) / Liczby oznaczone tą samą literą w kolumnie nie różnią się istotnie statystycznie (α = 0,05)
W – white, R – red, B – black / W – biała, R – czerwona, B – czarna.

Source/Źródło: own research/ badania własne.

The isolated starch (Table 2) demonstrated a 7-18-fold lower protein content ranging from 0.61% (black variety of Ecuador quinoa) to 1.57% (red variety of Ecuador quinoa), which is similar to the 0.95 reported by Jan et al., (2017). However, this protein content was still substantially higher than that found in cereal starches, such as wheat (0.3-0.4%) (Przetaczek et al., 2012; BeMiller, 2019), corn (0.21--0.5%) (Przetaczek, 2017; BeMiller, 2019), and tapioca (0.1%) starches (BeMiller, 2019).

Conversely, the origin of seeds in addition to their variety was proved to affect lipid content, both in the examined flours as well as in the obtained starch (Table 1). The lipid content of the analysed flours ranged from 6.16% (Bolivian red quinoa flour) to 8.25% (Bolivian white quinoa flour), which supports the findings reported by Nowak et al. (2016) (4.0-7.6%), Inglett et al. (2015) (6.07%) and Angeli et al., (2020) (5.9-7.9). The highest lipid content was determined in white quinoa seeds from Bolivia and Ecuador, as well as in the seeds of black quinoa grown in Ecuador (7.34-8.25%). Red seeds (irrespective of their origin) had the lowest lipid content (6.16% and 7.0% for Bolivian and Ecuadorian flours, respectively – see Table 1), which were however higher than these reported for other cereals: corn 1-4.7% (Inglett et al. 2015; USDA, 2023), wheat 1.4-2.3% (USDA, 2023), and rice 0.7-3.7% (USDA, 2023).

Table 2. Content of components of quinoa starch and the number of radicals
Tabela 2. Skład skrobi komosowej oraz liczba wolnych rodników

Sample/Próbka		Protein/Białko [%]	Fat/Tłuszcz [%]	Amylose/Amyloza [%]	Radicals/Rodniki [spins/g sample]
Bolivian starch/ Skrobia boliwijska	W	1.49^{a}	0.34^{a}	17.51^{a}	$2.06 \times 10^{19\ a}$
	R	1.54^{a}	0.43^{b}	15.89^{b}	$1.10 \times 10^{19\ b}$
	B	1.19^{a}	0.28^{a}	18.45^{a}	$1.05 \times 10^{19\ b}$
Ecuadorian starch/ Skrobia ekwadorska	W	1.51^{a}	0.66^{c}	18.03^{a}	$1.11 \times 10^{19\ b}$
	R	1.57^{a}	0.30^{a}	13.81^{c}	$1.08 \times 10^{19\ b}$
	B	0.61^{b}	0.55^{d}	16.76^{ab}	$1.06 \times 10^{19\ b}$

Values denoted in the columns by the same letters are not statistically significantly different (α = 0.05) / Liczby oznaczone tą samą literą w kolumnie nie różnią się istotnie statystycznie (α = 0,05)
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Source/Źródło: own research/ badania własne.

The starch isolated from quinoa seeds (Table 2) had a 10-25 times lower lipid content compared to flour. It ranged from 0.28% to 0.66% (db) similarly to the 0.40% reported by Jan et al. (2017), and was lower than in corn and wheat starch (0.8% and 0.9%, respectively) (BeMiller, 2019). The highest lipid content was reported in white and black quinoa starch from Ecuador (0.66% and 0.55%, respectively), while the lowest in the white (0.34%) and black (0.28%) quinoa seeds from Bolivia (Table 1).

The amylose content determined in the isolated starch ranged from 13.8% to 18.5% (Table 2) and was higher than 7.1-12.5% (FAO, CIRAD, 2015; Jan et al., 2017), but lower than the 25.4% reported by Tang et al. (2002). The lowest content of this fraction was found in the starch isolated from the red varieties of quinoa (13.81% for Ecuadorian and 15.89% for Bolivian quinoa), whilst there was no significant difference (α = 0.05) in the amylose content in the starch isolated from the white and black quinoa.

The amylose content was relatively low in comparison to potato starch at 23.5% (Rożnowski at al., 2021) and cereal starches: 29% in barley (Tang et al., 2002), 25-29% in wheat (Seung, 2020), and 22-30% in corn (Seung, 2020). The discrepancies in the values stated by various researchers may stem from the climatic and soil conditions during plant growth (Singh et al., 2003).

Previous analyses conducted with the EPR method (Bidzińska et al., 2004; Dyrek et al., 2007; Łabanowska et al., 2009) revealed that, depending upon its botanic origin and modifications, starch is susceptible to stable radicals formation during heating in the air at temperatures ranging between 150 and 250°C, which is why research into the mechanisms of radicals formation and their stability is of particular importance in the food industry due to the highly harmful effects of free radicals on the human body (Ciesielski and Tomasik, 1996; Gholap et al., 1993).

The analysis of starch with the use of electron paramagnetic resonance revealed that starch isolated from quinoa seeds, irrespective of its geographical origin and varieties, demonstrated a much higher content of radicals (1.05-2.06 × 10^{19} spins/g) compared to that found for maize starch (0.03 × 10^{19} spins/g) and spelt starch (0.32 × 10^{19} spins/g) (Bidzińska et al., 2004; Dyrek et al., 2007; Łabanowska et al., 2009), and for other starches like pumpkin starch (1.4-1.7 × 10^{15} spins/g) (Przetaczek et al., 2018). However, no significant influence (α = 0.05) of quinoa origin or variety was reported with regard to the content of free radicals in starch isolated from it.

However, no significant influence of quinoa origin or variety was observed regarding the content of free radicals in the isolated starch, as well as differences in the number of radicals between the initial flour and the obtained starch.

The results of the determinations of the water binding capacity (WBC) and solubility (S) of quinoa flours and starches in water at temperatures of 25°C, 40°C and 60°C are presented in Tables 3 and 4. The water binding capacity of the analysed types of flour increased with temperature, however the analyses showed no significant differences between the WBC determined at temperatures of 25°C and 40°C. A significant increase in the WBC of flour was noted at 60°C, which was 1.5-3.0 times higher than at lower temperatures. Conversely, temperature was observed to cause no significant (α = 0.05) effect on flour solubility in water (Table 3).

Table 3. Water binding capacity (WBC) and solubility (S) in water for quinoa flour at temp. 25, 40 and 60°C
Tabela 3. Zdolność wiązania wody (ZWW) i rozpuszczalność (R) mąki z komosy w wodzie w temp. 25, 40 i 60°C

Sample/Próbka		WBC [g/g db] at temperatures/ ZWW [g/g s.s.] w temperaturach			S[%] at temperatures/ R[%] w temperaturach		
		25°C	40°C	60°C	25°C	40°C	60°C
Bolivian flour/ Mąka boliwijska	W	1.50^{a}	1.54^{a}	4.28^{c}	11.36^{g}	11.16^{fg}	13.41^{k}
	R	1.44^{a}	1.49^{a}	2.92^{b}	9.87^{e}	10.17^{e}	11.96^{hi}
	B	1.60^{a}	1.52^{a}	3.73^{c}	11.04^{fg}	12.89^{jk}	12.80^{j}
Ecuadorian flour/ Mąka ekwadorska	W	1.34^{a}	1.47^{a}	3.03^{b}	9.34^{de}	9.35^{de}	9.78^{e}
	R	1.62^{a}	2.06^{b}	3.07^{b}	10.23^{e}	11.16^{fg}	10.80^{f}
	B	1.35^{a}	1.67^{b}	3.13^{b}	9.05^{d}	11.55^{gh}	12.51^{ij}

Values denoted in the columns by the same letters are not statistically significantly different (α = 0.05) / Liczby oznaczone tą samą literą w kolumnie nie różnią się istotnie statystycznie (α = 0,05)
W – white, R – red, B – black / W – biała, R – czerwona, B – czarna.

Source/Źródło: own research/ badania własne.

The water binding capacity of starch isolated from various types of quinoa flours increased 2-4 times at the higher temperature, i.e. 60°C, (Table 4) compared to temperatures of 25°C or 40°C. Along with the temperature increase, the swelling of the starch granules also increased with a change of solvent characteristics (Parker and Ring, 2001).

According to Pałasiński (1980), variety-related factors determine both the hydrophilic character and the water binding capacity of starch. Among the isolated starches, polymers obtained from Bolivian black quinoa showed the highest water binding capacity at all temperatures (Table 4). Other types of starch did not differ significantly from each other at the experimental temperatures with regard to their water binding capacity. At a temperature of 60°C, the analysed starches demonstrated at least three times higher WBC than potato or corn starch with similar solubility (Rożnowski et al., 2014). Starch isolated from black quinoa seeds imported from Ecuador demonstrated the lowest solubility in water (Table 4), while starch derived from black quinoa from Bolivia proved to be one of the most soluble starches among those analysed at all the temperatures. These results confirm the relation between both the variety and origin of starch and its solubility in water.

Table 4. Water binding capacity (WBC) and solubility (S) in water for quinoa starch at temp. 25, 40 and 60°C
Tabela 4. Zdolność wiązania wody (WBC) i rozpuszczalność (S) skrobi z komosy w wodzie w temp. 25, 40 i 60°C

Sample/Próbka		WBC [g/g db] at temperatures/ ZWW [g/g s.s.] w temperaturach			S[%] at temperatures/ R[%] w temperaturach		
		25°C	40°C	60°C	25°C	40°C	60°C
Bolivian starch/ Skrobia boliwijska	W	1.31^{a}	1.51^{ab}	5.34^{de}	0.96^{g}	1.07^{ghi}	1.66^{ij}
	R	1.13^{a}	1.27^{a}	4.78^{d}	1.58^{ij}	2.75^{kl}	3.38^{l}
	B	2.22^{bc}	2.64^{c}	6.13^{e}	1.80^{jk}	1.24^{ghi}	2.57^{kl}
Ecuadorian starch/ Skrobia ekwadorska	W	1.60^{ab}	1.67^{ab}	5.27^{d}	1.08^{ghi}	1.33^{hi}	2.27^{jk}
	R	1.54^{ab}	1.54^{ab}	5.37^{de}	0.48^{fg}	0.63^{fgh}	1.55^{ij}
	B	1.46^{a}	1.80^{ab}	5.14^{d}	0.22^{f}	0.42^{fg}	0.85^{fgh}

Values denoted in the columns by the same letters are not statistically significantly different (α = 0.05) / Liczby oznaczone tą samą literą w kolumnie nie różnią się istotnie statystycznie (α = 0,05)
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Source/Źródło: own research/ badania własne.

Kaukovirta-Norja et al. (1997) reported the effect of lipid content on the water binding capacity of starch and its solubility in water. In this study, no significant linear correlations were found between water binding capacity and lipid content, and between solubility in water and lipid content. Li et al. (2001) reported a correlation between amylose content and water binding capacity and solubility in water, but this was not corroborated here.

Starches isolated from seeds cultivated in Bolivia had much lower pasting temperatures than the polymers isolated from seeds imported from Ecuador (Table 5).

Table 5. Parameters of pasting characteristics of quinoa starches
Tabela 5. Parametry charakterystyki kleikowania skrobi z komosy

Sample/ Próbka		PT [°C]	PV [mPas]	TV [mPas]	BD [mPas]	FV [mPas]	SB [mPas]
Bolivian starch/ Skrobia boliwijska	W	50.4^{c}	3367^{d}	2037^{d}	1330^{d}	4922^{b}	2885^{a}
	R	55.9^{b}	4056^{c}	2715^{b}	1341^{d}	4842^{c}	2127^{d}
	B	50.7^{c}	2577^{e}	1149^{e}	1428^{c}	3698^{f}	2550^{b}
Ecuadorian starch/ Skrobia ekwadorska	W	57.4^{b}	3998^{c}	2738^{b}	1260^{e}	4374^{d}	1636^{e}
	R	61.1^{a}	4425^{b}	2596^{c}	1829^{b}	4230^{e}	1634^{e}
	B	56.0^{b}	5969^{a}	3003^{a}	2962^{a}	5358^{a}	2356^{c}

PT – pasting temperature, PV – peak viscosity, TV – trough viscosity, BD – breakdown, FV – final viscosity, SB – setback / PT – temperature kleikowania, PV – lepkość maksymalna, TV – minimum lepkości kleiku, BD – obniżenie lepkości, FV – lepkość końcowa, SB – wzrost lepkości w trakcie chłodzenia
Values denoted in the columns by the same letters are not statistically significantly different (α = 0.05) / Liczby oznaczone tą samą literą w kolumnie nie różnią się istotnie statystycznie (α = 0,05)
W – white, R – red, B – black / W – biała, R – czerwona, B – czarna.

Source/Źródło: own research/ badania własne

The starch characteristics were also affected by the quinoa variety. Starch isolated from red seeds had a higher pasting temperature (55.9°C and 61.1°C for Bolivian and Ecuadorian quinoa, respectively) than other quinoa starches (50.4-57.4°C). However, all the analysed starches demonstrated much lower pasting temperatures than commercial potato or maize starches (Fortuna et al., 2008). In the case of other pasting parameters, they were influenced by both the geographical origin and the variety of quinoa. The Ecuadorian quinoa starch had a higher value of peak viscosity (by 369-3392 mPas) and lower setback value (by 194-1249 mPas) than the same variety of Bolivian starch. In the case of quinoa starch isolated by Jan et al. (2017), on the RVA curve, a similar high gelatinisation peak (4637 mPas) was observed, followed by a significantly lower breakdown (943 mPas), and then an increase to a similar high viscosity (4869 mPas) in concluding the analysis.

In this study, no correlation was found between peak viscosity as the ability of starch to hold water (Bello--Pérez et al., 2010) and water binding capacity. Yanagisawa et al. (2006) and Kaukovirta-Norja et al. (1997) reported a correlation between pasting properties and amylose content, but no significant correlation was found by the authors in this respect. Moreover, solubility in water at 25°C was significantly strongly negatively correlated with peak viscosity ($r = -0.82$) and with breakdown viscosity ($r = -0.75$). In addition, a significant negative correlation between breakdown viscosity and protein content ($r = -0.86$) was observed. The starches isolated from white and red Bolivian quinoa seeds had significantly higher final viscosity (4922 mPas, 4842 mPas respectively) than the Ecuadorian ones (white 4374 mPas, red 4230 mPas). However, the highest value of the final viscosity was found for black Ecuadorian starch (5358 mPas), which was higher by 436-1600 mPas than in the other analysed starches.

Table 6 shows the DSC data of the starch samples. Among the examined polymers, the starch isolated from Bolivian seeds had lower gelatinization (1.4-4.4°C lower than those from Ecuador) and retrogradation temperatures (2.9-11°C lower than those from Ecuador) (Table 6). Values of the onset temperature (To_1), peak temperature (Tp_1) and endset temperature (Te_1) in starch gelatinisation (53.6°C, 61.9°C, and 70.0°C, respectively) and the onset temperature (To_2) and peak temperature (Tp_2) in starch retrogradation (46.8°C and 55.6°C respectively) determined for white Ecuadorian starch were all higher than for the other examined quinoa starches. The lowest gelation enthalpies of the Ecuadorian starches proved that gelatinisation of these starches was easier than that of the Bolivian ones. Starch from quinoa obtained through experimental cultivation in northern Poland (Pycia et al. 2019) exhibited higher gelatinisation temperatures (5-10°C higher) and enthalpy (10.1 J/g) compared to those from South America. Czuchajowski et al. (1998) reported that enthalpy was related to amylose content

Table 6. Thermodynamic parameters of quinoa starches
Tabela 6. Termodynamiczne parametry skrobi komosowych

Sample/ Próbka		Gelatinisation/Kleikowanie					Retrogradation/Retrogradacja					
		To_1 [°C]	Tp_1 [°C]	Te_1 [°C]	ΔH_1 [J/g]	PHI	To_2 [°C]	Tp_2 [°C]	Te_2 [°C]	ΔH_2 [J/g]	PHI	R [%]
Bolivia	W	49.8^{d}	57.5^{c}	66.9^{c}	8.35^{a}	1.08^{a}	43.9^{b}	50.9^{c}	56.5^{c}	0.31^{e}	0.04^{a}	3.7
	R	51.6^{c}	59.6^{b}	68.4^{b}	8.09^{b}	1.01^{a}	43.0^{b}	47.9^{d}	54.0^{d}	0.28^{e}	0.06^{a}	3.5
	B	48.5^{d}	56.9^{c}	66.0^{d}	6.64^{d}	0.79^{b}	42.8^{b}	51.3^{c}	52.5^{e}	0.42^{d}	0.05^{a}	6.3
Ecuador	W	53.6^{a}	61.9^{a}	70.0^{a}	7.50^{c}	0.90^{c}	46.8^{a}	55.6^{a}	62.4^{b}	1.02^{c}	0.12^{b}	13.4
	R	52.2^{b}	62.1^{a}	69.8^{a}	8.02^{b}	0.81^{b}	46.5^{a}	51.3^{c}	65.0^{a}	1.12^{b}	0.23^{b}	14.0
	B	51.9^{c}	59.3^{b}	67.6^{c}	6.87^{d}	0.93^{c}	46.8^{a}	54.7^{b}	61.2^{b}	1.69^{a}	0.21^{b}	24.6

To – onset temperature, Tp – peak temperature, Te – final temperature, ΔH – enthalpy of transition, R – retrogradation ratio / To – temperatura początku piku, Tp – temperatura piku, Te – temperatura końcowa, ΔH – entalpia przemiany, R – ułamek retrogradacji, W – white, R – red, B – black / W – biała, R – czerwona, B – czarna
Values denoted in the columns by the same letters are not statistically significantly different ($\alpha = 0.05$) / Liczby oznaczone tą samą literą w kolumnie nie różnią się istotnie statystycznie (α = 0,05).

Source/Źródło: own research/ badania własne.

in starch, however they found no correlation between enthalpy and amylose content. According to Noda et al. (2002) and Yasui et al. (2002) the molecular structure of amylopectin influences the DSC parameters to a greater extent than amylose content. The lower transition enthalpy values indicated shorter chain lengths and a lower molecular weight of the amylopectin (Pycia et al., 2019).

Retrogradation enthalpy of starch is usually 60-80% lower than that of gelatinisation enthalpy (Singh et al., 2003; Subaric et al., 2011), and in this study, the retrogradation enthalpy was 76-97% lower than the gelatinisation enthalpy (Table 6). The analysis of the ratio of the enthalpy of retrogradated starch (ΔH_2) to gelatinisation enthalpy (ΔH_1) indicated that it was much higher in the starches isolated from the seeds of Ecuadorian quinoa (14-24%) than in the polymers isolated from seeds originating from Bolivia (3-6%). It was also found that the ratio of enthalpies was significantly correlated with peak viscosity ($r = 0.84$, $\alpha = 0.05$) and breakdown viscosity ($r = 0.86$, $\alpha = 0.05$).

PHI is a numerical value describing the relative shape of the endotherm. The DSC curves during gelatinisation of all starches changed with a similar intensity both during the rise and decline of the gelatinisation peak, but many times slower than potato starch (Rożnowski at al., 2021). During the subsequent analysis of samples (after being stored under refrigeration conditions for a week), the signal increase was significantly weaker (2.6-4.3 times) in the Bolivian starch samples compared to the Ecuadorian ones, despite a significantly smaller temperature range of the transformation. This indicates the lower internal homogeneity of the Bolivian starch sample with a much smaller scope of retrogradation-induced structural changes in the starch gel.

5. Conclusion

The results of this study show that both the geographical origin and the variety of quinoa exert an influence on the quality of seeds as well as on the quality of the starch isolated from these seeds. Flour obtained from the varieties of quinoa was characterised by different content of lipids as well as water binding capacity at 60°C and solubility in water, whereas the flour obtained from seeds grown in Bolivia exhibited a higher water binding capacity and solubility at 60°C than flour from Ecuadorian seeds.

Starches isolated from quinoa seeds were characterised by different contents of lipids, amylose, and had different pasting and gelatinisation characteristics, which depended to a large extent on the geographical origin and variety of quinoa. Quinoa starch obtained from Bolivian seeds had lower temperatures of thermal transitions of starch, regardless of variety. The electron paramagnetic resonance analysis indicated that both the flour and starch isolated from quinoa seeds were characterised by considerable numbers of spins per gram. The starch obtained from red varieties (regardless of the region in which quinoa was cultivated), had the lowest amylose content, which may affect their technological significance and the potential use for modifications. These varieties of starch required higher gelatinisation temperature, which will result in higher financial costs. From a food technology perspective, white and black seeds starch varieties appear to be more advantageous because they require less energy for gelatinisation while yielding gels with an equal or higher final viscosity than red seeds starch. In turn, taking into account the stability of the pastes, the retrogradation progress in the Bolivian starch pastes was slower than in the Ecuadorian ones, and the white and red starch pastes retrograded more slowly than the white ones.

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Właściwości fizykochemiczne mąki i skrobi otrzymanych z różnych odmian komosy

Streszczenie: Obecnie obserwuje się wzrastające zainteresowanie tradycyjnymi, ludowymi produktami, zwłaszcza tymi o udowodnionych korzyściach zdrowotnych. Celem badań była ocena składu i właściwości mąk oraz skrobi pozyskanych z nasion różnych odmian komosy. Analizowane skrobie z komosy zawierały 7-18 razy mniej białka i 10-25 razy mniej lipidów niż mąki. Zawartość amylozy w skrobiach wynosiła od 15,9 do 18,5%. Próbki mąk i skrobi zostały również przebadane pod kątem właściwości termicznych (DSC), charakterystyki kleikowania (RVA) oraz ilości wolnych rodników (EPR). Skrobie z ekwadorskiej komosy charakteryzowały się znacznie wyższą temperaturą początkową (51,9-53,6°C) i temperaturą piku (59,3-62,1°C) niż skrobie boliwijskie (odpowiednio 48,5-51,6°C i 56,9-59,6°C). Wszystkie skrobie były podatne na tworzenie się wolnych rodników (1,05-2,06×10^{19} spinów/g) bez względu na ich pochodzenie geograficzne. Na inne właściwości mąk i wyizolowanych skrobi wpływ miały pochodzenie geograficzne i odmiana komosy.

Słowa kluczowe: komosa, skrobia, elektronowy rezonans paramagnetyczny EPR, reologia, retrogradacja