Physicochemical characterization of starches from seven improved cassava varieties: Potentiality of industrial utilization.

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ABSTRACT

Objective: The present study, which is in line with tropical crops increased value, aimed to highlight the industrial potential of starches from seven newly improved cassava varieties through their morphological, physicochemical and functional properties.

Methodology and results: Starches from seven improved cassava varieties encoded respectively V₅₄, V₅₅, V₆₄, V₆₆, V₆₉, and V₇₃ and V₄ were extracted and their physicochemical and functional characteristics were determined. The whole starches granules were ovoid and conical bearing a hilum on the truncated side. They contained relatively high amount of small granules (<10 µm size) and amylopectin. In addition, all the starches showed very strong water absorption capacity and began gelatinizing early (55 – 60 °C). However, the physicochemical characteristics significantly varied from one starch variety to another. The starches of V₅₄, V₆₄ and V₇₃ varieties showed an exceptional low (0.01 %) and stable syneresis after four weeks at 4 °C and -15 °C for V₅₄. The highest clarity was topped by varieties V₅₄ (78.54±3.30 %) and V₆₄ (76.27±6.72 %). Three starch varieties encoded V₅₄, V₆₄ and V₆₉ registered the higher amount of small granules (15.8±1.50, 16.60±0.90 and 14.40±0.90 % respectively). In contrast those encoded V₅₅, V₆₆ and V₇₃ with large granules, recorded the highest swelling power (30.10±3.00, 28.21±2.32 and 29.74±2.40 g/g respectively) and high amount of amylose (17.37±2.54, 20.86±2.36 and 19.03±2.45 %).

Conclusions and application of findings: The studied cassava starches varieties (particularly V₅₄, V₇₃, V₆₄, V₅₅ and V₆₆) could find a wide range uses in food and non-food industries as pharmaceuticals, cosmetics, textiles thanks to their interesting physicochemical and functional properties.

Key words: Cassava, starch, functional properties, industrial utilization.

INTRODUCTION

Cassava (Manihot esculenta Crantz) is the third most important source of energy after rice and maize, for human and livestock in the world (Fauquet & Tohme, 2008; FAO, 2008). It is grown for its edible roots, which serves as a food security and income-generating crop for millions of people in the developing countries (Sanni & Ayinde, 2002; Amani et al., 2005). In spite of all these potentialities, cassava is faced with a crucial problem of post-harvest storage. An excessive glut and harvest losses (approximately 50 %) occur at the peak of harvesting time (CORAF/WECARD,
Fresh cassava roots are highly perishable, with a shelf life of less than 3 days. Therefore, they are of poor market value. In this context, cassava roots are then processed into more storable forms (Phillips et al., 2004; FAO, 2008) such as starch following the Global Cassava Development Strategy advice in order to fulfill the global demand of cassava starch (FAO/IFAD, 2004). Starch is a multibillion-dollar business worldwide and is finding application in several industries. Indeed, outside the fact of being the main source of energy in the human diet, starch is also used in food industries and non-food industries such as manufacturing of adhesives, cosmetics, detergents, paper and textiles. In some foodstuffs, starch is used to influence or control such characteristics as aesthetics, moisture, consistency and shelf stability (De Cock, 1996; Ellis et al., 1998). This expansion of industrial uses justifies the incessantly increase in demand for starch (Davis et al., 2002). Potato, maize, wheat and cassava are the major sources of industrial starch but only around 10% of these starches derive from cassava (Manihot esculenta Crantz) roots. Although the uniqueness of starch physicochemical and functional characteristics, which is linked to its quality, varies according to its intended application (Svegmark & Hermansson, 1993), the significant differences among starch properties impose the search of new sources of starch with high and consistent qualities. In this respect, many research programs have implemented several strategies to develop high value cassava varieties (Ceballos et al., 2004; Ceballos et al., 2006). Some of these new cassava varieties obtained by bio fortification and introduced in Côte d’Ivoire by IITA (International Institute of Tropical Agriculture) showed a relatively high amount of starch (Koua et al., 2012).

MATERIALS AND METHODS

Raw Material: Seven improved varieties of cassava encoded respectively V56, V65, V64, V66, V69, and V73 (yellow colored pulp) and V4 (white colored pulp). These roots of eleven months old were kindly provided by the National Agricultural Research Center (CNRA) of Adiopodoumé (Côte d’Ivoire).

Starch Isolation: Cassava starches were extracted within 24 hours after harvesting according to Banks and Greenwood (1975) method. Samples of two kilograms (2 kg) of each cassava roots were washed, peeled and cut into small slices (4x4 cm) with stainless steel knife. The slices were blended and the paste dispersed in a sodium chloride (4%) solution to separate proteins from the starch during 24 h at 25±1 °C. The slurry was sieved successively through 500 µm, 250 µm and 100 µm sieves. The starch obtained in a separating funnel was then dried at 45 °C for 48 hrs in an electric oven (Memmert 700, Germany) with fan-forced ventilation. The dry products were ground, quantified and then stored for analyses.

Starch Granule Morphology: The starch granules morphology was determined by electron microscope. Isolated starch granules were mounted on the surface of a brass disk using double-sided adhesive silver-tape, coated with gold/palladium (60/40) and viewed under a scanning electron microscope (FEG Supra 40 VP Zeiss 2008) with an acceleration of 1 kV. The diameter distribution was determined on 500 granules using a calibrated micrometer.

Physicochemical Characteristics: The moisture and pH were carried out following the AOAC (1990) and Benesi et al. (2004) methods respectively. Amylose and amylopectin contents were carried out following the method described by Jarvis & Walker (1993): Defatted starch (0.1g) was dissolved in 5 ml of potassium hydroxide (1N) solution. The suspension was thoroughly mixed and 5 ml of HCl (1N) solution were added. The mixture was boiled in water bath for 15 min and the volume was adjusted to 10 ml. After centrifugation at 1000 rpm for 10 min, the supernatant was used for determination of amylose and amylopectin. For this, 0.05 ml of the supernatant was introduced in a test tube and 4.85 ml of distilled water, following by 0.1 ml of iodine reagent were added. The mixture obtained was left to stand for 10 min and the absorbance was read at 580 nm and 720 nm, respectively by using a spectrophotometer (Helios, Omega, UK). Standard curves of amylose and amylopectin were used as references.

Functional Properties:

Swelling power and solubility of the starch were determined by the method described by Ly & Yeh (2001) and Sosulski (1962) used to evaluate the samples water absorption capacity. Stability of starches samples to freezing was determined according to
Schoch (1968). Ten (10) g of paste sample were conditioned in a plastic tube at -15 °C and 4 °C, respectively for 4 weeks. Freezing stabilities were performed every week by measuring the percentage of water expelled after centrifugation at 2700 rpm for 30 min. The paste clarity of starch samples was carried out as described by Graig et al. (1989). Aqueous dispersions (1%) of starch were boiled at 100°C and constantly shaken for 30 min. The paste was cooled at ambient temperature and stored at 4 °C for 4 weeks.

**Statistical analysis:** All the experiences were performed in triplicate and the data were analyzed using the XLSTAT version 2007 Software and EXCELL. More precisely, in order to underline the differences between characteristics values means, Duncan’s test of the ANOVA was used at 95 % of confidence.

**RESULTS**

**Morphological and physicochemical characteristics:** the cassava starches granules (small and large sizes) were ovoid and conical with a truncated side bearing an eccentric hilum. The surface of the whole granules was smooth except for some granules of the variety V₆₄, which was, crumpled (Figure 1). Concerning the granule size distribution reported on Table 1, variety V₆₉ recorded the widest range (0.88 to 31.40 µm) when V₅₄ got the narrowest (6.5 to 25.37 µm). Moreover, variety V₄ topped the highest amount of small granules (31±2.00 %) in opposition to V₇₃ (03.40±0.65 %). The others varieties got intermediate values (7.40±0.6 % for V₆₆ to 15.8±1.5 % for V₅₄). About the amylose and amylopectin content (Table 2); the test of Duncan revealed a significant difference between varieties compared with moisture and pH that presented no difference. Indeed, amylose contents were inversely correlated (r = -0.88) with amylopectin, and both ranged from 14.20±1.98 % (V₅₄) to 25.31±2.5 % (V₅₄), and from 85.86±2.23 % (V₅₄) to 74.69±3.56 % (V₄), respectively.

**Figure 1:** Scanning electron micrographs of starches (Gx 400) of cassava varieties. *Legend: a – hilum in the truncated side; b – granules with rough surface*
Table 1: Starch granules distribution and proportion of small granules of cassava starches.

<table>
<thead>
<tr>
<th>Varieties</th>
<th>Granules size distribution (µm)</th>
<th>Proportion of small granules (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>V₄</td>
<td>3.51 – 24.35</td>
<td>31.00±2.00a</td>
</tr>
<tr>
<td>V₅₄</td>
<td>5.45 – 30.59</td>
<td>15.80±1.50bc</td>
</tr>
<tr>
<td>V₅₅</td>
<td>4.95 – 24.67</td>
<td>07.80±1.05d</td>
</tr>
<tr>
<td>V₆₄</td>
<td>6.50 – 25.37</td>
<td>16.60±0.90b</td>
</tr>
<tr>
<td>V₆₆</td>
<td>1.58 – 31.71</td>
<td>07.40±0.60d</td>
</tr>
<tr>
<td>V₆₉</td>
<td>0.88 – 31.40</td>
<td>14.40±0.90bc</td>
</tr>
<tr>
<td>V₇₃</td>
<td>4.99 – 23.77</td>
<td>03.40±0.65e</td>
</tr>
</tbody>
</table>

Data are represented as means±SEM (n=3). Mean with different letters in the same row are statistically different (p < 0.05) according to Duncan’s test.

Table 2: Physicochemical characteristics of cassava starches

<table>
<thead>
<tr>
<th>Varieties</th>
<th>Moisture (%)</th>
<th>pH</th>
<th>Amylose (%)</th>
<th>Amylopectin (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>V₄</td>
<td>12.95±0.30a</td>
<td>5.69± 0.21a</td>
<td>25.31±2.50a</td>
<td>74.69±3.56c</td>
</tr>
<tr>
<td>V₅₄</td>
<td>13.55 ±0.26a</td>
<td>4.83± 0.10a</td>
<td>14.20±1.98f</td>
<td>85.80±2.23a</td>
</tr>
<tr>
<td>V₅₅</td>
<td>13.30±0.53a</td>
<td>5.64 ±0.04a</td>
<td>17.37±2.54d</td>
<td>82.63±2.44bc</td>
</tr>
<tr>
<td>V₆₄</td>
<td>13.20±0.62a</td>
<td>5.80±0.10a</td>
<td>16.90±2.30d</td>
<td>83.10±1.76b</td>
</tr>
<tr>
<td>V₆₆</td>
<td>13.75±0.33a</td>
<td>5.57±0.11a</td>
<td>20.86±2.36b</td>
<td>79.14±2.09d</td>
</tr>
<tr>
<td>V₆₉</td>
<td>13.50±0.33a</td>
<td>5.66±0.13a</td>
<td>16.62±2.09e</td>
<td>82.38±2.45bc</td>
</tr>
<tr>
<td>V₇₃</td>
<td>12.80±0.31a</td>
<td>5.43±0.31a</td>
<td>19.03±2.45c</td>
<td>80.97±2.78c</td>
</tr>
</tbody>
</table>

Data are represented as means±SEM (n=3). Mean with different letters in the same row are statistically different (p < 0.05) according to Duncan’s test.

Legend: In bold, highest values; underlined, the weakest. Amylose and Amylopectin content are based on dry mater.

Functional properties: Concerning the swelling power (SP) as function of temperature, all the starches showed the same profile of Gaussian curve, with a peak at 80 °C for variety V₆₆ and at 85 °C for all the other varieties (Figure 2A). However, the Duncan’s test revealed significant differences concerning the maximum of SP of the seven varieties of cassava starches (Figure 2B). In fact, variety V₅₅ recorded the most important SP (30.19±3.00) in opposition to V₄ (24.53±2.50 g/g). The others varieties registered intermediary values ranging from 25.98±2.63 g/g (V₅₄) to 28.26±2.30 g/g (V₆₄).

Figure 2: Cassava starch swelling power evolution as function to the temperature and to the varieties. Legend: A – Swelling power evolution, B – Maximum of swelling power
The solubility profile (continuous increasing) was the same for all the varieties (Figure 3A). Starch solubility went increasing from 50 to 95 °C with two phases. From 50 to 70 °C, starches solubility rose more slowly than it did from 70 to 95 °C, for all the varieties. However, the maximum of solubility (at 95 °C) significantly (F=1473.085; p=0.0001) varied from a starch to another (Figure3B). Hence, variety V55 topped the highest value (8.44±0.65 %) while V73 had the lowest (6.04±0.83 %) at the same temperature (95°C).

The water absorption capacity (WAC) also showed a significant (F=4.281; p=0.012) difference among starches varieties (Figure 4). Indeed, the highest value was registered by V55 (119.94±0.57 %) and the slightest by V4 (107.08±0.50 %) followed by V54 (118.24±0.46 %). The others varieties obtained intermediary values ranging from 108.04±1.40 % (V66) to 118.24±0.46 % (V54).

About gel syneresis at -15 and +4 °C, the starches registered 0.00 % the first day (J0), then the syneresis increases continuously from the first week to the fourth one (Figure 5A and 5B). Nevertheless, varieties V54, V64 and V73 kept their very low syneresis (0.01 %) constant during the same period at +4 °C. V54 showed the same behaviour at -15 °C. Concerning variety V55, comparatively to varieties V4, V68 and V69 which syneresis values increased more rapidly from J0 to the fourth week, its syneresis rose very slightly (0.00 to 2.10 %) at +4 °C during the same period and from J0 to the first week (0.00 to 1.39±0.05 %) at -15 °C.
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As far as gels clarity, all the varieties recorded their highest values at J₀, and then decreased continuously until the fourth week (Figure 6A). It is worth underlining the varieties V₅₄ and V₆₄, which presented the most important value of clarity at J₀ and kept this same importance from the first to the fourth week. Moreover, the Duncan’s test showed a significant (F=789.258; p=0.0001) difference between varieties clarity at J₀ (Figure 6B). In fact, variety V₅₄ topped 78.54±3.30 % when V₅₅ registered 38.51±3.05 %. The other values ranged from 41.73±4.70 % (V₆₉) to 76.27±6.72 % (V₆₄).

DISCUSSION

Nowadays the food and non-food industry is faced with the challenge of providing quality foods and non-food products. For a product like starch, which is used as a basic material in many industries, quality can only be defined with reference to the end use. This exigency is generally referred to its functional and physicochemical properties (Aviara et al., 2010; Garsetti et al., 2005). Hence, higher starch swelling power is better for its involvement in food as thickeners and binding agent and in non-food industries as adhesive and pastes glues (Sanni et al., 2005). Indeed the loss of free water due to enormously swollen granules occupying more space contributes to improve the texture and the consistency of the starch heating system (Berry, 1997; Aviara et al., 2010). Cassava starch varieties V₅₅, V₆₆ and V₇₃ had strong swelling power at relatively low temperatures (80 °C and 85 °C) comparatively to corn starch usually employed as a raw material for manufacturing glues or pastes adhesives at higher temperature (more than 100 °C), could then be recommended for that purpose (Sanni et al., 2005). It is important to note that these starch varieties contained not only the highest amount of large granules but also the most important amylose content. These physicochemical properties would justify their behaviour in water, comparatively to the other varieties (Massaux et al., 2006; Nuwamanya et al., 2011). Furthermore, these cassava varieties could be suitable for preparations, which require precise temperatures of cooking. For instance, the variety V₆₆ could be
recommended as a composite additive to potato flour or starch as well as texturing and binding agent in the preparation of sausages with giblets whose precooking is made at 80 °C (Hendrick et al., 1994). The high swelling power of varieties starches $V_{55}$, $V_{66}$ and $V_{73}$ could be explained, according to Singh et al. (2003) and Wickramashinge et al. (2009) by the amount of large (> 10 µm) granules (for the whole varieties) and amylose. Indeed, water swelling (in heating condition) would be as higher as amylose content would be higher. This situation is confirmed by the results of the present study though the previous varieties registered the highest values of water swelling and amylose. Moreover, the two phases of solubility of starch varieties would suggest and underline the relative strongest of granules intra molecular structure due to the high stability of starch amylopectin structure (Graffham et al., 2000) mostly in the starch varieties $V_{66}$, $V_{54}$ and $V_{69}$. It is not worth précising here that these varieties contained more amylopectin and small granules than the other did, what would suppose an important crystalline structure, and would confirm that small granules are more robust than large ones (Massaux et al., 2006). About starch granules size, it should be essential for the cosmetic and pharmaceutical industries since the starch with higher small granule amount, could be used as a dusting agent in cosmetic and pharmaceutical industries (Massaux et al. 2006). According to the same authors, large granules would be better in plywood industry for plastic film manufacturing, so that the films would be biodegradable. Hence, based on their granules sizes, starch varieties of $V_{4}$, $V_{54}$ and $V_{64}$ could be used in the cosmetic and pharmaceutical industries as dusting agent, while $V_{55}$, $V_{66}$ and $V_{73}$ could be involved in plastic films. It would be worth recalling that all the cassava starch varieties also present interesting (more than 100%) swelling capacity at ??? ambient temperature. In fact, the increase in swelling capacity is indicative of suitability of a starch being used as a disintegrant agent in pharmaceutical industry (Chowdary, 2011). This property is generally exploited in potatoes (72.2 to 89.6 %) and corn (82.1 % to 97.7 %) starches (Kim et al., 1995; Zuluaga et al., 2007). Hence, it would be better to exploit the whole cassava starch in the tropical pharmaceutical industries, to reduce importations costs of potato and corn starch. Starch gel Syneresis is a parameter that represents the volume of water separated from the formed gel under storage at room temperature, refrigeration and freezing. This parameter characterizes the starch stability to these temperatures (Salwa et al., 2010). The lowest syneresis (highest resistance to freeze-thawing cycle) is obtained by gels of varieties $V_{54}$, $V_{55}$, $V_{64}$ and $V_{73}$ with negligible water exuded under refrigeration and freezing. This shows a very stable behaviour of these gels under storage quite similar to those obtained with waxy starches (maize, rice and cassava) which improved freeze–thaw stability compared to normal starches (Sanchez et al., 2010). So, these cassava starch varieties with such performance could be proposed as a substituent to waxy starches or other modified starches, which generally result from genetics manipulations and are expensive. However, it is important to notice that, contrary to the results of Schmitz et al. (2006) and Davies et al. (2008), no significant relation appeared between amylose content and syneresis, since varieties $V_{54}$ and $V_{64}$ got at far less amylose than varieties $V_{55}$ and $V_{73}$ but all of them adopted the same syneresis profile. This may be due to the higher weight-average molecular weight of the amylose fraction in cassava starches (Susuki et al., 1985) delaying the retrogradation. The latest phenomena would also be evaluated by gel clarity which would denote the starch purity (Masamba et. al., 2001; Nuwamanya et al., 2011), allowing its utilization in food and non-food products without interfering with their color and shelf life. The high clarity of the whole starch and the relative stability (for four weeks) of varieties $V_{54}$ and $V_{64}$ gels at +4 °C would confirm the aptitude of cassava starch to being utilized for its bright clarity (Masamba et. al., 2001). This aptitude of clarity stability ($V_{54}$ and $V_{64}$) could be due to their lowest amylose contents. Hence, if all the starch varieties could be exploited in the textile industry, varieties $V_{54}$ and $V_{64}$, might be used in food industry in creams, syrup and other preparations where high clarity is required (Sanni et al., 2005; Jyothi et al., 2007). In addition to their functional properties, other properties such as moisture, pH and amylose content are also important as they dispose starch to typical utilization under specific exigencies. Hence, the moisture content of the seven cassava starch varieties, which was within recommended range (10 to 20 %) for starches (Soni et al., 1993), might allow them for commercialization. Moreover, the pH values obtained by these cassava varieties might permit their use in the pharmacy, cosmetic and food industry (Nnemeka et al., 2009) where required pH is 3 to 9.
CONCLUSION
The whole cassava starch varieties would be apt to being exploited in pharmaceutical industry as disintegrant for tablets because of their strong water absorption capacity which was at far superior to those of potato and corn starch. However and preferentially, varieties $V_4$, $V_{54}$ and $V_{64}$ might be chosen for their highest amount of small granules which would permit their employment as dusting agent not only for pills but also for some cosmetics. Varieties $V_{56}$, $V_{66}$ and $V_{73}$ could interest the chemical industrial for glue and detergent manufacturing due to their high swelling power/solubility induced by their high amount of both amylose and large granule. Considering the high proportion of large granules, they could also be exploited in plywood industry for biodegradable plastic films confection. Varieties $V_{54}$, $V_{55}$, $V_{66}$, and at least $V_{73}$ could be involved in preparation which might be stored at fridge temperature 4 °C for the whole starches and in freeze (-15 °C) for $V_{56}$, due to their low and relatively stable syneresis and their high clarity. These varieties could then occur as raw material in the food industry as, thickeners texturing and binding agents, they could be exploited in textile industry due to the high clarity.

REFERENCES


