# New Starches. Properties of Five Varieties of Cowpea Starch<sup>1</sup>

E. TOLMASQUIM<sup>2</sup>, A. M. N. CORREA<sup>2</sup>, and S. T. TOLMASQUIM, Instituto Nacional de Tecnologia, Rio de Janeiro, Brazil

#### ABSTRACT

Starches were obtained from five varieties of cowpea: Brabham, Oscaroite, Plúmbeo, Pindamonhangaba, and Early Red. Their Brabender viscosities were quite similar with small differences, and their iodine affinities lower than those expected for legume starches. All the starch varieties presented single-stage swelling and solubility, Plúmbeo being more restricted than the others. Rate of solubilization in dimethyl sulfoxide, as well as ionic character, was determined. All of the starches were practically nonionic. These properties lend to the cowpea starches some technological applications.

The cowpea (Vigna sinensis) is not only consumed largely in the Brazilian Northeast, being one of the basic foods of that region, but is also used in several towns of the State of São Paulo for atmospheric nitrogen fixation in the inoculation of seeds of Leguminosae and the cowpea itself, kudzu, peanut, indigo tree, mucuna, pig bean, lima bean, adzuki, mung bean, guar, and lab-lab (1).

A detailed study of the starches of these Leguminosae was therefore needed, with a view to their possible technological utilization.

### MATERIALS AND METHODS

### Raw Material

The raw material utilized for this study consisted of five varieties of cowpea

Copyright © 1971 American Association of Cereal Chemists, Inc., 1821 University Avenue, St. Paul, Minnesota 55104. All rights reserved.

<sup>&</sup>lt;sup>1</sup>Contribution from the Instituto Nacional de Tecnologia, Rio de Janeiro, Brazil.

<sup>&</sup>lt;sup>2</sup>Fellows of Conselho Nacional de Pesquisas.

obtained from Instituto Agronômico de Campinas, São Paulo: Early Red, Pindamonhangaba, Oscaroite, Brabham, and Plumbeo. The seeds are long and cylindrical. Except for Plumbeo, which is 5 mm. long, all the other varieties are 7 mm. long. The Early Red beans are white with red spots; the Brabham, dark red with black spots; the Pindamonhangaba, reddish-brown; the Oscaroite, white with black spots; and the Plumbeo beans, as the name indicates, are lead-gray and black striped.

# Preparation of Starch

A method similar to that developed for the production of starch from gram (2) was followed.

The cowpea was steeped for 1 day at room temperature in water to which sodium bisulfite equivalent to 0.3% sulfur dioxide had been added. It was then ground in a blender with a small quantity of water, and the pulp obtained was washed with water on a 60-mesh screen. The residue was ground again. Three grindings were enough to extract most of the starch.

The wash liquids were combined and let stand until the next day. The starch was treated with 0.15% sodium hydroxide solution. After the starch had settled, the liquid was drawn off and the solid was washed with water. The starch was then suspended in water and separated by a 325-mesh screen. After settling, it was suspended in 0.1% sodium hydroxide solution, allowed to settle, and washed with water until the wash liquid was neutral. Then the starch was suspended in alcohol, filtered, and dried in the air.

### **Determinations**

Protein, Ash, Fat, and Moisture. The protein content was determined by a modified Kjeldahl method (3, p. 12) (conversion factor, 6.25). The samples were ashed according to the usual procedure (3, p. 284). The total free fat was determined by ether extractions (3, p. 287). Moisture content of starch was determined by drying to constant weight in a vacuum oven at 110°C. (3, p. 282).

Iodine Affinity. The starches obtained were defatted with methyl alcohol at 85%, under reflux, by doing three digestions of 1 hr. each (4).

Iodine affinity was determined by the procedure of Bates et al. (5) as modified by Schoch (6.7).

Swelling Power and Solubility were determined by a modification of the procedure described by Leach et al. (8).

A weighed starch sample was suspended in distilled water in a centrifuge bottle. The latter was heated for 30 min. at a specified temperature by immersion in a thermostatically controlled bath, meanwhile stirring gently to keep the starch granules suspended. The sample was then centrifuged, the aqueous supernatant removed, and the weight of the swollen sediment determined. The swelling power was calculated as the weight of sediment per gram of dry starch, and this value corrected for solubles to provide a measure of swelling of the undissolved portion of the starch. Dissolved starch substance was determined directly by drying and weighing an aliquot of supernatant. Swelling and solubility patterns were obtained by plotting data measured at 5°C. intervals over the pasting range of the starch (from 75° to 95°C.).

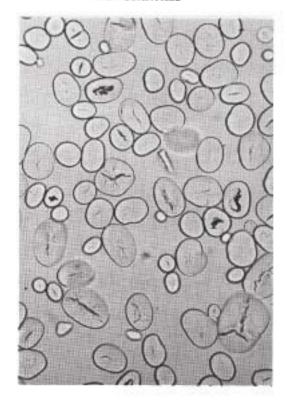


Fig. 1. Cowpea starch, var. Early Red; normal light (X about 700).

Kofler Gelatinization Temperature Range. The determination of the gelatinization temperature was made with a Kofler microscope hot stage.

Brabender Viscosity Curves. To determine Brabender viscosity, a Brabender amylograph with constant speed (Brabender, Ohg, Duisburg) was utilized, and the curves were plotted according to Mazurs et al. (9).

Starch concentrations of 4.0, 4.5, 5.0, and 6.0% were used, and the determinations were made at pH 6.0.

Solubility in Dimethyl Sulfoxide was determined by the procedure described by Leach and Schoch (10).

Ionic Character of these starches was determined by the technique described by Schoch and Maywald (11).

### RESULTS AND DISCUSSION

### Starch Granules

The starch granules obtained from the five varieties of cowpea are very similar; microphotographs of only one of them (Early Red) are given. Some of them are fissured and show darkened hilums with an average starch granule size between 10

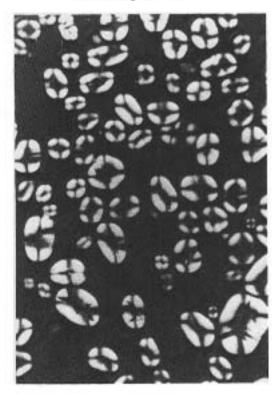


Fig. 2. Cowpea starch, var. Early Red; made with crossed polarizers (X about 700).

and 40  $\mu$  (Fig. 1), and strong, centric polarization crosses as shown in Fig. 2.

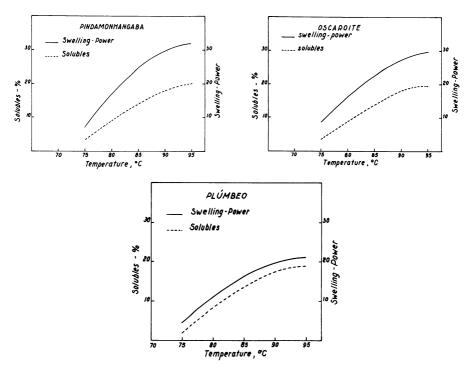
We also prepared the starches of five varieties by the (a) and (c) methods used by Schoch (12) for other legume starches. The results were similar to those obtained by using the process described here. The granules also presented fissures and the values of all the physicochemical determinations agreed.

# **Chemical Composition**

Analysis of the starches is shown in Table I, calculated on dry basis.

TABLE

1 MALE 1				
Starch		Gelatinization Range <sup>o</sup> C.		
Brabham	65.0	72.0	78.0	
Plúmbeo	66.0	73,0	77.0	
Pindamonhangaba	70.0	73.0	77.0	
Oscaroite	65.5	72.0	77.0	
Early Red	64.0	69.5	74.5	



Figs. 3 (upper left), 4 (upper right), 5 (bottom). Swelling power (g. of sediment per g. of dry starch) and solubility.

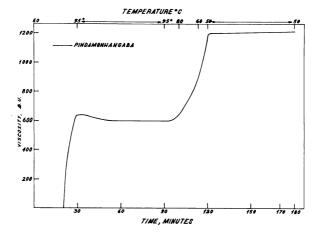


Fig. 6. Brabender amylogram of cowpea starch; concentration 5 g. per 100 ml. (Pindamonhangaba).

The chemical composition of these starches was practically the same, except for the Brabham variety which showed a lower ash content.

# **lodine Affinity**

The iodine affinity values are similar: Brabham, 5.52%; Early Red, 5.55%; Plúmbeo, 5.41%; Pindamonhangaba, 5.47%; and Oscaroite, 5.36%, but lower than those expected for legume starches (T. J. Schoch, personal communication), which are generally in the range of 6.0 to 7.5%.

### Swelling Power and Solubility

The solubility and swelling power are shown in Figs. 3, 4, and 5.

The percentage of solubles of the five varieties studied is similar, which does not agree with the swelling power.

The Pindamonhangaba and Early Red varieties showed similar swelling power, higher than the others, followed by Oscaroite and Brabham, and finally Plumbeo.

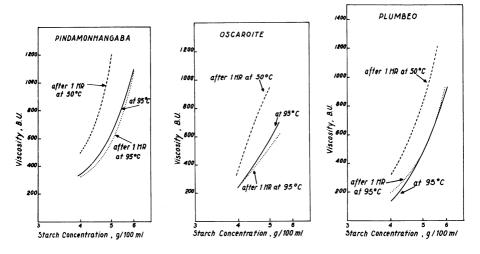
By microscopic examination, these starches, like other legume starches, seemed to undergo limited swelling when heated to a temperature above that of gelatinization. This behavior was not confirmed by swelling power determination.

# Kofler Gelatinization Temperature Range

The initial and final temperatures of gelatinization are very similar, with small discrepancies for the Pindamonhangaba and Early Red varieties. The values found are situated inside the limits normally presented by legume starches.

### Paste Viscosity

Curves of paste viscosity of the five varieties are similar, and show no swelling peak (Fig. 6). The viscosity at 95°C. is practically the same before and after 1 hr. of stirring, indicating the great resistance of the granules against mechanical disintegration. Increase in viscosity on cooling to 50°C. reflects a high



Figs. 7, 8, 9. Graphical analysis of Brabender curves.

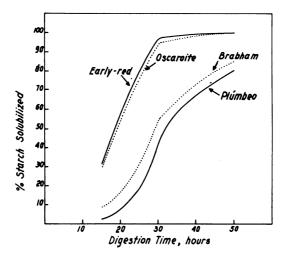


Fig. 10. Solubilities of granular starches in dimethyl sulfoxide.

retrogradation tendency. The set-back does not continue while holding the temperature at 50°C., indicating good stability of the cooled paste (Figs. 7, 8, and 9).

### Solubility in Dimethyl Sulfoxide

The rate of solubilization in DMSO (Fig. 10), as pointed out by Leach and Schoch, reflects differences in molecular bonding within the granules.

The Early Red and Oscaroite varieties attained complete solubilization in 30 hr., Brabham showed a lower degree of solutilization, followed by Plumbeo which is more resistant to DMSO action.

The structures of the starches of Early Red and Oscaroite are less homogeneous than those of the other three starches, Brabham, Plúmbeo, and Pindamonhangaba, for the velocity of solubilization of the former is greater than that of the latter ones.

### Ionic Character

Although the method is more useful for distinguishing starch mixtures than for establishing their ionic character, the results revealed that the starches are practically nonionic.

### CONCLUSIONS

In spite of the differences among the beans of the five varieties of cowpea, their starches are very similar in morphological aspects and physicochemical behavior.

The majority of legume starches presents moderately high linear content and consequently, a high iodine affinity so the low values obtained are unexpected. A difference occurs also in swelling power, solubility, and Brabender viscosity. They seem to have a degree of association between root and cereal starches, but are more uniformly associated than the latter, since they do not show multi-stage swelling.

As shown by Goering (13), the chunk pigweed starch also presents an amylose content slightly higher (4.9%) than corn starch and a highly unusual Brabender amylogram as it shows no cooking maximum and no break when the starch is cooled to 50°C. Goering suggests the presence of internal cross-linkages, or the failure of water to penetrate into the center of the large starch masses.

The granules present good resistance under shear at 95°C., and the paste, when cooled, shows a high viscosity. This represents a useful technological property, because with low starch concentrations it is possible to obtain viscous and stable pastes.

Therefore, in accordance with our physicochemical study, we can say that the unusual cooking curves of these starches suggest useful technological properties, for example, in the food industry, as sizes in the textiles industry, in the paper industry for coal bricks.

### Acknowledgments

The authors wish to express their thanks to Shiro Myasaka of the Instituto Agronômico de Campinas, São Paulo, for sending us the raw materials, to T. J. Schoch for the photomicrographs, to Eileen C. Maywald for the determinations of the temperatures of gelatinization, both from George Moffett Research Laboratory, Argo, Ill., and to Takeko Nakamura of the Starch Laboratory, Instituto Nacional de Tecnologia, Guanabara, for the fat, moisture, and protein determinations.

#### Literature Cited

- 1. NEME, N. A. Leguminosas para adubos verdes e forragem. Secretaria de Agricultura do Estado de São Paulo. Inst. Agronômico de Campinas, Campinas, Sao Paulo 109: 4 (1966).
- 2. SARIN, J. L., and QURESHI. Starch from gram. Ind. Eng. Chem. 30: 1318 (1938).
- 3. ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS. Official methods of analysis (9th ed.). The Association: Washington, D.C. (1960).
- 4.OTT, MARIETTE, and HESTER, E. ELIZABETH. Gel formation as related to concentration of amylose and degree of starch swelling. Cereal Chem. 42: 476 (1965).
- 5.BATES, F. L., FRENCH, D., and RUNDLE, R. E. Amylose and amylopectin content of starches determinated by their I complex formation. J. Am. Chem. Soc. 65: 142 (1943).
- 6. WILSON, E. J., Jr., SCHOCH, T. J., and HUDSON, C. S. Action of macerans amylase on the fractions from starch. J. Am. Chem. Soc. 65: 1380 (1943).
- SCHOCH, T. J. In: Methods in enzymology, ed. by S. P. Colowick and N. O. Kaplan, vol. 3, p. 13. Academic Press: New York (1957).
- 8. LEACH, H. W., McCOWEN, L. D., and SCHOCH, T. J. Structure of the starch granule. I. Swelling and solubility patterns of various starches. Cereal Chem. 36: 534 (1959).
- 9.MAZURS, E. G., SCHOCH, T. J., and KITE, F. E. Graphical analysis of the Brabender viscosity curves of various starches. Cereal Chem. 34: 141 (1957).
- 10.LEACH, H. W., and SCHOCH, T. J. Structure of the starch granule. III. Solubilities of granular starches in dimethyl sulfoxide. Cereal Chem. 39: 318 (1962).
- 11. SCHOCH, T. J., and MAYWALD, EILEEN C. Microscopic examination of modified starches. Anal. Chem. 28: 382 (1956).
- 12. SCHOCH; T. J., and MAYWALD, EILEEN C. Preparation and properties of various legume starches. Cereal Chem. 45: 564 (1968).
- 13. GOERING, K. J. New starches. II. The properties of the starch chunks from Amaranthus retroflexus. Cereal Chem. 44: 245 (1967).

[Received May 27, 1968. Accepted August 21, 1970]