Photodegradation of Cassava and Corn Starches

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The baking expansion properties of sour cassava starch (*Polvilho azedo*) are attributable to photochemical starch degradation induced by heterolactic fermentation after sun-drying. This study investigated the effects of UV irradiation on the different structural levels of cassava starch as compared to those of corn starch and dextrins. Photosensitive compounds excited at 360 and 290 nm in cassava starch were photodegraded when starch was exposed to sunlight or 360 nm irradiation. UV irradiation depolymerized cassava and corn starches, inducing modifications due, at least in part, to a mechanism involving free radicals. Lactic acid was also photodegraded. Photodegradation induced by UV absorption could have been due to fluorescent chromophores found in starches and nonfluorescent chromophores present in glucosidic units.

Keywords: *Sour cassava starch; photodegradation; UV irradiation; lactic acid; Polvilho azedo*

INTRODUCTION

Sour cassava starch (*Polvilho azedo*) is a natural-fermented and sun-dried cassava starch that shows expansion properties during baking. It is a traditional product used in Brazil and Colombia for snack foods and doughs and a potential ingredient of gluten-free breads for gluten-intolerant individuals. The biscuits produced with this starch have very high specific volumes (15−17 cm^3/g) and an alveolar structure and crispness similar to those of extruded snacks. Sour cassava starch production involves starch fermentation followed by sun-drying. The main acid resulting from cassava starch fermentation, lactic acid, is degraded by sun-drying (*1*), whereas acetic, propionic, and butyric acids remain as minor products (*2* and *3*).

The fermentation and sun-drying processes produce starch depolymerization (*1*) which is correlated with expansion ability (*4* and *5*). However, acidification of cassava starch with lactic, acetic, or butyric acid (*2, 3, 6*), followed by oven drying, failed to produce any great expansion ability after baking. Similarly, amylase depolymerization (*3*) or natural lactic fermentation (*1*) did not afford expansion properties to cassava starch. Consequently, it has been suggested that the expansion properties of sour cassava starch result, at least in part, from the combined effect of starch fermentation and sun-drying (*1, 6*−*8*). But, corn starch, after fermentation and sun-drying, showed no expansion during baking (*9*).

In laboratory studies, cassava starch acidified with lactic acid and subjected to UV irradiation expanded during baking (*4, 7, 8, 10*). Thus, expansion could be a result of the photochemical treatment. However, in contrast to UV-irradiated cassava starch, UV-irradiated corn starch showed no expansion during baking (*4*). The structural changes involved in the transformation of sour cassava starch dough are not clearly understood.

The first studies on starch photodegradation were performed in 1911 and 1912. Starch solutions irradiated with a mercury vapor lamp produced peroxide hydrogen, dextrins, and carbonyls (*11* and *12*), suggesting that glycosidic bonds are cleaved by UV irradiation (*13*). In this respect, formaldehyde, formic acid, and CO_2 are the principal components of photodegraded glucose and amylose solutions (*14* and *15*).

The present study describes the effects of UV irradiation on the different structural levels of cassava starch as compared to those of corn starch used as a model. The purpose was to provide a comprehensive study of the mechanisms involved in cassava starch changes.

MATERIALS AND METHODS

Sample Preparation. Cassava starch (*Manihot esculenta*) was obtained in two different batches from Lorenz Co., Ind. (São Paulo, Brazil), corn starch was obtained from Roquette Frères (Lestrem, France), and corn starch dextrins were from Fluka (# 31410). Cassava amylopectin and amylose were prepared as described by Banks and Greenwood (*16*). Sour cassava starch from Lorenz was used as a reference.

Starch samples were divided into acidified and control series. For acidification, starches, dextrin, and amylopectin were humidified (final moisture contents 50%) with 0.24 M lactic acid solution (dilution from Sigma # L1250 lactic acid; purity 98%). The final lactic acid content was calculated as 20 g/kg starch (dry basis). Humidified samples were maintained for 10 min at room temperature and dried in an oven at 25 °C for 10 h.

Control and acidified cassava (first batch) and corn starches, dextrins, and amylopectin were exposed to a mercury vapor lamp (HPK 125W; Philips, 1.15 A, 125 V, emission spectrum 200−600 nm; Philips, 1.15 A, 125 V, UV emitted energy 772 J/cm^2 after 16 h) in a closed reactor with a rotating plate and air circulation.

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Samples of control and acidified cassava starch (second batch) were subjected to irradiation by two other light sources, which were both used in a static reactor: 4 UV lamps with a discrete emission spectrum at 254 nm (UV-emitted energy 533 J/cm^2 after 24 h) and 3 UV black lamps with a continuous emission spectrum (maximum at 360 nm; UV-emitted energy 204 J/cm^2 after 24 h).

All samples were irradiated as 2-mm-thick layers at 65% relative humidity (RH). The moisture contents of nonirradiated and irradiated samples were determined by oven-drying at 130 °C for 2 h. All experiments were repeated three times.

Starch Depolymerization. The intrinsic viscosity of starch samples was measured with viscosimetric micro-Ubbelhode tubes at 35 °C in 0.2 N KOH (solvent elution time, 60 s). All measurements were performed in duplicate.

The average molecular weight $\overline{M_w}$ of native and irradiated (mercury vapor and 254 nm lamps) cassava starch samples was evaluated by high-pressure size-exclusion chromatography (HPSEC) with detection by multiangle laser light scattering (MALLS). Samples irradiated with a mercury vapor lamp were also evaluated after 4 h exposure (UV-emitted energy after 4 h, 193 J/cm^2). Samples were dispersed and solubilized as described by Bello-Pérez et al. (*17*). Carbohydrate concentrations after centrifugation and filtration were measured by the sulfuric acid−orcinol colorimetric method (*18*).

Dual detection of solutes was performed by a Multiangle Dawn DSP-F MALLS apparatus (Wyatt Technology Corporation, Santa Barbara, CA) with a differential refractive-index detector (Erma ERC-510, Japan) in series. HPSEC experiments were performed with a TSK-Gel G2000SW XL (30 cm × 7.8 mm i.d.) column and a TSK gel SWXL guard column (4.0 cm × 6.0 mm i.d.) at 30 °C, eluted with 0.02% sodium azide aqueous solution at a flow rate of 0.5 mL/min (*19*). This system allows the determination of the molecular weight distribution (MWD) and especially the weight-average $\overline{M_w}$ molar mass of each sample. $\overline{M_w}$ was calculated with ASTRA software, version 1.4 (*20*). A value of 0.146 mL/g was used as the refractive index increment (d*n*/d*c*) for starch. Calculations were performed using the Berry equation, with a second-order polynomial fit polymer (*21*).

Crystallinity and Thermal Properties of Cassava Starch. X-ray diffraction measurements of cassava starch samples (moisture contents, 14% and 30%) were recorded using Inel X-ray equipment operating at 40 kV and 30 mA. Cu$K_{\alpha 1}$ radiation (λ = 0.15405 nm) was selected using a quartz monochromator. A 120° (2θ) curved-position sensitive detector (CPS 120, INEL, France) monitored diffracted intensity during 2-h exposure periods. Samples were sealed between two aluminum foils to prevent any change in water content during measurement.

Differential scanning calorimetry (DSC) measurements of cassava starch samples were performed with a Setaram DSC 121. Samples were weighed in steel pans, and distilled water was added (moisture content 50%) before sealing. DSC profiles were performed from 30 to 180 °C at a heating rate of 3 °C/min. Dry aluminum powder was used as reference.

Chemical Analyses of Native and Irradiated Cassava Starch. Electronic spin resonance (ESR) of native and irradiated samples (360 nm and mercury vapor lamps) was recorded at room temperature on an EMS104 Bruker spectrometer. The following recording parameters were used: power, 4.99 mW; sweep width, 100 G; modulation, 8.02 G; sweep time, 5.24 s, and number of sweeps, 20.

The organic acids of the samples were extracted with sulfuric acid 5 mM (*22*), and their contents were determined by HPLC using an HPX 87H column (Biorad, Hercules, CA) at 55 °C, with 5 mM sulfuric acid at a flow rate of 0.6 mL/min. Detection was performed with a refractive index detector (Shimadzu RID-6A) and a spectrophotometric UV detector at 210 nm (Shimadzu, SPD-6A). Standard acid curves were obtained with pure solutions of lactic, propionic, formic, acetic, pyruvic, butyric, and isobutyric acids and with ethanol.

The number of carboxyl groups in starch samples was determined by the procedure described by Smith (*23*): through titration of hot gelatinized starch with 0.025 M sodium hydroxide solution until pH 8.3. Native starch samples were used as the titration control.

Aldehyde groups were identified by sample staining with Schiff's reagent for 15 min and then observed by a light microscope (Leica, model DMRKA). Photographs were performed (*x* 160) at 12 V with Konica VX film ISO100/21.

Spectral Analyses of Starch Samples. UV−Visible spectra of samples were recorded on a Perkin-Elmer double-beam Lambda 14 spectrophotometer equipped with a diffuse reflectance accessory (Labsphere, RSA-Perkin-Elmer 20).

Emission and synchronous corrected spectra of control and irradiated samples were recorded on an SLM4800C spectrofluorimeter (Aminco, Urbana, IL) equipped with a polarizer in neutral position for the excitation beam and a polarizer in vertical position for the emission beam. Glucose was used as reference. Front-surface geometry was used for the sample (incidence angle set at 56°), excitation and emission slit widths were set at 4 nm, and spectra were corrected from instrumental distortions in excitation using a rhodamine solution in the reference channel. Synchronous scanning was performed from 210 to 600 nm with a wavelength difference of 30 nm. On the basis of the peaks observed with the synchronous scanning spectrum, excitation wavelengths were selected to obtain the emission spectra. All spectra were recorded at room temperature (20 ± 1 °C).

Table 1. Intrinsic Viscosity of Cassava and Corn Starches Before and After Acidification and Light Exposure.

	intrinsic viscosity (mL/g)	
	cassava starch	corn starch
native starch	169	146
acidified starch	147	127
irradiated starch	113	123
acidified and irradiated starch	99	83
starch factor (S)	34.38[a]	
acidification factor (A)	110.09[a]	
light exposure factor (LE)	339.05[a]	
interaction S × A	ns	
interaction S × LE	19.56[a]	
interaction A × LE	ns	
interaction A × S × LE	13.71[a]	13.71**
standard error of residual (degree of freedom)	4.8 (8)	4.8 (8)

[a] Significant level at 1% for the Tukey test.

RESULTS

Starch Depolymerization. A decrease in intrinsic viscosity for corn and cassava starches was obtained with both acidification (A) and light exposure (LE) (Table 1). No significant interaction was observed between A and starch source (S) (Table 1) or between A and LE factors (Tables 1 and 2). However, a significant interaction between LE and S (Table 1) indicated that UV degradation changes as a function of the botanical source of starch. The decrease in intrinsic viscosity induced by UV irradiation was more effective for cassava than corn starch (Table 1). The intrinsic viscosities of cassava starch samples irradiated with mercury vapor (Table 1) were lower than those irradiated with 254 and 360 nm lamps (Table 2). The minor differences in viscosity values observed between native cassava starches (Tables 1 and 2) were attributable to the use of two starch batches.

After 35 s of heating, the extent of sample solubilization ranged from 91 to 99%. For HPSEC/MALLS analysis, the mass recovered after chromatography was 86−97%. The amylopectin fraction from cassava starch showed an elution peak at 5.4 mL, with a $\overline{M_w}$ of 3.8 ×

Table 2. Intrinsic Viscosity of Cassava Starches Before and After Acidification and Light Exposure

	intrinsic viscosity (mL/g)	
	control cassava starch	acidified cassava starch
nonirradiated starch	182	178
irradiated 360 nm	173	165
irradiated 250 nm	166	154
acidification factor (A)	7.17[a]	
light exposure factor (LE)	23.85[b]	
interaction A × LE	ns	
standard error of residual (degree of freedom)	5.8 (12)	

[a] Significant level at 5% for the Tuckey Test. [b] Significant level at 1% for the Tuckey Test.

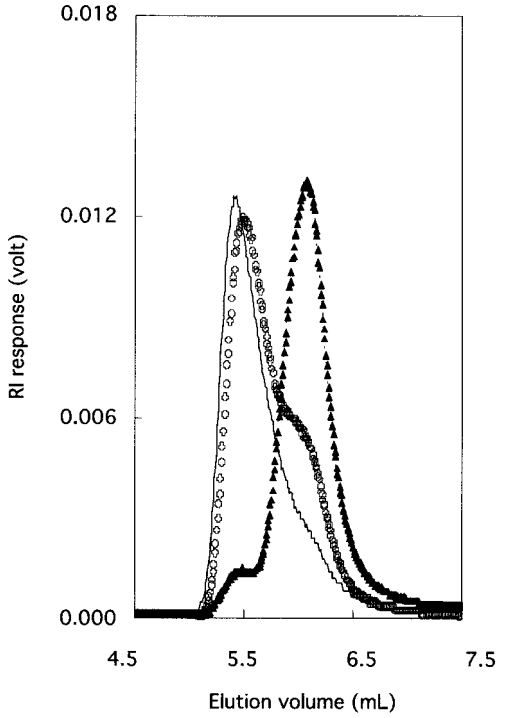

Figure 1. HPSEC profiles: (▲) amylose from cassava, (—) amylopectin from cassava, and (∗) native cassava starch.

10^8 g/mol, whereas the peak for amylose occurred at 6.1 mL, with a $\overline{M_w}$ of 3.2×10^6 g/mol. The small shoulder at 5.1−5.5 mL on the HPSEC profile indicated that the amylose sample contained a contaminant amylopectin fraction. Compared to HPSEC profiles of purified amylose and amylopectin (Figure 1), native cassava starch sample presented a profile with a strong overlapping of both fractions (Figure 1). The $\overline{M_w}$ of native cassava starch was 4.2×10^8 and 2.5×10^8 g/mol for the first and second batches, respectively. The RI profile of native cassava starch showed a major peak at V_e 5.4 mL, followed by an overlapped peak at V_e 5.8 mL (Figure 1).

Starch degradation by acidification (Figure 2) was indicated by a small shoulder at V_e 6.0 mL and the lower peak area V_e 5.4 mL. Acidification induced a decrease of $\overline{M_w}$ from 2.5×10^8 to 1.6×10^8 g/mol. A similar degradation was observed for acidified starches after irradiation at 254 nm (Figure 2). For samples irradiated with mercury vapor lamps for 4 h, the reduction of the first peak and the increase of a shoulder at V_e 6.0 mL were more pronounced (Figure 3). Samples irradiated for 16 h exhibited more marked peak displacement (V_e 5.7 mL and V_e 6.1 mL) than those irradiated for 4 h (Figure 4). The $\overline{M_w}$ of samples irradiated for 4 and 16 h decreased from a $\overline{M_w}$ of 4.2×10^8 to 2.8×10^8 and 7.3×10^7 g/mol, respectively (Figure 4).

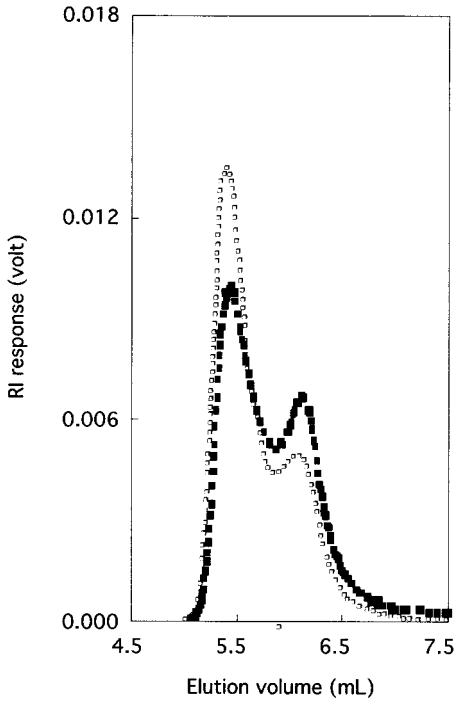

Figure 2. HPSEC profiles: (□) acidified cassava starch and (■) acidified cassava starch irradiated at 250 nm.

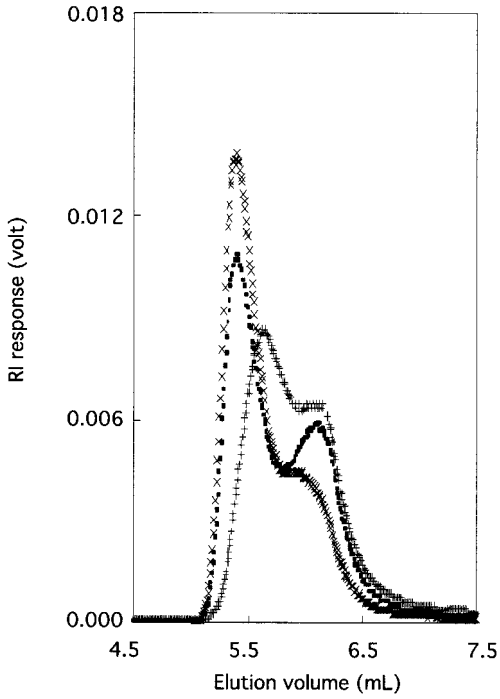

Figure 3. HPSEC profiles: (×) native cassava starch, (●) cassava starch irradiated for 4 h, and (+) cassava starch irradiated for 16 h.

Starch Crystallinity and Thermal Properties. No differences were observed between the X-ray diffraction patterns of native and acidified and/or irradiated cassava starch samples (Figure 5). Cassava starch showed characteristic C-type crystallinity as in previous studies (*3*, *6*, *24*, *25*). The most intense bands corresponded to Bragg angles (2θ): 15°, 17°, 18.1°, 22°, 23.3°, and 24°.

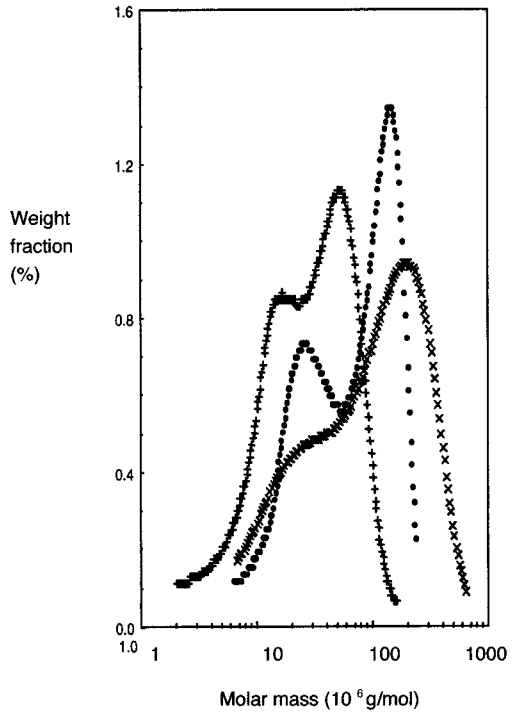

Figure 4. Molecular weight distributions: (×) native cassava starch, (●) cassava starch irradiated for 4 h, and (+) cassava starch irradiated for 16 h.

Irradiated and acidified cassava starch samples, at 50% moisture content, showed thermograms similar to those recorded for native cassava starch. Melting endotherms ranged between 47 and 94 °C, with maximum temperature between 59 and 61 °C and enthalpy of 16.5 $J \cdot cm^{-1}$ ($\sigma \pm 0.927$) (data not shown).

Chemical Analyses. *Free Radical Formation.* The nonirradiated starches, amylopectin, and dextrin samples gave no ESR signal. Cassava and corn starches irradiated with a mercury vapor lamp gave an ESR signal of the AA′/BB′ type (*26*), centered around 3500 G (Table 3). The BB′ signal, previously reported in gamma-irradiated starches, was attributed to $-RO_2^{\bullet}$ radicals (*26* and *27*). The AA′ signal was most apparent in irradiated dextrins. Unlike samples irradiated with a mercury vapor lamp, those irradiated at 360 nm exhibited no signal.

Organic Acid Contents. After irradiation, the lactic acid contents of acidified cassava starch samples decreased by 32% with the mercury vapor lamp and by 12% with the lamp at 254 nm. Conversely, no significant decrease in lactic acid content was observed for samples irradiated at 360 nm. Traces of formic and pyruvic acid were also detected in the irradiated samples.

Irradiation also produced a significant decrease in the lactic acid contents of corn starch and dextrin. Similar extents of lactic acid disappearance were observed for both starches irradiated with the mercury vapor lamp, i.e., 32−30% of initial lactic acid content in the acidified samples. For acidified dextrins, a decrease of 48% of lactic acid content was found (Table 4).

Content of Carboxyl Groups. The starch content of carboxyl groups was high only for acidified samples irradiated with the mercury vapor lamp, whereas samples subjected to either acidification or irradiation showed no increase of carboxyl group content. The contents of carboxyl groups were 0.038% and 0.043% for acidified, irradiated cassava starch and corn starch, respectively. The absence of carboxyl groups in samples irradiated at 254 and 360 nm indicated that higher UV energy was required for carboxylation. Carboxyl group content was too low to allow quantification with the analytical method used.

Aldehyde Group. Nonirradiated samples treated with Schiff's reagent showed no staining, and the same was true for acidified cassava starch samples or those irradiated at 254 and 360 nm. However, acidified or native cassava and corn samples irradiated with the

Table 3. Characteristics of AA′ and BB′ Lines Induced by UV Irradiation

	AA′ line		BB′ line	
	g factor	peak to peak width (mT)	*g* factor	peak to peak width (mT)
cassava starch	2.0050	23.3	2.0051	9.0
corn starch	2.0052	26.1	2.0055	8.8
cassava amylopectin	2.0056	20.3	2.0060	7.9
dextrin	2.0053	19.7		

Table 4. Lactic Acid Content (average of three replicate extractions) of Acidified Cassava and Corn Starch Samples Before and After UV Irradiation

	lactic acid content (mg/g samples db)	
acidified samples	nonirradiated	irradiated
cassava starch	16.8	11.4
corn starch	18.3	12.9
dextrin	14.0	7.3

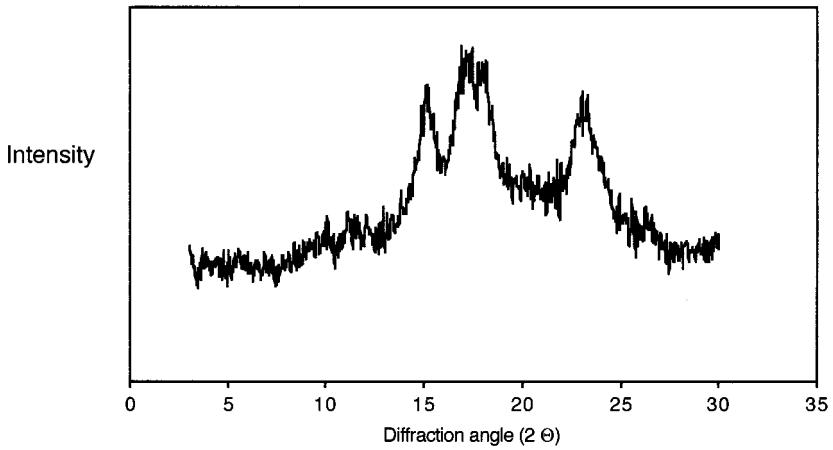

Figure 5. X-ray diffraction pattern of acidified cassava starch irradiated at 250 nm.

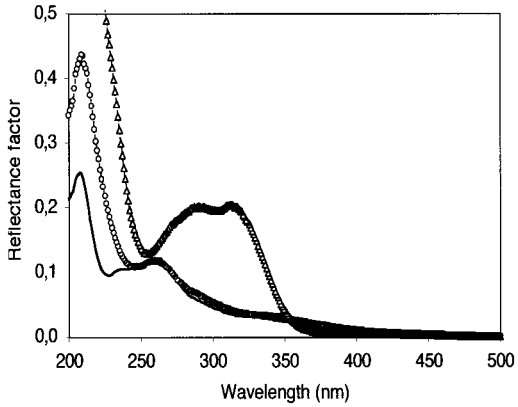

Figure 6. UV-visible diffuse reflectance spectra of (—) native cassava starch, (○) acidified cassava starch, and (△) corn starch.

mercury vapor lamp showed red staining similar to that frequently observed for periodate−starch reaction.

Starch UV Absorption and Presence of Chromophores. *Diffuse Reflectance Spectra.* Control cassava starch samples showed an intense and sharp absorption band, with a maximum at 210 nm (band I), followed by a medium intensity band resulting from the overlap of several peaks at 260−290 nm (band II). The latter band exhibited low intensity, with a maximum in the vicinity of 350 nm extending up to the visible region (band III). The patterns of acidified and irradiated samples were very similar to those of controls. However, an increase in absorbance occurred at 210 nm for acidified samples (Figure 6). In corn starch, a UV absorption band was also observed at 210 nm, which was more intense than that for cassava starch. A second band, overlapping between 260 and 360 nm, was also observed in the corn starch spectrum, with an excitation maximum at 290 and 310 nm (Figure 6).

Front-Surface Fluorescence Spectra. The synchronous scanning spectrum of native cassava starch showed two major peaks (Figure 7) associated with luminescence emission. The first was related to band II of the diffuse reflectance spectrum. An excitation wavelength set at 290 nm led to fluorescence emission, with a maximum at 330 nm. The second peak of the synchronous spectrum had a maximum located in band III of the diffuse reflectance spectrum, with excitation at 365 nm and maximal emission at 410 nm. A small peak excited at 460 nm was also observed. The pattern showed no differences between acidified, 254 nm irradiated, and control samples. Conversely, for samples irradiated with the 360 nm or mercury vapor lamps, the peaks excited at 290 and 365 nm showed reduced intensity. The same effect was detected for sour cassava starch. The spectra of glucose and amylopectin from cassava starch samples also showed no fluorescence.

Corn starch spectra also showed a large peak at 290 nm, corresponding to an emission at 330 nm (Figure 8) and relating to the overlapped bands at 260−370 nm observed in the diffuse reflectance spectrum for corn starch (Figure 3). The peak at 290 nm, which showed reduced intensity in the spectra of irradiated cassava starches, remained unchanged after irradiation of corn starch. The peak observed under excitation at 365 nm in cassava starch (Figure 7) was not clearly distinguish-

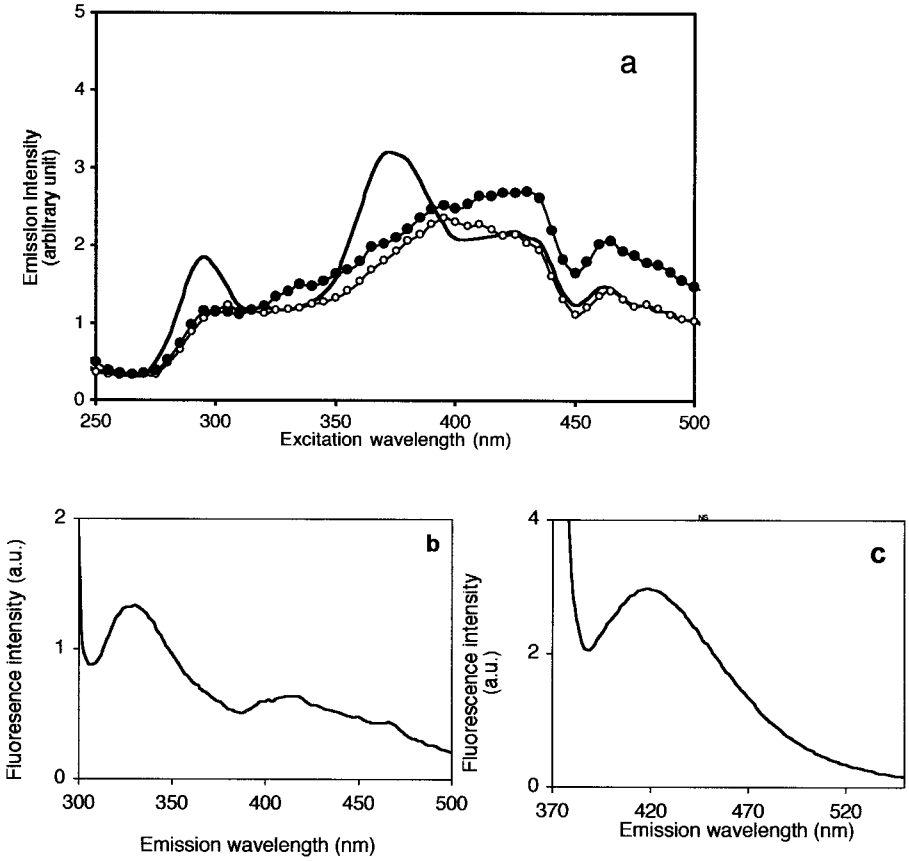

Figure 7. (a) Emission/excitation synchronous scanning spectra of cassava starch (—), irradiated cassava starch (●), and sour cassava starch (○); (b) emission fluorescence spectra, excitation at 290 nm; (c) emission fluorescence spectra, excitation at 365 nm.

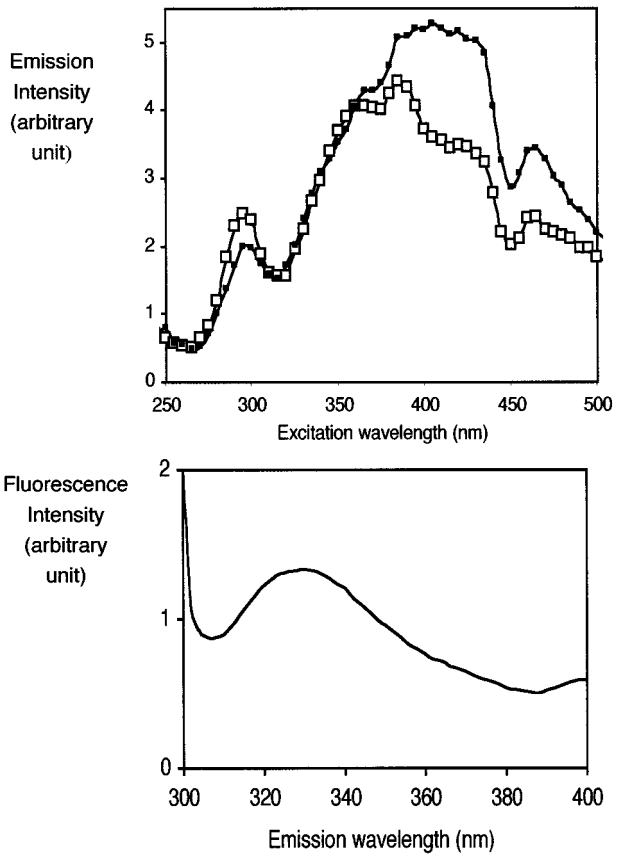

Figure 8. Top, emission/excitation synchronous scanning spectra of corn starch (□) and irradiated corn starch (■); bottom, emission fluorescence spectra, excitation at 290 nm.

able in the corn starch spectrum (Figure 8), overlapping another peak excited at 375 nm.

DISCUSSION

Effects of UV Irradiation on Starches. UV irradiation induced cassava starch depolymerization more effectively at 254 nm than at 360 nm (Table 2). The lack of interaction between acidification and starch factors suggests that acidification induced similar depolymerization for corn and cassava starches. However, the significant interaction between light exposure and starch factors indicated that the botanical origin of starch influences the extent of UV depolymerization. Indeed, cassava starch appeared to be more susceptible than corn starch to UV depolymerization.

The $\overline{M_w}$ values confirmed the starch depolymerization observed for intrinsic viscosity. The HPSEC/MALLS profiles showed random degradation by UV irradiation. In the HPSEC profiles of irradiated samples, the displacement of the first peak indicated depolymerization of amylopectin fraction. Amylose depolymerization was not so clearly apparent because the peak attributed to the depolymerized amylopectin fraction overlapped with the peak attributed to the amylose fraction. The decrease of $\overline{M_w}$ became greater when UV exposure with the mercury vapor lamp was increased from 4 to 16 h. These results differ from those reported by Fiedorowicz et al. (*28*) who found a higher $\overline{M_w}$ value for the amylopectin fraction in corn starch suspensions when UV-irradiation time was increased, suggesting that a starch cross-link occurred after 5 h of exposure.

The unchanged thermograms and diffraction patterns of cassava starch samples indicate that lactic acid treatment and UV irradiation did not change the crystalline structure of cassava starch. These observations are consistent with those of Mestres and Rouau (*22*) and Plata-Oviedo and Camargo (*6*), who found similar DSC thermograms for native, fermented, and sun-dried cassava starches. This finding suggests that starch photodegradation induced by UV irradiation or sun-drying is limited to amorphous regions of granules.

These changes give an explanation for the difference between native and sour starches. Because of the depolymerization event, sour cassava starch is likely to have lower viscosity and E′ than native cassava starch, enabling higher scores in baking expansion (*5*).

Photodegradation Mechanism in Starches. Staining with Schiff's reagent revealed the formation of aldehyde groups in starches photodegraded by the mercury vapor lamp. For starch photooxidation, some degraded forms could be similar to those encountered during starch oxidation by periodate ions. This observation is consistent with the notion that UV irradiation induces starch photooxidation, which would start with breakage of the C_2-C_3 bond of glucopyranose, producing a starch dialdehyde, followed by the formation of formaldehyde, formic acid, and CO_2 after UV irradiation (*13* and *14*).

Both cassava and corn starches were depolymerized by exposure to the mercury vapor lamp, leading to formation of AA′/BB′ type free radicals. The BB′ signal, as reported for gamma-irradiated starches (*27*), is attributable to $-RO_2^{\bullet}$ radicals and to the action of gaseous oxygen traces on free radicals resulting from the cleavage of glycosidic links (*27*).

The absence of the ESR signal in cassava starch samples irradiated at 360 nm, and the lack of carboxyl groups in cassava starch samples irradiated at 360 and 254 nm, indicated that free radicals and carboxyl groups, if present, were not detectable by these methods. Indeed, ESR signal intensity and free radical lifetime decrease with increases in the moisture contents of starch and with a reduction of total irradiation energy (*27*). Irradiation of samples at 360 and 254 nm was carried out with higher final water contents (12−13%) than for samples irradiated under the mercury vapor lamp (9−10%). Moreover, the energies emitted at 360 and 254 nm were lower than those observed for the mercury vapor lamp. Thus, the higher moisture contents and lower irradiation energy received by samples exposed to 360 and 254 nm could have been responsible for the lack of an ESR signal and carboxyl groups. Carboxyl groups formed only in samples acidified and then irradiated under the mercury vapor lamp.

However, the role of lactic acid and its effects on starch photodegradation remain unclear. Given the decrease in lactic acid content after UV irradiation, photodegradation of lactic acid should have taken place during UV exposure. As sample temperature during light exposure was never higher than 40 °C, it is unlikely that lactic acid was vaporized. The notion that lactic acid was photolyzed is in agreement with the hypothesis of Mestres and Rouau (*22*) that lactic acid is converted to another product during sun-drying of starch. Much earlier works (*29* and *30*) reported a degradation of lactic acid solutions by sunlight and UV irradiation, resulting in the formation of formaldehyde, acetaldehyde, acetic acid, peroxides, formic acid, carbon

monoxide, carbon dioxide, hydrogen, methane, and pyruvic acid. These reports might explain the traces of formic acid observed in the samples after UV exposure. Formic acid could be generated from lactic acid or by starch photodegradation. The increase in the intensity of the peak at 210 nm in the reflectance spectra of acidified samples might have been due to lactic acid. In fact, maximum absorption was observed at 210 nm for lactic acid solutions (*14* and *30*).

The existence of fluorescence chromophores in native cassava starch was evidenced by excitation at 290 and 360 nm. The disappearance of this fluorescence after irradiation with mercury vapor and 360 nm lamps suggests that these components are degradable by UV irradiation. The lack of these peaks in the spectrum for sour cassava starch suggests that the same effect could be induced by the high-energy part of the sun spectrum. Conversely, the presence of fluorescence chromophores in samples irradiated at 254 nm indicates that fluorescent chromophores in cassava starch are apparently insensitive to photolysis by irradiation at 254 nm.

The diffuse reflectance and fluorescence spectra for corn starch samples were quite different from those for cassava starch. The strong band observed at 320 nm in the reflectance spectrum of corn starch (Figure 6), which was lacking in cassava starch, did not lead to fluorescence emission (Figure 8). In particular, the peak present at 290 nm was not affected by UV irradiation. Thus, it is possible that the excited components at 290 nm were not the same for cassava and corn starch samples. Despite these differences, both starches were depolymerized by lactic acid and UV irradiation. In depolymerization, the interaction related to starch origin and light exposure (Table 1) is indicative of the different behavior of cassava and corn starches during UV irradiation. Cassava starch is considered more susceptible than other cereal starches to oxidative depolymerization (*31*), which could be due to the absence of lipids. As lipids are more easily oxidized, they would be photoxidized before starch and could thus play a protective role in starch depolymerization by UV irradiation.

Cassava starch samples showed an absorption spectrum similar to that of amylopectin extracted from cassava. However, both amylopectin and dextrin samples showed no fluorescence when excited at 290 or 360 nm, indicating the absence of fluorescent chromophores. The multistep treatment required for amylopectin extraction or dextrin production could remove the natural substances present in starch and/or change the crystallinity level, with the concomitant loss of fluorescence. This result would also mean that the fluorescence observed in cassava starch was not due to the D-glucosyl structure.

However, the presence of free radicals in irradiated dextrins and amylopectin indicated that UV absorption occurred for these samples. Given the complex molecules present in cassava, competition could occur between several photochemical pathways. One pathway could relate to UV absorption by fluorescent chromophores excited at 290 and 360 nm in cassava starch. The other, leading to the formation of free radicals in starch, amylopectin, and dextrin, could correspond to the breakage of glucose bonds present in all these samples. With this pathway, the D-glucose molecule would absorb UV irradiation (*15*), thereby playing the role of a nonfluorescent chromophore.

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