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# Characterization of Starches from Tuber of *Pinellia ternata* (Thunb.) Breitenbach, Rhizome of *Alisma orientale* Juzepczuk and Seed of *Coix lacryma-jobi* Linné var. *ma-yuen* Stapf

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**Abstract: Various physicochemical properties were investigated to assess the potential of starches from the residual crude drugs after extraction. The powdered crude drugs (C) differed from each other in harvest time or district of cultivation. Starches (S) were prepared from tubers of *Pinellia ternata* (Thunb.) Breitenbach (PT), rhizomes of *Alisma orientale* Juzepczuk (AO) and seeds of *Coix lacryma-jobi* Linné var. *ma-yuen* Stapf (CL). C-PTs, C-AOs and C-CLs contained 41.1–77.5, 12.5–40.5 and 1.5–5.8% starch, respectively. S-PT, S-AO and S-CL granules measured were 8.2±0.2–16.0±0.4, 6.1±0.2 and 11.5±0.4–13.5±0.4 μm, respectively, in average diameter. S-PTs, S-AOs and S-CLs were classified as CA-type. The amount of P in S-PTs, S-AOs and S-CLs was 62–330, 93–110 and 75–210 μg/g, respectively. That of Ca was 320–530, 48–260 and 18–33 μg/g, respectively. S-PT-1, S-AO-2 and S-CL-2 showed endothermic curves from 67.3 to 85.0, 58.9 to 84.2 and 59.2 to 81.0°C, their enthalpy being 3.4±0.3, 4.2±0.0 and 4.5±0.2 J/g, respectively. S-PT-1, S-AO-2 and S-CL-2 are expected to be available for starch gelatinized at low energy. The digestibility of raw S-PTs, S-AOs and S-CLs by α-amylase was 35.3±2.4, 38.3±2.3 and 62.2±5.2%, respectively, at 72 h. The main oligosaccharide products from the raw starches (digestibility: S-PT-1, 2.4%; S-AO-2, 5.8%; S-CL-2, 7.1%) digested by α-amylase were maltotriose (35.8–40.0%) and maltose (35.8–42.8%). The main product from the starches (digestibility: S-PT-1, 4.8%; S-AO-2, 12.1%; S-CL-2, 18.7%) digested by glucoamylase was glucose (97.6–99.5%). The digested S-PT-1, S-AO-2 and S-CL-2 granules (digestion time, 1 h) were roughly eroded by α-amylase all over the surface and the starches digested by glucoamylase maintained their original form with a few fine grains on their surface. A few granules of S-CL-2 digested by glucoamylase lost their original form. The S-PT-1(A), S-AO-2 (A) and S-CL-2(A) digested by α-amylase are expected to be available as an adsorbent, because of their porosity. The results of gelatinization temperature and enthalpy suggest that the thermostability of S-PT-1, S-AO-2 and S-CL-2 digested by α-amylase was higher than that of the starches digested by glucoamylase.**

**Key words: pinellia tuber starch, alisma rhizome starch, coix seed starch, physicochemical property, digestibility by amylase**

The traditional Chinese herbal remedies Pinellia Tuber, the tuber of *Pinellia ternata* (Thunb.) Breitenbach (PT), Alisma Rhizome, the rhizome of *Alisma orientale* Juzepczuk (AO) and Coix Seed, the seed of *Coix lacryma-jobi* Linné var. *ma-yuen* Stapf (CL), have been used as a stomachic, a diuretic and an antifebrile anodyne antiphlogistic agent, respectively. They are the most useful crude drugs in traditional Chinese medicine. In 2001 and 2002, quantitative imports of PT, AO and CL totaled 250, 200 and 6972 to 8693 tons, respectively.[1)] CL has been consumed abundantly as a raw material for health teas in recent years. The adsorption of water[2)] and dyes[3)] by crude drug starches of PT, AO and CL has also been investigated. PT, AO and CL starches were superior to potato starch in the capacity to adsorb anionic methyl orange at 25°C.[3)] The physicochemical properties of starches from AO cultivated in Japan have been examined.[4)]

Crude drugs have been utilized as a raw material for extracts and in powdered form. The purpose of this study was to make profitable the use of starch after extraction of the active ingredients of the crude drugs PT, AO and CL, as well as *Panax ginseng* C.A. Meyer (PG) and *Panax notoginseng* (Burk.) F.H. Chen (PN).[5)] This paper reveals physicochemical properties such as particle size distribution, crystalline structure, gelatinization property, mineral content and digestibility by α-amylase or glucoamylase, which are essential to any application. The SEM observation of the starch before and after amylase digestion can provide information on the starch granular structure by enzymatic treatments. The physicochemical characteristics of PT, AO and CL starches were examined.

## MATERIALS AND METHODS

***Materials.*** Tubers of *Pinellia ternata* (Thunb.) Breitenbach (PT), rhizomes of *Alisma orientale* Juzepczuk (AO) and seeds of *Coix lacryma-jobi* Linné var. *ma-yuen*

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Abbreviations: PT, tuber of *Pinellia ternata* (Thunb.) Breitenbach; AO, rhizome of *Alisma orientale* Juzepczuk; CL, seed of *Coix lacryma-jobi* Linné var. *ma-yuen* Stapf; DSC, differential scanning calorimeter; SEM, scanning electron microscope; C, powdered crude drug; S, starch.

Stapf (CL) were purchased in November 2000 and 2001 from Fukuda Ryu Co., Ltd. (Osaka, Japan). The PTs, AOs and CLs were: PT-1 (number of spherical tubers per unit dried weight, 1400–1600 grains/kg, Sichuan, China, harvested in Oct. 1998), PT-2 (2700–3000 grains/kg, Guizhou, China, harvested in Oct. 1999), PT-3 (3000 or more grains/kg, Guizhou, China, harvested in Feb. 1999), PT-4 (700–800 grains/kg, Sichuan China, harvested in Oct. 1998), AO-1 (Sichuan, China, harvested in Dec. 2000), AO-2 (Sichuan, China, harvested in Apr. 1998), AO-3 (Sichuan, China, harvested in Aug. 1998), AO-4 (Sichuan, China, harvested in Mar. 2001), AO-5 (Sichuan, China, harvested in Feb. 1998), CL-1 (Guizhou, China, harvested in Apr. 1998), CL-2 (Thailand, harvested in Apr. 1998) and CL-3 (Thailand, coated with astringent skin, harvested in Apr. 1998). Enzymes, α-amylase and glucoamylase, and all other reagents were the same as those used previously.[5] Glucoamylase from *Aspergillus niger* (EC 3.2.1.3; 53 U/mg protein, 13 mg protein/mL; assay, spectrophotometric stop rate determination method.) was purchased from Sigma Chemical Corporation ST. Louis, MO, USA. The enzymes were used without further purification or enzyme assay. PT-1, AO-2 and CL-2 starches were the same samples used in adsorption experiments.[2,3] In this study, they were particularly used in DSC analysis, SEM and determination of oligosaccharide products present after digestion by amylase.

***Methods.*** The powdered crude drugs (C) and their starches were prepared as described in a previous paper.[2] DSC analysis, SEM, X-ray crystallography, and analyses of the components of crude drugs, distribution of particle size, inorganic elements of crude drug starches, digestibility of raw starch by α-amylase, and oligosaccharide products present after digestion by α-amylase or glucoamylase were conducted as described in a previous paper.[5]

## RESULTS AND DISCUSSION

### *Components of powdered crude drugs.*

The typical components of dried powdered crude drugs (C) PT, AO and CL were examined (Table 1). C-PTs contained a large amount of starch (41.1–77.5%) and crude protein (5.5–7.0%). The number of spherical tubers per unit dried weight (grains/kg) of PTs, as shown in Table 1, ranked in decreasing order as follows: PT-3, PT-2, PT-1 and PT-4. The amount of starch in C-PTs did not correlate with tuber grain size. C-AOs contained 12.5–40.5% starch and 21.8–25.1% crude protein. The starch yield of AO cultivated in Japan was approximately 14% of the fresh tissue.[4] C-CLs contained a small proportion, 1.5–5.8% starch, 15.3–15.9% crude protein and a large proportion, 8.4–13.0% crude fat. C-PTs, C-AOs and C-CLs contained 0.6±0.2 to 1.2±0.1% crude fiber, less than (3.3–4.3%) *Panax ginseng* C.A. Meyer (PG) and *Panax notoginseng* (Burk.) F.H. Chen (PN).[5] It was obvious that the starch contents in C-PTs, C-AOs and C-CLs differed by the harvest time or the district of cultivation.

### *Physicochemical properties of starch.*

The size distribution of particles is shown in Fig. 1. Low and high peaks of PT starch granules were observed in the range of 0.5 to 3 μm and of 3 to 40 μm, respectively. Particles of PT-4 starch had an average diameter of 16.0±0.4 μm, being twice as large as those of PT-2 starch (8.2±0.2 μm) and PT-1 and PT-3 starches (9.6±0.0 μm). Particle sizes of five kinds of AO starches were distributed in the same range, 2 to 15 μm, without particles of 20 μm or larger. The average diameter was 6.1±0.2 μm. The average diameter of starch from AO cultivated in Japan was approximately 4.7 μm.[4] The particle sizes of starches from AOs harvested in a different month or year at Sichuan, China were all the same, being 1.3 times as large as that[4] of starch from AO harvested at Japan.

**Table 1.** Components of powdered crude drugs PT, AO and CL.

| Powdered crude drug sample | Loss on drying (%) | Crude fat (%) | Crude protein (%) | Crude fiber (%) | Starch (%) |
|---|---|---|---|---|---|
| PT-1 | 11.2 | 0.6 | 7.0 | 1.2 | 77.5 |
| PT-2 | 11.1 | 0.4 | 5.5 | 1.1 | 41.1 |
| PT-3 | 11.8 | 0.5 | 5.6 | 1.4 | 72.7 |
| PT-4 | 11.4 | 0.5 | 6.0 | 1.2 | 63.8 |
| Mean±SD | 11.4±0.3 | 0.5±0.1 | 6.0±0.7 | 1.2±0.1 | 63.8±16.1 |
| AO-1 | 6.4 | 5.1 | 25.1 | 0.8 | 34.0 |
| AO-2 | 8.1 | 5.3 | 21.8 | 1.6 | 12.5 |
| AO-3 | 6.6 | 4.1 | 22.5 | 0.9 | 25.2 |
| AO-4 | 7.1 | 5.0 | 23.8 | 1.0 | 40.5 |
| AO-5 | 7.5 | 4.7 | 24.0 | 1.2 | 25.0 |
| Mean±SD | 7.1±0.7 | 4.8±0.5 | 23.4±1.3 | 1.1±0.3 | 27.4±10.6 |
| CL-1 | 9.9 | 8.4 | 15.3 | 0.4 | 1.5 |
| CL-2 | 9.1 | 11.5 | 15.9 | 0.7 | 5.8 |
| CL-3 | 8.4 | 13.0 | 15.5 | 0.7 | 3.3 |
| Mean±SD | 9.1±0.7 | 11.0±2.3 | 15.5±0.3 | 0.6±0.2 | 3.5±2.2 |

PT, tuber of *Pinellia ternata* (Thunb.) Breitenbach; AO, rhizome of *Alisma orientale* Juzepczuk; CL, seed of *Coix lacryma-jobi* Linné var. *ma-yuen* Stapf; PT-1 (number of spherical tubers per unit dried weight, 1400–1600 grains/kg, Sichuan, China, harvested in Oct. 1998); PT-2 (2700–3000 grains/kg, Guizhou, China, harvested in Oct. 1999); PT-3 (3000 or more grains/kg, Guizhou, China, harvested in Feb. 1999); PT-4 (700–800 grains/kg, Sichuan, China, harvested in Oct. 1998); AO-1 (Sichuan, China, harvested in Dec. 2000); AO-2 (Sichuan, China, harvested in Apr. in 1998); AO-3 (Sichuan, China, harvested in Aug. 1998); AO-4 (Sichuan, China, harvested in Mar. 2001); AO-5 (Sichuan, China, harvested in Feb. 1998); CL-1 (Guizhou, China, harvested in Apr. in 1998); CL-2 (Thailand, harvested in Apr. 1998); CL-3 (Thailand, coated with astringent skin, harvested in Apr. 1998).

One high and two low peaks of CL starch granules were observed in the ranges of 3 to 30, 0.5 to 3, and 35 to 100 μm, respectively. The modal diameters of CL-1, CL-2 and CL-3 starches were 11.35, 13.98 and 13.98 μm, respectively (Fig. 1), however, the average diameters of CL-1, CL-2 and CL-3 starches were 12.6±0.2, 13.5±0.4 and 11.5±0.4 μm, respectively. It was concluded that the particle sizes of starches from PTs and CLs differed by the harvest time or the district of cultivation.

PT-1, AO-2 and CL-2 starches alone were observed by means of SEM (Fig. 2). The granular sizes of S-PT-1, S-AO-2 and S-CL-2 were approximately 7–11, 4–6.5 and 6–15 μm, respectively. S-PT-1, S-AO-2 and S-CL-2 granules broke into pieces when they were being prepared, and displayed irregular shapes, that is, oval and spherical (Fig. 2). Rounded humps in oval form were observed on

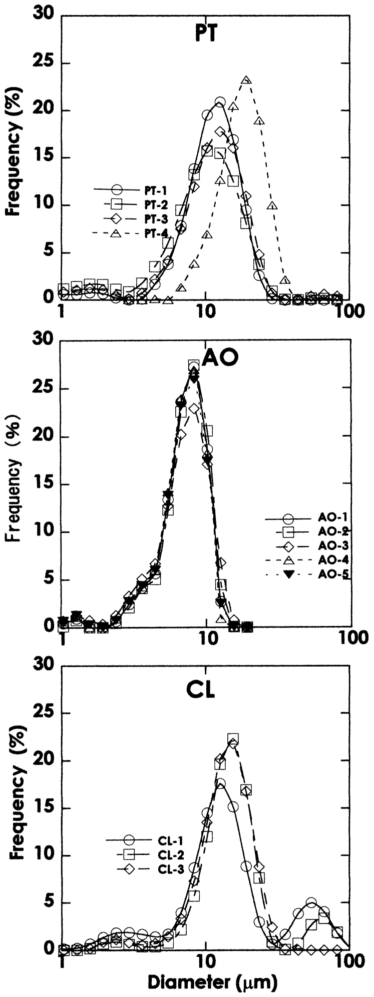

**Fig. 1.** Particle size distribution of PT, AO and CL starch granules.

For abbreviations see Table 1.

the oval body surface of S-AO-2 and S-CL-2 granules. Granules with small hollows on their surface were also observed in the S-CL-2 preparation. The starch of AO has been reported to be similar in shape to that of sweet potato.4)

In the X-ray diffractograms (Fig. 3), PT, AO and CL starches all had a sharp peak 3, peak 4 with two 4a and 4b peaks and a sharp peak 6. Since the three definite peaks 6a, 6b and 6c were not observed in Fig. 3, they were classified as type $C_A$.6) AO starch had been reported to be type $C_A$4) (a mixture of 80% type A and 20% type B).6)

Mineral contents of PT, AO and CL starches were measured (Table 2). The amounts of P in PT, AO and CL starches were in the range of 62 to 330, 93 to 110, and 75 to 210 µg/g, respectively. The amount of P in starch of AO cultivated in Japan has been reported to be 210 µg/g,4) being 2 times as much as that (104±8 µg/g) in AO starches harvested in China. The amounts of P in PT and CL starches differed by the harvest time or the district of cultivation. The amount of Ca in PT, AO and CL starches was in the range of 320 to 530, 48 to 260, and 18 to 33 µg/g, respectively. That the amount of Ca (439±98 µg/g) was large in comparison with amounts of other minerals contained in PT starches can be explained by the coexistence of raphides of calcium oxalate and starch particles in mucous cells of PT.7) A positive correlation ($p<0.01$) was obtained between the Ca and Mg contents in AO starches, indicating that Mg may be taken in proportionately with the amount of Ca taken up by AO starch while alismatis rhizoma grows in soil.

The gelatinization properties of undigested starches are shown in Table 3. PT-1, AO-2 and CL-2 starches at the gelatinization temperature were in the same range of those of sweet potato starches8) or endosperm starches of rices.9) However, in enthalpy they were very much lower (3.4 to 4.5 J/g) than those (13.4±0.9 J/g, $n=30$) of sweet potato starches8) or those (11.8±1.2 J/g, $n=65$) of endosperm starches of rices.9) It is expected that PT-1, AO-2 and CL-2 starches will be available for starch gelatinized at low energy.

### *Digestibility of raw starch by α-amylase, thermal properties of digested starch and composition of oligosaccharides after digestion by α-amylase or glucoamylase.*

The digestibility of PT, AO and CL starches by α-amylase was measured at 37°C to estimate the susceptibility to α-amylase of the raw starch contained in granules, pills or tablets2) prepared from both the powdered crude drug and its extract (Fig. 4). The digestibility of PT and CL starches increased gradually reaching limits of 33–38% (35.3±2.4%) and 56–65% (62.2±5.2%), respectively, at 72 h. On the other hand, the digestibility of AO starches increased uniformly up to 25%, and then approached 35–41% (38.3±2.3%) at 72 h. CL starch was most susceptible to α-amylase, followed by AO starch and then PT starch. It was concluded that the raw starches from PT and AO were not available for the vehicle in granules, pills or tablets, because of low digestibility.

From observations made by SEM (Fig. 2), it was found that the exterior of S-CL-2(A) granules was more roughly eroded by α-amylase than that of S-PT-1(A) or S-AO-2(A) granules, with many holes of 1 µm or less observed on the irregular surface. No negative correlations were observed between digestibility by α-amylase at 72 h (Fig. 4) and average granular size (Fig. 1) or $\Delta H$ (Table 3), which is inconsistent with results published previously.8)

A suspension of starch digested by an enzyme consists of water-insoluble residue and water-soluble oligossaccharides.10) The thermal properties of the water-insoluble residue after attack by α-amylase were measured (Table 3). The endothermic curves of the digested PT-1, AO-2 and CL-2 starches shifted slightly to higher temperatures and their enthalpy decreased 1/2 to 4/5, compared to that of the raw starches. Monma *et al.*11) reported that starch granules are basically made of the susceptible part and the less susceptible part against amylase digestion. Noda *et al.*8) indicated that the higher the content of crystalline structure, the lower the digestibility by amylase. Since the digested starch was largely composed of the part less susceptible to amylase digestion,11) that is, the crystalline part,8) it was suggested that the onset temperature ($T_o$) of the digested PT-1, AO-2 and CL-2 starches had been shifted higher. The PT-1(A), AO-2(A) and CL-2(A) starches digested by α-amylase were observed to be more porous by α-amylase (Fig. 2), like the digested starches

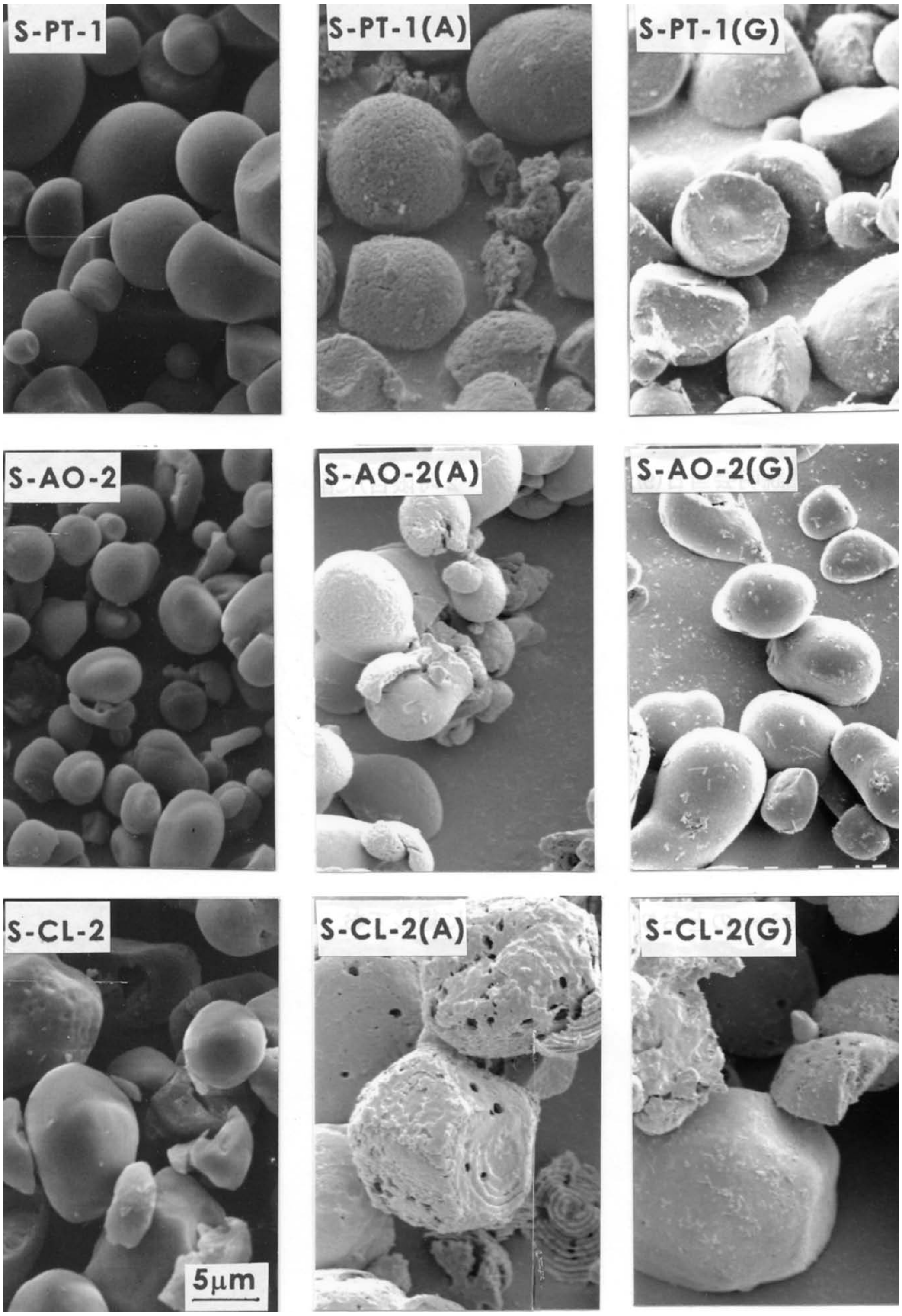

**Fig. 2.** Scanning electron micrographs of PT-1, AO-2 and CL-2 starches and the same starches digested by α-amylase or glucoamylase for 1 h.

S-PT-1, undigested PT-1 starch; S-PT-1(A), PT-1 starch digested by α-amylase for 1 h; S-PT-1(G), PT-1 starch digested by glucoamylase for 1 h; S-AO-2, undigested AO-2 starch; S-AO-2(A), AO-2 starch digested by α-amylase for 1 h; S-AO-2(G), AO-2 starch digested by glucoamylase for 1 h; S-CL-2, undigested CL-2 starch; S-CL-2(A), CL-2 starch digested by α-amylase for 1 h; S-CL-2(G), CL-2 starch digested by glucoamylase for 1 h.

from roots of PG and PN.[5] We suggested that the decrease in enthalpy had been mainly caused by the porosity of the digested starch. The digested PT-1(A), AO-2(A) and CL-2(A) starches are expected to be available as an adsorbent, because of their porosity.[3]

The types and composition of oligosaccharide produced by α-amylase were examined in order to investigate the water-soluble products from different kinds of starches (Table 4). The total amount of oligosaccharide from each of the PT-1, AO-2 and CL-2 starches was 594.8, 457.1 and 704.7 μg, respectively. Maltose or maltotriose was the most abundant (35.8–42.8%), followed by glucose (5.0–6.0%), maltotetraose through maltoheptaose (1.4–5.8%) and isomaltose (1.1–2.0%). The result of products by α-

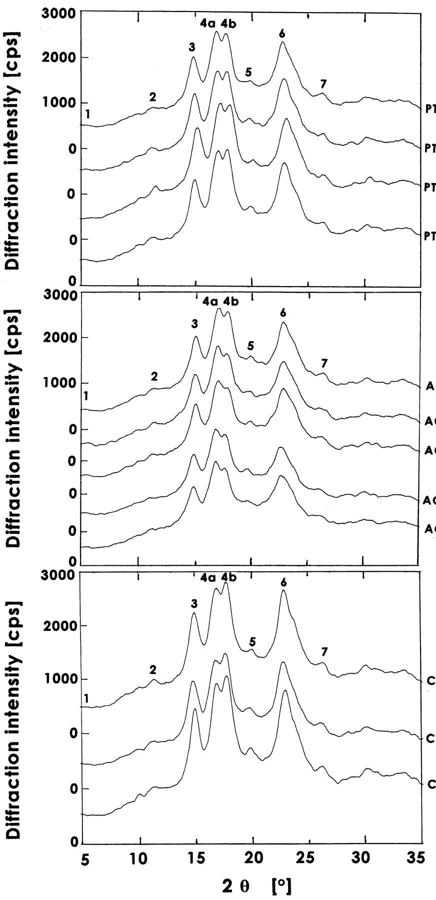

**Fig. 3.** X-ray diffractograms of PT, AO and CL starches.

For abbreviations see Table 1. The numbering is based on a reference.[6]

**Table 2.** Mineral contents of PT, AO and CL starches.

| Starch sample | Mineral content (μg/g) | | | | |
|---|---|---|---|---|---|
| | P | K | Na | Ca | Mg |
| PT-1 | 330 | 2.1 | 4.8 | 390 | 29 |
| PT-2 | 150 | 9.4 | 7.1 | 530 | 48 |
| PT-3 | 62 | 5.2 | 9.8 | 320 | 92 |
| PT-4 | 110 | 3.9 | 9.6 | 500 | 52 |
| Mean±SD | 163±117 | 5.0±3.1 | 8.0±2.4 | 439±98 | 55±27 |
| AO-1 | 110 | 20 | 3.4 | 54 | 32 |
| AO-2 | 110 | 51 | 9.8 | 48 | 34 |
| AO-3 | 110 | 43 | 6.2 | 260 | 150 |
| AO-4 | 97 | 23 | 6.3 | 86 | 38 |
| AO-5 | 93 | 54 | 2.0 | 120 | 60 |
| Mean±SD | 104±8 | 38±16 | 5.5±3.0 | 114±87 | 62±50 |
| CL-1 | 75 | 2.5 | 8.6 | 33 | 14 |
| CL-2 | 210 | 1.6 | 5.4 | 18 | 22 |
| CL-3 | 140 | 13 | 18 | 19 | 25 |
| Mean±SD | 142±68 | 6.0±6.3 | 11.0±6.5 | 23±8 | 20±6 |

For abbreviations see Table 1.

amylase suggested that types and compositions of oligosaccharide from 3 kinds of starches were almost the same, being independent of the origin of the starches.

The thermal properties of the water-insoluble residue after attack by glucoamylase were measured (Table 3). The endothermic curves of the PT-1, AO-2 and CL-2

**Table 3.** Gelatinization properties of PT-1, AO-2 and CL-2 starches digested by α-amylase or glucoamylase.

| Starch sample | $T$o (°C) | $T$p (°C) | $T$f (°C) | $\Delta H$ (J/g) |
|---|---|---|---|---|
| Undigested | | | | |
| PT-1 | 67.3±0.1 | 73.3±0.5 | 85.0±0.4 | 3.4±0.3 |
| AO-2 | 58.9±3.9 | 70.1±1.7 | 84.2±0.5 | 4.2±0.0 |
| CL-2 | 59.2±1.8 | 68.2±0.3 | 81.0±0.7 | 4.5±0.2 |
| Digested by α-amylase* | | | | |
| PT-1 | 71.3±0.1 | 77.2±0.4 | 90.0±0.4 | 2.8±0.3 |
| AO-2 | 69.0±0.1 | 75.2±0.1 | 84.3±0.5 | 2.0±0.3 |
| CL-2 | 67.2±0.3 | 75.2±0.3 | 87.4±0.2 | 2.4±0.1 |
| Digested by glucoamylase** | | | | |
| PT-1 | 69.6±0.6 | 74.2±0.1 | 79.5±0.2 | 3.9±1.1 |
| AO-2 | 67.2±0.6 | 70.9±0.1 | 75.3±0.1 | 1.9±1.0 |
| CL-2 | 68.5±0.1 | 72.3±0.1 | 78.2±0.4 | 1.4±0.3 |

$T$o (°C), onset temp.; $T$p (°C), peak temp.; $T$f (°C), final temp.; $\Delta H$ (J/g), enthalpy. Values are means±SD ($n$=3). *Digested by α-amylase for 1 h at 37°C (digestibility: PT-1 starch, 2.4%; AO-2 starch, 5.8%; CL-2 starch, 7.1%). **Digested by glucoamylase for 1 h at 37°C (digestibility: PT-1 starch, 4.8%; AO-2 starch, 12.1%; CL-2, 18.7%).

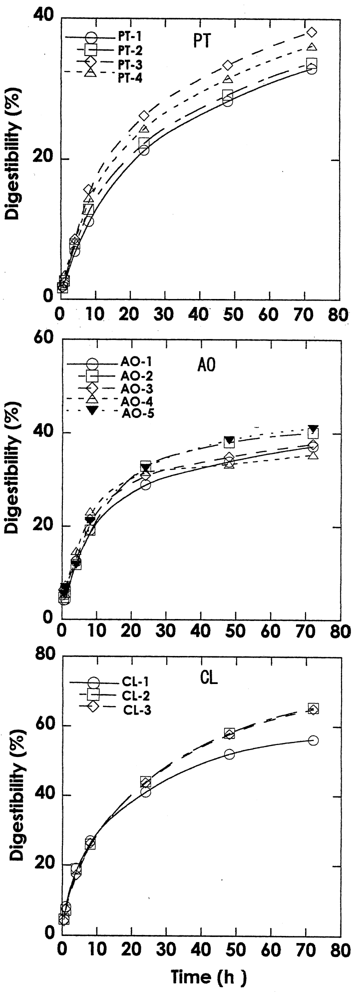

**Fig. 4.** Digestibility of PT, AO and PN raw starches by α-amylase.

For abbreviations see Table 1. The digestibility was calculated by dividing the amounts of reducing sugars (mg) formed in the elapsed time from 50 mg of raw starch. The digestibility of PT, AO and CL raw starches was 35.3±2.4, 38.3±2.3 and 62.2±5.2%, respectively at 72 h.

**Table 4.** Types of oligosaccharides produced from PT-1, AO-2 and CL-2 starches by α-amylase.

| Oligosaccharide | Amount of oligosaccharide (μg) | | |
|---|---|---|---|
| | PT-1 | AO-2 | CL-2 |
| Maltoheptaose (G-7) | 8.3( 1.4%) | 9.9( 2.2%) | 17.5( 2.5%) |
| Maltohexaose (G-6) | 26.7( 4.5%) | 16.0( 3.5%) | 41.2( 5.8%) |
| Maltopentaose (G-5) | 23.9( 4.0%) | 13.3( 2.9%) | 36.0( 5.1%) |
| Maltotetraose (G-4) | 21.4( 3.6%) | 14.5( 3.2%) | 29.3( 4.2%) |
| Maltotriose (G-3) | 213.0(35.8%) | 182.9(40.0%) | 271.8(38.6%) |
| Maltose (G-2) | 254.3(42.8%) | 192.6(42.1%) | 252.6(35.8%) |
| Isomaltose (iso-G-2) | 11.1( 1.9%) | 5.1( 1.1%) | 14.4( 2.0%) |
| Glucose (G-1) | 36.1( 6.0%) | 22.8( 5.0%) | 41.9( 6.0%) |
| Total | 594.8 | 457.1 | 704.7 |

The solution of digestibility (PT-1 starch, 2.4%; AO-2 starch, 5.8%; CL-2 starch, 7.1%) was used. The value in parentheses is a percentage of each oligosaccharide (G-1–G-7). G-2, 35.8–42.8%; G-3, 35.8–40.0%; G-1+iso-G-2+G-4+G-5+G-6+G-7, 17.9–25.6%.

**Table 5.** Types of oligosaccharides produced from PT-1, AO-2 and CL-2 starches by glucoamylase.

| Oligosaccharide | Amount of oligosaccharide (μg) | | |
|---|---|---|---|
| | PT-1 | AO-2 | CL-2 |
| Maltoheptaose (G-7) | 0.0( 0.0%) | 0.0( 0.0%) | 0.0( 0.0%) |
| Maltohexaose (G-6) | 0.0( 0.0%) | 0.0( 0.0%) | 4.6( 0.5%) |
| Maltopentaose (G-5) | 0.0( 0.0%) | 0.0( 0.0%) | 0.0( 0.0%) |
| Maltotetraose (G-4) | 2.2( 0.6%) | 2.1( 0.3%) | 4.7( 0.5%) |
| Maltotriose (G-3) | 1.3( 0.3%) | 0.6( 0.1%) | 3.2( 0.3%) |
| Maltose (G-2) | 1.9( 0.5%) | 0.8( 0.1%) | 1.8( 0.2%) |
| Isomaltose (iso-G-2) | 3.8( 1.0%) | 0.0( 0.0%) | 3.0( 0.3%) |
| Glucose (G-1) | 368.7(97.6%) | 671.4(99.5%) | 992.4(98.2%) |
| Total | 377.9 | 674.9 | 1009.7 |

The solution of digestibility (PT-1 starch, 4.8%; AO-2 starch, 12.1%; CL-2 starch, 18.7%) was used. The value in parentheses is a percentage of each oligosaccharide (G-1–G-7). G-1, 97.6–99.5%; iso-G-2+G-2+G-3+G-4+G-5+G-6+G-7, 0.5–2.4%.

starches moved to higher temperatures following digestion by glucoamylase. The gelatinization temperatures of the starches after digestion by α-amylase were higher than those after digestion by glucoamylase. The temperature range of the endothermic curves was narrower after digestion by glucoamylase (8–10°C) than after digestion by α-amylase (15–20°C). The PT-1 starch digested by glucoamylase did not differ in enthalpy from its raw form. The enthalpy of the AO-2 and CL-2 starches decreased 1/3 to 1/2 on digestion by glucoamylase. The enthalpy of the starches except PT-1 starch after digestion by α-amylase were larger than after digestion by glucoamylase. The results of the gelatinization temperature and the enthalpy suggest that the thermostability of the PT-1, AO-2 and CL-2 starches digested by α-amylase was greater than that of the starches digested by glucoamylase, being contrary to the results of PG and PN starches.[5)]

From observations made by SEM (Fig. 2), it was found that the S-PT-1(G), S-AO-2(G) and S-CL-2(G) digested by glucoamylase maintained their original forms with a few fine grains on their surface. A few granules of S-CL-2(G) lost their original form. Very small pores were also observed on the surface of S-CL-2(G).

The types and composition of oligosaccharide produced by glucoamylase were examined in order to investigate the water-soluble products from three kinds of starches (Table 5). The total amount of oligosaccharide from each of the PT-1, AO-2 and CL-2 starches was 377.9, 674.9 and 1009.7 μg, respectively. Glucose was most abundant (97.6–99.5%), while maltose through maltoheptaose were detected in small amounts (0.5–2.4%). The types and compositions of oligosaccharide from the 3 kinds of starches were similar to that of PG-4 starch,[5)] being independent of the origin of the starches. Glucoamylase cuts starch into glucose units from the non-reducing end. The detection of the small amounts of maltose through maltoheptaose and isomaltose suggested that the glucose residue is slightly phosphor-esterified.[12)]

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# 生薬ハンゲ，タクシャ，ヨクイニン由来の澱粉の特性

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生薬の抽出残渣に含まれている澱粉の有用性を評価するため，澱粉の物理化学的な諸特性を調べた．生薬は収穫時期あるいは栽培地の異なるものを用いた．澱粉(S)は，*Pinellia ternata* (Thunb.) Breitenbach の塊茎，ハンゲ(PT)，*Alisma orientale* Juzepczuk の塊茎，タクシャ(AO)，*Coix lacryma-jobi* Linné var. *ma-yuen* Stapf の種子，ヨクイニン(CL)から調製した．PT，AO，CL の粉末生薬には，澱粉が 41.1–77.5，12.5–40.5，1.5–5.8% 含まれていた(Table 1)．S-PT，S-AO，S-CL の平均粒子径は 8.2±0.2–16.0±0.4，6.1±0.2，11.5±0.4–13.5±0.4 μm であった(Fig. 1)．S-PT，S-AO，S-CL の結晶型は CA 型であった(Fig. 3)．S-PT，S-AO，S-CL それぞれの燐含量は 62–330，93–110，75–210 μg/g，カルシウム含量は 320–530，48–260，18–33 μg/g であった(Table 2)．S-PT-1，S-AO-2，S-CL-2 の吸熱曲線は 67.3–85.0，58.9–84.2，59.2–81.0°C の範囲内に観察され，エンタルピーはそれぞれ 3.4±0.3，4.2±0.0，4.5±0.2 J/g であった(Table 3)．これらの澱粉は低エネルギー糊化デンプンとしての利用が期待できる．生澱粉 S-PT，S-AO，S-CL の α-アミラーゼによる 72 時間後の分解率は 35.3±2.4，38.3±2.3，62.2±5.2% であった(Fig. 4)．α-アミラーゼにより生澱粉から生成した(分解率：S-PT-1，2.4%；S-AO-2，5.8%；S-CL-2，7.1%)主な糖類は，三単糖(35.8–40.0%)とマルトース(35.8–42.8%)であった(Table 4)．グルコアミラーゼにより生澱粉から生成した(分解率：S-PT-1，4.8%；S-AO-2，12.1%；S-CL-2，18.7%)主な糖は，グルコース(97.6–99.5%)であった(Table 5)．S-PT-1，S-AO-2，S-CL-2 は，1 時間分解後，α-アミラーゼによって粒子の表面全体が凸凹に侵食されたが，グルコアミラーゼによっては原型をとどめており粒子表面に小粒が付着していた．S-CL-2 の粒子には，グルコアミラーゼによってその原型を失っているものもみられた(Fig. 2)．α-アミラーゼにより分解された S-PT-1(A)，S-AO-2(A)，S-CL-2(A)は，多孔性のゆえに吸着剤としての利用が期待できる(Fig. 2)．糊化温度とエントロピーの結果から，α-アミラーゼによって分解された S-PT-1，S-AO-2，S-CL-2 の方が，グルコアミラーゼによるものよりも，熱安定性の高いことが推察された(Fig. 2，Table 3)．