



## Physicochemical and functional properties of starches from sorghum cultivated in the Sahara of Algeria

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### ABSTRACT

Pure starches were isolated from white and red sorghum cultivated in Tidikelt, a hyper arid region situated in south Algeria. Amylose content, X-ray pattern and rheological properties of starches were examined. The amylose content in white sorghum starch (27.1%) was slightly higher than that in red sorghum (24.8%). The swelling power and the solubility behavior of both starches were nearly similar below 65 °C. At higher temperatures, starch isolated from the white sorghum cultivar showed higher swelling power and lower solubility index than pigmented sorghum starch. The pasting properties of starches determined by RVA, Rapid Visco Analyser showed different viscosity peaks. Red sorghum starch had a higher value (4731 cP) than white sorghum starch (4093 cP). For both sorghum, X-ray diffractograms exhibit an A-type diffraction pattern, typical of cereal starches and the relative degrees of crystallinity were estimated at 22.72% and 28.91%, respectively, for local white and red sorghum starch. DSC analysis revealed that sorghum starches present higher temperatures at the peak (70.60 and 72.28 °C for white and red sorghum starches, respectively) and lower gelatinization enthalpies (9.087 and 8.270 J/g for white and red sorghum starches, respectively) than other cereal starches.

The results showed that physicochemical and functional properties of sorghum cultivar starches were influenced by the genotype and the environment.

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### 1. Introduction

Starch is the main reserve polysaccharide in plants. It is found as semi-crystalline granules of widely different shapes and sizes depending on the botanical source.

It is composed almost entirely of the polysaccharides amylose and amylopectin. The physical arrangement of amylose and amylopectin and the interaction between starch molecules and other food components determine the physicochemical and functional properties of starch. These properties affect the quality of starch-based products and are essential to determine potential applications of starch as its enzymatic transformation.

Algeria through the national programs of research has drawn up strategies to inventory the genetic resources of sorghum and de-

velop their crop production for its available added-value, giving grain quality and potential applications of their starch.

The approach was the determination of functionality and physicochemical properties of isolated starch from local sorghum cultivars for their competitive potential to satisfy specific technological and nutritional needs for target market and understand how these sorghum starch properties affect enzymatic hydrolysis.

Sorghum (*Sorghum bicolor* (L.) Moench) examined is cultivated in Tidikelt in the Sahara of Algeria bordering the Sahel countries such as Niger and Mali, known to be important sorghum producer countries (FAO & ICRISAT, 1997).

The particularity of these cultivars lies to their growth in hyper arid ecosystem where the maturity temperature is very high reaching a monthly mean of 45.2 °C and their irrigation using saline underground water. They are also known for their high drought resistance and capacity to grow using low-input agricultural fertilizers.

The most important sources of starch are cereals. Corn, wheat and potato starch has been extensively characterized but little interest has been given to the sorghum starches (Robyt, 1998) and even less to Algerian sorghum starch.

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It is the major storage form for carbohydrate in sorghum, making up about 60–80% of normal (non waxy) kernels (Abd Elmoneim, Burkhard, & Rita, 2004). The starch content is ranged between 60–77% and 55.6–75.2% according to Whistler and Pascall (1967) and Jambunathan (FAO & ICRISAT, 1997), respectively. For its processing and industrial utilization, further characterization is needed.

Data on Algerian sorghum starch properties were nonexistent so the aims of this study were isolation and partial characterization of starches from two predominant cultivars of white and red sorghum grown under hyper arid conditions of Sahara regions. Some physicochemical and functional properties such as amylose content, swelling power, solubility, crystallinity and pasting properties were determined and compared to properties of starches from other botanical sources and from sorghum cultivars growing in different environmental conditions. Genotypic and growth environment are known to influence starch characteristics (Rhymer, Ams, Malcolmson, Brown, & Duguid, 2005) therefore the characterization of sorghum starches issued from hyper arid ecosystem of Algerian Sahara and local genotypes is particularly relevant before considering their industrial utilization which is important to preserve the local sorghum varieties and enhance the sorghum cultivation and contribute to the socioeconomic development of these regions.

## 2. Materials and methods

### 2.1. Materials

Sorghum grain cultivars were grown in Tidikelt a hyper arid region situated in the Sahara of Algeria and known to have temperatures ranging from 7.8 to 45.2 °C and very low annual rainfall rate (16.9 mm) compared to the 700–800 mm in France, the most important sorghum producer in Europe. White and red sorghum were purchased from the 2004 harvest. The length/breadth ratio of sorghum kernel was 1.17 and 1.27 and the density (g/l) was  $692.8 \pm 0.6$  and  $736.5 \pm 0.2$ , respectively, for white and pigmented sorghum. The average weight of 1000 kernels was  $33.1 \pm 0.5$  g for white sorghum and  $27.7 \pm 0.1$  g for pigmented sorghum.

All most chemical products were purchased from sigma chemical Co (St. Louis, MO) and Merck certified grade.

### 2.2. Methods

#### 2.2.1. Starch isolation and purification

Starch was isolated from the two sorghum cultivars by alkali extraction as proposed by Pérez Sira and Amaiz (2004), Beta, Coke, Rooney, and Taylor (2000) and Beta and Coke (2001) with few modifications.

For white sorghum, 500 g of grains were steeped for a night in 0.25% NaOH solution. They were washed and then crushed using a warring blender (Eberbach, Michigan, USA) at full speed during 10 min. The suspensions were passed through sieves (355, 50  $\mu$ m). The filtrates were centrifuged (5000 rpm during 20 min). The layer of residual proteins, fibers and lipids was scraped each time. The operation was repeated four times until disappearance of the sludge layer. The starch was centrifuged in pure ethanol and finally in distilled water. The extract was then dried overnight at 40 °C.

For red sorghum, the grains were soaked in 467 ml of 5.25% NaOCl solution and 50 g of KOH and heated at 60 °C during 7 min under agitation. The starch was then isolated as described earlier but the mixture was cooled at room temperature and the grains were washed until the red color disappeared.

#### 2.2.2. Starch content

The starch contents were determined polarimetrically by and Ewers method (ISO 10520:1997). This method includes the determination of the optical activity of soluble sugars in 40% ethanol and of the solution obtained after treatment of the sample by the diluted hydrochloric acid at high temperature, defecation and filtration.

#### 2.2.3. Starch color

The color of the extracted starches was determined using a spectrophotometer Miniscan of Hunterlab (Virginia, USA). Standard white and black plates are used beforehand to calibrate the apparatus. This measurement is quantified by Hunterlab (1958) system given by **L**, **a**, and **b** parameters.

#### 2.2.4. Amylose content

Apparent amylose content was estimated a modified iodometric method of Morrison and Laignelet (1983). A weight of 50 mg of the starch (db) were dispersed in 5 ml of urea-dimethylsulfoxide (1:9 v/v). The starch suspension in screw-capped tubes was vortexed and placed in a water bath at 95 °C for 60 min under agitation until complete solubilization and cooled at room temperature. A volume of 100  $\mu$ l of the soluble starch solution is added to 9.7 ml of distilled water and 200  $\mu$ l of iodine solution (0.5 g KI and 0.05 g I<sub>2</sub> in 25 ml of distilled water). The blend was immediately mixed and placed in the darkness during 20 min. The absorbance of the formed blue complex was then measured at 635 nm using a Shimadzu spectrophotometer UV-2401 (Kyoto, Japan). Amylose content was calculated from a standard curve prepared using blends of pure potato amylose and pure maize amylopectin from ICN biomedical Inc. (OHIO, USA). Three replicate samples were used in this analysis.

#### 2.2.5. Swelling power and solubility index

The estimation of swelling power SP and water solubility index WSI was done according to the Radosta, Kettlitz, Schierbaum, Reh-bucke, and Gernat (1991) and Tang, Mitsunaga, and Kawamura (2004) method with some modifications. A suspension of 0.1 g of starch and 6 ml of distilled water was heated in the range 55–95 °C in a water bath for 30 min. The suspension was then cooled rapidly at room temperature and centrifuged (8000 rpm, 20 min).

Water solubility index WSI is reported as the ratio of dry mater supernatant to dry starch sample whereas swelling power SP is reported as the ratio of swelling starch granules sediment to dry starch. Three replicate samples were used in this determination.

#### 2.2.6. Rapid Visco Analyzer (RVA)

RVA (Newport scientific Pty. Ltd., Warriewood, Australia) was employed to measure the pasting properties of starch ( $3 \pm 0.01$  g db, 28 g total weight). Experiments were performed using the ICC-Draft-Standard method (1995).

The temperature-time conditions included a heating step from 50 °C to 95 °C for 10 min, a holding phase at 95 °C for 10 min, a cooling step from 95 °C to 50 °C for 10 min and a holding phase at 50 °C for 5 min. The speed was 860 rpm for the first 10 s, then 160 rpm for the remainder of analysis. Peak viscosity, final viscosity, minimal viscosity, breakdown, setback, peak time, and pasting temperature of isolated starches were obtained from pasting curves. Viscosities of setback and breakdown were calculated.

#### 2.2.7. X-ray diffractometry and relative crystallinity

The analysis was carried out using an X-rays diffractometer, model BRUKER D8 ADVANCE (Karlshuhe, Germany) 40 kV, 40 mA, 1600 W with Bragg Brentano configuration assembly to specific beam parallel mirror of GOEBEL on the outlet side of the tube radiation and equipped with copper anticathode wavelength

$\text{CuK}\alpha = 154,056 \text{ \AA}$ , type 2Th/Th, step  $0.050^\circ$ , step time 6 s, temperature  $25^\circ\text{C}$ . The diffracted intensity was measured from 5 at  $35^\circ$  as a function of 2Th. The relative degree of crystallinity was estimated by determining the ratio of the area, in counts, under five major diffraction peaks to the total area under the curve between  $8^\circ$  and  $35^\circ$  2Th according to the Hayakawa method (Chakraborty et al., 2004). The areas were determined by weighting the two sections. The areas were calculated by comparison of their weights with the weight of known areas prepared using the same paper (Köksel, Sahbaz, & Özboy, 1993).

### 2.2.8. Differential scanning calorimetry

The thermal behavior of the starch samples is evaluated using an analyzer enthalpy differential DSC 2920 (TA Instruments, New Castle DE, USA). The apparatus is calibrated in temperature and enthalpy with eicosane ( $T_o = 36.8^\circ\text{C}$  and  $\Delta H = 247.4 \text{ J/g}$ ) and indium ( $T_o = 156.6^\circ\text{C}$  and  $\Delta H = 28.71 \text{ J/g}$ ). Calorimetric measurements are led on samples of 5 mg (db) loaded into  $10 \mu\text{l}$  of distilled water. The samples were hermetically sealed in aluminum capsule and allowed to stand 1 h at room temperature. The suspensions were then heated in DSC at a rate of  $5^\circ\text{C/min}$  from 10 to  $120^\circ\text{C}$ . An empty aluminum pan is used as reference. Temperature of onset ( $T_o$ ), peak ( $T_p$ ), and conclusion ( $T_c$ ) of gelatinization and endothermic enthalpy ( $\Delta H$ ) are given starting from the thermograms.

## 3. Results and discussion

### 3.1. Isolated starch

Starch content in sorghum kernels of the white cultivar ( $66.8 \pm 0.3\%$ ) was higher than the red one ( $65.3 \pm 0.1\%$ ). The two starch cultivar contents were inferior to the mean value of  $69.5\%$  given by Jambunathan ([www.unu.edu/unupress/food](http://www.unu.edu/unupress/food)). This observation supposes that starch content was reduced by elevated maturation temperature as reported by Matsuki, Yasui, Kohyama, and Sasaki (2003). The analysis on 160 sorghum genotypes showed that starch was comprised between  $55.6\%$  and  $75.2\%$ .

The starch isolation methods from sorghum cultivars still present some difficulties especially in proteins separation stages. The role of sorghum endosperm matrix protein and cell wall components in limiting extraction is a research focus; however the starch purity was high  $93.3\%$  and  $94.1\%$  for red and white sorghum, respectively.

### 3.2. Starch color

The data of color parameters are shown in Table 1. The extracted starches had a high degree of whiteness; the  $L$  values were  $92.91$  and  $91.06$ , respectively, for white and red sorghum with low  $a$  and  $b$  values confirming the high purity of isolated starches; Wang, White, Pollak, and Jane (1993) estimated that a value higher than  $90$  gives a satisfactory whiteness for the starch purity. Pérez Sira and Amaiz (2004) using similar process of steeping, obtained a higher value for the starch isolated from white sorghum ( $91.3$ ) but lower for the starch of pigmented sorghum ( $78.4$ ). The values of  $b$  were  $3.58$  and  $4.15$ , respectively, for white sorghum and red sorghum starches; they express a tendency of color towards yel-

low. These values were lower than those found by Pérez Sira and Amaiz (2004) which were  $10.1$  for white sorghum starch and  $16.5$  for the pigmented sorghum starch, leading to suppose that the local varieties had less yellow pigment and that the residual protein and lipid content was weaker.

The starch extracted from the pigmented sorghum had a negative value for  $a$  after treatment with sodium hypochlorite showing that the red color disappeared by tannins extraction as result of the effect of the bleach treatment. The high degree of whiteness of the isolated starch can provide many opportunities of food and industrial applications.

### 3.3. Amylose content

The amylose content of starches isolated from the two sorghum cultivars showed a significant difference. The highest amylose content of  $27.1\%$  was observed for white sorghum starch. Red sorghum starches contained  $24.8\%$  of amylose. The sorghum starches analyzed were considered as normal types since the yield ranged from  $21\%$  to  $34\%$  (Beta et al., 2000). Similar values of amylose content have been reported for maize and wheat ( $28\%$ ) (FAO, 1995; Jenkins & Donald, 1998). For Zimbabwe sorghum and three sorghum genotypes growing in Indiana (USA), the amylose content was ranged, respectively, between  $20.9$ – $30.2\%$  and  $19.2$ – $22.4\%$  (Beta et al., 2001; Benmoussa, Suhendra, Aboubacar, & Hamaker, 2006). The results found using 160 genotypes where the mean value of  $26.9\%$  (FAO, 1995) was given showed that the amylose content of local white sorghum starch was not markedly affected by high maturity temperature in opposition to the local pigmented sorghum starch.

The amylopectin content and ratio were  $72.9\%$ ,  $0.4$  for white sorghum and  $75.2\%$ ,  $0.3$  for pigmented sorghum. The amylose content has been reported to vary with the botanical source of the starch and is affected by the climatic and soil conditions during grain development (Singh, Kaur, & Singh Sandhu, 2006).

### 3.4. Swelling power (SP) and water solubility index (WSI)

The SP and WSI at different temperatures ranging between  $55$  and  $95^\circ\text{C}$  are, respectively, presented in Figs. 1 and 2.

The SP and WSI of both starches increased with increasing of temperature. At temperatures lower than  $65^\circ\text{C}$ , the SP of the white and red sorghum starches were similar whereas above this temperature, the SP of pigmented sorghum starch was higher than that of white sorghum. For the white sorghum starch, the variation was nearly linear. The difference was caused by the higher amylopectin content. Indeed, swelling behavior of cereal starches is primary due to the property of their amylopectin content, amylose acts as

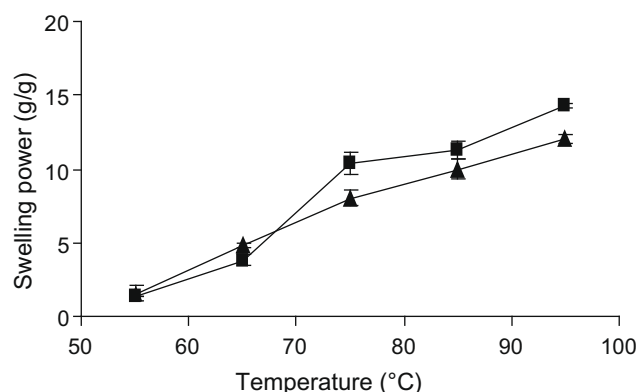


Fig. 1. Swelling patterns of native white ▲ and red ■ sorghum starches.

Table 1  
Color parameters of white and red sorghum starches.

Color parameters	White sorghum starch	Red sorghum starch
<b>L</b>	$92.91 \pm 0.00$	$91.06 \pm 0.04$
<b>a</b>	$-0.26 \pm 0.00$	$-0.48 \pm 0.02$
<b>b</b>	$3.58 \pm 0.03$	$4.15 \pm 0.00$

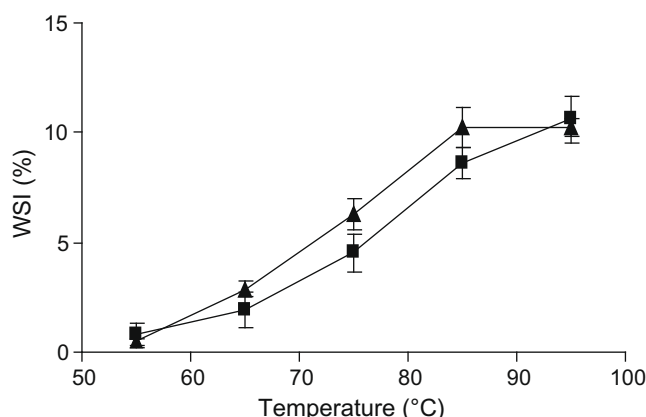


Fig. 2. Water solubility index patterns of native white  $\blacktriangle$  and red  $\blacksquare$  sorghum starches.

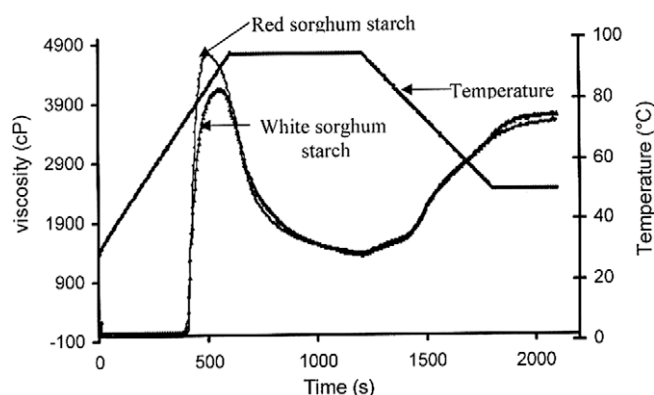


Fig. 3. RVA-viscograms of native white and red sorghum starches.

inhibitor of swelling, especially in the presence of lipids (Tester & Morrison, 1990).

The WSI variation profiles for both starches were similar. It levelled off at temperature between 85 and 95 °C. According to the results of Radosta et al. (1991), the solubility of corn and potato starches, was very different and it was constant between 60 and 85 °C followed by a fast increase. The potato starch had a higher swelling power and solubility than wheat, rice and corn starch (Singh et al., 2006), the solubility index is the highest 25% at 95 °C (Radosta et al., 1991). Vansteelandt and Delcour (1999) obtained a maximum swelling power and a solubility index of 11.3 g/g and 13.3% for wheat starch.

### 3.5. Pasting properties

The pasting properties of sorghum starches using a Rapid Visco Analyzer RVA are presented in Fig. 3 and Table 2.

Both sorghum starches had the same thermal behavior except at the peak, the pigmented sorghum starch viscogram showed the highest viscosity value at the peak (4731 cP) and the same minimal and final viscosity data as shown in Table 2. Beta et al. (2000)

found, for the four varieties of sorghum cultivated in Zimbabwe, lower peak times (300–450 s) and lower peak viscosities than those obtained for the starches isolated from the two local sorghum cultivars. The genotype and the environmental conditions can explain these differences.

Compared to viscosities of sorghum starches, the potato starches showed a similar behavior. However, they presented at the peak a higher viscosity than wheat starch where the peak is nearly absent; on the other hand the breakdown viscosity was then quite higher for the starches of sorghum, millet and potato (Roudot, 2002).

### 3.6. X-ray diffraction pattern and relative crystallinity

White sorghum and red sorghum starch showed an A-type diffraction pattern, typical of cereal starches. The diffractograms had the same profiles (Figs. 4 and 5). The area under the diffraction angle 2 $\theta$  in the range 13.0–25.0° indicates the crystallinity of starches. The peaks for the white and pigmented sorghum starches appeared at 15°; 17°; 18°; 23° (2 $\theta$ ). The same peaks were found for Korean raw waxy sorghum starch with the exception of a peak at 11.5 (Shin et al., 2004).

The crystallinity degrees were 22.72% and 28.91%, respectively, for white and red sorghum starch. Pigmented starch exhibited higher crystallinity than white sorghum starch and wheat starches had lower crystallinity. Chakraborty et al. (2004) found that the degree of crystallinity of 11 wheat genotypes ranged between 10.1–15.3% and D. opposite Thunb cultivars presented a higher values ranged from 34.3% to 43.1% (Shujun et al., 2008). Degree of crystallinity is reported to be one of several factors that determine starch digestibility in animals (Benmoussa et al., 2006). The degree of crystallinity perfection according to Tester and Morison is impacted by the molecular structure of amylopectin (unit chain length, extent of branching, molecular weight, and polydispersity) (Bao, 2004) however, no experimental proof exists to exclude the presence of amylose in the crystalline regions Amylose molecule can crystallize under various conditions: retrogradation or preparation of crystal novo of amylose A, B and V (Buléon, Colonna, & Leloup, 1990).

### 3.7. Gelatinization characteristics

The gelatinization transition temperature [ $T_o$  (onset),  $T_p$  (peak) and  $T_c$  (conclusion)] and the enthalpy of gelatinization  $\Delta H$  of white and red sorghum starches are presented in Table 3.

Significant differences of gelatinization temperature and enthalpy between white and pigmented sorghum starches were obtained. The red sorghum starch showed a higher gelatinization temperature than white sorghum starch however the enthalpy of gelatinization was weaker.

Compared to results obtained by Jenkins and Donald (1998), Jane et al. (1999), Singh, Singh, Kaur, Sodhi, and Gill (2003) for other starches of other botanical sources as potato, corn, rice and wheat, local sorghum starch showed higher temperature of onset and peak and lower gelatinization enthalpy.

Sorghum starch gelatinization temperature ranges of 67–73 °C have been reported for sorghum grown in South Africa and 71–81 °C for sorghum grown in India (Taylor, Schober, & Bean, 2006)

Table 2  
Pasting properties of native starch from white and red sorghum cultivars.

Starch source	Peak viscosity (cP)	Minimum viscosity (cP)	Breakdown (cP)	Final viscosity (cP)	Setback (cP)	Peak time (min)	Pasting temperature (°C)
White sorghum	4093 $\pm$ 9.9	1330 $\pm$ 15.5	2763	3718 $\pm$ 14.8	2388 $\pm$ 30.4	9.6 $\pm$ 0.6	73.8 $\pm$ 0.4
Red sorghum	4731 $\pm$ 36.5	1372 $\pm$ 42.4	3359 $\pm$ 94.0	3593 $\pm$ 43.1	2221 $\pm$ 27.7	8.5 $\pm$ 0.0	74.7 $\pm$ 0.6



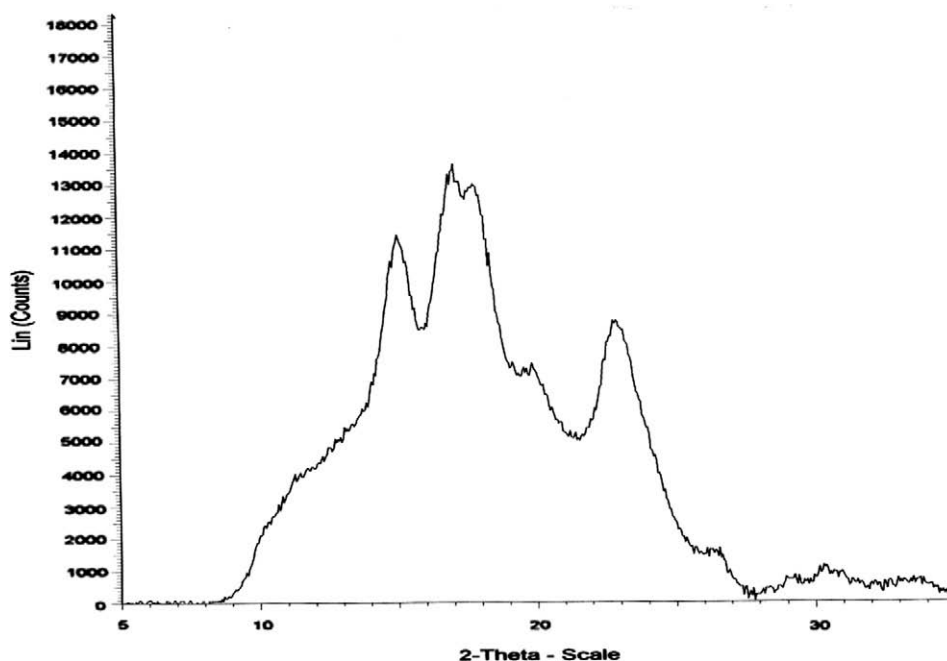


Fig. 4. X-ray diffractogram of native white sorghum starch.

and 73.2 for Korean waxy sorghum (Choi, Kim, & Shin, 2004). High temperature gelatinization can be an indication of the higher stability of starch crystallites in starch molecules (Moorthy, 2002). Starch gelatinization temperature is influenced by many factors; in particular the lengths of the various chains in the amylopectin molecule with gelatinization temperature increasing with longer chain length (Taylor et al., 2006). Moorthy (2002) reported that gelatinization enthalpy depends on number of factors such as crystallinity intermolecular bonding, and it also depends on genetic and environmental factors, so it can be deduced that hyper arid environment has affected gelatinization properties of sorghum starch by increasing peak temperature. Similar observation was done previously for wheat and other species but gelatinization enthalpy was found increasing (Matsuki et al., 2003).

#### 4. Conclusion

Starches were isolated from white and pigmented sorghum kernels with a high purity and great clearness in spite of the difficult extraction.

The sorghum starches of two cultivars grown under similar growth location and hyper arid ecosystem of Algerian Sahara were normal type and showed significant differences in physicochemical properties, which ultimately affect the functional properties of the isolated starches.

White and red sorghum starches showed a high viscosity peaks. The variations on properties between the two cultivar starches show the effects of genotype on starch properties and end-product quality as reported by many researchers. The effects were reported

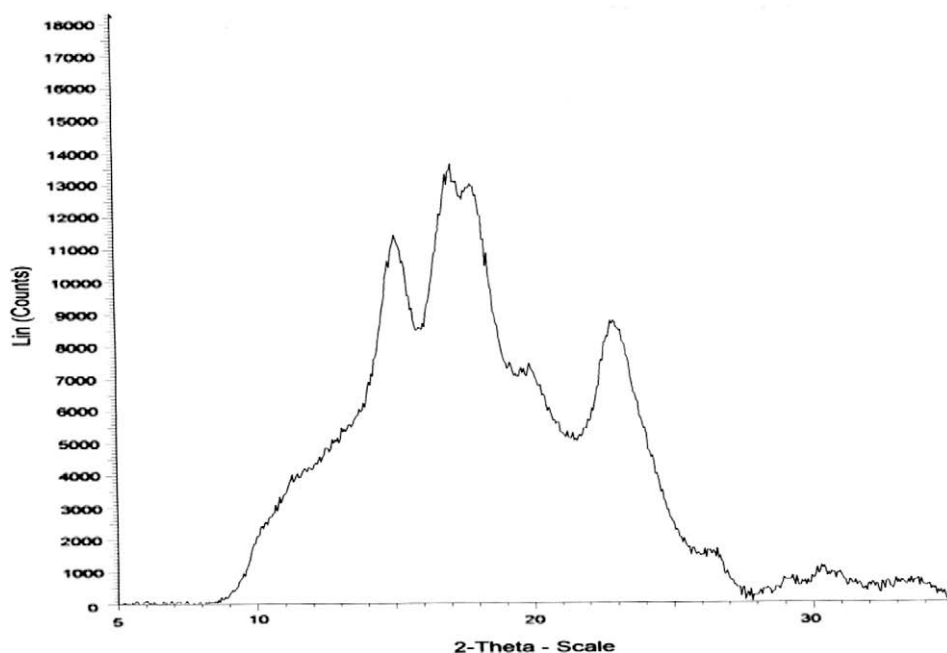


Fig. 5. X-ray diffractogram of native red sorghum starch.

**Table 3**

Gelatinization characteristics of native white and red sorghum starches.

Starch source	$T_o$ (°C)	$T_p$ (°C)	$T_c$ (°C)	$\Delta H$ (J/g)
White sorghum	66.60 ± 0.18	70.60 ± 0.27	76.78 ± 0.06	9.087 ± 0.011
Red sorghum	68.43 ± 0.06	72.29 ± 0.08	77.09 ± 0.04	8.270 ± 0.032

$T_o$ ,  $T_p$  and  $T_c$  indicate the temperature of the onset, peak and conclusion of gelatinization,  $\Delta H$  enthalpy of gelatinization.

earlier for other botanical source starches. The local sorghum starches characteristics data found were within the values interval given for sorghum cultivated in other countries in Africa, India and America. Compared to starch of other botanical sources, the results show that for white sorghum, amylose content is slightly different than maize and wheat however for both sorghum starches, the solubility, and swelling power are higher than those found for wheat, rice and corn starch. The crystallinity degree and viscosity are also higher than wheat starch and the thermal behavior is similar to potato starch.

The NaOCl addition was effective for the pigmented sorghum starch bleaching and had not affected on the principal physico-chemical and functional properties examined (size and shape of granule starches, viscosity, swelling, solubility).

The local sorghum starch studied exhibited very interesting functional properties suitable to be used in food products as thickening and gelling agent for their higher values of viscosity. Significant effect of hyper arid environmental on sorghum starch properties was observed especially by reducing starch granule size and increasing gelatinization temperature.

More research is required to understand the relationship between characteristics, industrial applications, and end-product quality and to extend the investigations on starch functional properties for other sorghum cultivars over the Sahara regions of Algeria. This study suggest further research is needed on amylopectin and amylose fine structure in order to contribute to the understanding of structural and functional property relationships and the environmental and genetic effect on starch properties.

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