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Study of the chemical and physical modification of starch obtained from white carrot *(Arracacia xanthorrhiza)* and sweet potato *(Ipomoea batatas)*

Estudio de la modificación química y física de almidón obtenido de zanahoria blanca (*Arracacia xanthorrhiza)* y camote *(Ipomoea batatas)*

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ABSTRACT

Starch is an abundant and accessible source of biological raw materials, widely used in the food, medical and textile industries. The objective of the present study was to analyze the chemical and physical modification of starch obtained from white carrot (*A. xanthorrhiza*) and sweet potato (*I. batatas*). To do this, a completely randomized design with multiple factors was used, using white carrot and purple sweet potato. To verify the normality of the factors, the Kruskal Wallis technique was used, using the statistical programs InfoStat and R Studio. The results showed that white carrot starch, through chemical modification, had a higher amylose content (37.49); total starch (56.06) and whiteness index (89.08); while, the starch obtained by physical modification showed higher humidity (12.14), water absorption index (5.79); solubility (0.63) and swelling power (5.83). On the other hand, in sweet potato, the physically modified starch obtained a higher concentration of amylose (40.96); humidity (9.87), water absorption index (3.56); swelling power (3.64), compared to the chemical method, which determined a higher whiteness index (89.29).

Keywords: starch; alternative; amylose; amylopectin; nutritional

RESUMEN

El almidón es una fuente abundante y accesible de materias primas biológicas, ampliamente utilizada en las industrias alimentaria, médica y textil. El presente estudio tuvo como objetivo analizar la modificación química y física de almidón obtenido de la zanahoria blanca (*A. xanthorrhiza)* y camote *(I. batatas).* Para ello, se utilizó un diseño completamente al azar con múltiples factores, empleando zanahoria blanca y camote morado. Para el contrasté de normalidad de los factores se utilizó la técnica Kruskal Wallis, mediante los programas estadísticos InfoStat y R Studio. Los resultados demostraron que, el almidón de zanahoria blanca por medio de modificación química presentó mayor contenido de amilosa (37,49); almidón total (56,06) e índice de blancura (89,08); mientras que, el almidón obtenido por modificación física mostró mayor humedad (12,14), índice de absorción de agua (5,79); solubilidad (0,63) y poder hinchamiento (5,83). Por otro lado, en el camote, el almidón modificado físicamente obtuvo mayor concentración de amilosa (40,96); humedad (9,87), índice de absorción de agua (3,56); poder de hinchamiento (3,64), en comparación al método químico, que se determinó un mayor índice de blancura (89,29).

Palabras clave: almidón modificado; amilosa; amilopectina; caracterización parcial; propiedades funcionales; nutricional

1. INTRODUCTION

Roots and tubers are an excellent source of starch (16-24%), providing 75-80% of total caloric intake, and are used as raw material in the production of noodles, bakery products, confectionery, snacks, starch syrups, among others (León-Méndez et al., 2020). The white carrot is a tuber native to South America, belonging to the Apiaceae family, and contains about 67.29 g of starch per 100 g of dry matter (Parra et al., 2015). In Ecuador, it is cultivated in the inter-Andean valleys from 700 to 3200 m.a.s.l. It is the only vegetatively propagated umbellifera domesticated in the Americas (Aracelly, 2016).

Sweetpotato, on the other hand, is one of the main food crops in the world, mainly in tropical and subtropical areas (Shubhendu et al., 2015). In Ecuador, it is cultivated by small farmers, mainly in the Sierra with 42 %, Coast with 47 % and Amazon with 11 %, being the provinces of Santa Elena, Guayas and Manabí the ones with the highest production of this tuberous root.

Starch is one of the most abundant natural biopolymers in nature, it is found in a great variety of tissues of botanical origin (tubers, seeds and leaves) (Peñaranda et al., 2018). Structurally, starch is a polymer of D-glucose units), composed of a mixture of polysaccharides made up of amylopectin (80%), amylose (20%) and a minority fraction (1- 2%) of non-glucosidic conformation such as lipids and minerals, depending on its botanical origin (León-Méndez et al., 2020).

Native starch also has some limitations, such as tendency to retrogradation, low freeze-thaw stability and pH sensitivity (Ocaña, 2019). Starch modification is carried out to improve the positive attributes and eliminate the deficiencies of native starches. Several methods have been developed to produce a variety of modified starches with a variety of characteristics and applications (Omodunbi-Ashogbon & Temitope-Akintayo, 2023).

Physically modified starches are simple and inexpensive because they can be produced without chemicals or biological agents (Martins-Fonseca et al., 2021). In contrast, chemical modification is possible due to the ubiquitous hydroxyl groups in starches that have been exploited for more than a century, mainly in the preparation of starch esters and ethers, but also in more subtle alterations, e.g., to adjust the structure of starches for specific applications (Omodunbi-Ashogbon & Temitope-Akintayo, 2023).

All these techniques tend to alter the highly flexible starch polymer with modified physicochemical properties and modified structural attributes of high technological value for food and non-food industries (Zia-Ud et al., 2017). Starch modification is a constantly evolving industry with numerous possibilities to generate new starches that include new functional and value-added properties as demanded by the industry (Ocaña, 2019).

Therefore, the objective of the present research was studying the chemical modification (acetylation) and physical modification (microwave) of starch obtained from white carrot (*Arracacia xanthorrhiza*) and sweet potato (*Ipomoea batatas*).

2. MATERIALS AND METHODS

2.1. Material

Xanthorrhiza starch from was obtained from roots grown at La Pradera Experimental Farm, located in Chaltura, Imbabura province. Sweet potato starch was obtained from roots grown at the Portoviejo Experimental Station, located at Km 12, Via Santa Ana, Canton Portoviejo. Starch extraction was carried out at the Nutrition and Quality Department, located at the Santa Catalina Experimental Station, latitude: 0°22'S, longitude: 78°33'0, altitude of 3050 m.a.s.l.

2.2. Statistical analysis

Results were analyzed by applying a completely randomized multifactorial design. The analyses were performed in triplicate. Two species and two types of starch modifications were evaluated. To determine the significant difference between the means of the treatments, the Tukey statistical test was used with a confidence level of 95 %, using the statistical software InfoStat.

2.3. Obtaining native starch

To obtain the starch, 8 kg of each raw material was used, free of impurities and damaged roots. The selected roots were washed, peeled and cut into thin slices, which were crushed in an "OSTER-BLSTMG-W00-013" blender. The whole was then filtered, performing several washes of the residue with distilled water to separate all the starch. The filtrate was left to stand for 4 h to promote the sedimentation of the starch, which was separated from the supernatant and dried in a "MEMMERT" oven for 24 h at 48°C. The recovered starch was ground and passed through a 90 µm sieve and stored in hermetically sealed polypropylene bags of 0.002 mm caliber.

2.4. Modification of native starch

Physical Modification

25 g of starch was placed and 15 ml of distilled water was added, stirred for 5 minutes and microwaved for 40 seconds. The gelled starch was placed in plastic containers with lids and frozen for 24 hours. The frozen sample was freeze-dried for 5 days, then crushed and ground, prior to the different analyses.

Chemical modification

A modification by acetylation was performed, following the methodology established by Montero-Peralta, (2018) with some modifications. 5 g of starch sample was taken, to which 25 ml of distilled water was added, stirred constantly for 30 minutes. Then pH was adjusted with NaOH 0.1 N, 0.15 g of acetic acid was slowly added until pH between 8-8.5 was reached using NaOH 6N. The reaction was maintained for 3 min and stopped by adding 0.4 N HCl. The starch was washed with distilled water and centrifuged for 15 min at 1500 rpm. Three washes were performed to remove the acidity. The whole was centrifuged and the precipitated starch was recovered, which was placed in a Petri dish and dried in an oven at 50 ºC for 30 minutes. The dehydrated starch was ground and sieved in a 90 µm sieve.

2.4. Starch characterization

Amylose content: It was determined following the methodology established by Carrasquero-Durán & Navas, (2015) with some modifications. It was weighed 100 mg of sample and placed in a 100ml volumetric balloon, then added 1 ml of ethanol (95 %) with 9 ml of 1 N sodium hydroxide. For the gelatinization process it was left to stand for 24 hours at room temperature, at the end of the elapsed time 100 ml of distilled water was added, followed by 1 ml of 1 N acetic acid and 2 ml of 2 % iodine solution. The reaction was left to take place at room temperature, in darkness, for 20 minutes, the reading of the absorbance at 620 nm was taken.

For the preparation of the blank, 50 ml of distilled water with 5 ml of 0.09 N NaOH was added in a 100 ml volumetric balloon, followed the above process, where 1 ml of 1 N acetic acid and 2 ml of 2% iodine solution were added and 100 ml of distilled water was added. For the standard curve: 100 mg of amylose and 100 mg of amylopectin were weighed in 100-ml volumetric balloons, then 1 ml of ethanol (95 %) and 9 ml of 1 N NaOH were added, left to stand for 24 hours at room temperature, and the standard curve was prepared according to Table 1.

Table 1.
Preparation of the standard curve to determine the amylose content

Mixture composition			
Amylose (%)	**Amylose standard (mL)**	**Amylopectin (mL)**	**0.09 N NaOH (mL)**
0	0	9	1
10	1	8	1
20	2	7	1
30	3	6	1
40	4	5	1
50	5	4	1

Functional properties: Water absorption index, solubility and swelling power: 2.50 g of starch was weighed into a centrifuge tube containing a magnetic stirrer, 30 ml of water was added to each tube and stirred for 30 minutes. It was centrifuged by 5000 rpm, 20 minutes. The supernatant was decanted into a graduated centrifuge tube and the volume was measured, followed by filtration of the supernatant. Then 10 mL of the filtrate was taken and placed to dry by 24 h at 90 °C. The remaining gel was weighed (Urbina-Dicao et al., 2023) and the following equations were applied for the calculation.

Calculations

- Water Absorption Index (WIA)

$$IWIA = \frac{Gel\ Weight\ (g)}{Sample\ Weight}$$

- Water Solubility Index (WSI)

$$WSI = \frac{Solubles\ Weight}{Sample\ Weight}$$

- Swelling power (SP)

$$SP = \frac{Gel\ weight}{Sample\ weight - Soluble\ weight}$$

Moisture determination (%): It was determined by oven, where 25 g of sample was placed at a temperature of 130 °C by 3 h (Alvis et al., 2008).

3. RESULTS AND DISCUSSION

Table 2, shows the results of the physicochemical (amylose, starch, moisture) and functional (water absorption index, solubility and swelling power) characteristics of native and modified starch from white carrot (*Arracacia xanthorrhiza*).

For amylose content, a significant difference ($p<0.05$) was determined between the starches of the two species under study, showing that the highest content corresponded to the chemically modified starch (37.49 %), while the native starch obtained the lowest amount of amylose (29.53 %). One aspect that affects starch resistance is the size and type of granules (Martins-Fonseca et al., 2021). On the other hand, according to Rocha et al., (2020) in their research they determined an amylose content of 18.7 % in white carrot starch and 28.9 % in potato starch. Generally most starches contain between 20 - 30 % amylose (Villarroel et al., 2018).

In relation to total starch content, it was shown that native starch (87.22 %) was statistically superior to physically modified starch (50.21 %). There was a significant decrease in its content when it was subjected to modification. Coinciding with Gercekaslan, (2020) who determined in yam starch (Dioscorea alata) obtained 98.27 % and in starch modified by alkaline treatment, 94.67 %. In addition, Pinzon et al. (2020) established values ranging from 96.80 to 98.40 % of total starch for the subvariety of Arracacha amarilla (Xanthorrhiza bancroft).

Regarding the moisture content in the different starch stages, when presenting significant difference ($p<0.05$), they placed a range between 6.94 - 12.14 % for native and physically modified starch. Martins-Fonseca et al. (2021), when evaluating treated potato and sweet potato starches (physical modification), obtained a moisture content of 10 and 15 %. Sharma et al. (2022) also presented a starch content of 10 % in yellow carrot.

The water absorption index content presented significant differences ($p<0.05$), where the highest water absorption was found in the physically modified starch with 5.79 %, compared to the native starch that obtained 2.38 %. According to Gercekaslan (2020), physically modified starches have a higher water absorption rate, due to the larger size of the granules. As well as, several authors in the physical modification of carrot pomace starch determined a water absorption rate of 5.25 % (Kaisangsri et al., 2016).

Starch modification has resulted in an increase in one or more of the following properties: increased digestibility, emulsifying agent, emulsion stabilizer, encapsulating agent, cold water swellability, charged starch molecules, enhanced cooking characteristics, film formation, wall materials for encapsulation, improved

Regarding water solubility index, it was determined that physically modified starch (0.63 %) obtained a higher solubility compared to the native state (0.20 %) and chemically modified (0.58 %). These results are related to Valcárcel et al., (2019) who studied Andean tuber starches in native and modified state and obtained 0.32 and 0.59 for oca (*Oxalis tuberosa*); 0.22 and 0.91 in olluco (*Ullucus tuberosus*) and 0.15 and 0.72 in mashua (*Tropaeolum tuberosum*).

As for the swelling power, it was shown that the highest incidence was found in the physically modified starch (5.83 g water/g starch) as opposed to native starch, which had a lower value (2.38 g water/g starch). This variable is closely related to the absorption index, where native starch absorbs more water and therefore has a higher swelling power of the granules. (2020) who presented a swelling capacity of 6.80 (g water/ g starch) in starches annealed from germinated sorghum. Modified starches are characterized by excellent their ability to swell when subjected to industrial food processes with the main characteristic sought to be achieved is the ability to trap as much water within it (Bashir & Aggarwal, 2019).

The native and chemically modified starch presented a higher whiteness index with values of 89.27 % and 89.09% respectively, being statistically different ($p<0.05$) to the physically modified starch that obtained 86.01%. Authors such as Agredo et al., (2017) presented a lower whiteness index in extruded and fermented starches (82 and 89%) compared to native starch (91%). It is necessary to emphasize that, the higher the starch whiteness and brightness, the more acceptable it is for industrial processes, the oxidation of unsaturated carbon chains influences coloring bodies (Gercekaslan, 2020).

Table 2.

Effect of modification on the physicochemical characteristics and functional properties of A. xanthorriza starch

Parameter	Native starch	Microwave modified starch	Acetylated starch
Amylose(%)	29.52±0.05[a]	33.17±0.05[b]	37.49±0.05[c]
Starch (%)	87.22±2.49[c]	50.21±2.49[b]	56.06±2.49[a]
Moisture (%)	11.06±0.21[b]	12.14±0.21[c]	6.94±0.21[a]
Water absorption Index (%)	2.38±0.18[a]	5.79±0.18[c]	3.04±0.18[b]
Water solubilityIndex (Water g /Starch g)	0.20±0.03[a]	0.63±0.03[b]	0.58±0.03[b]
Swelling power (%)	2.40±0.18[a]	5.83±0.18[b]	2.98±0.18[b]
Whiteness index	89.27±0.13[b]	86.1±0.13[a]	89.08±0.13[b]

Note: Different lower case letters associated with values within the same column indicate a significant difference at the p<0.05.

Table 3 shows the results of the physicochemical characteristics (amylose, starch, moisture) and functional properties (water absorption rate, solubility and swelling power) of native and modified starch from purple sweet potato (Ipomoea batatas).

Regarding amylose content, a significant difference (p<0.05) was found between the types of starches studied, with the highest value being found in microwave-modified sweet potato starch (40.96 %) compared to acetylated starch, which had a lower amylose content of 32.26 %. For this parameter, it was determined that physical modification leads to an increase in amylose content. These results are opposite to those determined by Benelli et al., (2019) who reported a lower amylose content in potato and corn starches modified by physical means with values of 19.00 to 19.90 % respectively. Guzman-Condarco (2018) reported 24 % amylose in starch obtained by chemical modification.

Regarding the total starch content, it was observed that native starch presented 83.70 %, a statistically higher value than starches obtained by physical and chemical modification with values of 65.88 and 65.93 respectively. These results are within the reported range of 45 to 80 % for roots and tubers in their natural state (García-Méndez et al., 2016). Other authors such as Indrianti & Pranoto (2018) reported 56 % and 65 % total starch in sweet potato modified by heat and wet treatment. This parameter is important as it determines the application of starch in different food products (Anchundia et al., 2019).

Moisture content showed significant difference (p<0.05) and varied between 7.71 and 9.87 % in native and physically modified starch. The higher amount of moisture in microwave-treated starch is related to the degree of gelatinization, which allows it to absorb more or less water. The experimental values are lower than those determined by (Chen et al, 2022) who reported a variable moisture content between 11.03-15.12% in sweet potato starch. Indrianti & Pranoto (2018) reported 12.34 % in native starch of purple sweetpotato.

The water absorption index presented significant differences (p<0.05), the highest value corresponded to microwave-treated starch with 3.56 %, while, the lowest index (1.91 %) was determined in native starch. The decrease in water absorption rate is influenced by the method of starch modification, which in turn is related to the pre-gelatinization or gelatinization of the starch, a state that determines the greater or lesser ability of the granule to absorb water. These values agree with those reported by Babu et al., (2018) for sweet potato starches, native (1.82%) and modified with organic and inorganic acids (2.46%) for the water absorption index. In the water solubility index, the type of starch did not have a significant influence (p>0.05), determining values ranging from 0.62 to 0.96 %. These results are lower than those reported by Murillo-Martínez et al., 2021) who mention values of 2.91 and 0.92 for purple and yellow sweet potato starch. Starch solubility depends on several factors such as extraction source, modification method, inter-associative strength between molecules and swelling capacity (Manzanillas-Rojas, 2018; Zhang et al., 2018).

In relation to swelling power, a significant difference ($p<0.05$) was determined between starches according to the modification method. The highest value corresponded to physically modified starch with 3.64 g water/starch; whereas, native starch and chemically modified starch presented similar values with 1.96 and 2.33 g water/starch. The swelling power is related to the water absorption capacity of starch, which in turn varies depending on the nature of the starch, the method of extraction and modification (Jia et al., 2023). Several investigations mention a swelling capacity between 0.19 - 0.23 for canary bean and chocho guaranguito flour (Sánchez et al., 2023). According to Majzoobi & Farahnaky (2021) granulated starch showed a lower swelling capacity compared to modified starch.

Regarding the whiteness index, it was determined that the chemically modified starch with 89.29 % was statistically different ($p<0.05$) from the physically obtained starch, which showed 87.18 %. This result could be attributed to the chemical modification that prevents starch oxidation. Wang et al. (2022) reported an average whiteness index of 95 % for sweet potato starch modified with microwave-assisted L-malic acid. Physically modified and native starch have some limitations such as retrogradation, low process tolerance and gel turbidity, which limit their use in the food industry (Bashir & Aggarwal, 2019).

Table 3.

Effect of modification on the physicochemical characteristics and functional properties of I. batata starch

Parameter	Native starch	Microwave modified starch	Acetylated starch
Amylose(%)	40.06±0.1^{b}	40.96±0.1^{c}	32.26±0.1^{a}
Starch (%)	83.70±1.98^{b}	65.88±1.98^{a}	65.93±1.98^{a}
Moisture (%)	7.71±0.3^{a}	9.87±0.31^{c}	8.78±0.3^{b}
Water absorption Index (%)	1.91±0.1^{c}	3.56±0.14^{a}	2.4±0.12^{b}
Water solubilityIndex (Water g /Starch g)	0.96±0.20^{a}	0.63±0.21^{a}	0.62±0.21^{a}
Swelling power (%)	1.96±0.13^{a}	3.64±0.11^{b}	2.33±0.17^{a}
Whiteness index	88.29±0.18^{b}	87.18±0.18^{a}	89.29±0.18^{c}

Note: Different lower case letters associated with values within the same column indicate a significant difference at the $p<0.05$.

CONCLUSIONS

Chemical modification of carrot starch significantly affected amylose content and whiteness index. While, physical modification helped to retain more moisture, which in turn affected the water absorption rate and water solubility index. The microwave-modified sweet potato starch showed higher amylose content, moisture content, water absorption rate, solubility and swelling power; however, the chemical modification had a positive effect on the higher whiteness index of the starch. The technique of modifying white carrot and sweet potato starches is an interesting alternative to increase and diversify their possibilities of use in the food industry.

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CONFLICTO OF INTEREST

There is no conflict of interest related to the subject matter of the work.

CONTRIBUTION OF THE AUTHORS

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