Variability in starch physicochemical and functional properties of yam (*Dioscorea* sp) cultivated in Ivory Coast

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Abstract: Native starches were extracted from 21 cultivars of four yam species representative of the yam population of Ivory Coast. They were first characterized for their proximate composition, starch physico-chemical properties (amylose content, particle size distribution, crystallinity, thermal properties and intrinsic viscosity). Some functional properties (swelling, solubility and pasting behaviour and paste clarity) were then determined. Analysis of variance and principal component analysis showed that three homogenous groups could be distinguished, mainly based on starch physico-chemical properties. The first group contained all yam starches of the D alata and the D cayenensis-rotundata complex species. It was characterized by a large diameter grain (approximately 25 µm), a high amylose content (around 25% db), a high intrinsic viscosity (mean of 190 cm³ g⁻¹), and a high apparent viscosity and clarity of the paste. The second group contained the D esculenta varieties, characterized by a small granule size (diameter $6\,\mu m$), a low intrinsic viscosity (121 cm 3 g $^{-1}$), a high gelatinization enthalpy change (19 J g $^{-1}$) and a low paste viscosity. The D dumetorum sample differed from the D esculenta group by having a pure A-type crystalline form and an opaque paste. A multiple regression showed that the volume fraction of the dispersed phase and native granule size (or amylose content) could account for close to 80% of the variability of paste apparent viscosity. Gel clarity appeared mainly linked to granule size, small granules from D dumetorum and D esculenta giving the most opaque gels.

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Keywords: yam; Dioscorea sp; starch; physicochemical properties; functional properties; paste clarity

INTRODUCTION

Yams are important root crops cultivated in the humid and sub-humid tropics. They belong to the Dioscorea genus, which includes some 600 species. Coursey¹ and Léon² mention four distinct centres of origin for the edible yam: firstly the Indochina Peninsula, where the greater or water yam (D alata), the lesser yam (D esculenta), the aerial or potato yam (D bulbifera), the intoxicating yam (D hispida), D nummularia and D pentaphylla are grown; secondly South China, where the more temperate-adapted species, the Chinese yam (D opposita) and D japonica, originated; thirdly the Caribbean area, the origin of the cush-cush yam (D trifida), with a subsidiary centre in South America; and finally a location ranging from the West African forest belt to the savannah, the centre of origin of the yellow yam (D cayenensis), the white or guinea yam (D rotundata), the bitter yam (D dumetorum) and the aerial or potato yam (D bulbifera). Recent studies have shown that D cayenensis and D rotundata are part of the same botanical complex, properly named the D cayenensis-rotundata complex.^{3,4}

World vam production amounts to 38×10^6 tonnes per year. The bulk of edible yam production comes from the 'yam zone' in West Africa, which extends from Nigeria to Ivory Coast and accounts for about 91% of world production.⁵ In these countries, yam is of major importance as a staple food and consumption is around 100 kg per person per year. Despite the high levels of yam production noted in the above countries and the high starch content of the yam (70-80% dry basis (db)),^{6,7} this starch resource is not used for starch production on an industrial level. Within the starch industry, which represents a world market of between 33 and 36 million tonnes, potato in temperate climates and cassava and sweet potato in tropical areas are the only roots and tubers undergoing real industrial development for starch production because of their specific physicochemical and functional properties.⁸

Yam starch has received little attention from researchers in terms of its industrial potential. Its physicochemical and nutritional properties have been investigated by several teams in relation to yams produced in Ghana, 1,9-11 Cameroon 6,12,13

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and Nigeria. $^{14-16}$ These studies also compared such functional properties as swelling and solubility patterns and the rheological and gelling properties of starches extracted from one or several *Dioscorea* species. Major variability was observed in yam starch characteristics such as amylose content (from 10 to 25% db) or granule size (from several to $45\,\mu m$), but inter-comparisons between the different sets of data are not possible as the methodologies often differ.

In Ivory Coast, the third largest yam producer in the world, the traditional cultivars of the Dioscorea cayenensis-rotundata complex have been listed, described¹⁷ and classified,¹⁸ but there have, up to now, been few studies of the physicochemical and functional properties of the vam starches of the varieties cultivated there. The present study examines a large set of physicochemical and functional properties of 21 types of native starches representative of the major vam species cultivated in Côte d'Ivoire (Dioscorea alata, the D cayenensis-rotundata complex, D dumetorum and D esculenta). This will help to propose new industrial ways to utilize and add value to this unconventional starch source. In addition to presenting an exhaustive comparison of these cultivars, the study aims to determine the physicochemical basis of starch functional properties: this will be emphasized in the light of the great variability of the starches concerned without lipid interactions as for cereal starches. The present study reports the first step of this programme; several further publications based on the same material will deal with the evaluation of various technological and functional properties and the characterization of macromolecular starch structure.

MATERIALS AND METHODS

Raw materials

Twenty-one native starches were extracted from four species of yam tubers: five cultivars (cv) of Dioscorea alata ('Bodo', 'Daminangba', 'Florido', 'Soglan' and 'Suidié'), 11 cultivars of the Dioscorea cayenensis-rotundata complex ('Assawa', 'Assobayérè', 'Frou', 'Kangba', 'Kouba', 'Kpassadjo', 'Kpokpokpo', 'Kponan', 'Krenglè', 'Lokpa' and 'Sopèrè'), one cultivar of Dioscorea dumetorum ('Dumetorum') and a four-clone selection of Dioscorea esculenta ('Esculenta 154', 'Esculenta 5', 'Esculenta 6' and 'Esculenta 7'). The raw material was obtained from the experimental farm of the Genetics Department (FAST) of the University of Abidjan (in the forest zone) or (in the case of Assobayérè, Kangba, Kpassadjo, Kpokpokpo, Lokpa, Sopèrè, Dumetorum and Esculenta 154) from the National Institute of Agronomical Research (IDESSA) in Bouaké, about 400 km north of Abidjan in the centre of Ivory Coast (in the Savanna zone). The tubers were harvested 10 months after planting and stored at ambient temperature before starch extraction.

Methods

Starch isolation

The starches were purified according to the procedure previously described by Amani. Yam tubers were peeled and immediately cut into small pieces. The freshly cut pieces were suspended in distilled water containing 0.1% w/v sodium metabisulphite. The material was crushed in a Warring blender (Moulinex, Lyon, France) and suspended in a large excess of distilled water containing 4% NaCl. The slurry was filtered through a $100\,\mu\mathrm{m}$ sieve. The starch was allowed to settle and the supernatant decanted off. The starch granules of *D dumetorum* were centrifuged at $2660 \times g$ for $15\,\mathrm{min}$. This process was repeated four times and the recovered white prime starch was then oven-dried at $45\,^{\circ}\mathrm{C}$.

Proximal composition 2 Moisture content was determined by oven-drying for 2 h at 130°C, lipid content by hexane extraction and ash content by incineration at 550°C using the AOAC method.²⁰ Crude protein content was calculated from the nitrogen content $(N \times 6.25)$ obtained by the Kjeldhal method. Total cellulose was determined by the BIPEA method.²¹

Particle size analysis

Particle size analysis was performed using a low-angle laser light-scattering technique employing a Coulter LS 230 laser granulometer (Coulter Corporation, Miami, FL, USA). About 10% w/v of sample was suspended in ethanol. The sample was placed in an ultrasonic bath for 30 s for preliminary agitation to disperse any agglomerates. The particle size parameters were read after 90 s of agitation. Data on starch granule distribution were computed (mean, median and perpendicular bisector in percentage of volume).

Scanning electron microscopy (SEM)

Starch samples were freeze-dried, then gold coated with an ion sputtering device (Jeol JFC 1100; Jeol Ltd, Akishima, Japan) and examined under a scanning electron microscope (Jeol JSM 840A; Jeol Ltd, Akishima, Japan) working at an accelerating voltage of 10 keV.

Differential Scanning Calorimetry (DSC)

DSC analyses were performed on a Perkin Elmer DSC 7 device (Perkin Elmer, Norwalk, CT, USA) using sealed stainless steel pans. The sample pan (10-11 mg) of starch and $50 \,\mu\text{l}$ of lyso-phospholipid 2% w/v in water) and the reference pan $(50 \,\mu\text{l})$ of ultrapure water) were heated from 25 to $160\,^{\circ}\text{C}$ at a scanning rate of $10\,^{\circ}\text{C}$ min $^{-1}$, held for 2 min at $160\,^{\circ}\text{C}$ and cooled to $60\,^{\circ}\text{C}$ at $10\,^{\circ}\text{C}$ min $^{-1}$. The gelatinization enthalpy (ΔH) and the gelatinization onset temperature (GT) of each sample were then determined on the thermograms. Amylose content was measured from the energy of amylose–lyso-phospholipid complex formation using a differential scanning calorimeter. All analyses were performed in duplicate and mean values were calculated.

Intrinsic viscosity

Intrinsic viscosity (η) was measured at 35 °C in 0.2 M KOH solution using an Ubbelohde viscometer, according to the procedure described by Mestres and Rouau.²³ The samples (50–60 mg db) were solubilized in freshly prepared and nitrogen-deoxygenated KOH (1.0 M, 2 cm³) under constant agitation at 20 °C for 6 days. An 8 cm³ aliquot of ultrapure water was then added and the samples agitated for 1 day. The samples were filtered through a 5 μ m sieve using a Millipore Filter (Durapore Membrane filter, Ireland) prior to determination of intrinsic viscosity by extrapolation to zero concentration of reduced and inherent viscosities.

X-ray diffraction measurements

Starches were observed respectively in the dry state and after conditioning at a water activity of 0.9 (over a saturated salt solution of barium chloride at 25 °C) up to sorption equilibrium. Samples (15–20 mg) were sealed between two aluminium foils to prevent any significant change in water content during measurement. Diffraction diagrams were recorded using a transmission technique with a XRG 3000 X-ray generator (Inel Orléans, France) operating at 40 kV and 30 mA. CuK α 1 radiation (λ = 0.15405 nm) was selected using a quartz monochromator. A curved position-sensitive detector (CPS120, Inel) was used to monitor the diffracted intensities, with a 2 h exposure period.

Relative crystallinity was determined on hydrated samples (16% < water content < 18% on a dry basis) after all recorded diagrams had been brought to the same scale by normalizing the total scattering between 3 and 30° (2 θ). It is assumed that total scattering between two 2θ limits, which are usually chosen on either side of the amorphous halo, is independent of the crystallinity and proportional to the sample amount involved in the scattering.²⁴ The respective amounts of A- and B-types were determined using a multilinear regression, assuming that the experimental normalized diagrams are a linear combination of elementary patterns of amorphous, A- and B-types, following a method derived from Gernat et al.25 The normalized diffraction contributions of purely crystalline A and B polymorphs were obtained from highly crystalline spherolitic crystals of low DP amylose while dry extruded starch was used as the amorphous standard.

Pasting properties

A 4% db dispersion (28 g) of starch was placed in a Rapid Visco Analyzer, model 3D (Newport Scientific, Narrabeen, Australia). Viscosity was recorded in accordance with the following temperature profile: holding at 30 °C for 1 min, heating from 30 to 90 °C at 6 °C min⁻¹, holding at 90 °C for 5 min, and then cooling to 50 °C at 6 °C min⁻¹ with continuous stirring at 160 rpm. Three parameters were measured: pasting temperature (PT), viscosity at the start of the 90 °C plateau (12 min, V_{90}) and final viscosity at 50 °C (23 min, $V_{\rm f}$).

Swelling power, solubility and dispersed volume fraction measurements

Swelling power and solubility patterns were determined using 4% db (w/w) starch dispersions. The Rapid Visco Analyzer (RVA) was used to prepare the pastes as described above, but the experiment was stopped either after 12 min (1 min after the start of the 90 °C plateau) or after 23 min at the end of experiment (at 50 °C). The paste was immediately transferred to a 50 cm³ centrifuge tube. After centrifugation for 5 min at $5000 \times g$ at 25 °C, the supernatant and sediment were collected and weighed (Wsu and Wse, respectively). They were then dried at 100 °C for 24 h (Wsu) and 48 h (Wse) and their dry matter mass was determined (Dsu and Dse, respectively). As in the study of Mestres et al,26 three parameters were calculated: concentration of solubilized material in the supernatant (ie solubility), swelling power and dispersed phase volume fraction (Φ) , according to formulas (1), (2) and (3), respectively:

solubility (g dm⁻³) =
$$Dsu/(Wsu - Dsu)$$
 (1)

swelling power
$$(g g^{-1}) = (Wse - Dse)/Dse$$
 (2)

$$\Phi = (27.625 - (\text{Wsu} - \text{Dsu}))/27.625 \tag{3}$$

where 27.625 is the calculated total volume (cm 3) of the paste, assuming the specific density of the starch to be $1.5 \,\mathrm{g}\,\mathrm{cm}^3$.

Viscosity measurement

Twenty-eight grams of 4% (db, w/w, pH 7) paste was prepared using an RVA. The experiment was stopped after 12 min in accordance with the profile previously described in the previous section. The paste was transferred to a Haake Viscotester VT-550 (Thermoelectron Corp, Waltham, USA), using the NV module. Gel viscosity was measured at 30 °C at a shear rate of 140 s⁻¹.

Determination of paste clarity

The procedure of Craig et al^{27} and Zheng et al^{28} was used to determine starch paste clarity. A 1% db aqueous dispersion of starch was boiled at 100 °C for 30 min under constant stirring. Percentage transmittance was measured after cooling to 30 °C at 620 nm.

Statistical analyses

One-way analysis of variance (ANOVA) and principal components analysis (PCA) were conducted with the help of Statgraphics software (Version 2.1). Multiple regressions were performed using Statitcf (Boigneville, France).

RESULTS

Starch chemical characteristics

Chemical analysis of the starch extracted from the different yam tubers generally showed very low (<0.3% db) non-starchy residual component contents

(ie ash, cellulose, proteins and lipids; Table 1). The extraction technique used gave yam starch samples with a mean purity of 99%.

Amylose content varied significantly with the species (Table 2), and two groups of starches could be distinguished. Those with a high amylose content (around 26% db), grouping together the starches of *D alata* and the *D cayenensis-rotundata* complex, and those with a low amylose content (16% db), consisting of the starches of *D esculenta and D dumetorum*. Each group was quite homogeneous, with an internal standard deviation (standard deviation of the residual, SDR) of 1.0.

Morphological and physicochemical properties

Starch grain size and shape

Analysis of variance distinguished three types of yam starches according to their mean volume particle size. The starch granules from the D cayenensisrotundata complex cultivars had the largest mean diameter (26.4 μ m, Table 2) and were flattened ovoid (Fig 1(a)). Those of the D alata cultivars formed the second group, with a mean diameter of 21.5 μ m, and were more or less rounded ovoid granules (Fig 1(b)). D esculenta and D dumetorum had the smallest granules, less than 7μ m in diameter, with a polygonal shape (Figs 1(c) (d)). It should be noted that it was impossible to establish the distribution curve for D dumetorum starch by light-scattering because of aggregate formation, thus its mean granule size was evaluated by electron microscopy.

Particle size distribution was quite large within each sample, and particularly so in the case of starches from the *D cayenensis-rotundata* complex cultivars; for 'Daminangba', for instance, starch granule size

distribution ranged from 10 to 60 µm (Fig 2). Granule size was also quite heterogeneous within each group (SDR of 3.1), with some cultivars having granule sizes typical of a different species group. 'Florido' (*D alata*), for instance, had a large starch granule size typical of *D cayenensis-rotundata* complex cultivars, while the opposite was observed with 'Kouba'.

Crystallinity and crystalline type

Important differences were observed in the crystalline type of the yam starches. Only one sample was 100% A-type (*D dumetorum*). The starches of the *D cayenensis-rotundata* complex were a mixture of crystalline types, with a mean value of 70% B-type. They were significantly different from the *D alata* starches, which presented a mean value of 93% B-type, while starches from *D esculenta* cultivars were in an intermediate group (mean value of 83% B-type). However, the variability within each group was high (SDR of 17) and two cultivars from the *D cayenensis-rotundata* complex had 100% B-type starch, while Florido starch was the only *D alata* starch with partial A-type crystallinity.

The degree of crystallinity ranged from 26 to 45%, with a mean value of 36%. Although variations were apparent within each species (the *D cayenensis-rotundata* complex contained both a very low crystalline starch, 'Assawa', and the most crystalline one, 'Kponan'), *D esculenta* starches had a significantly lower crystallinity (31%) than the other vam starches.

Intrinsic viscosity

The starches of the different cultivars of the D cayenensis-rotundata complex and of the D alata

Table 1. Yam starch proximate analysis

Cultivars	Botanical name	Ash (g 100 g ⁻¹ db)	Cellulose (g 100 g ⁻¹ db)	Proteins $(g 100 g^{-1} db)$	Lipids (g 100 g ⁻¹ db)
Bodo	D alata	0.08	0.36	0.35	0.09
Daminangba	D alata	0.18	0.38	0.21	0.11
Florido	D alata	0.13	0.38	0.19	0.11
Soglan	D alata	0.38	0.36	0.20	0.09
Suidié	D alata	0.17	0.37	0.23	0.10
Assawa	D cayenensis-rotundata	0.09	0.38	0.18	0.10
Assobayérè	D cayenensis-rotundata	0.22	0.35	0.20	0.05
Frou	D cayenensis-rotundata	0.19	0.27	0.11	0.07
Kangba	D cayenensis-rotundata	0.09	0.36	0.22	0.03
Kouba	D cayenensis-rotundata	0.26	0.31	0.22	0.04
Kpassadjo	D cayenensis-rotundata	0.06	0.37	0.19	0.10
Kpokpokpo	D cayenensis-rotundata	0.11	0.36	0.26	0.06
Kponan	D cayenensis-rotundata	0.12	0.37	0.15	0.10
Krenglé	D cayenensis-rotundata	0.07	0.37	0.26	0.10
Lokpa	D cayenensis-rotundata	0.04	0.09	0.23	0.09
sopèrè	D cayenensis-rotundata	0.07	0.05	0.21	0.08
Dumetorum	D dumetorum	0.02	0.35	0.68	0.08
Esculenta 154	D esculenta	0.22	0.06	0.37	0.07
Esculenta 5	D esculenta	0.22	0.05	0.39	0.09
Esculenta 6	D esculenta	0.23	0.09	0.07	0.06
Esculenta 7	D esculenta	0.21	0.10	0.18	0.09

Crystallinit $36^{a} \pm 4.9$ 27 36 35 35 39 41 45 42 35 38 pattern (% B) Crystalline $93^a \pm 15.7$ 70 65 65 65 65 60 50 100 100 100 change (J g⁻¹) $16.3^{b} \pm 1.3$ $14.9^{\circ} \pm 0.8$ Enthalpy 20.3 19.5 16.7 14.4 15.9 14.4 15.2 14.9 16.1 14.3 14.9 13.7 14.9 19.7 14.3 temperature (°C) Gelatinization $^{7}5.4^{b} \pm 0.4$ $^{7}3.3^{6} \pm 2.4$ 69.9 76.9 71.9 81.7^a 72.3 73.6 72.7 75.6 76.5 73.6 71.0 75.8 70.9 73.4 onset 72.1 74.4 viscosity (cm³ g⁻¹) $86^{a} \pm 13$ Intrinsic 195 185 180 189 197 199 134 Particle size $21.5^a \pm 4.4$ $26.4^{a} \pm 3.0$ 6.0 20.0 28.8 25.8 30.9 29.3 25.0 27.0 18.6 19.7 28.1 25.9 23.4 20.4 25.4 Amylose (%) $26.8^{a} \pm 0.8$ $26.4^{a} \pm 1.1$ 26.8 27.4 16.6^b 26.0 27.1 25.2 25.9 27.2 26.8 25.4 14.8 27.1 25.3 27.1 26.2 28.8 26.7 25.2 15.7 D cayenensis-rotundata D cayenensis-rotundata Table 2. Yam starch physicochemical properties Botanical name D dumetorum D esculenta D esculenta Mean value D alata D alata SDR Mean value ± SDT Mean value ± SDT Mean value ± SDT Esculenta 154 Daminangba Dumetorum Esculenta 5 Esculenta 6 Esculenta 7 Assobayérè **Apokpokpo** Kpassadjo All groups Cultivars Assawa Kangba Kponan Krenglé Kouba sopèrè Lokpa Florido Sogian Bodo Suidlé Frou

Means with different letters in each column are significantly different at ho < 0.05 using LSD test

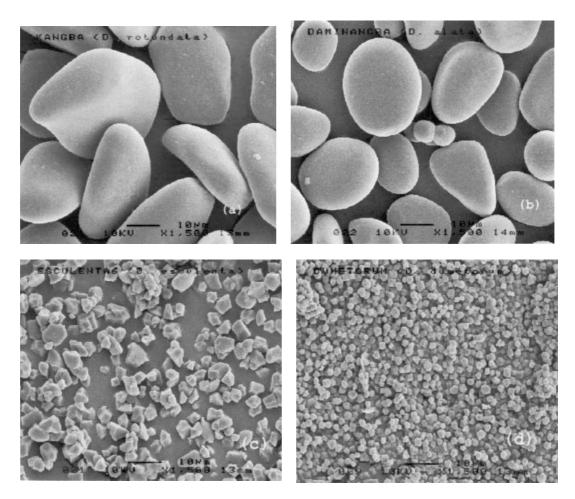


Figure 1. Scanning electron micrographs of yam starch granules. (a) 'Kangba' (*D cayenensis-rotundata*); (b) 'Daminangba' (*D alata*); (c) Esculenta 6 (*D esculenta*); (d) *Dumetorum* (*D dumetorum*).

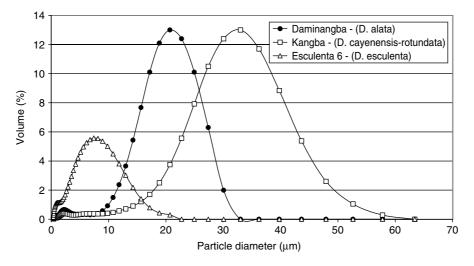


Figure 2. Granule size distribution of native yam starch.

cultivars had a similar, high, intrinsic viscosity (around $190 \,\mathrm{cm^3\,g^{-1}}$), significantly different from that measured for the *D* esculenta and *D* dumetorum cultivars, the mean value of which was close to $130 \,\mathrm{cm^3\,g^{-1}}$ (Table 2).

Gelatinization enthalpy and gelatinization temperature The gelatinization enthalpy change (ΔH) was greatest for the *D* esculenta starches (18.0–20.3 Jg⁻¹), with

a mean of $19.4\,\mathrm{J\,g^{-1}}$ (Table 2). The lowest $\Delta H\mathrm{s}$ were observed with the starches of the *D cayenensis-rotundata* complex (mean of $14.9\,\mathrm{J\,g^{-1}}$). The *D dumetorum* and *D alata* starches presented intermediate values of around $16.5\,\mathrm{J\,g^{-1}}$. Each group was quite homogeneous with an SDR of $1.0\,\mathrm{J\,g^{-1}}$, with the exception of 'Florido', which had a low enthalpy change $(14.4\,\mathrm{J\,g^{-1}})$ typical of *D cayenensis-rotundata* complex starch.

The gelatinization onset temperature varied little between yam species, with a global mean value of $74.1\,^{\circ}$ C. Only the *D dumetorum* starch presented a significantly higher gelatinization temperature (81.7 $^{\circ}$ C, Table 2).

Functional properties

Solubility, swelling power and dispersed volume fraction No significant difference between species (Table 3) was observed for swelling power, solubility and volume fraction occupied by the dispersed phase (Φ), during pasting. At 90 °C the yam starches, taking all species together, absorbed a mean 14.2 g water g⁻¹ dry matter, thus occupying 72% of the volume fraction for a 4% dry matter dispersion, with a mean concentration of solubilized material of 9.8 g dm⁻³. After cooling to 50 °C (23 min on the RVA profile), a slight (8%) increase in mean swelling power and a major (40%) increase in mean solubility were noted, the latter rising to 13.7 g dm⁻³ of solubilized matter.

The starch of the 'Krenglè' (D cayenensis-rotundata) cultivar was the most soluble ($23.2\,\mathrm{g\,dm}^{-3}$ of dry matter at $50\,^\circ\mathrm{C}$) and also had one of the highest swelling rates ($16.5\,\mathrm{g\,g}^{-1}$). On the other hand, the three starches with the lowest swelling power and solubility

('Assobayérè', 'Kangba' and 'Lokpa') belonged to the same species complex.

Pasting behaviour

The pasting temperature (PT) of the yam starches for 4% starch suspensions was around $80\,^{\circ}\text{C}$ (Table 4). The highest pasting temperature ($87\,^{\circ}\text{C}$) was measured for the starch of *D dumetorum*, and the lowest for *D esculenta* starches (mean value of $78.7\,^{\circ}\text{C}$). Starches from *D alata* and the *D cayenensis-rotundata* complex had an intermediate position, with a mean PT value close to $83\,^{\circ}\text{C}$.

Analysis of variance showed two different homogeneous groups of yam starch according to their apparent viscosity (measured by RVA). The pastes obtained from the starches of D alata and the D cayenensis-rotundata complex were the most viscous (mean V_{90} close to 24 RVU), while those of the D esculenta and D dumetorum group had a low viscosity (9 and 2.5 RVU, respectively, at V_{90}). On cooling, the apparent viscosities of the yam starches increased by over 40% to reach a mean final viscosity ($V_{\rm f}$) of 29.2 RVU (Table 4). Similar results were obtained for the viscosity measured using the Haake Viscotester, the D alata starch pastes having a mean viscosity of 292.8 mPa s while that of D dumetorum

Table 3. Yam starch swelling power, solubility and volume fraction of the dispersed phase for 4% dry matter dispersions prepared in the RVA after 12 and 23 min pasting

		At 90 °C (12 min)			At 50 °C (23 min)		
Cultivars	Botanical name	Swelling power (g g ⁻¹)	Solubility (g dm ⁻³)	Φ	Swelling power (g g ⁻¹)	Solubility (g dm ⁻³)	Φ
Bodo	D alata	13.8	7.3	0.70	15.4	8.1	0.77
Daminangba		15.2	11.3	0.77	16.8	12.9	0.86
Florido		15.0	12.3	0.75	15.7	14.1	0.81
Soglan		15.3	10.9	0.76	15.8	13.0	0.83
Suidlé		16.0	13.5	0.82	16.8	21.4	0.92
Mean value \pm SDT	D alata	$15.1^{a} \pm 0.8$	$11.1^{a} \pm 2.3$	$0.8^{a} \pm 0.01$	$16.1^{a} \pm 0.7$	$13.9^{a} \pm 4.8$	$0.84^{a} \pm 0.1$
Assawa	D cayenensis-rotundata	14.0	8.0	0.72	16.8	10.8	0.81
Assobayérè		10.8	7.2	0.55	11.8	8.6	0.59
Frou		15.4	8.9	0.79	16.7	11.6	0.86
Kangba		11.7	6.9	0.57	12.4	9.6	0.62
Kouba		14.6	9.1	0.75	15.2	11.0	0.80
Kpassadjo		13.4	8.3	0.65	13.6	17.0	0.71
Kpokpokpo		14.0	8.6	0.73	15.6	14.1	0.84
Kponan		15.2	10.0	0.77	15.4	15.1	0.84
Krenglé		16.4	11.4	0.86	16.7	23.2	0.93
Lokpa		12.6	6.1	0.63	14.8	16.8	0.80
sopèrè		14.6	11.1	0.79	14.8	17.3	0.80
Mean value \pm SDT	D cayenensis-rotundata	$13.9^{a} \pm 1.7$	$8.7^{a} \pm 1.7$	$0.70^{a} \pm 0.1$	$14.9^{a} \pm 1.7$	$14.1^{a} \pm 4.3$	$0.78^{a} \pm 0.1$
Dumetorum	D dumetorum	13.7a	12.4a	0.70a	15.1a	12.2a	0.77a
Esculenta 154	D esculenta	14.3	12.5	0.70	14.8	15.1	0.76
Esculenta 5		14.1	12.4	0.73	15.7	16.5	0.83
Esculenta 6		13.9	7.3	0.70	14.9	7.1	0.76
Esculenta 7		14.8	9.9	0.75	16.1	11.2	0.82
$\text{Mean value} \pm \text{SDT}$	D esculenta	$14.3^{a} \pm 0.4$	$10.5^{a} \pm 2.5$	$0.70^{a} \pm 0.01$	$15.4^{a} \pm 0.6$	$12.6^{a} \pm 4.2$	$0.8^{a} \pm 0.04$
All groups	Mean value	14.2	9.8	0.72	15.28	13.65	0.79
- ·	SDR	1.3	2.0	0.08	1.35	4.14	0.08

Means with different letters in each column are significantly different at p < 0.05 using LSD test.

Table 4. Yam starch pasting properties and gel clarity

Cultivars	Botanical name	Pasting temperature (°C)	V ₉₀ RVA viscosity at 12 min (RVU)	V _f RVA viscosity at 23 min (RVU)	Viscosity (mPa s)	Clarity (% transmittance)
Bodo	D alata	84.7	20.3	31.0	328	23.8
Daminangba		81.5	25.7	35.4	219	62.7
Florido		85.4	18.5	26.7	318	36.7
Soglan		83.7	22.1	32.6	234	36.3
Suidlé		79.3	31.7	38.7	364	27.3
Mean value \pm SDT	D alata	$82.9^{b} \pm 2.5$	$23.7^{a} \pm 5.2$	$32.9^{a} \pm 4.5$	$292.8^{a} \pm 62.9$	$37.4^{b} \pm 15.2$
Assawa	D cayenensis-rotundata	83.7	31.0	41.7	197	42.0
Assobayérè		86.4	4.8	14.0	99	21.0
Frou		81.0	31.4	45.4	208	45.5
Kangba		84.8	9.8	17.7	50	42.0
Kouba		80.7	25.1	35.0	172	44.7
Kpassadjo		85.6	15.0	25.1	148	51.8
Kpokpokpo		83.0	29.0	43.5	242	29.0
Kponan		82.9	33.5	42.9	232	26.5
Krenglé		80.4	38.0	41.9	311	41.5
Lokpa		83.4	16.8	30.2	142	58.6
Sopèré		76.3	39.1	45.6	301	44.9
Mean value \pm SDT	D cayenensis-rotundata	$82.6^{b} \pm 2.8$	$24.9^{a} \pm 11.6$	$34.8^{a} \pm 11.4$	$190^{\rm b} \pm 80$	$40.7^{a} \pm 11.1$
Dumetorum	D dumetorum	87.5a	2.5b	5.0b	61b	8.9c
Esculenta 154	D esculenta	76.6	13.1	20.4	167	13.2
Esculenta 5		77.1	11.5	19.2	178	21.8
Esculenta 6		82.8	6.1	11.4	76	26.3
Esculenta 7		78.2	5.6	10.1	113	37.6
Mean value \pm SDT	D esculenta	$78.7^{b} \pm 2.8$	$9.1^{b} \pm 3.8$	$15.3^{b} \pm 5.3$	$130^{b} \pm 47.8$	$24.7^{bc} \pm 10.2$
All groups	Mean value	82.1	20.5	29.2	198	35
	SDR	2.8	9.4	9.3	71	12

Means with different letters in each column are significantly different at $\rho < 0.05$ using LSD test.

was 61 mPa s. Moreover, considerable variability in Haake viscosity was noted with the pastes of the *D* cayenensis-rotundata complex, where both high and low viscosity pastes were found (301, 311 and 232 mPa s for 'Sopèrè', 'Krenglè' and 'Kponan', respectively, as against 99 and 50 mPa s, respectively, for 'Assobayérè' and 'Kangba').

Gel clarity

The clarity of the starch gels was very variable (from 8.9 to 62.7%), with an overall mean transmittance of 35%. Analysis of variance gave three groups: the clearest starch gels (mean transmittance of around 40%), grouping together the cultivars of the D cayenensis-rotundata complex and those of D alata; opaque gels (8.9% transmittance), represented by the starch of D dumetorum; and an intermediate group consisting of the starches of the D esculenta species, with a mean transmittance of 24% (Table 4). Despite this classification, a very large withingroup variability was observed (SDR of 12): the first group, for instance, contained not only the clearest gels, from 'Daminangba' (D alata) and 'Lokpa' (D cayenensis-rotundata complex), but also starches giving very opaque ones (close to 20% transmittance).

DISCUSSION

The relatively low amylose content (around 6% db) of the D esculenta and D dumetorum starches and the high amylose content (around 6% db) of the D cayenensisrotundata and D alata starches are in agreement with numerous previous studies.^{9,12-16,29-31} The low particle size and the polygonal shape of the D esculenta and D dumetorum starches have likewise already been described by Rasper and Coursey, Delpeuch et al¹² and Farhat et al,16 who also found ovoid or ellipsoid shapes and mean sizes of between 20 and 35 µm for the D cayenensis-rotundata complex and D alata varieties. However, the latter were also the first to report the lower intrinsic viscosity of D esculenta and D dumetorum starches in comparison with other yam starches. Emiola and Delarosa, 14 on the other hand, found that D dumetorum starch had an intrinsic viscosity similar to that of other yam starches. It should be noted, however, that these authors found a high amylose content (25% db) for their D dumetorum starch, in contradiction to results from other sources. 9,12,30,31

The gelatinization onset temperature of the yam starches was high (74 °C) compared with that of other tuber starches: close to 60 °C for potato³² and cassava starches,²³ and around 67 °C for sweet potato and tania starches.³³ This result agrees with previous ones^{33,16} and particularly with the results of Farhat

et al, 16 who found a higher gelatinization temperature for D dumetorum than for D cayenensis-rotundata (83.1 as against 75 °C). The pasting temperature (PT) of the yam starch suspensions was likewise high (over 80 °C), which also agrees with previous results^{9,16,34} particularly for D dumetorum, as already mentioned by Rasper.¹¹ The gelatinization enthalpy change of the starches was in the range previously described by Farhat *et al*¹⁶ and around the values $(17-18 \,\mathrm{Jg}^{-1})$ measured for potato and cassava starches. 32,23 The great variation in yam starch crystallinity, in particular the unique A-type pattern of D dumetorum, have been noted by Delpeuch et al, 12 Farhat et al 16 and Gallant et al, 30 but the present study is the first to assess the relative ratio of the two polymorphs and their degree of crystallinity. It should be noted that no correlation exists between crystalline type and degree of crystallinity.

The swelling power of yam starch at $90\,^{\circ}\text{C}$ was in the same range $(10.8-16.4\,\mathrm{g\,g^{-1}})$ as that mentioned by Emiola and Delarosa¹⁴ (around $15.5\,\mathrm{g\,dm^{-3}}$ for *D dumetorum*, *D alata* and *D cayenensis-rotundata* at $90\,^{\circ}\text{C}$) and Rasper¹¹ (between 13.9 and $24.9\,\mathrm{g\,g^{-1}}$ at $95\,^{\circ}\text{C}$ for the same species as in this study). Yam starch had an intermediate swelling power, between the low values measured for cereals and the high values measured for other tuber starches such as cassava and potato.

A principal components analysis (PCA) was performed based on the physicochemical characteristics and the swelling and solubility behaviour of the 21 yam cultivars. The first three axes explained 38.4, 27.5 and 13.4% of the variability, respectively. Four main starch

physicochemical characteristics were represented on the first axis: granule size, amylose content and intrinsic viscosity contrasted with enthalpy change. These variables were highly correlated, due in particular to the specific characteristics of the D esculenta and D dumetorum starches for these parameters. Swelling and solubility behaviour were represented on the second axis while the third one represented variables representative of starch crystallinity (crystalline type opposed to gelatinization temperature; Fig 3). Figure 4 shows a representation of the different cultivars on axes 1 and 3 of the PCA that allows the best discrimination between yam species; yam species could not in fact be distinguished by their swelling and solubility behaviour, represented on axis 2. Ivory Coast yams could thus be classified into three homogenous clusters based on starch physicochemical characteristics. One cluster, in the top left-hand quarter, groups together the four clones of D esculenta (\blacksquare). This cluster is characterized by starches with small granules, low amylose content and intrinsic viscosity and high gelatinization enthalpy change. The *D dumetorum* cultivar (\blacklozenge) was remote in the low left-hand quarter. This starch has properties similar to those of the D esculenta cluster, but is differentiated from it by the 100% A-type crystalline type and high gelatinization temperature. The other species are grouped in a cluster on the right-hand side of the graph, distributed around axis 1. The *D alata* cultivars (\triangle) are positioned in the left-hand part of the cluster because of lower particle size and higher gelatinization enthalpy change.

It should be noticed that this discrimination is based on samples collected within two zones (forest

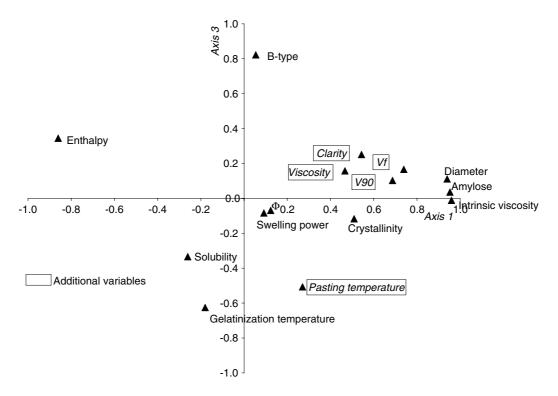


Figure 3. Score plot of principal components 1 and 3 of 10 variables of physicochemical properties of yam starches. Clarity, Haake viscosity (viscosity), final viscosity (V_f), viscosity at 90 °C (V_{90}) and pasting temperature were considered as additional variables.

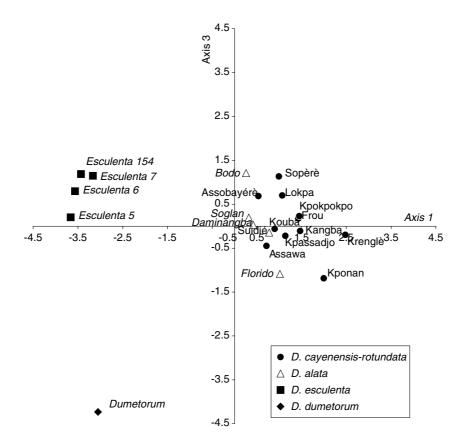


Figure 4. Sample plot of principal components 1 and 3 of 21 cultivars of *D alata, D cayenensis-rotundata* complex, *D dumetorum* and *D esculenta* starches.

and Savanna zones), ie in different agroecological conditions. Indeed, agroecological conditions may also have an influence on yam starch physico-chemical and functional properties. As a first approach of this problem, we could test this effect on D cayenensisrotundata samples that originated partly (five samples) from forest zone and partly (six samples) from the Savanna. An analysis of variance was performed considering the various cultivars as replications in the same zone. It thus showed that only swelling power could be significantly influenced by agro-ecological conditions: starches from the Savanna region exhibited lower swelling power. However, this was not linked to any physico-chemical starch characteristic, hence the main differences evidenced in yam starches studied can be considered as originating mainly from the genotype.

With regard to yam starch functional properties, the viscosity results agree with those of Farhat $et\ al$, 16 who classified yam starches by their hot paste viscosity as follows, in descending order: $D\ alata > D\ cayenensis-$ rotundata $> D\ esculenta > D\ dumetorum$. Viscosity variables were plotted on PCA axes as additional variables (Fig 3) and appeared mainly linked to axes 1 and 2. The viscosity variables were highly positively correlated to amylose content and granule size (axis 1) and to swelling power and volume fraction of the dispersed phase (Φ , axis 2). A predictive model of V_{90} was designed using linear multiple regression analysis. It incorporated two variables (significant at less than 0.001), giving the following equation with a

determination coefficient of 0.88 (Fig 5):

$$V_{90} = -72.1 + 106 \times \Phi + 0.76 \times \text{particle size (} \mu\text{m})$$

Similarly, two variables were sufficient for predicting 79% of the variability of the apparent viscosity at $50 \,^{\circ}\text{C}$ (V_{f}):

$$V_{\rm f} = -75.3 + 1.75$$
 $imes$ amylose content (%db) + 78.8 Φ

The key role of Φ in the consistency of starch pastes and gels is well known³⁵⁻³⁷ and the viscosity of a maize paste can be predicted by Φ .²⁵ On the other hand, previous results obtained using various tropical starches extracted, in particular, from roots and tubers have demonstrated that paste viscosity increases with native starch granule size.³⁸ In addition, Rao et al^{39} have pointed out the role of starch granule size distribution in starch paste consistency. The predictive model obtained is thus in agreement with the literature. Again, the direct effect of amylose on the aggregation and gelification phenomenon occurring during starch paste cooling and storage and its consequence on paste setback and gel strengthening have also been well described. 40-43 It thus appeared natural that starch paste viscosity after cooling (V_f) should be positively correlated to starch amylose content. With regard to paste clarity, our results are in the same range as those of Moorthy³⁴ and Rodriguez-Sosa and Parsi-Ros, 44 who reported around 60%

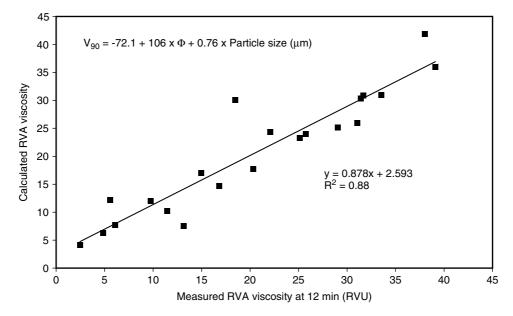


Figure 5. Viscosity predictive model at the start of the 90 °C plateau (V_{90}).

transmittance for *D* alata and *D* rotundata starch gels. Yam starch gels are not as clear as potato and cassava starch gels (96 and 73% transmittance respectively), but in some cases they are clearer than maize starch gels (41% transmittance).²⁷ Clarity was plotted to the right of axis 1 close to the position of the viscosity variables on the PCA graph (Fig 3). Paste clarity was positively correlated to $V_{\rm f}$ (r = 0.44), confirming the results of Dufour et al.38 Furthermore, a highly positive correlation coefficient was found between paste clarity and granule size (r = 0.53), small granules from D dumetorum and D esculenta giving more opaque gels (Table 4). This is in agreement with the findings of Craig et al²⁷ who showed that paste opacity is primarily due to light refraction on starch ghosts: in small granule pastes, the number of refraction possibilities is higher than in large granule pastes of the same starch concentration, and consequently the refraction index is higher. The second factor favouring paste opacity is light-scattering on polymers and particularly on the polymer network that forms after amylose gelation. We could not confirm this relationship as the starch samples having a small granule size in our experiment (D dumetorum and D esculenta starches) also had a low amylose content. It can be hypothesized, however, that paste clarity is a very complex functional property depending on numerous factors, such as granule size and swelling power, amylose content and amylose macromolecular properties (molecular size and degree of branching). The first two determine the actual size of the granule ghost in the paste, while amylose content and the amylose macromolecular properties determine not only the gelation power but also the viscosity and shear rate, which play a role in the disintegration of granule ghosts during paste preparation. This hypothesis will be investigated in a further work, which will also compare the ability of various yam starches to resist a number of technological stresses.

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