Preparation and Properties of Various Legume Starches

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ABSTRACT

Special methods have been devised for the isolation of purified starches from the following seven legumes: lentil, yellow pea, navy bean, garbanzo, mung bean, lima bean, and wrinkled-seeded pea. The first four of these starches show restricted swelling patterns when pasted in water over the temperature range of 65°–100°C.; they also give stabilized Brabender hot-paste viscosities similar to those of cross-bonded starches. These properties are attributed to a relatively high content (30–40%) of linear fraction in these starches. However, lima-bean starch (with a comparably high linear content) shows higher swelling during pasting, and gives a Brabender viscosity similar to that of corn starch. Wrinkled-pea starch (containing approximately 75% linear fraction) behaves similarly to high-amylose corn starch. The interrelations between granule swelling, fragility of the swollen granule, and hot-paste viscosity are discussed.

The literature contains very little information on the isolation and properties of various legume starches. Perhaps the most extensive study is that by Kawamura and his associates (1,2), but most of the legumes which they examined are unknown in this country. The cooking qualities of various peas and beans are probably influenced by the pasting characteristics of their starchy component (3). Hence, the present study was undertaken to obtain basic information on the nature and behavior of the purified starches from various common North American legumes. Special methods were devised for separating the starch from seven legumes, and these starches were characterized with respect to their iodine affinities (indicative of content of linear fraction), Brabender viscosities, and the patterns of granule swelling and solubilization during pasting.

MATERIALS AND METHODS

Sources of Legumes

The following common dried legumes were obtained from local grocery stores: lima beans, lentils, garbanzos ("chick-peas"), split yellow peas, and white navy beans ("pea beans"). To ensure that the isolated starches were truly representative of the species, at least two samples of each legume were separately processed, different brands being chosen from packers located in different sections of the country. In all cases, the starches prepared from different batches of the same legume had essentially identical physical properties.

Mung-bean starch was prepared from beans purchased on the Chicago market and of domestic origin. In addition, starches were prepared from Hong Kong and Philippine mung beans ("green gram"), and a sample of refined starch submitted by Dr. Ei Yamamura (Agricultural Experiment Station, Taniyama City, Kagoshima Prefecture, Japan) was also examined. These four starches were quite similar, though they showed minor differences in properties, possibly due to variety or conditions of growth.

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For the wrinkled-seeded garden peas, dried seed peas of the Laxton's Progress variety were obtained from a local seed company, and batches from the 1963 and 1964 crops were processed separately. Properties of these two starches were identical.

With certain legumes, separation of pure starch is difficult because of the presence of a highly hydrated fine fiber fraction (presumably from the cell walls enclosing the starch granules) and also the high content of insoluble protein. Hence, optimum methods had to be found for each species of legume. The following procedures were found most suitable.

Isolation of Starches: Method A

Mung beans, garbanzos, and dehulled split yellow peas are most easily processed, and pure starch can be obtained simply by steeping in warm water, grinding, and sedimenting in water medium. A 5-lb. lot of the dried legume was wetted with 50 ml. of toluene, then covered with 6 to 8 liters of distilled water, and steeped overnight in a thermostatted bath at 50°C. In all cases, the pH throughout steeping was within the range of 5.9 to 6.3, which precludes any acidic hydrolysis (4). When toluene was omitted in one preliminary run, pronounced fermentation occurred during steeping, and the pH of the steep liquor dropped to 4.4. The isolated starch had a very low Brabender viscosity (indicative of acidic degradation) and was therefore discarded.

The steep liquor was decanted; the swollen and softened legumes were washed with water and then ground (in four to six portions) for 3 min. in distilled water (approximately 2 liters per portion) in a 1-gal. Waring Blendor operated at low speed. (Longer grinding causes overheating.) The ground magma was screened through 60-mesh silk bolting cloth. and the pulp was liberally washed on the cloth with distilled water, then hand-squeezed as dry as possible. The residual pulp was again ground for 3 min. in the blender with fresh water, and rescreened. The combined starch suspension was then screened through 220-mesh nylon bolting cloth (53-μ pore size) into 10-gal. Pyrex jars. This method of double-screening (i.e., first through 60-mesh, then through 220-mesh) is much more rapid than direct screening through fine bolting cloth, and in addition gives better starch yields.

The suspension was allowed to settle for 2 to 3 hr., or until a dense, firm starch layer of maximum depth was deposited. The supernate was siphoned off, and the starch was resuspended in water, screened again through 220-mesh nylon, and then sedimented three more times in 5-gal. volumes of distilled water or until the supernate layer was substantially free of color and suspended haze. (Alternatively, the starch may be separated by "tabling," as described under method B.) The final starch slurry was adjusted to pH 6.0, and the starch was filtered, dried in a thin layer at room temperature, and powdered to pass 80-mesh.

Isolation of Starches: Method B

Lentils, lima beans, and white navy beans are more difficult to process, because of the presence of insoluble flocculent protein and highly hydrated fine fiber which slow down sedimentation and cosettle with the starch to give a light, loose deposit. These legumes were steeped in water, ground, and screened as above described. The aqueous slurry was settled overnight, the supernatant liquid siphoned off, and the sediment resuspended in 4–5 gal. of 0.2% sodium hydroxide solution (this medium dissolves most of the protein but does not gelatinize the starch). The alkaline suspension was screened through 220-mesh nylon to remove a portion of the fine fiber and then slowly flowed down an inclined "table." The latter was a flat, shallow trough of heavy-gage stainless-steel sheet, 8 ft. long, 4 in. wide, with a total slope of 0.5 in.; the surface of this table was lightly scored with a rotary disk sander to provide anchorage for the sedimented starch. The lighter fine fiber and any undissolved protein remained suspended and passed off in the overflow. The deposited starch was resuspended in 4–5 gal. of 0.2% sodium hydroxide, again screened through 220-mesh, and retabled. After two or three such tablings, the settled starch gave a firm, dense deposit on the table and was substantially free of fine fiber (as detected by acidifying, staining with methylene blue, and examining under the microscope). Total contact time of the starch with alkali was about 20 hr. This alkalinity did not appear to be detrimental to the starch, since samples of mung-bean starch prepared by methods A and B had identical Brabender viscosities and swelling and solubility patterns.

The final alkaline deposit of starch was suspended in distilled water, neutralized to pH 6.0 with hydrochloric acid, filtered on a Büchner funnel, and thoroughly washed on the filter with water. To further reduce salt content, the filter cake was again suspended in distilled water, readjusted if necessary to pH 6.0, filtered, and washed. The starch was dried as previously described.

Isolation of Starches: Method C

The above two processes are not applicable to wrinkled-seeded peas, since water-steeping is apparently inadequate to soften the peas and to weaken the cells enclosing the starch granules. Conventional steeping in metabisulfite solution as used for corn was totally ineffectual, and only alkali steeping gave a low-protein starch. A 5-lb. lot of the dried peas was steeped overnight at room temperature in 8 liters of 0.3% sodium hydroxide solution. The pH of the final steep liquor dropped to 7–8 on various batches, presumably because of consumption of alkali by the protein. The greatly swollen peas were washed with water, then ground for 3 min. in the Waring Blendor in 0.2% sodium hydroxide solution previously chilled to 5°C. Since 3-min. grinding in the blender at low speed produced a temperature rise of about 15°C., the use of cooled alkali avoided excessive heating which might cause gelatinization of the starch. The ground magma was screened through 60- and 220-mesh cloth as previously described, and the suspension settled overnight. The loose, bulky deposit was resuspended in 4–5 gal. of 0.2% sodium hydroxide, screened through 220-mesh, and allowed to settle. These steps of screening and settling were repeated three or four more times, or until the supernate was free of color and haze and the starch showed a negligible amount of fiber under the microscope. Alternatively, the alkaline suspension may be tabled two or more times, until the overflow from the table shows negligible fiber. Sedimentation of wrinkled-pea starch is much slower than with other starches, probably because of lower density of the granules. Also, a high proportion of fine fiber interferes with starch deposition. Consequently, total contact time with alkali (including steeping) was about 40 hr. The final starch was neutralized, washed, and dried as previously described under method B.

Comments on the Four Methods

The dry lentil starch was a pale cream color; all others were pure white. Yields and analyses of the separated starches are given in Table I. Yields from different lots of the same legume are quite consistent, and these values probably represent practical limits of starch recovery. Ash contents are very low, and protein levels (as Kjeldahl nitrogen) are generally lower than most cereal starches.

TABLE I

Analysis and Properties of Legume Starches[a]

Starch	Yield	Ash	Nitrogen	Fat	Iodine Affinity	Gelatinization Range
	%	%	%	%	%	°C.
Lima bean	30	0.13	0.039	0.10	6.59	72 – 76 – 81.5
	22	0.085	0.036	....	6.56	70 – 75 – 85
	23	0.067	0.070	0.10	6.60	....
Lentil	....	0.054	0.031	....	6.95	65 – 68.5 – 71.5
	38	0.060	0.031	0.09	6.99	64 – 69 – 74
Yellow pea	40	0.013	0.034	....	7.44	64 – 67.5 – 73
	44	0.032	0.033	0.05	6.95	63 – 67 – 73.5
Navy bean	24	....	0.046	....	6.67	67 – 69 – 73.5
	27	0.051	0.041	0.11	6.58	66 – 70 – 77
Garbanzo	40	0.042	0.047	0.11	6.15	66 – 69.5 – 72
	38	0.053	0.044	0.12	6.70	62.5 – 65 – 68
Mung bean[b]						
U.S.	37	0.06	0.01	0.17	5.95	64 – 69 – 76
U.S.	43	0.01	0.01	0.18	....	65 – 70 – 76
Hong Kong	32	0.01	0.02	....	5.87	66 – 70 – 74
Philippine	39	0.01	0.01	....	6.02	66 – 70 – 74
Yamamura	....	0.02	0.02	0.17	6.01	60 – 66 – 78
Wrinkled pea[c]	18 18 22	0.102	0.070	....	15.16	....
	18 19	0.047	0.065	0.19	15.20	69 – ? – 83[d]

[a] Data are given for individual batches of starch in most cases.

[b] The first batch of domestic mung beans was processed in alkali by method B, the other batches in water by **method A.**

[c] Owing to low yields, the starches from various batches of wrinkled-pea starch were composited as indicated.

[d] The midpoint in the gelatinization range of wrinkled-pea starch cannot be accurately determined.

Physical Characterization of Starches

Brabender viscosities were run on each starch at four to six different concentrations, for best delineation of both the hot-paste viscosity and the setback on cooling. Variation between different batches of the same starch was minor. Certain general precautions in the operation of the amylograph should be mentioned: The thermoregulator may occasionally become maladjusted by as much as 3°–4°C., causing substantial differences in the height and shape of the curve. Hence, the cover of the Brabender cup was drilled to accommodate a short-stemmed, calibrated thermometer, positioned on the opposite side of the thermoregulator from the cooling element. Temperatures were regulated by this auxiliary thermometer with an accuracy of ± 0.5°C. Tests showed that the presence of the thermometer had no effect on the viscosity curve. As a second precaution, water should be circulated through the cooling element only during the cooling period from 95° to 35°C.; if used at any other time, local congelation of the starch paste may give erratic results.

Swelling and solubility patterns during pasting were determined in duplicate by the method of Leach *et al.* (5); 10- to 12-g. samples were used for wrinkled-pea starch and 5- to 6-g. for the other starches. Precision of results (calculated as average deviation from the mean) was ± 0.18 unit for the swelling power and ± 0.25% for the solubility. Swelling patterns are shown in Fig. 1, and representative solubilities at intervals of 10°C. are given in Table II.

Gelatinization ranges were determined with the Kofler hot stage on a polarizing microscope (6), and are expressed as initiation, midpoint, and completion of extinction of the interference crosses in the granules (Table I).

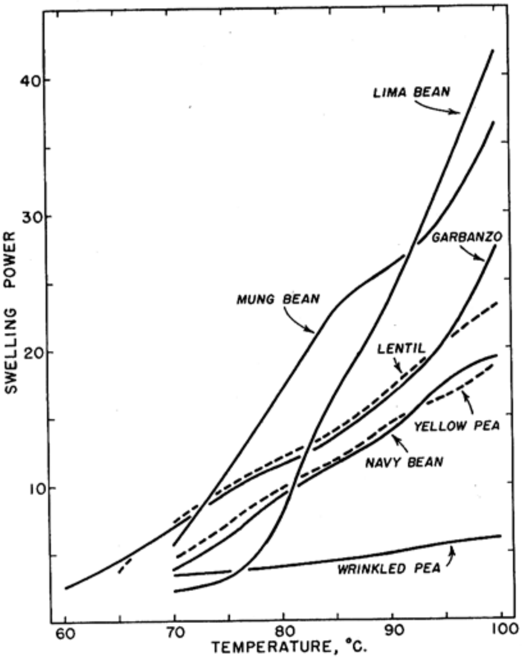


Fig. 1. Swelling patterns of various legume starches, corrected for solubles.

TABLE II
TYPICAL SOLUBILITY-TEMPERATURE PATTERNS OF LEGUME STARCHES

STARCH	SOLUBILITY AT INDICATED TEMPERATURE 70°C.	80°C.	90°C.	100°C.
	%	%	%	%
Lima bean	0	3.5	14.0	25.0
Mung bean	1.5	10.1	18.7	28.6
Garbanzo	4.9	10.3	14.3	23.5
Lentil	6.0	13.9	20.0	24.8
Navy bean	0.6	7.5	12.6	17.5
Yellow pea	2.0	13.4	20.5	26.1
Wrinkled pea	2.8	7.8	15.5	25.4

Iodine affinities were determined by electrometric titration (7), with samples which had previously been defatted by Soxhlet extraction for 48 hr. with 95% ethyl alcohol (Table I).

Fat content of the starches was determined on 50- to 100-g. samples by a procedure involving acid hydrolysis, filtration, and drying of the insoluble residue, and solvent extraction of this dried residue (8). Two minor changes were made in the published procedure. First, the time of acid hydrolysis was increased to 4 hr. to overcome excessive insoluble "sludge" which presumably was due to the higher content of linear fraction in these legume starches (particularly that from wrinkled peas). Second, carbon tetrachloride was substituted for petroleum ether as the fat extractant, solely for safety reasons.

Protein was determined by conventional Kjeldahl. Since the factors for the specific legume proteins are not known, results are here reported as percent nitrogen on dry-starch basis.

All seven legume starches were nonionic, as judged microscopically by the absence of any staining with either methylene blue or light-green SF yellowish (6).

RESULTS AND DISCUSSION

The Brabender hot-paste viscosity patterns of various starches appear to be determined by two factors: 1) the extent of swelling of the starch granules, and 2) the resistance of the swollen granules to dissolution by heat or fragmentation by shear. The viscosity patterns of "thick-boiling" starches can be roughly classified into four types:

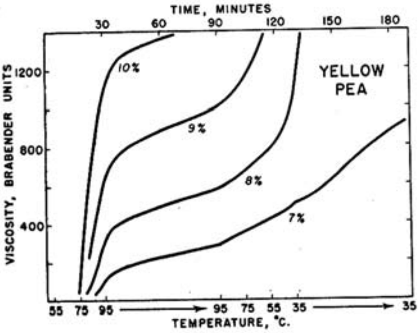
Type A: High-swelling starches, e.g., potato, tapioca, the waxy cereals, and ionic starch derivatives. The granules of these starches swell enormously when cooked in water, and the internal bonding forces become tenuous and fragile toward shear. Hence the Brabender shows a high pasting peak followed by rapid and major thinning during cooking.

Type B: Moderate-swelling starches, e.g., normal cereal starches. Because the granules do not swell excessively to become fragile, these starches show a lower pasting peak and much less thinning during cooking.

Type C: Restricted-swelling starches, especially chemically cross-bonded products. Cross-linkages within the granule markedly reduce swelling and solubilization, and stabilize the swollen granule against mechanical fragmentation. Hence the Brabender curve shows no pasting peak, but rather a very high viscosity which remains constant or else increases during cooking.

Type D: Starches with highly restricted swelling, especially "high-amylose" corn starches containing 55–70% linear fraction. Because of the internal rigidity imparted by the high content of associated linear molecules, the granules of these starches do not swell sufficiently to give a viscous paste when cooked in water at normal concentrations. Hence, the amount of starch must be increased two- or threefold to give a significant hot-paste viscosity of type C. However, such high-amylose starches give a type A or B viscosity pattern when cooked in media which cause greater granule swelling, e.g., 0.1*N* sodium hydroxide.

Four of the legume starches (yellow pea, navy bean, lentil, and garbanzo) gave type C Brabender curves, with no pasting peak and with constant or increasing viscosity during cooking at 95°C. (Figs. 2–5). While Tolmasquim



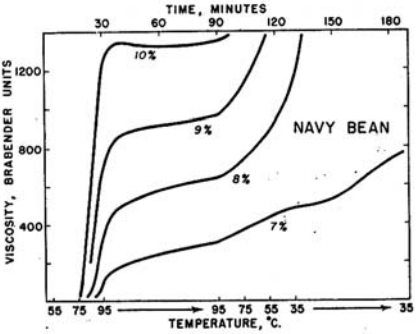
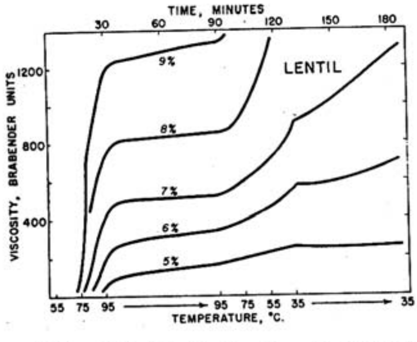


Fig. 2 (left). Brabender viscosity of yellow-pea starch. Concentrations are given in percent (w./v.) of dry-basis starch.

Fig. 3 (right). Brabender viscosity of navy-bean starch.



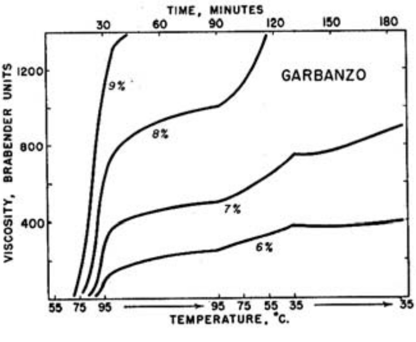
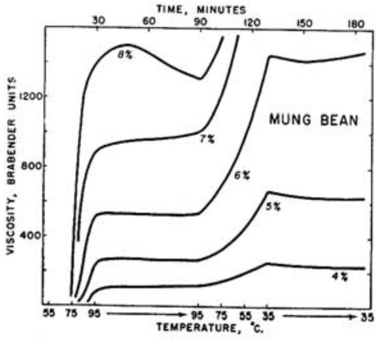


Fig. 4 (left). Brabender viscosity of lentil starch.

Fig. 5 (right). Brabender viscosity of garbanzo starch.

and his co-workers (9,10) have observed a type C viscosity pattern for garbanzo starch, this behavior has not been reported with any other unmodified starches cooked in water at 95°C. However, type C curves have been obtained by undercooking normal starches (e.g., corn starch run at 75° or 85°C.), or by cooking in a medium which restricts granule swelling (e.g., corn starch in 7–9% sodium sulfate solution at 95°C.). Similarly, Medcalf and Gilles (11) have observed that sulfate stabilizes the Brabender hot-paste viscosity. As shown in Fig. 1, the swelling power of these four legume starches at 95°C. is somewhat restricted (i.e., in the range of 16 to 20), and this appears to be a factor contributing to their stabilized viscosity pattern.

Mung-bean starch shows substantially higher swelling (29 at 95°C.). It has a somewhat mixed viscosity pattern (Fig. 6), type C at lower concentrations, and type B at higher concentration. Lima-bean starch has a still higher swelling power (33 at 95°C.) and shows a definite type B viscosity at all concentrations (Fig. 7). In addition, it has a high gelatinization temperature and shows an unusual single-stage swelling at relatively high temperature. To account for the two-stage swelling of corn starch, it has been speculated (5) that the granules are held together by two sets of bonding forces, a weak association relaxing at 65°–75°C., and a second and stronger association relaxing at 85°–100°C. By similar reasoning, the granules of lima-bean starch might be considered as internally associated only by relatively strong bonding forces.



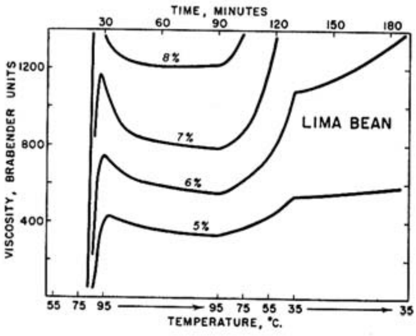


Fig. 6 (left). Brabender viscosity of mung-bean starch.

Fig. 7 (right). Brabender viscosity of lima-bean starch.

Wrinkled-pea starch was the first of the high-amylose starches to be discovered (3). Iodine affinity of the Laxton's Progress variety is 15.2%, indicating at least 75% content of linear fraction. Its Brabender viscosity (Fig. 8) and its swelling curve are very similar to those of Amylomaize VII corn starch (American Maize-Products Co.), which contains about 70% linear fraction. Hence, wrinkled-pea starch has a type D viscosity, with no special or unusual characteristics.

Tolmasquim *et al.* (9,10) attribute the restricted swelling and type C viscosity of garbanzo starch either to natural cross-bonding or to the influence of fatty acid. However, the presence of natural cross-linkages in a native

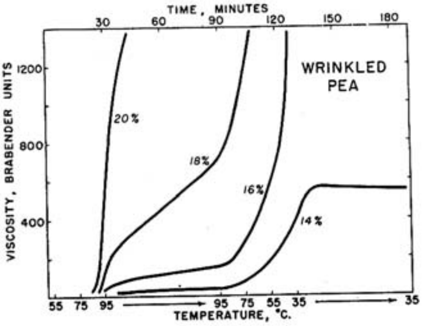


Fig. 8. Brabender viscosity of wrinkled-pea starch.

starch would seem rather unlikely, and no enzyme mechanism can be visualized for the introduction of such linkages. Also, these legume starches show high solubility patterns (Table II), while commercial cross-bonded products always have greatly reduced solubilities. With respect to fatty acid, the legume starches prepared in the present studies contained only about 0.1% fatty acid, an amount insufficient to have any significant effect on either the Brabender viscosity or the swelling pattern (12).

Deatherage *et al.* (13) have reported that various normal legume starches have a rather high content (30–36%) of linear fraction, and the high iodine affinities of the present starches are in accord with this previous observation. It seems plausible that the swelling would be restricted and the hot-paste viscosity stabilized as the content of linear fraction increases. Thus, in the series of waxy maize, normal corn starch, and high-amylose corn starch, the progressive decrease in swelling and increase in viscosity stability may be attributed to the reinforcement imparted by long linear-chain molecules meandering through the granule structure. But lima-bean starch does not show the restricted swelling and type C viscosity of the other normal legume starches, even though its content of linear fraction is comparably high. Mung-bean starch has a substantially lower content of linear fraction (iodine affinity = 6.0%) than the other legume starches, which may plausibly account for its mixed types B and C viscosity pattern.

The type of hot-paste viscosity simply reflects the resistance or fragility of the swollen granules toward shear, and this latter quality is certainly influenced to a major degree by the swelling power, particularly within a group of related starches. However, the relation between granule fragility and swelling power is not necessarily strict and absolute, and hence two widely different starches may have similar swelling powers but quite different viscosity patterns. Disturbing factors may possibly include the size and shape of the granules, the kind and degree of crystallinity within the granules, the ionic charge on the starch, the presence of fat and protein, and perhaps even the molecular size and degree of branching of the starch fractions. As an extreme case, studies will shortly be reported by the present authors on the properties of "shoti" starch (derived from a variety of Pakistan curcuma tuber), which gives a mixed type B and C viscosity pattern despite a high swelling power of 50–70 at 95°C.

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