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Carbohydrate Polymers 49 (2002) 63–70

Carbohydrate Polymers

www.elsevier.com/locate/carbpol

Three underutilised sources of starch from the Andean region in Ecuador Part I. Physico-chemical characterisation

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Received 14 March 2001; revised 4 July 2001; accepted 4 July 2001

Abstract

The physico-chemical aspects of three native Andean starches from *Arracacha xanthorriza*, *Canna edulis* and *Oxalis tuberosa* were investigated. Scanning electron microscopy-investigations showed that granules of *A. xanthorriza* were the smallest with irregular shape and sizes between 7 and 23 μm, whereas granules of *O. tuberosa* and *C. edulis* were both ovally shaped with granular sizes between 20 and 55 μm and 35–101 μm, respectively. All three starches revealed a B-type X-ray diffraction pattern. The gelatinisation behaviour was investigated using differential scanning calorimetry (DSC). The gelatinisation enthalpy was 14.6 J/g of starch for *O. tuberosa*, 15.7 J/g for *C. edulis* and 17.6 J/g for *A. xanthorriza*, and the peak temperature of the endothermic DSC-transition was 55.9, 61.2 and 60.1°C, respectively. The amylose content determined by gel permeation chromatography after debranching with isoamylase was 4% for *A. xanthorriza*, 18.4% for *O. tuberosa*, and 23.8% for *C. edulis*. The amylopectin showed different structures among the three starches with a β-amylolysis limit of 67.6% for *C. edulis*, 64.5% for *O. tuberosa* and 56.6% for *A. xanthorriza*. The average chain length of the amylopectin was highest for *A. xanthorriza* (22.6), followed by *O. tuberosa* with 22.4, and lowest for *C. edulis* (21.9). The complexation ability of the three starches was investigated by adding sodium dodecyl sulphate (SDS), and the amylose content was positively correlated with the enthalpy of the amylose–SDS complex.

Keywords: *Arracacha xanthorriza*; *Canna edulis*; *Oxalis tuberosa*; Gelatinisation; Chain length distribution; Amylose–lipid complex; Ecuador

1. Introduction

Starch is a very useful raw material with a wide field of applications from gelling systems of foods to manufacturing of paper and adhesives (Swinkels, 1985). The source of starch production varies all over the world depending on local traditions and climatic conditions, but it is more or less only starch and starch derivatives of maize and potato that are of commercial interest (Swinkels, 1985). Only a few percentages of the world crop of starch is used in its native state, and to fit into specific industrial processes the main part of starch is chemically modified by degradation, substitution or cross-bonding (Koch & Röper, 1988). There are also possibilities of using genetically modified crops enriched in one of the starch components, such as high-amylopectin potato (Visser, Suurs, Steeneken & Jacobsen, 1997.

However, there is always a concern about using different kinds of modified starches for food production, and consumers' request of non-modified foods are constantly increasing. Another aspect is that many countries lack their own domestic production of starch, even though they have conceivable conditions for it (National Research Council, 1989). It can therefore be of wide interest to characterise new and unconventional sources of native starch. Potato that is used as a source of starch and starch derivatives originates from the Andean region in South America, but the use of other Andean crops as sources of starch has not yet been fully investigated. This is most likely a result of incomplete knowledge of the characteristics of such starches. Some reports in the literature (Cortella & Pochettino, 1995; Hizukuri 1985; Pérez, Breene & Bahnassey, 1998; Snyder 1984) include information on the properties of gelatinisation, starch granule size and the distribution of the chain length of amylopectin of *Arracacha xanthorriza*, *Canna edulis*,

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Abbreviations: Differential scanning calorimetry (DSC); Size-exclusion chromatography (SEC); Scanning electron microscopy (SEM); Sodium dodecyl sulfate (SDS); cultivar (cv)

0144-8617/02/$ - see front matter
PII: S0144-8617(01)00305-8

and *Oxalis tuberosa*, but much more knowledge of the functional properties of these starches is required before they can be commonly used. In the present study of the physicochemical properties, such as morphology, crystallinity and gelatinisation, three Andean starches extracted from *A. xanthorriza*, *C. edulis* and *O. tuberosa* were investigated. Moreover, the chemical composition in terms of amylose and amylopectin was characterised.

2. Materials and methods

2.1. Materials

Tubers of *A. xanthorriza,* cultivar FB-001, and *C. edulis*, cultivar MH-1173, were both identified and obtained from International Potato Centre (CIP), Quito, Ecuador, whereas *O. tuberosa* was bought directly at the local grocery market in Quito, Ecuador.

The starch was isolated after rinsing the tubers in water and grinding in a Rietz RP-8-115 disintegrator (Rietz Manufacturing Company). The slurries obtained were wet-sieved (mesh 1 mm, 0.5 mm and 150 μm) to exclude non-starch components by repeated washing cycles. The suspensions with a concentration of approximately 0.007 Kg/l were then stirred in containers (0.75 m × 0.75 m × 0.60 m), and allowed to form a sediment before the supernatant was removed. The necessary time to obtain a sediment was approximately 24 h, 1 h and 30 min for *A. xanthorriza*, *O. tuberosa* and *C. edulis*, respectively. After the sedimentation procedure was repeated at least three times, the pure starch sediments were dried in an oven at 30°C for 15 h.

Dimethylsulfoxide (DMSO) and sodium dodecyl sulfate (SDS), specially purified for biochemical work, were purchased from BDH Chemicals (Poole, England). Iodine, potassium iodide and urea were obtained from E. Merck (Darmstadt, Germany). Sepharose CL-6B was purchased from Amersham Pharmacia Biotech (Uppsala, Sweden). The isoamylase EC 3.2.1.68 used was the crystalline form from *Pseudomonas amyloderamasa*, 71,000 U/mg protein, obtained from Hayashibara Biochemical Labs. (Okayama, Japan) and β-amylase (EC 3.2.1.2, 880 U/mg protein) from Sigma Chemical, St Louis, MO, USA. Aluminium oxide, Al_2O_3, 90 active, neutral for column chromatography was obtained from E. Merck (Darmstadt, Germany). Double distilled and deionised water was used for all experiments.

2.2. Methods

2.2.1. Scanning electron microscopy (SEM)

A thin layer of starch granules was mounted on an aluminium specimen holder by double-sided tape. The specimen holder was loaded in a Balzers SCD 004 Gold Sputter Coater for 120 s at 15 mA. During these conditions a thin cover of gold with a thickness of approximately 20 nm will be obtained. The specimen holder was then transferred to a JEOL JSM-840A scanning electron microscope and the starch samples were examined at 20 kV.

2.2.2. Wide-angle X ray scattering technique (WAXS)

A flat-film camera arrangement (Stenhagen, 1951) was used for the WAXS determinations. The X-ray camera was equipped with a Philips PW 2273/20 LFF copper anode X-ray tube (Philips, The Netherlands), giving an average radiation wavelength of 0.154 nm, and operated at 40 kV and 20 mA. Characteristic *d*-spacings in the wide-angle area for the β-form of tristearine were used for the calibrations.

The starch samples were weighed into small tubes and mixed with water to a water/starch ratio of 1:1 (w/w). The samples were equilibrated at room temperature for 1 h before they were mounted in designed X-ray cassettes with O-rings and windows of mica. The X-ray scattering was registered on medical X-ray film, CEA Reflex 25 (CEA AB, Strängnäs, Sweden), and processed according to recommendations of the manufacturer.

2.2.3. Differential scanning calorimetry (DSC)

The gelatinisation properties of the different starches were analysed on a Seiko SII 6200 DSC (Seiko, Japan) equipped with standard software. The investigations were made in the temperature range 17–97°C, at a scanning rate of 10°/min. The samples were investigated in excess of water with a starch to water ratio of 1:3 (w/w) in coated pans from TA Instruments (TA Instruments, USA). An empty pan with double lids was used as a reference. The enthalpies of gelatinisation (ΔH) are presented in J/g starch and calculated on dry matter basis, that was determined by puncturing and drying the pans in an oven at 105°C for 2 h. The endothermic DSC-transition temperatures, registered in °C, are given as the onset temperature (T_o), the peak temperature (T_m) and the final temperature (T_c). The results given are the average of three measurements.

For studying the complexation of SDS with amylose, starch samples were weighed directly into the pans. An SDS solution (5% w/w) was added to give a water-starch relation of 2:1 (10% SDS (w/w) on starch basis). The pans were prepared just before the measurement was made. A pan with aluminium oxide (Al_2O_3) was used as reference. The melting enthalpy of the amylose-SDS complex (ΔH_{cx}) and its melting peak temperature (T_{cx}) were determined and calculated on their dry matter basis, determined as previously described. The results given are the average of three measurements. The heating processes used for the experiments was adapted from Gudmundsson (1992): heating from 20 to 150°C at a rate of 10°/min, stop for 3 min at 150°C, then cooling from 150 to 20°C at a rate of 50°/min, before a second heating cycle between 20 and 140°C at a rate of 10°/min, stop for 1 min at 140°C, and finally cooling from 140 to 20°C at a rate of 50°/min.

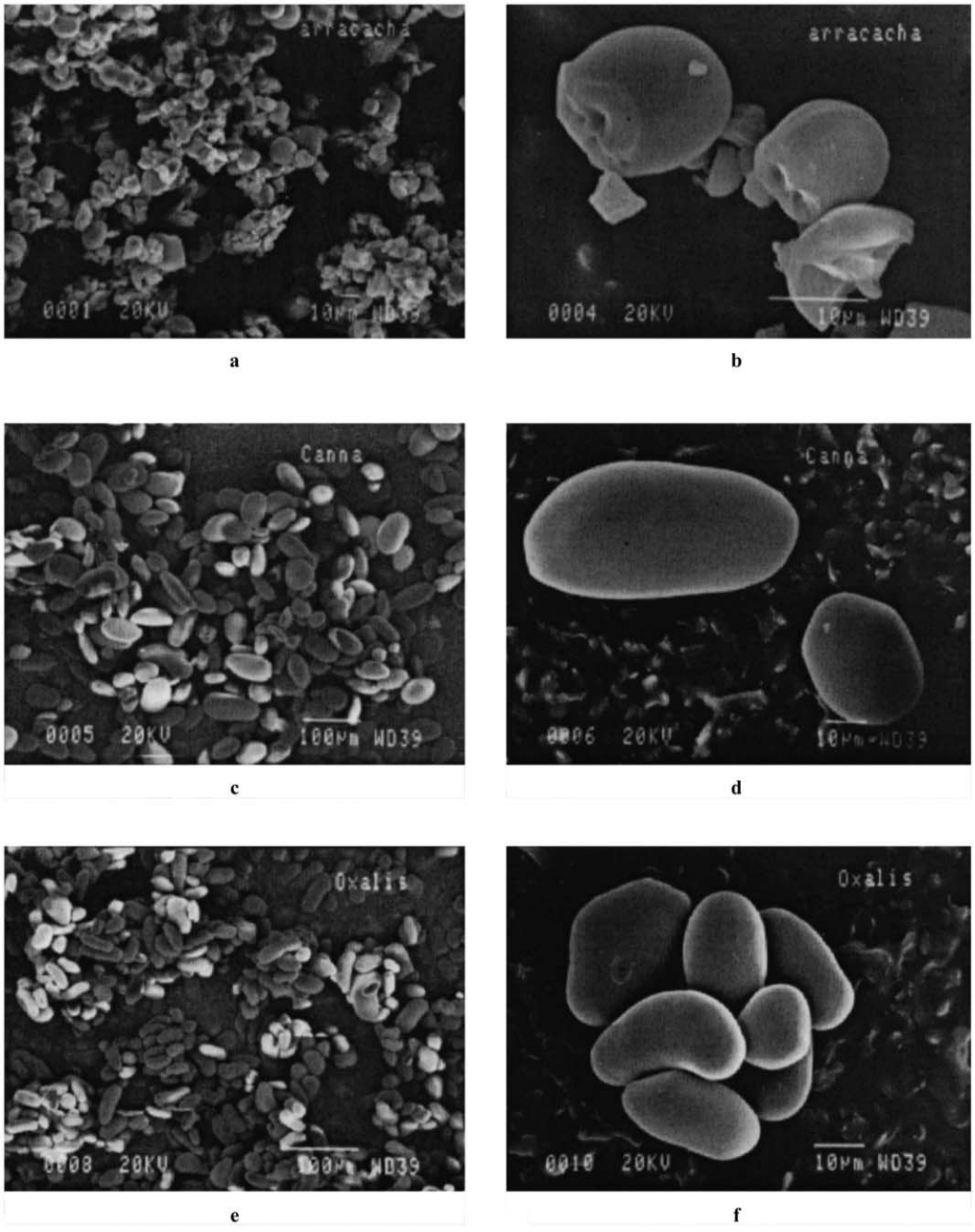

Fig. 1. SEM micrographs of starch granules from: (a), (b) *A. xanthorriza*, (c), (d) *C. edulis* and (e), (f) *O. tuberosa*.

2.2.4. Determination of blue value and maximum wavelength (λ_{max})

Blue values and λ_{max} were determined according to Morrison and Laignelet (1983). Starch or amylopectin samples were dissolved in a mixture of nine volumes of DMSO and one volume of 1 M urea. An aliquot of starch-urea-dimethylsulphoxide (UDMSO) was dissolved with an appropriate amount of water, then a I_2–KI solution was added and the resultant solution was mixed immediately. Solution absorbances were measured at 635 nm 15 min after addition of I_2–KI reagent. The absorption curves were also determined in the range 400–800 nm. Calculation and temperature corrections of blue values were done according to Morrison and Laignelet (1983).

2.2.5. Isolation of amylopectin

Fifty milligrams of starch was dissolved in 1 ml of 1 M NaOH, and 9 ml of distilled water were added in steps during 4 h. The polysaccharide product was fractionated on a Sepharose CL-2B (Amersham Pharmacia Biotech, Uppsala, Sweden) column (70 cm × 1.6 cm) using 0.01 M NaOH as eluent at a flow rate of 0.4 ml/min. The elution profile was monitored by refractive index (RI detector R-403, Waters Associates, Milford, MA, USA) and the

Table 1
Physico-chemical properties together with λ_{max} and β amylolysis of the amylopectin fraction of *A. xanthorriza*, *C. edulis* and *O. tuberosa*

Isolated amylopectin								
Source	Shape	Size (μm)	X-ray pattern	Amylose content (%)	Blue value[a]	λ_{max} (nm)		β amylolysis[a] (%)
A. xanthorriza	Irregular	7–23	B	3–5	0.42 ± 0.02	559	551	56.6 ± 1.1
C. edulis	Oval	35–101	B	23.4–24.2	0.92 ± 0.04	613	574	67.6 ± 3.0
O. tuberosa	Oval	22–55	B	17.4–19.4	0.85 ± 0.04	598	560	64.5 ± 0.6

[a] Mean value and standard deviation of measurements made at triplicate.

amylopectin fraction isolated and freeze dried (Lloyd, Hedley, Bull & Ring, 1996).

2.2.6. β-Amylolysis limit

β-Amylolysis was performed according to Andersson, Rydberg, Larsson, Andersson and Åman (2001). Amylopectin (5 mg) was dissolved in 200 μl DMSO in a boiling water bath. The sample was then diluted with 1 ml 0.1 M sodium acetate, pH 4.8 and 1μl of β-amylase (22,880 U/ml) was added. The incubation at 25°C was stopped after 5 h by boiling the sample for 5 min. The sample was diluted 1:1 with water prior to injection on a Biogel P-2 column (1.6 cm × 90 cm) eluted with water. Carbohydrates in collected fractions (0.9 ml) were detected by the phenol–sulphuric acid method (Dubois, Gilles, Hamilton, Rebers & Smith, 1956). The β-amylolysis limit was calculated as the proportion of carbohydrates with a $dp < 4$.

2.2.7. Determination of the amylose content

Starches from *A. xanthorriza*, *C. edulis* and *O. tuberosa* were prepared essentially according to the method described by Torneport, Salomonsson and Theander (1990). The samples (6 mg) were dissolved in 1 ml DMSO in a boiling water-bath for 30 min, and then transferred to an oven at 100°C for an additional 60 min. The starch was then precipitated with 9 ml ethanol (95% (v/v)) and centrifuged for 5 min at 1000 × *g*. The precipitates were dissolved in 0.5 ml DMSO with heating, and incubated in 3.5 ml 0.06 M sodium acetate buffer (pH 3.6) and 5 μl isoamylase at 38 °C in a shaking water-bath over night. The debranched samples were then applied to a Sepharose CL-6B (65 cm × 1.6 cm). The elution procedure was performed with 0.25 M KOH at a flow-rate of 23 ml/h. Fractions of 2 ml were collected, and the amylose–amylopectin ratio was determined by carbohydrate detection using the phenol–sulphuric acid method (Dubois et al., 1956).

2.2.8. Determination of the chain length distribution of amylopectin

Amylopectin was isolated according to Koch, Andersson and Åman (1998), and debranched by isoamylase according to the methods described by Fredriksson, Andersson, Koch and Åman (1997). The chain length distribution was analysed with high performance anion exchange chromatography on a Dionex DX 500 (Sunnyvale, CA, USA) equipped with a ED 40 pulsed amperometric detector, a CarboPac PA-100 anion exchange column (250 mm × 4 mm) in combination with a CarboPac PA-100 guard column, and an autosampler (Spectra-Physics, Freemont, CA, USA), Koch et al. (1998). The detector response of the PAD is not quantitative with respect to carbohydrate content. Therefore the individual peaks of (1 → 4)-α-D-glucans in the amylopectin chromatograms were corrected for by their relative molar PAD response (Koch et al., 1998). The longest chains that could be quantified had a CL of 56.

3. Results and discussion

By SEM investigations the starch granular sizes were observed to be remarkably different for the three starches of *A. xanthorriza*, *C. edulis*, and *O. tuberosa* (Fig. 1, Table 1). The granules of *C. edulis* are the largest with measured lengths between 35 and 101 μm. Even larger granules of *C. edulis* have been reported in the literature (Snyder, 1984). The granules can be partly compared with those of potato starch with sizes of 10–100 μm (Snyder, 1984). Granules of both *O. tuberosa,* and *A. xanthorriza* have more modest sizes in the range 22–55 and 7–23 μm, respectively. The size of granules for *O. tuberosa* is similar to that reported by Cortella and Pochettino (1995). The SEM investigations also showed the presence of pores along the equatorial region of native granules of *A. xanthorriza* (see Fig.1b). The pores had an estimated diameter around 2 μm. A similar arrangement of pores has also been observed on potato starch granules, and granules from wheat, rye and barley (Fannon, Hauber & BeMiller, 1992). No such pores were however observed on granules from *C. edulis* or *O. tuberosa*.

All three starches exhibited similar X-ray patterns (Table 1) with one strong *d*-spacing at 1.58 nm, a very weak spacing at 0.93 nm, two weak spacings at 0.64 and 0.59 nm, a strong one at 0.52 nm, three medium strong spacings at 0.47, 0.41 and 0.37 nm, and finally a weak spacing at 0.34 nm. The X-ray diffraction pattern of the spacings is characteristic for the B type, which is reported to be typical for almost all kinds of root and tuber starches, like potato (Zobel, 1988).

The amylose content, measured by SEC, was highest for *C. edulis* with 23.8% followed by *O. tuberosa* 18.4%, and *A. xanthorriza* 4% (Table 1). The amylose levels can be

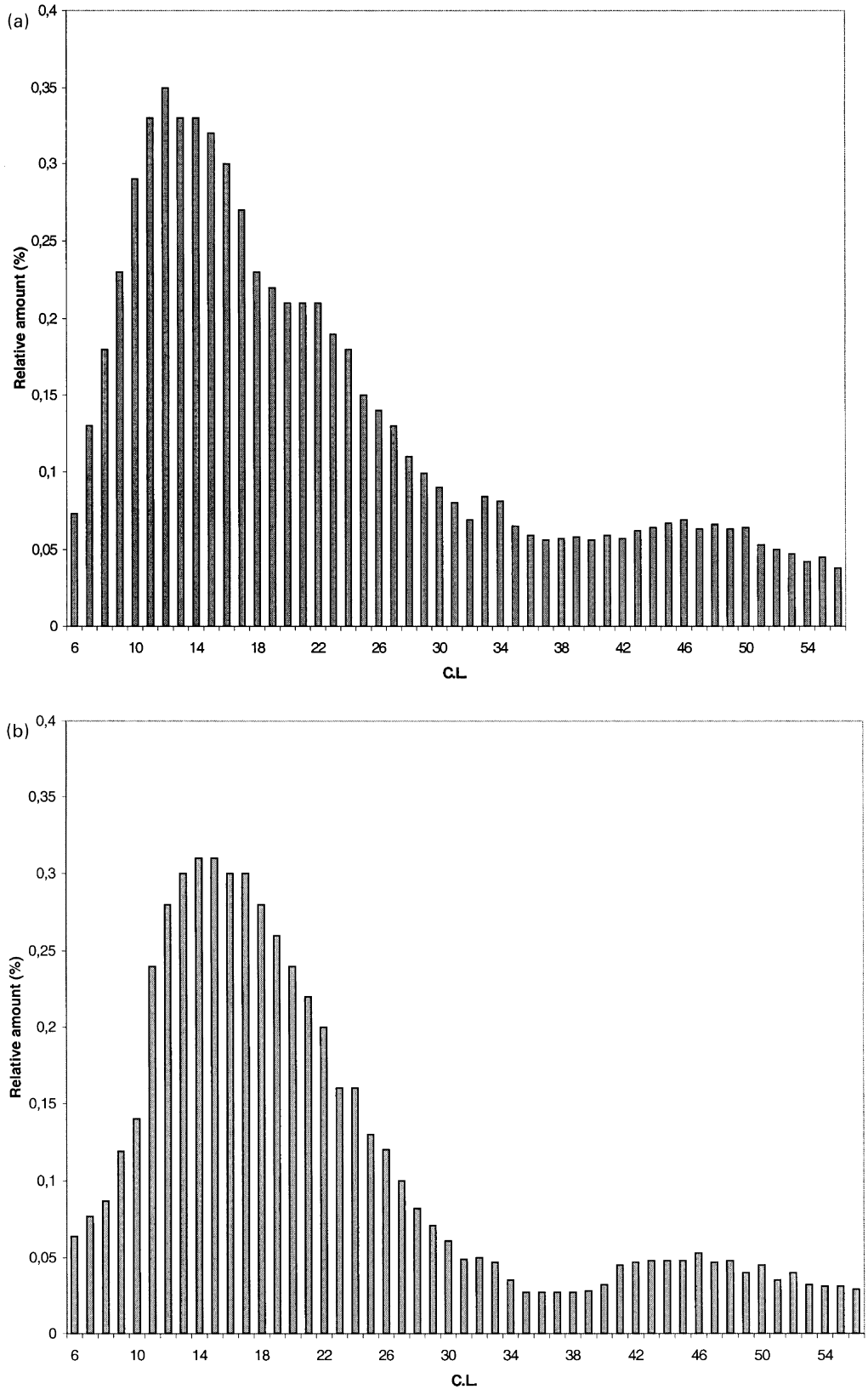

Fig. 2. (a) Amylopectin unit chain length distribution of *A. xanthorriza* by high-performance anion-exchange chromatography. (b) Amylopectin unit chain length distribution of *C. edulis* by high-performance anion-exchange chromatography. (c) Amylopectin unit chain length distribution of *O. tuberosa* by high-performance anion-exchange chromatography.

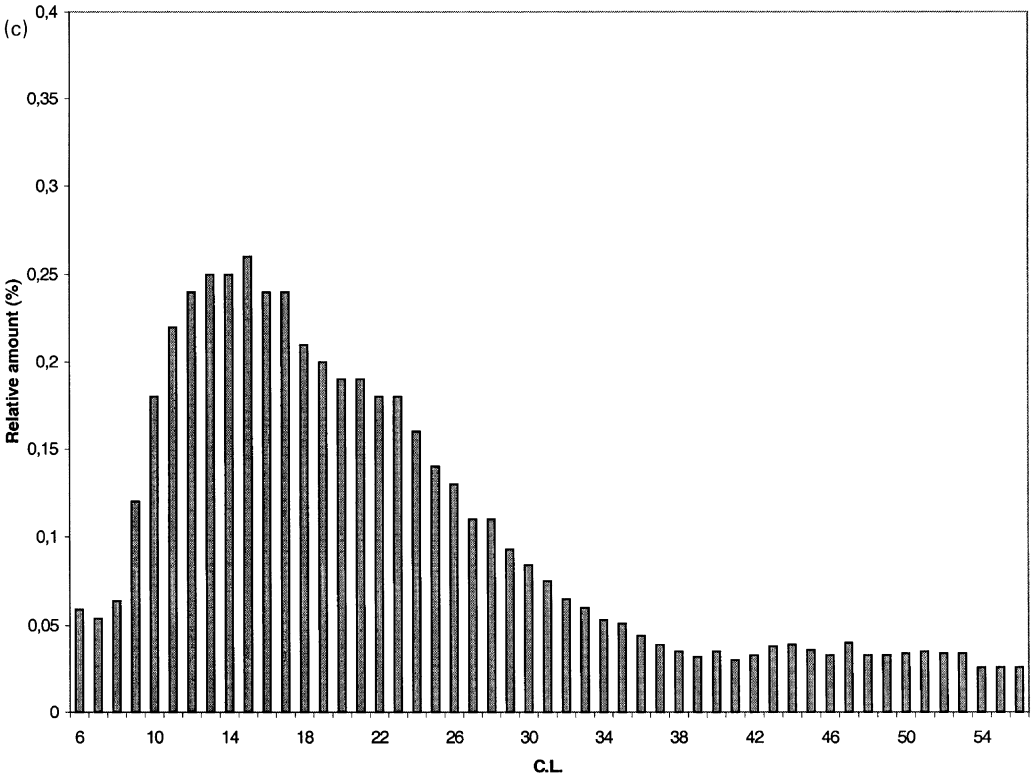

Fig. 2. (continued)

compared with the ones found for some starches, e.g. potato (Fredriksson, Siverio, Andersson, Eliasson & Åman, 1998), normal and waxy maize (Hizukuri, 1996), with values of 21, 25.8–32.5 and 1.4–2.7%, respectively.

Blue value and λ_{max} of the whole starch showed a tendency similar to the amylose content, being 0.92 and 613 nm for *C. edulis*, 0.85 and 598 nm for *O. tuberosa* and 0.42 and 559 nm for *A. xanthorriza*.

Isolated amylopectin of *C. edulis* had the highest β-amylolysis limit and λ_{max} (67.6% and 574 nm), whereas the values for *O. tuberosa* (64.5% and 560 nm) were between those of *C. edulis* and *A. xanthorriza* (56.6% and 551 nm). These values are comparable to that obtained for commercial maize, being 59% and 554 nm for β-amylolysis limit and λ_{max}, respectively (Hizukuri, 1996). The lower β-amylolysis limit and λ_{max} values of *A. xanthorriza* compared to *C. edulis* and *O. tuberosa* suggest shorter outer chains for the first one. Moreover, a low β-amylolysis limit of *A. xanthorriza* could suggest extensive branching in the amylopectin, whereas the higher value of *C. edulis* and

Table 2
Gelatinisation parameters of *A. xanthorriza*, *C. edulis* and *O. tuberosa* with and without SDS showing enthalpy (ΔH), onset (T_o), peak (T_m) and final (T_c) temperatures of gelatinisation together with T_{cx} and ΔH_{cx} of the amylose-SDS complex (n.d.: not detected)

Starch	T_o[a] (°C)	T_m[a] (°C)	T_c[a] (°C)	ΔH[a,b] (°C)	T_{cx}[a] (°C)	ΔH_{cx}[a,b] (J/g)
A. xanthorriza						
Without SDS	53.8 ± 0.1	60.1 ± 0.1	65.9 ± 0.8	17.6 ± 0.3	n.d.	n.d.
With SDS[c]	48.3 ± 0.3	54.6 ± 0.2	–[d]	12.0 ± 0.9	99.7 ± 0.6	0.2 ± 0.1
C. edulis						
Without SDS	56.8 ± 0.0	61.2 ± 0.1	67.7 ± 0.9	15.7 ± 0.2	n.d.	n.d.
With SDS[c]	54.6 ± 0.5	60.0 ± 0.2	–[d]	6.7 ± 1.1	97.9 ± 1.5	2.7 ± 0.4
O. tuberosa						
Without SDS	50.2 ± 0.1	55.9 ± 0.2	63.3 ± 0.4	14.6 ± 0.2	n.d.	n.d.
With SDS[c]	45.3 ± 0.1	50.5 ± 0.4	–[d]	7.3 ± 0.1	98.7 ± 1.9	2.0 ± 0.4

[a] Mean value and standard deviation of measurements made at triplicate.
[b] Expressed as J/g starch.
[c] With 10% SDS (w/w, starch basis).
[d] Not determined.

O. tuberosa could indicate a less branched structure (Madhusudhan, Gowda & Tharanathan, 1996).

The chain length distribution of the amylopectins showed a trimodal distribution profile for all three starches (Fig. 2a–c). *C. edulis* and *O. tuberosa* had smaller amounts of chains between CL 6 and 9 than *A. xanthorriza*. Small amount of chains with CL 6 to 9 together with the absence of a maximum at CL 12 of *C. edulis* and *O. tuberosa* were the main differences with *A. xanthorriza*. The chain length distribution patterns for chains between CL 6 to 9 seem to be characteristic of each species (Hanashiro, Abe & Hizukuri, 1996; Koizumi & Fukuda, 1991). *C. edulis* and *O. tuberosa* showed similar distribution patterns between CL 12 and 15 whereas *A. xanthorriza* had a peak at CL 12. The three starches showed a shoulder at CL 22–24. The long chains of *A. xanthorriza* and *C. edulis* had a maximum at CL 46 whereas *O. tuberosa* showed no distinct population in the region CL 40–55. The cereal amylopectins of rye and waxy barley showed a similar distribution pattern to the one of *A. xanthorriza*, with a peak at CL 12 and a marked shoulder at CL 19–20 (Silverio, Fredrikson, Andersson, Eliasson & Åman, 2000). Potato Desiree has a slightly similar pattern to *C. edulis* and *O. tuberosa* for CL between 10 and 20 (Silverio et al., 2000). The weight average chain length was the highest for *A. xanthorriza* with 22.6, followed by *O. tuberosa* with 22.4, and *C. edulis* with 21.9. Obviously, the weight average chain length values did not correspond to the β-amylolysis limit and the λ_{max}. Similar weight average chain lengths of *A. xanthorriza* and *O. tuberosa* showed differences of β-amylolysis, λ_{max} and consequently a different chain length distribution of amylopectin. The results could suggest a similar degree of branching of *A. xanthorriza* and *O. tuberosa* with a different pattern of branching.

DSC-results of the three starch samples showed that the peak temperature (T_m), often referred to as the gelatinisation temperature, was 55.9°C for *O. tuberosa*, 60.1°C for *A. xanthorriza*, and 61.2°C for *C. edulis* (Table 2). The gelatinisation enthalpies ranged from 14.6 J/g of amylopectin for *O. tuberosa* to 17.6 J/g for *A. xanthorriza*. The gelatinisation properties for *A. xanthorriza* were similar to those reported by Pérez et al. (1998). Fredriksson et al. (1998) have shown that enthalpy and temperature of gelatinisation only could be correlated in starches from similar genetic origin.

The native starches of *A. xanthorriza*, *C. edulis* and *O. tuberosa* do not contain lipids, and no endotherm due to a transition of the amylose–lipid complex was observed in the DSC thermogram. To obtain information about the lipid complexation ability of the starches, their interaction with SDS was investigated. SDS was chosen as a model surfactant as it does not give rise to any endotherms by itself in the temperature range of interest (Evans, 1986). It was found that the enthalpy of gelatinisation decreased in the presence of SDS (Table 2). Such a reduction could be explained by an exothermic complex formation between SDS and amylose (Gough, Greenwell & Russell, 1997b; Villwock, Eliasson, Silverio & BeMiller, 1999). Also the temperature range of gelatinisation was altered in the presence of SDS. The peak temperature decreased for *C. edulis* from 61.2 to 60.0°C, from 55.9 to 50.5°C for *O. tuberosa*, and from 60.1 to 54.6°C for *A. xanthorriza*. The complex between amylose from *A. xanthorriza*, *C. edulis* and *O. tuberosa* starches and SDS at saturated conditions (Evans, 1986) show melting peaks (T_{cx}) between 97.9°C for *C. edulis* and 99.7°C for *A. xanthorriza* (Table 2). The enthalpy of the transition of the complex, ΔH_{cx}, was positively correlated to the amylose content, being the highest for *C. edulis*, 2.7 J/g, followed by *O. tuberosa* and *A. xanthorriza* with enthalpies of 2.0 and 0.2 J/g, respectively.

The present investigation has clearly demonstrated that there were considerable differences in the physico-chemical properties between the three starches examined from the Andean region of Ecuador. The three starches exhibited the same B-type X-ray crystallinity pattern, but differed in the gelatinisation properties. Isolated amylopectins of *A. xanthorriza* and *O. tuberosa* showed to have a similar degree of branching with a different pattern of branching. Starch from *A. xanthorriza* with a natural amylose content of 4% could be an interesting alternative to waxy starches. For practical applications it is of interest to examine the rheological and gel-forming properties of three starches and this will be published in a separate paper.

Acknowledgements

This research has been financed by grants from International Program In the Chemical Sciences (IPICS). The authors thank Dr P. Åman and Dr R. Andersson for help and discussion in preparing the manuscript.

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