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Physicochemical factors affecting cooking and eating quality of nonwaxy rice

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Physicochemical factors affecting cooking and eating quality of nonwaxy rice

by

Young Eun Lee

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of the
Requirements for the Degree of
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Iowa State University
Ames, Iowa

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I. INTRODUCTION

A. Preamble

Rice (Oryza sativa L.) has been cultivated for centuries and produced in many countries. The major rice-producing Asian countries are the Peoples Republic of China, India, Indonesia, Bangladesh, Thailand, Burma, Japan, Korea, Vietnam, and the Philippines. The major areas of production other than Asia are Brazil, the United States, the Malagasy Republic, Egypt, Colombia and Italy (Juliano, 1984). In the United States, 94% of the total rice crop is produced in Arkansas, Louisiana, Texas, and California, and the balance of the production is in Mississippi and Missouri (Adair, 1972).

Rice is very important in the world food economy in that it is the main staple food for 1/2 to 2/3 of the world's population, and it accounts for 1/3 to 1/2 of the daily caloric intake in many Asian countries, including Korea and Japan. Indeed, it is also the major source of protein for the masses of Asian people. Furthermore, rice is becoming a main staple food in many of the African and Latin American countries. It also plays an important role in the economies of many countries such as Thailand, Burma, Vietnam, Egypt, and to some extent the United States (Lu and Chang, 1980).

Domestic consumption of rice in the United States continues to expand, and indications are that this strong upward trend will continue (Holder and Martella, 1980; Holder and Dorland, 1982). Among three major outlets - direct food use (i.e., without further processing),

processed foods, and beer - rice used directly for food is, by far, the leader, accounting for about 60% of domestic consumption. Direct food use includes raw, parboiled, and precooked milled rice. Processed foods include cereals, packaged foods, baby foods, soups, etc. (Webb, 1985).

There are more than 20,000 rice varieties in the world. However, in the United States, because of the close cooperation between industry and breeders, there are only a few varieties released into commercial production (Webb and Stermer, 1972). Rice varieties in the United States are classed for marketing purposes as long-, medium-, and short-grain types based upon kernel shape (mainly length-width ratio). Historically, and now through planned breeding, each grain type is associated with specific cooking, eating, and processing characteristics. Grains of typical long-grain varieties cook dry, fluffy, and remain separate when cooked and are preferred for use in such prepared products as parboiled rice, quick-cooking rice, canned rice, canned soups, dry soup mixes, frozen dishes, and other convenience-type rice-containing foods. Typical short- and medium-grain types, on the other hand, cook moist, chewy and clingy and are preferred for such products as dry breakfast cereals and baby foods, and for brewing uses. All three grain types and their qualities are in rather widespread demand by both the domestic and foreign trades. Most consumers in the United States prefer the texture of the typical long-grain types, although some prefer the texture of the typical short- and medium-grain types (Webb, 1985).

With but few exceptions, the grains of all rice varieties in commercial production in the United States are described as straw-hulled, nonpigmented pericarp, translucent, nonscented, nonwaxy (common) types containing varying ratios of amylose and amylopectin starch and possessing a mild, bland taste and flavor (Webb, 1985). One exception is the limited production of waxy (glutinous) short-grain rice. This rice, also called "sweet rice," is characterized by an opaque endosperm containing virtually all amylopectin-type starch. When cooked, it tends to lose its shape and be very glutinous. Waxy rice has been produced primarily for several commercial product formulations, including sauces, gravies, salad dressing, desserts, pizza shells, and batter dips for fried chicken (Webb, 1985). Recently, waxy rice has been largely replaced by various modified corn starches in many uses.

Another exception is scented (aromatic) long-grain rice produced on small acreage as a specialty product. This rice has an aroma similar to that of roasted popcorn or nuts and has a flavorful, nutty taste similar to that of the much-sought-after Basmati class of varieties in Pakistan and India. Its translucent grain contains relatively high levels of amylose-type starch. A major constituent responsible for the unique flavor of this type of rice was recently identified as 2-acetyl-1-pyrroline, which is present in the volatile oil fraction of cooked rice (Buttery et al., 1983).

A third exception, also produced in limited amounts for localized specialty markets in the United States, is the so-called "Toro" type of rice. This rice has the grain size and shape of U.S. long-grains but

possesses the cooking behavior and eating characteristics of U.S. short- and medium-grain rices.

More recently, a long-grain rice with superior processibility, referred to as "Newrex" type quality, was developed (Bollich et al., 1980) to satisfy the rice industry's need for a drier and fluffier table rice with improved processibility for manufacturing into canned, quick-cooking, and frozen types of rice products. "Newrex" type quality represents the first major improvement in U.S. long-grain quality and is the forerunner of rices of superior processibility.

B. Statement of the Problem

Encouraging progress has been made in the last two decades in rice research, especially with emphasis on rice grain quality and the parboiling process. However, much more work is needed to understand different rice grain qualities due to the varietal differences, especially different cooking and eating qualities among varieties with similar physicochemical properties in terms of amylose content and gelatinization temperature. Barber et al. (1979) recommended two priority research areas for the assessment of grain quality, one of which is cooked rice properties.

Rice is the only cereal whose primary use is through cooking and consumption of the whole grain. The cooking of rice results primarily in the gelatinization and swelling of the starch in the rice endosperm, with absorption of water. Although rice starch may increase as much as 60 times in volume when cooked in excess water (Little and Dawson,

1960), the rice kernel swells no more than 4 times even in excess water, the nonstarch constituents obviously suppressing this swelling (Juliano et al., 1964a). Juliano et al. (1964a) suggested that aside from the composition of starch and the nonstarch constituent, the physical structure of the starch granule also appears to be important. Since there have been observations of different endosperm cell arrangements of rice grains, loosely-packed and compactly-packed ones (Rosario et al., 1968; Evers and Juliano, 1976), it appears that the physical structure of rice grain might be important, too.

So far, most of the research has been directed toward the major component, starch, which accounts for about 90% of the dry weight of milled rice (Juliano, 1972a). More research needs to be directed toward the milled rice itself to understand its different cooking and eating qualities.

It is now generally believed that the amylose·to amylopectin ratio is the most important determinant affecting the cooking and eating qualities of milled rice. Since these differences exist among varieties with similar amylose content, some additional indices are needed to differentiate among them, especially in breeding programs. In the United States, the National Rice Quality Laboratory, Beaumont, TX, routinely tests gelatinization temperature of starch and alkali spreading value, water uptake capacity at 77°C, amylographic gelatinization and pasting characteristics, and protein content of milled rice in addition to amylose content. The International Rice

Research Laboratory, Philippines, uses two additional indices, gelatinization temperature and gel consistency of milled rice.

The structural changes of starch granules during gelatinization can be evaluated with the light microscope or the scanning electron microscope (SEM). Recently, SEM has been used increasingly to investigate gelatinization phenomena of several starches other than rice starch (Miller et al., 1973; Hill and Dronzek, 1973; Chabot et al., 1976; Hoseney et al., 1977, 1978; Lineback and Wongsrikasem, 1980; Bowler et al., 1980; Holmes and Soeldner, 1981; Christianson et al., 1982). Studies on the gelatinization and swelling pattern of isolated rice starch and of milled rice are limited (Little and Dawson, 1960; Bechtel and Pomeranz, 1980; Wirakartakusumah, 1981; Damir, 1985). Even most of the in situ gelatinization studies were done during the parboiling process rather than during the cooking of boiled rice.

Gelatinization temperatures of rice starch vary widely among varieties. Distribution of granule size, degree of crystallinity, and amylose content may affect the gelatinization temperature of starch. But there are contradictory results or lack of evidence, which necessitates more research.

The existing knowledge of what occurs during rice cooking is still incomplete, and the exact physicochemical role of the constituents of the rice grain, as influenced by variety, is still speculative. Further studies are required to elucidate the physicochemical changes during cooking and their relationship to the texture of cooked rice. The use of SEM may help to clarify the role of starch and nonstarch constituents

and the effect of rice grain structure on determining cooking and eating qualities of rice.

C. Objectives of the Study

There are many rice varieties with diverse characteristics throughout the world and there is a distinct preference for rice based on race and region. Therefore, previous studies on rice research have been mainly aimed at developing quick and good indices for predicting rice grain qualities (cooking, processing and eating qualities) in breeding programs in the countries that consume the most rice. Unfortunately, there are few studies dealing with the role of starch and nonstarch constituents and the effects of physical changes of isolated rice starch and milled rice on the cooking and eating qualities of rice.

The following objectives were formulated for the present study for nonwaxy rices with diverse and extreme characteristics:

1) evaluate the physicochemical properties of rice starch and milled rice and examine the relationships among them;
2) observe the changes in physical appearance of starch granules heated in excess water and evaluate their effects on the development of rheological properties and viscosity;
3) observe the changes in physical appearance of milled rice during heating and evaluate their effects on the cooking and eating qualities of rice;
4) investigate factors affecting gelatinization temperature (birefringence end-point temperature; BEPT) of rice starch.

II. LITERATURE REVIEW

A. Gelatinization Phenomena of Starch

Starch is the main source of carbohydrate in human diet. Its importance in food processing is based on the fact that over 80 percent of all food crops are composed of cereals and other starchy crops. One of the most consumed cereal grains is rice (Greenwood, 1979). If rice is processed through a hydrothermal treatment, gelatinization will occur.

In order to understand the phenomenon of gelatinization, it is necessary to understand the components and structure of the starch granule.

1. Starch molecule

Starch is an α-glucan that has two major structurally distinct components: amylose and amylopectin. A third component, often referred to as the intermediate fraction, has been identified in some starches (Banks et al., 1971; French, 1984). The percentage of the intermediate fraction varies from 5 to 10 percent in most cereal starches. Its structure is currently not known and may vary with botanical source (Banks and Greenwood, 1975; Greenwood, 1979).

a. Amylose For a long time amylose was thought to consist entirely of a linear polymer of D-glucose with α-(1→4) glycosidic linkages (Figure 1). However, this concept changed when small amounts of branching through α-(1→6) linkages were reported in amylose (Banks

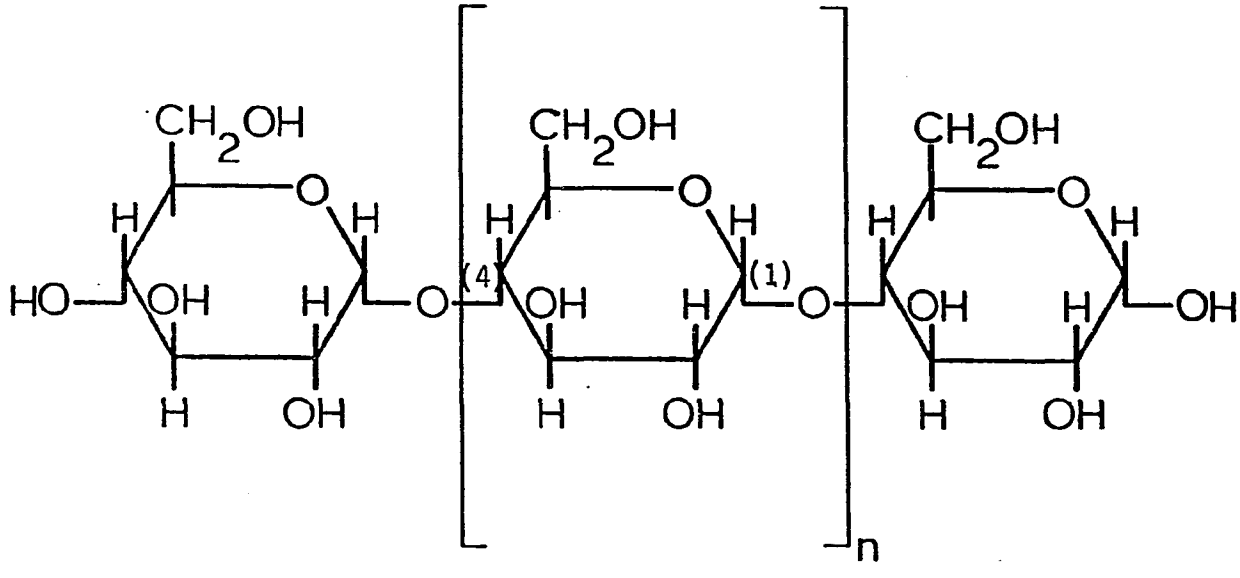


Figure 1. Amylose

and Greenwood, 1967). It is now concluded that amylose consists of a mixture of linear molecules and molecules with limited, long-chain branching involving α-(1→6) linkages. The branches may occur in the order of one per 500 glucose residues and be multiply branched (Banks et al., 1973; Banks and Greenwood, 1975; Greenwood, 1979; Hood, 1982). Amylose molecules have degrees of polymerization (DP) of 350-1000 compared with amylopectin with a DP of several thousand or more (Whistler and Daniel, 1985).

One of the most important features of amylose in foods is its ability to form inclusion complexes with a wide variety of complexing agents, such as lipids, iodine and most primary aliphatic alcohols. With these complexing agents, amylose possesses a helical structure, of 6 or 7 glucose residues per turn, and the complexing molecules occupy the central cavity of the helix (Figure 2). The ability of amylose to interact with iodine, forming a characteristic deep-blue complex, has been used extensively in the characterization of starch (Banks et al., 1973; Banks and Greenwood, 1975). In the absence of complexing agents and in dilute solution, or in gel form, amylose adopts a randomly coiled structure (Banks et al., 1973).

b. Amylopectin Amylopectin is a highly branched fraction of starch containing 94-96% α-(1→4) and 4-6% α-(1→6) linkages. The average chain length in each branch is 20-26 glucose units (Greenwood, 1979; Hood, 1982).

Three model structures were proposed for amylopectins based on the chemical analyses soon after the branched nature of amylopectin was

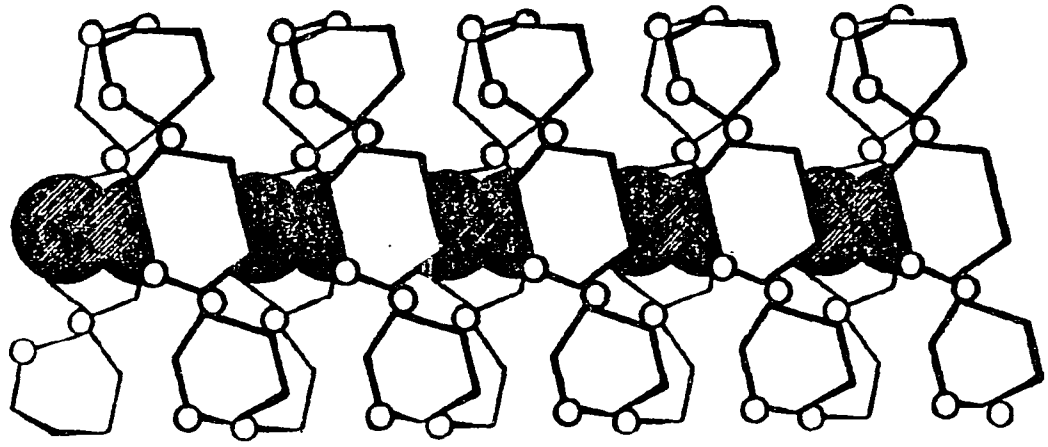
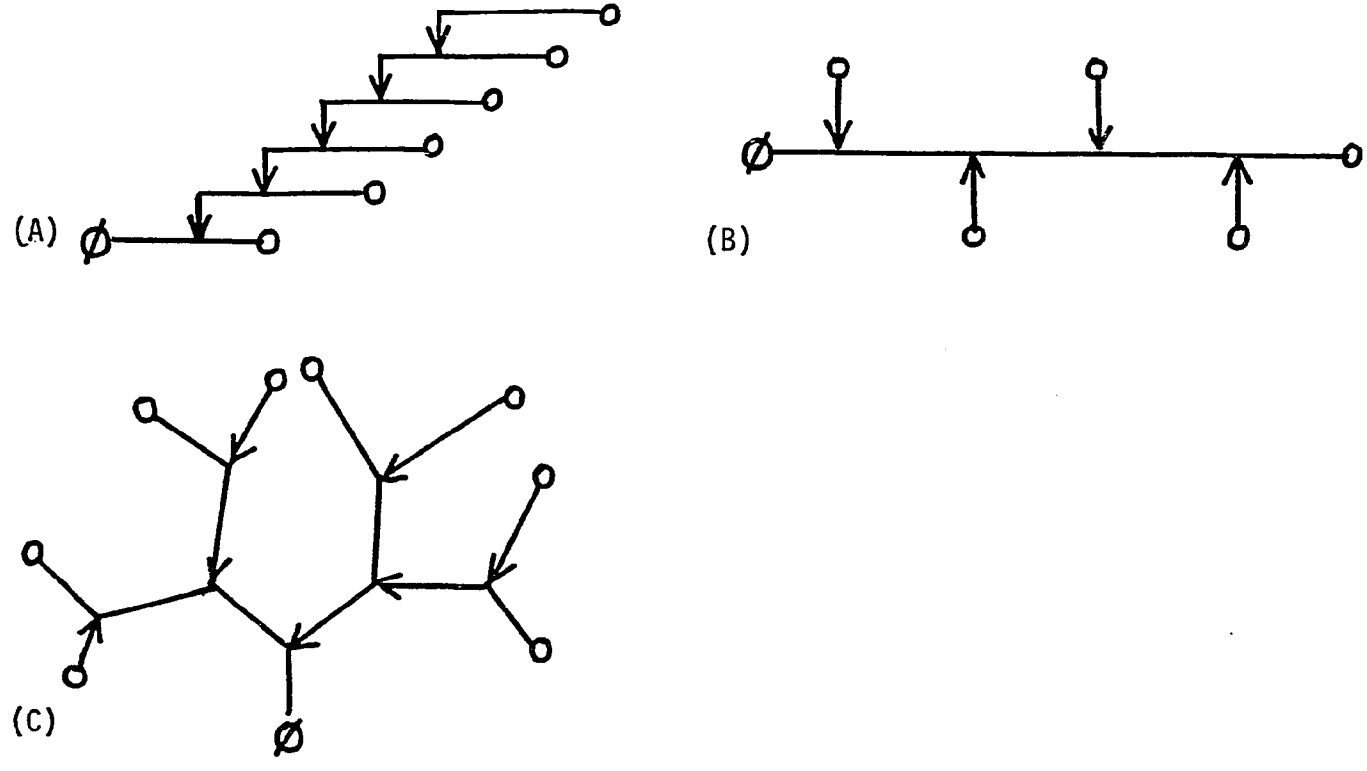


Figure 2. Helical structure of amylose in the presence of complexing agents (adapted from Rundle et al., 1944)

recognized (Figure 3). Among these models, the randomly branched structure proposed by Meyer and Bernfeld (1940) was generally accepted as agreeing best with the evidence then available for the arrangement of chains in amylopectin. With the development of new biochemical and chromatographic techniques in the 1950s, however, the Meyer model has been considerably modified further. Recently, Robin et al. (1974, 1975) have proposed a model for amylopectin based on the "cluster" structure of Nikuni (cited in Nikuni, 1978) and French (1972) (Figure 4). In this model, the A and B chains are linear and have mean degrees of polimerization ($\overline{DP}$) of 15 and 45, respectively. The B chains form the backbone of the amylopectin molecule and extend over two or more clusters. Each clusters contains two to four closely associated A chains. The associated clusters of A chains are primarily responsible for the crystalline regions within the granule. The intercrystalline (amorphous) areas occur at 60-70 Å intervals (Kassenbeck, 1978; French, 1984), contain the majority of the α-(1→6) linkages and are relatively susceptible to hydrolysis by enzyme and acid. The amylopectin molecule of waxy maize starch was reported to be 100-150 Å in diameter and 1200-4000 Å long (Yamaguchi et al., 1979).

2. Starch granule

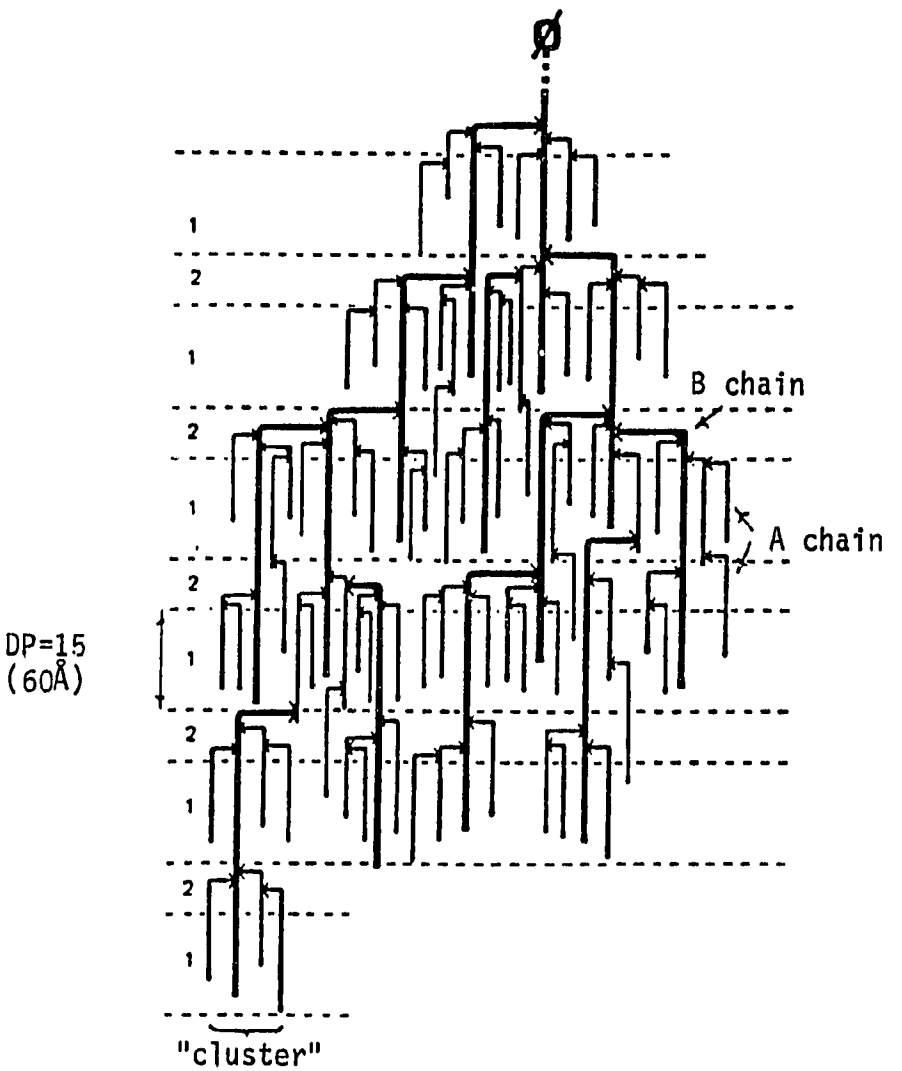
Of all polysaccharides, starch is the only one universally produced in small individual packets called granules (Whistler and Daniel, 1985). They may be spherical, ellipsoidal or irregular in shape and vary in



(A) Laminated structure (Haworth et al., 1937)
(B) Herring-bone structure (Staudinger and Husemann, 1937)
(C) Randomly branched structure (Meyer and Bernfeld, 1940)

ø = Reducing end group
o = Nonreducing end group
→ = α-(1→6) branch points
- = α-(1→4) linkages

Figure 3. Early models proposed for amylopectin (adapted from Hood, 1982)



1 = Crystalline area
2 = Amorphous area
ø = Reducing end group
→ = α-(1→6) branch points
– = α-(1→4) glucan

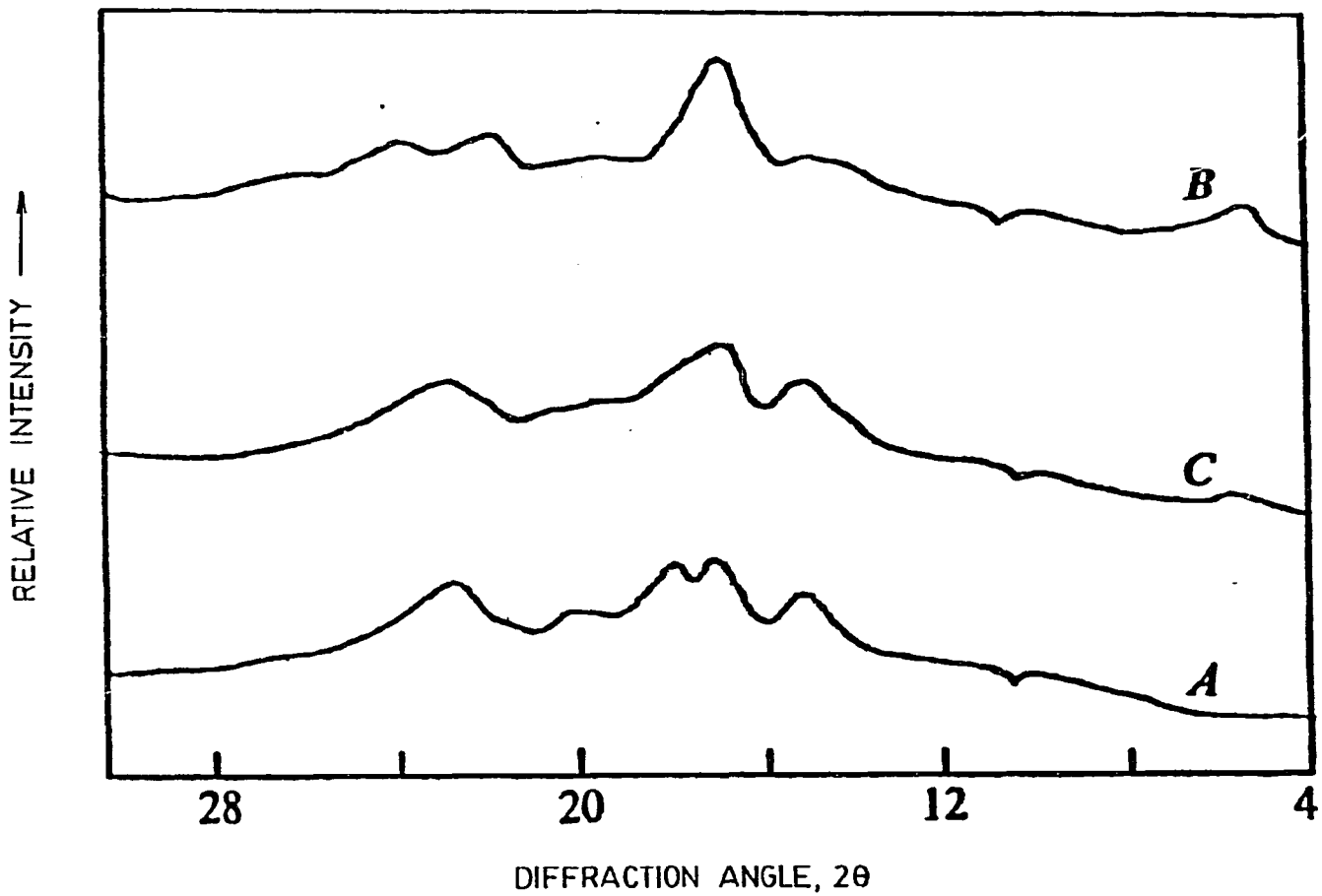
Figure 4. Currently accepted structure for amylopectin (adapted from Robin et al., 1974)

size from 2 μm in pollen starch to 175 μm in canna starch (Banks and Greenwood, 1975).

In addition to the simple type of starch granule in which a plastid gives rise to a single nucleus and consequently one granule, a second type of granule is also found in many species. This is the compound granule, in the formation of which a plastid must contain several nuclei to be developed to multipart granule.

When intact granules are examined under a polarizing microscope, they exhibit a well-defined birefringence pattern with a dark cross (Maltese cross), implying a high degree of molecular orientation within the granule (Greenwood, 1979). It would appear that amylopectin is responsible for the crystallinity since waxy starches with essentially no amylose are very birefringent, while many of the granules in high-amylose starch are nonbirefringent (Greenwood, 1979; Hood, 1982).

Many attempts have been made to explain the crystallinity of the starch granules as shown by characteristic x-ray diffraction patterns, differing in interplanar spacings and intensities of diffractions (Sterling, 1978). Starch has been regarded as a semicrystalline material composed of crystalline and amorphous regions since the classic work of Katz in the 1930s. Katz and Itallie (cited in Banks and Greenwood, 1975) distinguished three types of crystalline structure which depends on the botanical source of the starch (Figure 5): the A-pattern by most cereal starches; the B-pattern by most tuber starches; and the C-pattern by some pea and bean starches. The C-pattern is, in fact, an intermediate form between A and B types. Waxy-starch granules



A = Cereal starches
B = Tuber starches
C = Pea and bean starches

Figure 5. Typical x-ray diffraction patterns for starches (adapted from Banks and Greenwood, 1975)

also exhibit a strong x-ray diffraction pattern (Maniñgat and Juliano, 1979).

Starch granules tend to possess radial symmetry and often exhibit well-defined rings or lamellar structure. However, the starch granules obtained from maize, wheat, and barley seldom exhibit rings unless pretreated by acid or by amylolytic enzymes (Banks et al., 1973; Evers and McDermott, 1970; Mussulman and Wagoner, 1968). Recently Chabot et al. (1978) supported the existence of the concentric lamellar structure with the freeze-fracturing procedure with waxy maize starches. The acid or enzyme-resistant rings represent crystalline regions, while the amorphous regions are more labile to the acid and enzyme hydrolysis (Hood, 1982). According to Yamaguchi et al. (1979), the rings occur at irregular 1200-4000 Å intervals and probably represent the overall length of individual amylopectin molecules, suggesting that a single amylopectin molecule commence at one growth ring and terminates at the next. Each amylopectin molecule is made up of many 70 Å clusters (Figure 6). The presence of lamellar structures fits with the theory that starch granules grow during biosynthesis by apposition of successive tangential layers to produce an "onion-like" layered structure.

The molecular structure of starch is related to the crystalline properties of the granule. It is now well accepted that the starch molecules are radially oriented within the granule. According to Kainuma and French (1972), pairs of the outer $\overline{DP}$ 15 chains of amylopectin (Figure 4) can form double helices and contribute to the

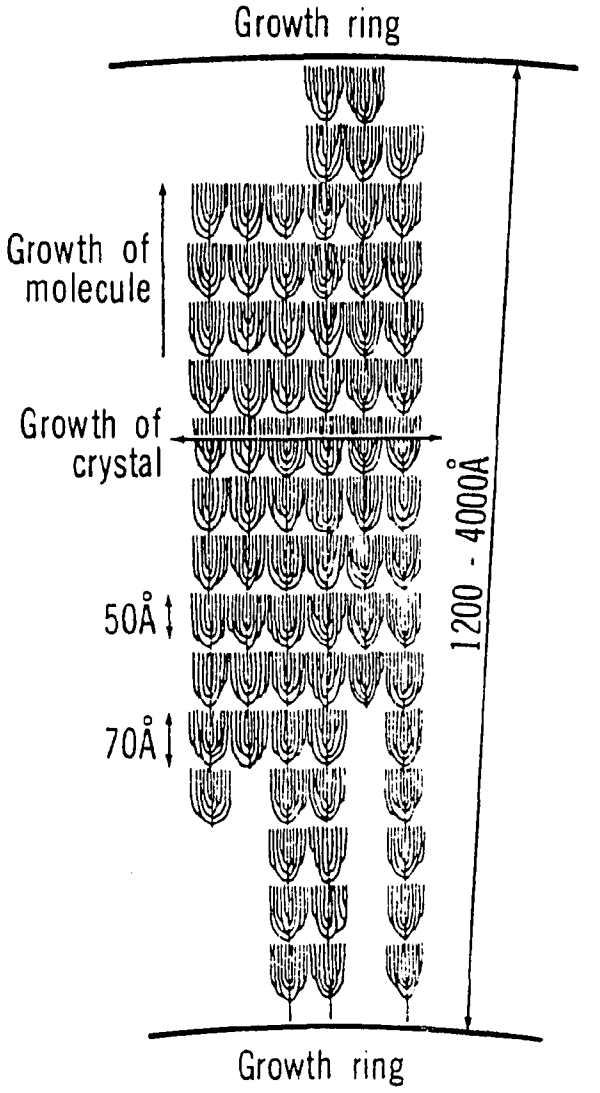


Figure 6. Schematic presentation of the arrangement of amylopectin molecules within a growth ring (adapted from French, 1984)

crystalline properties of starch granules. As mentioned earlier, the (1→6) linkage-rich regions of amylopectin are relatively amorphous (Robin et al., 1974, 1975).

In spite of the progress in determining the molecular and granular structure of starch, knowledge of the arrangement of amylose and amylopectin molecules within the granule is still relatively meager. However, it has been suggested that amylose may be located between amylopectin molecules and contributes to the high degree of order in the crystalline regions of the amylopectin within the granule (Hood, 1982).

3. Gelatinization of starch

Undamaged starch granules are not soluble in cold water, but can reversibly imbibe water and swell slightly. The percentage increase in granule diameter ranges from 9.1% for normal corn starch to 22.7% for waxy corn (Whistler and Daniel, 1985). However, as the temperature is increased, starch molecules vibrate more vigorously, breaking intermolecular bonds and allowing their hydrogen-bonding sites to engage more water molecules. This penetration of water makes swelling irreversible and the structure of the granule altered significantly (Leach et al., 1959; Leach, 1965; Whistler and Daniel, 1985). The process is called "gelatinization" and the temperature at which gelatinization occurs is called "gelatinization temperature." It usually occurs over a narrow temperature range (5°-10°C), indicating that some granules in a sample exhibit different gelatinization temperatures (Schoch and Maywald, 1956). At this temperature, the

granule loses its birefringence and materials from the granule diffuses into the water (Greenwood, 1979).

The term "gelatinization" is used to describe the initial rapid swelling of the granules accompanying the loss of birefringence by the more precise chemists. However, this term also has been used to describe both the initial and subsequent swelling and hydration of granular starches by others.

Based on changes of starch granules during and after heating in aqueous medium, Olkku and Rha (1978) summarized the steps of gelatinization as follows:

1) granules hydrate and swell to several times their original size;
2) granules lose their birefringence;
3) clarity of the mixture increases;
4) rapid increase in viscosity occurs and reaches a maximum;
5) starch molecules, primarily linear, dissolve and diffuse from ruptured granules;
6) upon cooling, uniformly dispersed matrix forms a gel or paste-like mass.

a. Viscosity changes during gelatinization Aside from swelling during gelatinization, the viscosity of the medium also increases. Both the molecular and granular structures contribute to the increase in viscosity. Heat disrupts the intermolecular hydrogen bonds that maintain the structural integrity of the granule. The more accessible and amorphous regions hydrate initially (Hood, 1982). Water molecules solvate the liberated hydroxyl groups and the granule continues to

swell. As a consequence of severe disruption of hydrogen bonds, the granule will be fully hydrated and finally the micellar network separates and diffuses into the aqueous medium (Leach, 1965; Glicksman, 1969; Greenwood, 1979; Hood, 1982). Viscosity increases concomitantly with the increasing granule size. When the granule swells to the point that internal bonding can no longer maintain its integrity, it ruptures and the viscosity declines. This increase and decrease of viscosity during gelatinization can be readily followed by using a Brabender amylograph. From comparative ultrastructural-viscosity studies, Miller et al. (1973) and Allen et al. (1977) reported that amylose leaches from the granule and forms an extragranular network. The increase in viscosity in the early heating stages is due mainly to this extragranular material; in latter stages when maximum viscosity is approached, it is due to both the swollen granules and the extragranular material except in extremely concentrated starch suspension. Since gelatinization depends on water infiltration into the granule, granules in limited water systems (i.e., bread) will be less swollen and thus the final viscosity will be lower (Hood, 1982)

b. Morphological changes of starch granules during gelatinization

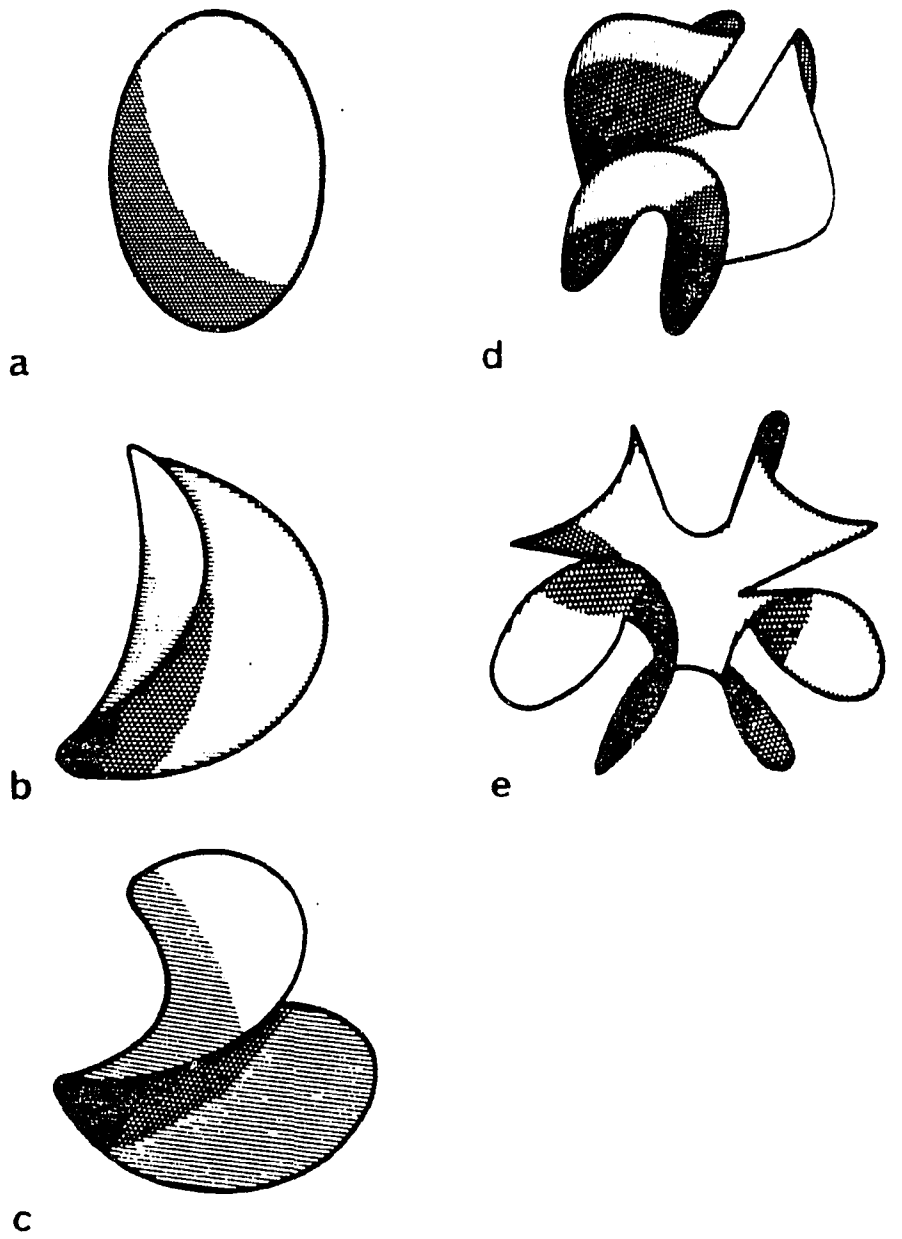
From the observations with potato starch, Bear and Samsa (1943) indicated that swelling of starch granule is tangential rather than isotropic or radial. A radial contraction during swelling cannot be ruled out. From present knowledge of starch granule structure, it seems likely that the tangential swelling is due to the hydration and lateral expansion of amylopectin crystallites. The amylopectin molecule as a

whole cannot expand radially, that is, along its molecular axis. Radially oriented amylose molecules, whether in the crystallites or in the amorphous phase, also restrict swelling along their molecular axis (French, 1984).

A unique swelling and gelatinization pattern is seen with wheat and related starches (Woodruff and Webber, 1943; Derby et al., 1975; Bowler et al., 1980). From study of lenticular wheat starch granules, Bowler et al. (1980) concluded that swelling is a two-stage process, which occurs primarily in the plane of the two major axes only. The process involves radial expansion to form a flattened disc followed by tangential expansion to produce a complex puckered granule (Figure 7). Banana starch is somewhat intermediate between wheat and potato in its swelling pattern.

Christianson et al. (1982) investigated the swelling pattern of the corn starch granules, basically spherical with some granules having faceted sides. Corn starch granules begin to swell radially, then undergo radial contraction and random tangential expansion. They form complex geometrical structures between the range of 67°-70°C unlike the more uniform single-dimensional tangential swelling of lenticular wheat starch. At higher temperatures, when starch begins to solubilize, corn starch granules lose their distinct ridges and appear to melt into thin flat discs.

There have been few investigations on the swelling pattern of rice starch which is similar to corn starch in shape and much smaller in size.



(a) 50°-60°C
(b) 60°-70°C
(c) 70°-80°C
(d) and (e) above 80°C

Figure 7. Diagramatic representation of the changes occurring due to tangential swelling of the lenticular wheat starch granule (adapted from Bowler et al., 1980)

From the hot water swelling and gelatinization patterns of the various types of starch granules, French (1984) theorized that the swelling of amorphous regions contributes to the disruption of the crystalline regions by uncoiling of double-helical regions and break-up of amylopectin crystallite structure. The liberated side chains of amylopectin become hydrated and swell laterally, further disrupting crystalline structure. The starch molecules are unable to stretch longitudinally, and actually may have a tendency to contract to approach a random coil conformation. This provides a constraint against swelling in the chain direction. Increased molecular mobility with further hydration permits a redistribution of molecules, and the smaller, linear amylose molecule diffuse out. Further heating and hydration weaken the granule to the point where it can no longer resist mechanical shearing or hydrothermal stress, and a sol results.

c. Application of thermodynamics to the study of starch gelatinization Because the starch granule may be considered as a semicrystalline polymer (spherulite) which contains both crystalline and amorphous regions, gelatinization may be viewed as a melting process. In the allied field of synthetic polymers, Flory (1953) has devised an expression to relate the melting temperature of a crystalline polymer (starch granule in this case) to the concentration of diluent in the system (water in this case). Such an equation has relevance to the problem of starch gelatinization. It was with these ideas in mind that Lelievre (1973) examined the relationship between the gelatinization temperature of the starch granule under equilibrium conditions and the

water content of a dispersion of starch granules. A similar analysis using Flory's equation has been used on the results from DSC (differential scanning calorimetry) studies on potato starch (Donovan, 1979), various legume starches (Biliaderis et al., 1980) and rice starch (Wirakartakusumah, 1981).

A concept to explain gelatinization and the effect of water content that is compatible with DSC data is schematically summarized in Figure 8 according to Biliaderis et al. (1980) and Biliaderis (1983). If excess water is present, extensive hydration and swelling of the amorphous regions facilitate melting of the starch crystallite upon heating. This occurs over a very narrow temperature range, and therefore results in a single endotherm (lower temperature endotherm). The melting of the crystallites may involve a solvation assisted helix-coil transition of the polymer chains, going from the ordered form to the random conformation. This solvation process offsets the stabilization forces (hydrogen bonding) in the crystallites. Extensive swelling accompanies the disruption of the crystallites and results in an increase in viscosity following the loss of birefringence.

In more concentrated starch solutions, however, the destabilizing effect of the amorphous regions decreases because of the limited amounts of water present and only partial melting of crystallites occurs resulting in a smaller area of the lower temperature endotherm. Upon further heating, subsequent redistribution of the water around the unmelted crystallites will assist the complete melting of the granule. Donovan (1979) and Biliaderis et al. (1980) further suggested that water

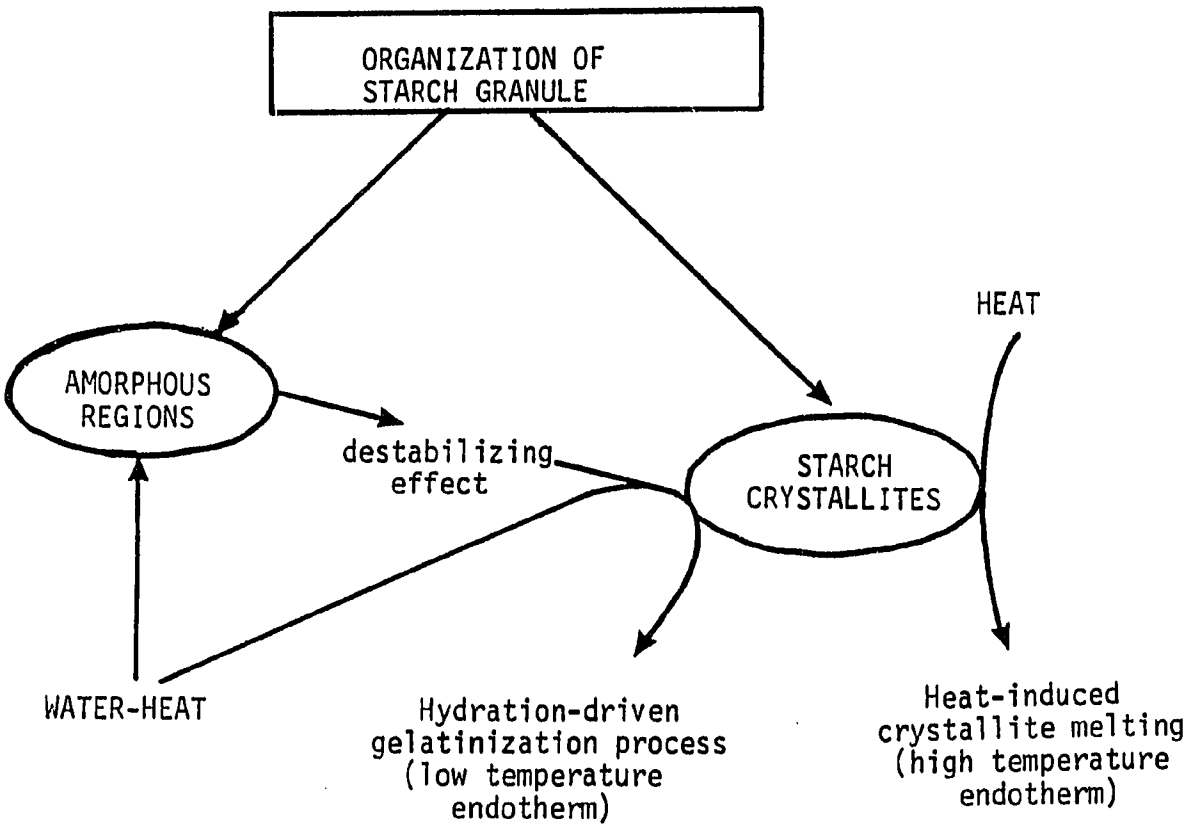


Figure 8. Schematic representation of phase transition mechanism of granular starch (adapted from Biliaderis, 1983)

mobilization may take place toward the unmelted crystallite. Finally, under extreme conditions, where no moisture is present in the system, and the only denaturant is heat, melting of the starch crystallites would be expected to occur at temperatures close to the estimated true melting point of undiluted polymer ("true-melting" of crystallites).

The successful application of these ideas and equations of polymer physics into the study of starch gelatinization as a basis for reconciling a larger number of experimental studies and results is encouraging. Food processes in general are, however, nonequilibrium in character, and therefore the criticism might well be evolved against this type of work that it is divorced from industrial reality. Therefore, the application of nonequilibrium thermodynamics to the study of starch gelatinization has been considered.

Merchant and Blanshard (1978) postulated three constituent processes for starch gelatinization based on nonequilibrium dynamics: 1) diffusion of water into the starch granules, 2) a hydration-facilitated helix coil transition which is a melting process, and 3) swelling as a result of crystallite disruption. Blanshard (1979) reported that total exchange of water between a starch granule and the environment at ambient temperature occurs in about one second. Based on this observation and the temperature dependence of gelatinization, the initial diffusion process is not responsible for starch gelatinization. Using small-angle light scattering technique to further study melting and/or swelling processes, the results showed that gelatinization may be described as a "semicooperative process." Each starch granule has its

own degree of crystallinity with its unique energy characteristics. The imposition of a 2°C temperature jump may result in certain starch granules being totally gelatinized but, in others, only some of the crystallites will gave their gelatinization threshold exceeded. Within such partially gelatinized granules, there is the possibility of a rearrangement of the polymer chains of amylose and amylopectin. With such arrangements, the energy characteristics of adjacent crystallites will also be moderated and some of these may then fall within the temperature range where melting occurs, with a consequent loss of x-ray order and birefringence. It is this process of rearrangement which is believed to be responsible for the slow, time-dependent process.

4. Methods for determining starch gelatinization

Starch gelatinization can be determined qualitatively and/or quantitatively by physical, chemical and biochemical methods.

a. Light microscopy The many methods that had been proposed prior to 1950 for measuring the gelatinization temperature of starch have been discussed in detail by Kerr (1950). Three different criteria had been used to detect the gelatinization temperature: loss of birefringence, increase in optical transmittance, and rise in viscosity. Measurement of the loss of birefringence is more sensitive, accurate, and reproducible technique than the methods based on the other two criteria. The Koefler electrically-heated microscopic hot stage and polarizing microscope provide a simple and rapid means for detecting degree of gelatinization (Watson, 1964). It is limited, however, to

dilute granule suspension (0.1-0.2% aqueous starch suspension). With this instrument, sigmoidal gelatinization curves may be obtained by graphing the percentage of granules that have lost birefringence against the temperature (Figure 9; Leach, 1965). In practice, usually only initial and 98% loss temperature (birefringence end-point temperature; BEPT) are recorded. Berry and White (1966) modified Watson's method to follow the progress of gelatinization by recording the light output on a photocell as a function of hot stage temperature.

Microscopic examination of granules undergoing gelatinization permits one to observe swelling duration, degree of swelling, and swollen granule integrity and size. Collison (1961) used a photomicrograph technique to measure the swelling of individual granules directly.

b. Electron microscopy Structural changes occurring during gelatinization have been reported with the scanning electron microscope (SEM) (Miller et al., 1973; Hill and Dronzek, 1973; Chabot et al., 1976; Hoseney et al., 1977, 1978; Lineback and Wongsrikasem, 1980; Holmes and Soeldner, 1981; Bowler et al., 1980; Christianson et al., 1982).

Despite the importance of gelatinized granule morphology in the functional properties of many foods, such studies on gelatinized granules have raised a number of questions that are not resolved yet. Investigations on concentrated systems or on completely pasted starches have problems with artifacts owing to the well-known phenomenon that starch molecules aggregate during drying or freezing. These effects

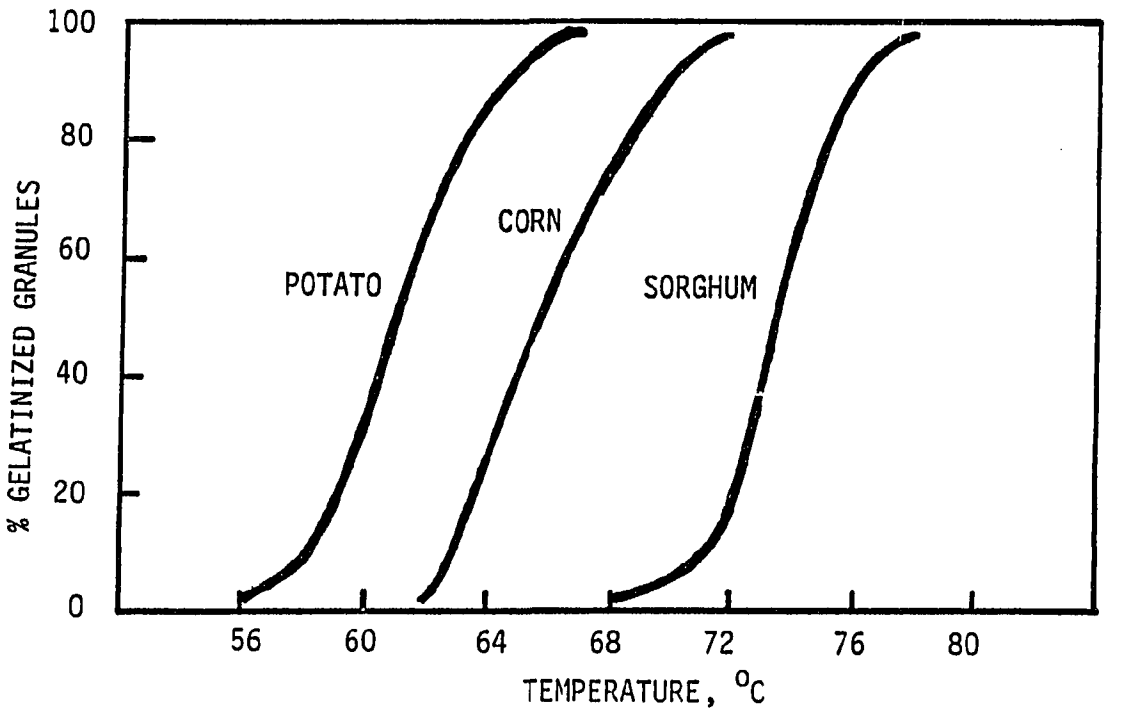


Figure 9. Graph of the gelatinization temperature ranges of various native starches (adapted from Leach, 1965)

were investigated by Berghofer and Klaushofer (1976) and recognized and discussed by Miller et al. (1973) and Chabot (1979).

Scanning electron microscopy is an important technique in food science, but its true value rests on scientists learning to control avoidable artifacts and recognizing the range of effects produced by different processing and preparation procedures.

c. Viscometry In common practice, the most widely used method for determining the degree of gelatinization is based on changes in viscosity during gelatinization.

A Brabender Visco/amylo/Graph provides information, not only on gelatinization, but also on the properties of the cooked paste. This instrument records the torque required to balance the viscosity that develops when a starch slurry is subject to a programmed heating and cooling cycle (rate of 1.5°C/min). The temperature at which the first major rise in viscosity occurs is highly dependent on starch concentration and is generally higher than gelatinization temperatures obtained by loss of birefringence. Halick et al. (1960) indicated that when high concentrations (20%) of rice flour are used, the Brabender curve leaves the baseline at the same temperature as the BEPT.

Amylograph viscosities are profoundly affected by pH of the starch or flour suspension (Hodge and Osman, 1976; Tipples, 1982; Zobel, 1984) (Figure 10). Therefore, to examine native starches or flours at as-is pH, the pH should be in the range of 5.0 to 6.0. In practice, pH of the starch or flour suspensions may be adjusted to this range by dropwise addition of acid or alkali (1.0 N HCl or NaOH).

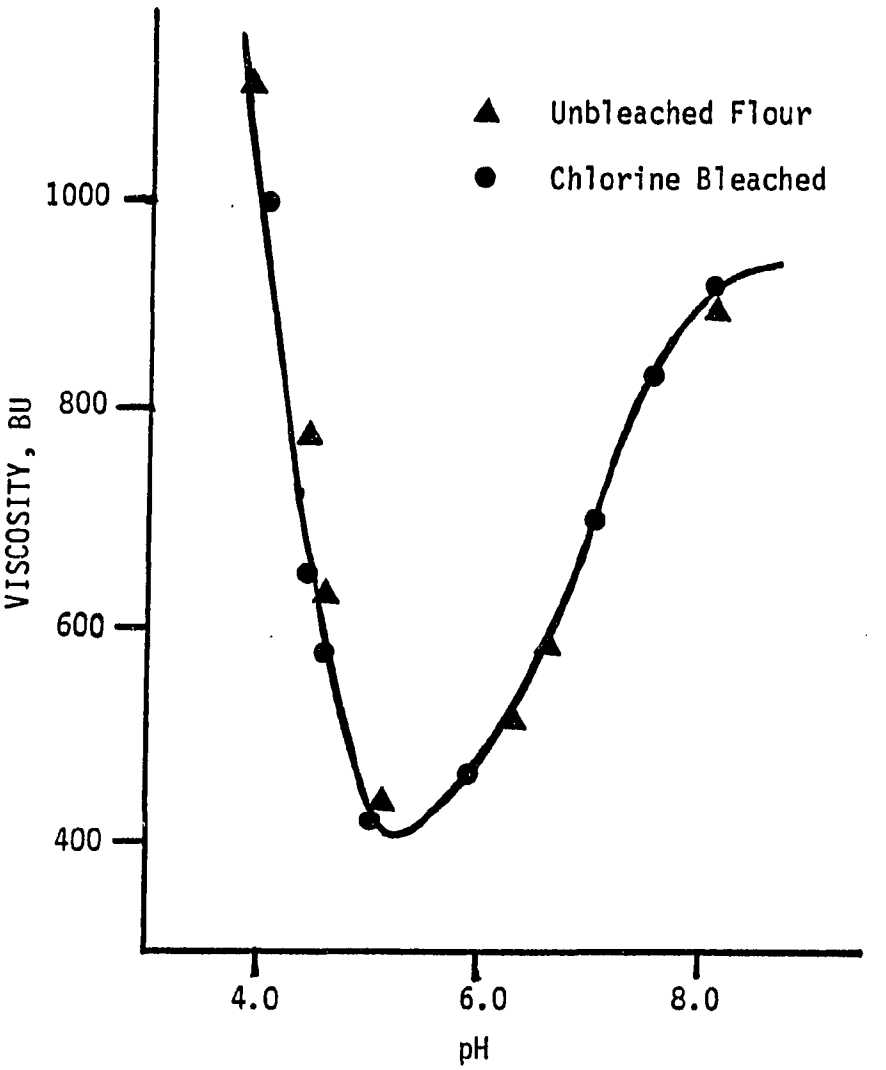


Figure 10. Effect of pH on amylograph peak viscosity of wheat flour (adapted from Tipples, 1982)

In addition to the Brabender Visco/amylo/Graph, the Corn Industries Viscometer, which was developed by Kesler and Bechtel (1947), is another rotational instrument designed especially for continuous measurement of viscosity during the preparation of a starch paste under standard conditions (Leach, 1965).

Freeman and Verr (1972) measured gelatinization and paste development by heating starch in a closed bottle submerged in a water bath with a shaking mechanism. At specified times or temperature, samples were removed and viscosities determined with a Brookfield Synchro-Lectric viscometer.

d. Swelling and solubility determination The primary event that occurs when starch is gelatinized in an aqueous medium is granule swelling (Leach, 1965).

Leach et al. (1959) developed swelling power and solubility curves to characterize potato, corn, waxy and cross-linked (-bonded) corn and other starches over the swelling range of the starch. Swelling power, in this case, is a measure of hydration capacity, since the test is a weight measure of swollen granules and their occluded water. As a direct result of granule swelling, there is a parallel increase in starch solubility, paste clarity, and paste viscosity.

The major factor that controls the swelling behavior of starch is the strength and character of the micellar network within the granule, which in turn is dependent on the degree and kind of association. On a molecular level, many factors may influence the degree of association, as well as the size, shape, composition, and distribution of the

micellar areas in the internal lattice. These factors include the ratio of amylose to amylopectin, the characteristics of each fraction in terms of molecular weight, molecular weight distribution, degree of branching, conformation, and the length of the outer branches in the amylopectin. The presence of naturally occurring noncarbohydrate impurities (i.e., fatty acids, ionizable esterified phosphate groups) is also a highly important factor.

Normal corn, rice, and sorghum starches show restricted swelling when compared to their waxy counterparts. This suggests that the linear fraction reinforces the internal network. It is well known that the shorter amylose molecule are preferentially solubilized and leached from swollen starch granules.

e. Amylose/iodine blue value method It was previously described that amylose complexes with iodine, producing a brilliant blue color. This characteristic has been used as an analytical tool for measuring amylose content.

A quantitative method to determine the amount of amylose present in solution has been developed by McCready and Hassid (1943) and modified by Gilbert and Spragg (1964). The absorbance of the blue color is measured with a spectrophotometer at 600 nm. However, it was suspected that the blue color may not fully develop if retrogradation or incomplete solubilization of amylose is encountered. Under these conditions a more rigorous method of mixing is required (Gilbert and Spragg, 1964). Thus, the method that gives the maximum absorbance should be chosen. In spite of these weaknesses, the iodine blue value

method provides a rapid determination of amylose content that is adequate for most purposes (Banks et al., 1974; Banks and Greenwood, 1975; Juliano, 1979b). For starches containing intermediate fractions with chain lengths between 50-100 glucose units (i.e., amylomaize), the simple iodine blue value method overestimates the amylose content (Banks et al., 1974).

Roberts et al. (1954) applied the amylose/iodine blue value method to determine soluble starch in water at 55°C as an index of parboiling in rice. However, this method itself was not applicable to parboiled rice since gelatinized rice flour was insoluble in water (Birch and Priestley, 1973). Modification of this method by dissolving the amylose in alkali solution and then subsequently neutralizing it with acid solution has been practiced (Birch and Priestley, 1973; Birch et al., 1973). The alkali treatment dissolves amylose in an aqueous solution. A critical concentration of alkali was found for gelatinized starch (0.2 M KOH) while it was higher (0.5 M KOH) for raw starch. They used this optimum concentration to distinguish between raw and gelatinized starch. After addition of iodine reagent, the absorbance was measured with a spectrophotometer at 600 nm. The ratio of the absorbance of these two different mixtures (0.2 M vs. 0.5 M KOH) is proportional to the degree of gelatinization. Bakshi and Singh (1980) applied this method to measure the degree of gelatinization in parboiled rice.

f. X-ray diffraction In certain cases, x-ray patterns can be used to differentiate between native starches and to detect changes in crystallinity brought about by physical or chemical treatment of starch

granules (Zobel, 1964). The method has been used as a tool to measure the extent of gelatinization (Varriano-Marston et al., 1980; Owusu-ansah et al., 1982).

In principle, there are two methods of recording patterns in an x-ray diffraction unit: 1) the diffractometer method, in which rays scattered from the sample are received by a Geiger-Müller counter tube, with the output then amplified and plotted by chart recorder; and 2) the photographic method, in which the pattern is recorded on a photographic film (Zobel, 1964).

X-rays are a form of electromagnetic radiation with a wavelength typically between 0.1 and 1.0 nm (1-10 Å), which is comparable to the molecular spacing in a crystal. When an x-ray beam impinges on the crystal which is held in a special mount that allows the crystal to be rotated with respect to the incident beam, diffraction occurs. Diffraction phenomenon occurs whenever a wave motion interacts with an obstacle. The diffracted beams are recorded to obtain information on the structure of the crystal and the molecules with the crystal (Sherwood, 1976).

X-ray diffraction can give information not only about the crystal structure of the crystallites of starch granules, but also about the relative amounts of crystalline and amorphous phases. However, interpretation of x-ray data has been difficult, owing to the inadequate amount of data, the small crystallite size, the imperfection of the crystallites, and the large unit cells (French, 1984).

In x-ray analysis of starch granules, satisfactory results are obtained if the specimen are properly prepared and mounted. Coarse powder gives less intense patterns. Therefore, the samples have to be less than 200 mesh (57 μm) in size and packed as densely as possible into a sample holder. The finished surface must be smoothed and flushed. The patterns are analyzed based on their interplanar spacings and relative intensities of the diffraction lines. It was mentioned previously that for starch granules the patterns can be classified as A, B, and C patterns (Zobel, 1964).

g. Differential scanning calorimetry Differential scanning calorimetry (DSC) has been applied to study gelatinization of starch by considering gelatinization of starch to be the analog of a melting process for a crystal (Banks and Greenwood, 1975). Stevens and Elton (1971) applied DSC to measure heat of gelatinization of several native starches.

DSC is a thermoanalytical technique for monitoring changes in physical or chemical properties of materials as a function of temperature by detecting the heat changes associated with such processes.

This system was originally patented by the Perkin-Elmer Corp., and termed 'Differential Scanning Calorimetry.' This name subsequently has been applied to some calorimetric DTA (differential thermal analysis) instruments by other manufacturers.

In DSC, the measuring principle is to compare the rate of heat flow to the sample and to an inert material (reference) which are heated or

cooled at the same rate. Changes in the sample that are associated with absorption or evolution of heat cause a change in the differential heat flow which is then recorded as a peak. The area under the peak is directly proportional to the change of enthalpy (heat content) and its direction indicates whether the thermal event is endothermic or exothermic. In addition to the enthalpy determination, DSC also provides information on initial, peak, and conclusion temperatures of the reaction and the heat capacity of the sample (Biliaderis, 1983).

DSC is particularly well suited to investigate the heat-induced phase transitions of starch/water systems, because it allows: 1) use of a small sample which minimizes the thermal lag within the system; 2) no change of sample concentration due to evaporation of water during measurement because the sample is enclosed in a sealed container; 3) study of starch gelatinization over a wide range of temperatures and moisture contents; and 4) estimation of transition enthalpies (Biliaderis et al., 1980; Biliaderis, 1983).

h. Other methods Other methods in addition to those previously described are available, e.g., enzymatic digestibility (Shetty et al., 1974), nuclear magnetic resonance (Lelievre and Mitchell, 1975), laser light scattering (Merchant et al., 1977), light transmission (Cook and Axtmayer, 1937), absorption of congo-red measurements (Carrol and Cheung, 1964). However, these methods are less popular due to the difficulties in their procedures or degree of accuracy in measuring the degree of gelatinization.

5. Factors affecting extent and temperature of gelatinization

Gelatinization of starch is a hydrothermal process. Therefore, the conditions during gelatinization and the physicochemical properties of starch itself may affect the extent and temperature of gelatinization.

a. Conditions during gelatinization The extent and temperature of gelatinization may be affected by water content (water/starch ratio), heating rate, and temperature during steeping.

Amylography and BEPT measurement are applied to only limited concentrations of starch suspension. The temperature at which initial viscosity rise occurs in the amylograph decreases as starch concentration increases.

DSC studies with various water/starch ratios showed a progressive shift of gelatinization endotherm to higher temperature as water content decreases. In excess water, a single endotherm is observed, but it develops a tailing shoulder and this shoulder shifts progressively toward high temperature as water content decreases. At sufficiently low water content, this shoulder becomes the only endotherm observed. Until the shoulder becomes the only endotherm observed, the lower temperature endotherm occurs at constant temperature (Donovan, 1979; Eliasson, 1980).

Stevens and Elton (1971) reported the effect of heating rate on gelatinization characteristics of several starches using DSC. As heating rate increases, the temperature range for gelatinization also increases as the result of decreasing the onset temperature and increasing conclusion temperature. Similar observations were reported

by Wooton and Bamunuarachchi (1979). Heidemann (1978) suggested that, as the heating rate was decreased and the time for water imbibition was increased, granules with different degrees of disorganization could "recrystallize" to produce a more ordered granule, increasing onset temperature. The increase in conclusion temperature with increasing heating rate may be due to the greater thermal lag experienced by the sample.

Steeping is carried out during isolation of starch to soften the grain to facilitate wet milling or during parboiling of rice. The gelatinization temperature (GT) of the starches increased and the range of temperatures narrowed as the temperature and duration of steeping at a specific temperature increased as shown in Table 1 (Gough and Pybus, 1971; Lorentz and Kulp, 1980).

Since starch is a semicrystalline material consisting of amorphous and crystalline regions, holding a suspension of granules just below the gelatinization temperature would be expected to give rise to more perfectly ordered crystals. This occurs by realignment of starch chains in the amorphous or gel phase, and some additional crystallization and increase the gelatinization temperature like the annealing process of semicrystalline polymers (Banks and Greenwood, 1975; French, 1984). Also in the high-temperature (90°-110°C) moisture treatment (Sair and Fetzer, 1944; Sair, 1967), the crystallites melt, at least in part, and during cooling assume a more stable and more highly associated form than in the native granule (Osman, 1967; French, 1984). In synthetic polymers, exposure to an appropriate temperature and solvent environment

Table 1. Gelatinization temperatures of wheat starch for various steeping times and temperatures[a]

Treatment	Gelatinization temperature, °C		
	Onset (T_o)	Peak (T_p)	Conclusion (T_c)
Untreated	57.2	60.5	62.6
24 hrs. at 25°C	58.0	61.4	63.8
72 hrs. at 25°C	58.8	62.0	63.5
24 hrs. at 40°C	59.5	62.4	64.4
72 hrs. at 40°C	63.0	64.5	65.5
24 hrs. at 50°C	66.0	68.4	69.5
72 hrs. at 50°C	67.0	69.0	69.5

[a]Adapted from Lorentz and Kulp (1980).

causes a spontaneous ordering of the polymer molecules, which is known as annealing and generally occurs at a temperature near the melting point of the polymer.

b. Physicochemical properties of starch If standard conditions for gelatinization during cooking are fixed, the extent and temperature of gelatinization of starch will be governed by varietal differences in physicochemical properties of starches, such as granule size, degree of crystallinity, and amylose content.

Within a single type of starch, the size of granule varies, i.e., from 2 to approximately 35 μm in wheat starch. Even though the presence of different sizes of granules in one type of starch has been shown, the effect of granule size on gelatinization is still unclear. Banks and Greenwood (1959) suggested that in any one population the larger granules appear to be the more susceptible to gelatinization, while the smaller granules are more resistant. Similar observations were reported by other investigators (Radley, 1960; Stevens and Elton, 1971; Rockland et al., 1977). However, Goering et al. (1974) reported no significant effect of granule size on the distribution of temperature of gelatinization. Careful observation using a polarizing microscope at higher magnification showed that both large and small granules lost birefringence simultaneously. Examination of hot-pasting peaks using a Brabender amylograph also suggested no effect of granule size (Goering, 1978; Dengate et al., 1979). On the contrary, Wirakartakusumah (1981) reported that larger rice starch granules are more resistant to gelatinization, since smaller granules (4-5 μm) have a lower enthalpy of

gelatinization (10.9 J/g) and a lower gelatinization temperature of 69.3°-77.5°C, as compared to those of unfractionated granules (12.6 J/g, 72.0°-81.3°C, respectively). Also Merca and Juliano (1981) reported that among two crops of seven waxy rices, the two samples with high gelatinization temperature (74.5°-77°C) had a larger mean starch granule size (7.2-7.4 μm) than the five samples with low gelatinization temperature (63°-65.5°C), which had a mean granule size of 5.3-5.8 μm. Among samples from two crops of seven intermediate-amylose rices (20-25% amylose), only one sample with the highest gelatinization temperature (74°C) had a larger mean granule size (6.9 μm) than the other six samples (mean granule size; 5.8-6.0 μm) with intermediate gelatinization temperature (70°-74°C) and low gelatinization temperature (58°-69.5°C).

The starch granule is generally considered as a semicrystalline polymer which contains both crystalline and amorphous regions. The gelatinization temperature is thus a measure of the degree of orderliness of the granule organization (Juliano, 1972a).

Four-day Lintnerization loss of rice starch granules correlates negatively with final gelatinization temperature of starch regardless of amylose content (Kongseree and Juliano, 1972; Evers and Juliano, 1976). The recovery of Lintnerized starch after 15 days of treatment in 2.2 M hydrochloric acid at 35°C ranged from 7 to 21% and was greater for starches with high BEPT. Lintnerized starch had sharper x-ray diffraction peaks than did native starch (Maniñgat and Juliano, 1979). There is some evidence that the degree of starch crystallinity and the diffraction intensity of the amylose of rice may have some relation to

its gelatinization temperature (Lugay and Juliano, 1965; Juliano et al., 1969).

In a single type of starch, amylose content also varies widely, especially in rice: from less than 2% in waxy to 7-33% among nonwaxy varieties.

Although BEPT and amylose content are known to be independent properties of rice starch and are affected by environmental factors, only the following BEPT types are common among various types: waxy, low and high BEPT; low-amylose, low and high BEPT; intermediate-amylose, low and intermediate BEPT; and high amylose, low and intermediate BEPT. The intermediate BEPT type (70°-74°C) is rare in waxy (<2% amylose) and low-amylose rices (7-20%), whereas the high BEPT type (74.5°-79°C) is rare for intermediate (20-25%) and high-amylose (25-33%) rices (Juliano, 1984).

It is believed that each granule possesses individuality and thus differs from each other in its structure as well as in its properties (Greenwood, 1979; Meredith, 1981). Because of contradictory and/or insufficient evidence on the effect of granule size, degree of crystallinity and amylose content on gelatinization characteristics, these factors require further investigation.

B. Properties of Rice Starch and Milled Rice

1. Chemical and molecular properties of rice starch

The chemical and molecular properties of rice starch are probably similar to those of other cereal starches used for human consumption

(Juliano, 1984). Within rice varieties there are two types of rice based on the ratio of amylose to amylopectin: waxy rice which contains only 1-2% amylose, and nonwaxy rice which contains from 7 to 33% amylose. The nonwaxy rice can be further classified as low, 7-20%; intermediate, 20-25%; and high, 25-33% (Juliano, 1979a; Juliano, 1985a).

Iodine binding capacity (IBC) of rice amylose (Table 2) is close to those of amyloses from other starches (19-20%). Purity of isolated amylose tends to decrease with increasing amylose content of the starch. The same is also true for amylopectin. Hence, waxy amylopectin has a lower IBC than nonwaxy amylopectin. Gel filtration on Sepharose CL-2B of recrystallized low-IBC amyloses from high-amylose rices suggested contamination of the amylose with amylopectin or with a fraction intermediate in branching between amylose and amylopectin (Juliano, 1985a). This is consistent with the relatively higher $\overline{DP}$ and the larger number of branches for amyloses from high-amylose starches than for those from low-amylose starches (Hizukuri et al., 1983b)

Ultracentrifugation provides the best means for comparing the molecular sizes of amylopectin and amylose. Sedimentation constants are 4-14 S for amylose and 20-520 S for amylopectin (Table 2). $\overline{DP}$ measured by reducing end methods showed values of 180-630 glucose units for amylose and 260-1,050 glucose units for amylopectin (Juliano, 1966, 1967). Recently, Hizukuri et al. (1983b) obtained $\overline{DP}$ value of 530-790 glucose units for seven once-recrystallized amylose samples. The reducing end method is not sensitive enough for determining $\overline{DP}$ value of amylopectin because of contamination with low-molecular-weight

Table 2. Range of molecular properties of amylose and amylopectin from nonwaxy and waxy rices[a]

Property	Amylose	Amylopectin	
		Nonwaxy	Waxy
Iodine binding capacity,[b] %	17.4-20.0	0.37-2.74	0.07-0.09
ß-Amylosis limit,[c] %	72-84	49-58	49-59
Sedimentation constant,[d] $S_{20,w}$, Svedbergs	4-14	20-510	60-520
Mean degree of polymerization,[e] glucose units	530-790	260-880	330-1,050
Mean chain length,[f] glucose units per branch	100-160	18-28	18-27

[a]Adapted from Juliano (1985a).
[b]Measured by potentiometric iodine titration.
[c]Measured by ß-amylase hydrolysis.
[d]Measured by ultracentrifugation.
[e]Measured by reducing end method.
[f]Measured by periodate oxidation method.

amylodextrin, which may explain in part the low $\overline{DP}$ values reported for amylopectin (Juliano cited in Juliano, 1985a).

Because of its linear nature, amylose has a longer mean chain length ($\overline{CL}$) than amylopectin (Table 2). Seven once-recrystallized amyloses with $\overline{DP}$s of 530-790 glucose units had a $\overline{CL}$ of 100-160 glucose units per branch (nonreducing end), corresponding to 3.4-7.5 branches per molecule or 6.4-9.9 branches per 1,000 glucose units (Hizukuri et al., 1983b). Rice amylose seems to be more branched than potato, tapioca, and kuzu amyloses, with two to six branches per 1,000 glucose units (Hizukuri et al., 1981). Such branching may explain the incomplete action of α-amylase on rice amylose (Table 2). Periodate oxidation (Hizukuri et al., 1983a) reveals $\overline{CL}$s of amylopectin of 18-28 glucose units, similar for both waxy and nonwaxy amylopectin (Table 2).

2. Physical, gelatinization and pasting properties of rice starch

Gelatinization temperature (GT) of rice starch varies widely among rice varieties and is classified in rice (Juliano, 1979a) as low (58°-69.5°C), intermediate (70°-74°C), and high (74.5°-79°C). The variation probably reflects the compactness of the rice endosperm, as gelatinization temperature is indexed in the breeding programs with the alkali spreading value of milled rice in which low-GT rices are completely disintegrated, intermediate-GT rices show some degree of disintegration, and high-GT rices just swell in 1.7% KOH at 30°C after 23 hrs soaking (Little et al., 1958). Gelatinization temperature range

for rices varies from 2° to 12°C and tends to be narrower for waxy rices (Juliano et al., 1969; Reyes et al., 1965).

Ambient temperature during grain development can also affect the BEPT and amylose content of the rice starch (Resurreccion et al. cited in Juliano, 1985a). High temperature decreases amylose content, but increases BEPT, while cool temperature has the opposite effect.

Differential scanning calorimetry (DSC) of nonwaxy rice starch showed well distinguished amorphous and crystalline transition. The thermal behavior of rice starch appears to be consistent with the data obtained using the waxy corn starch model (Maurice et al., 1985). Russell and Juliano (1983) reported that there were varietal differences in enthalpy of gelatinization among rice starch granules (11.3-17.3 J/g), but the heat of cooking, energy required to heat the starch:water mixture (1:4, dry basis) from 20° to 100°C, showed no varietal differences within experimental error (1,405-1,563 J/g). The enthalpies of gelatinization are correlated positively with the gelatinization temperatures found by photometry and DSC (63°-76°C and 63°-78.4°C, respectively).

Water absorption and solubility pattern of starch show that differences between samples with low- and high-GT occur mainly below 70° or 75°C (Juliano et al., 1969). Water absorption and dissolution start at a lower temperature in the starches with low gelatinization temperature. Nonwaxy starch gives lower values than waxy starch.

Milled rice flour or rice starch shows characteristic Brabender amylograph curves (Halick and Kelly, 1959; Juliano et al., 1964a,

1964b). The peak viscosities of waxy rices occur at lower temperature than those of nonwaxy rices. Carboxymethyl cellulose (0.9%)-starch (6.25%) amylography (Sandstedt and Abbott, 1964) of nonwaxy rice starch showed the typical two-stage gelatinization of cereal starches (Juliano and Perdon, 1975), whereas waxy rice starch showed one-stage gelatinization and a higher peak viscosity than nonwaxy rice starch (Juliano, 1984; Figure 11) in conformity with results on corn starches (Sandstedt and Abbott, 1964).

Amylograph peak viscosity of milled rice flour is affected by many factors, such as aging or storage of the sample, protein content, and amylose content. The relationship of amylograph peak viscosity of milled rice flour and protein content is negative, probably due to suppression of gelatinization (Juliano et al., 1964a, 1964b; Juliano and Pascual, 1980). Correlation with amylose content is conflicting (Halick and Kelly, 1959; Juliano et al., 1964a, 1964b; Juliano and Pascual, 1980). Breakdown viscosity during heating is correlated with amylose content (Juliano et al., 1964b). Amylograph final viscosity at 95°C, viscosity on cooling to 50°C, setback, and consistency of milled rice flour are all positively correlated with amylose content (Juliano et al., 1964a, 1964b; Juliano and Pascual, 1980).

Differences in pasting behavior are most pronounced among high-amylose rices and starches, as shown by Brabender amylograph pasting viscosity (Perez and Juliano, 1979). However, rices with hard gel consistency of milled rice flour and low gelatinization temperature, such as IR 8 and IR 42, have higher amylograph peak viscosity, setback,

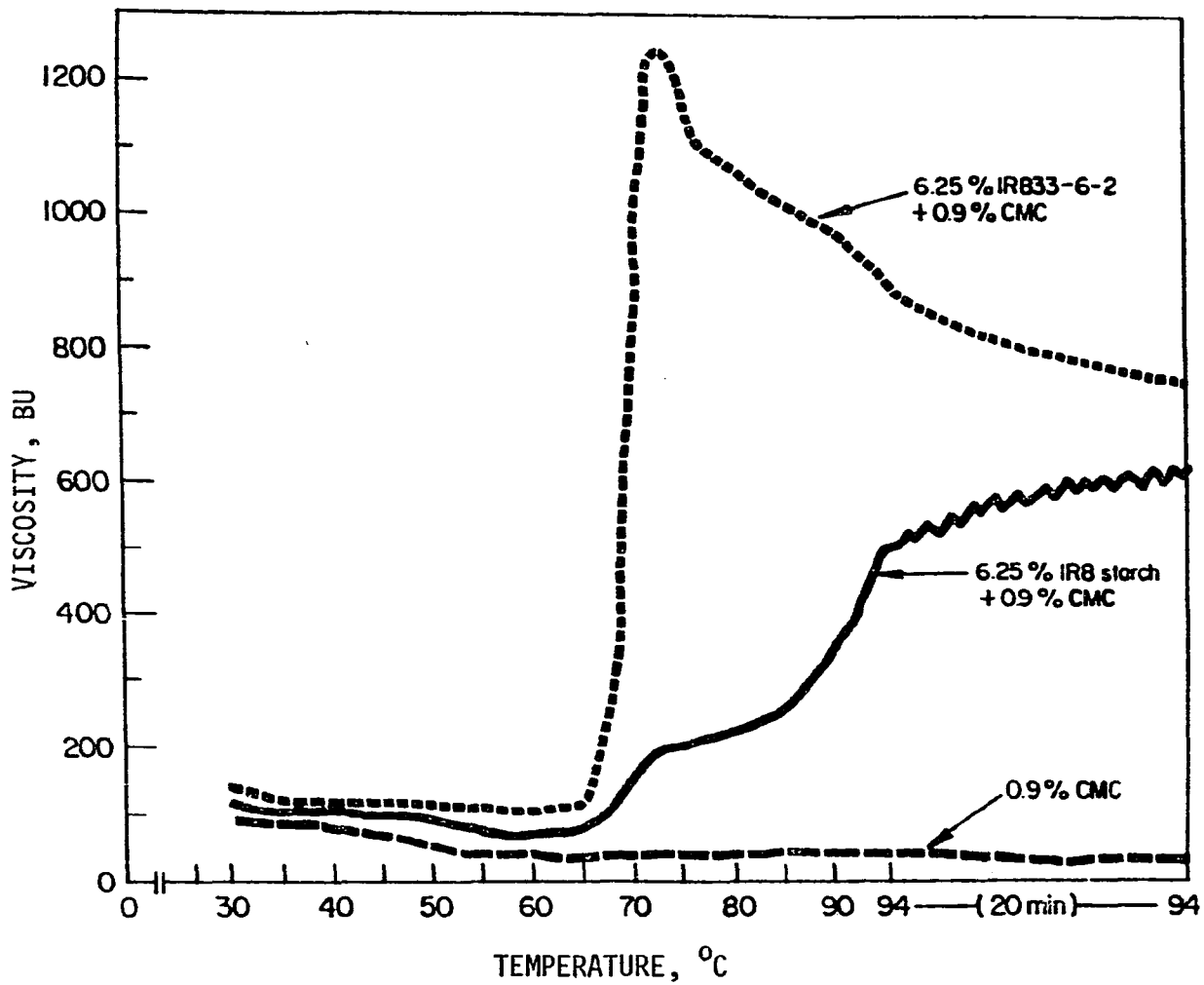


Figure 11. Typical 0.9% carboxymethylcellulose - 6.25% (wet basis) starch amylograms of nonwaxy (IR 8) and waxy (IR 833-6-2) rice starch (adapted from Juliano, 1984)

and consistency of milled rice flour than other high-amylose rices with soft gel consistency of milled rice flour and intermediate gelatinization temperature, such as IR 5 and IR 32 (Juliano, 1979a).

3. Cooking and eating qualities of milled rice

The cooking and eating qualities of milled rice are mainly determined by the properties of its starch, because starch accounts for about 90% of the dry weight of milled rice. The ratio of amylose to amylopectin is generally accepted as the major determinant of cooking qualities, i.e., water absorption, volume expansion, and solids in the cooking water, and of eating qualities, i.e., stickiness, tenderness, color (whiteness), gloss, and aroma.

However, differences in eating quality also exist among varieties of similar amylose content. Therefore, some other additional quality factors other than amylose content are needed to differentiate among varieties, especially in breeding programs.

In the United States, at the USDA National Rice Quality Laboratory, Beaumont, TX, rice cooking and processing qualities are assessed in terms of physicochemical properties, which then serve as indices of rice cooking and processing behavior. These indices and test methods include: 1) amylose content, 2) alkali spreading value of whole milled grains in contact with dilute alkali - an indication of gelatinization temperature, 3) amylographic gelatinization and paste viscosity characteristics, 4) water uptake capacity at 77°C, 5) birefringence end-point temperature, 6) protein content, 7) parboiling-canning stability,

and 8) specific brewing cookability of rice with malt diastase (Webb, 1975, 1985).

Among these quality indicators, amylose content and gelatinization temperature have been considered the most important characteristics for predicting rice cooking and processing behavior (Halick and Keneaster, 1956; Williams et al., 1958; Webb, 1975, 1980; Juliano, 1979a).

Some rice cooking and processing quality predictors for typical long-, medium-, and short-grain U.S. rices are given in Table 3 (Webb, 1985). Typical U.S. long-grain varieties, which cook dry and fluffy, are characterized by relatively high amylose content, slight-to-moderate alkali spreading reaction of whole-grain milled rice in dilute alkali, moderate water uptake capacity at 77°C, and intermediate gelatinization temperature. Amylographic paste viscosity characteristics of the typical long-grain varieties usually show an intermediate peak height and a relatively high cooled-paste viscosity. Canning stability of parboiled grains of typical long-grain varieties in terms of solid loss during canning are relatively low (desirable) and canned grains show a minimum splitting and fraying of edges and ends. Long-grain types, in terms of specific brewing cookability with malt diastase, are relatively resistant to starch liquefaction.

By way of comparison, typical U.S. short- and medium-grain varieties, which cook moist and clingy, are characterized by comparatively low amylose content, extensive spreading reaction of whole-grain rice, relatively low gelatinization temperature and relatively high water uptake capacity at 77°C. Amylograms of the

Table 3. Range of average chemical and physical (quality) characteristics[a] among typical U.S. long-, medium-, and short-grain rice types[b]

Endosperm characteristics	Grain type		
	Long	Medium	Short
Amylose content, %	23-26	15-20	18-20
Alkali spreading value, average	3-5	6-7	6-7
Gelatinization temperature,[c] °C	71-74	65-68	65-67
Gelatinization temperature class	Intermediate	Low	Low
Water uptake at 77°C, ml/100g	121-136	300-340	310-360
Protein (N x 5.95), %	6-7.5	6-7	6-6.5
Parboiling-canning stability, solids loss %	18-21	31-36	30-33
Amylographic paste viscosity, BU			
Peak	765-940	890-980	820-870
Cooked 10 min at 95°C	400-500	370-420	370-400
Cooled to 50°C	770-880	680-760	680-690
Brewing cookability of rice with malt diastase, Zahn sec	120+	5-15	5-10

[a]Based on measurements of fully developed mature grains of typical varieties within each grain type.
[b]Adapted from Webb et al. (1979).
[c]Birefringence end-point temperature.

typical medium- and short-grain varieties usually show comparatively low cooled-paste viscosities. The parboil canning characteristics of typical short- and medium-grain types show high (undesirable) solids loss on canning, the canned grains show extensive splitting and fraying of edges and ends, and they show relatively high susceptibility to starch liquefaction in specific brewing cookability tests with malt diastase.

The association of grain type with specific cooking and processing behavior occurs primarily in the United States and is a result of planned breeding (Webb, 1985). Throughout the world, varieties of grain type possessing nontypical cooking and processing qualities exist.

In the Philippines, the Rice Quality Laboratory of the IRRI (International Rice Research Institute) Plant Breeding Department routinely measures the following starch properties: amylose content by calorimetric iodine assay (Perez and Juliano, 1978); gelatinization temperature of milled rice by alkali digestibility test (Little et al., 1958); gel consistency of by the flow characteristics of milled rice gel (100 mg of milled rice flour) in 2 mL 0.2 N KOH (Cagampang et al., 1973). Based on amylose content and gelatinization temperature, milled rice is classified into several categories, as mentioned earlier. Also gel consistency of milled rice flour is classified based on the length of the cold horizontal gel in mm in a 11 X 100 mm test tube (Juliano, 1979a) as hard (26-40 mm), medium (41-60 mm), and soft (61-100 mm). This classification correlates with amylograph consistency or the increase in viscosity of the rice paste on cooling from 94° to 50°C.

Rice grown in various countries differ widely in the combination of these three starch properties.

a. Cooking quality Cooking and processing characteristics are among the most important quality components that establish the economic value of the rice grain.

i. Cooking methods Rice is cooked in various ways throughout the world. Batcher et al. (1963a) classified cooking methods into: oven method, small amount of water, medium amount of water, large amount of water, steaming, steaming with oil added, and cooking in water with oil added. Taste panel scores of the rice prepared by different methods suggested that the palatability characteristics of the cooked product from a given sample or region were similar regardless of cooking method used (Batcher et al., 1963a, 1963b).

ii. Volume expansion and water absorption during cooking Water absorption is usually determined by the increase in weight of rice during treatment (Juliano, 1985b) or by the decrease in volume of cooking water (Halick and Kelly, 1959).

Volume expansion and water absorption during cooking are directly affected by amylose content. Waxy rice expands the least during cooking, and its cooked grain has the heaviest bulk density (Juliano, 1979a).

The water-rice ratio in the double boiler method for acceptable soft texture (less than 10 kg of Instron hardness) increases with increasing amylose content: 0.9-1.1 for waxy rice, 1.2-1.4 for low-amylose rice, 1.5-1.6 for intermediate-amylose rice, and 1.7-2.0 for

high-amylose rice (Juliano and Perez, 1983). Thus, for a screening technique, a constant-water-rice ratio of 1.7-2.0 would be most sensitive for samples covering all the amylose types. Even though rices are cooked with this adjusted water-rice ratio based on amylose content, amylose content is still correlated with cooked-rice Instron hardness ($r=0.59^{**}$, n=266) and stickiness ($r=-0.82^{**}$, n=268) (Juliano and Pascual, 1980). Because of adjusted water-rice ratio used, volume expansion and water absorption correlated positively with amylose content.

However, volume expansion and water absorption of rice in the excess water method were affected by differences in cooking time among only nonwaxy varieties because waxy starch shows only a one-stage gelatinization and reaches peak viscosity in the amylograph shortly after the onset of gelatinization, while nonwaxy starch has a two-stage gelatinization probably reflecting the melting of the amylose-lipid complex (Juliano, 1985c).

With an arbitrary cooking time longer than the optimum cooking time, water absorption will relate not only to amylose content, but also to rates of cooking. Although Bhattacharya and Sowbhagya (1971) observed that all rice varieties have about 73% water content on cooking to optimum cooking time in excess water, differences in water content of samples (71-76%) are observed that are traceable to differences in cooking time and to differences in starch gelatinization temperature and also to grain thickness (Juliano et al., 1981; Juliano and Perez, 1983; Juliano et al., 1984).

Water absorption values determined below the boiling temperature do not correspond to actual water absorption during cooking, but they do differentiate rices based on starch gelatinization temperature. Water uptake at 77°C (Halick and Kelly, 1959) used by the USDA National Rice Quality Laboratory distinguishes between low-GT and intermediate- to high-GT rices, since only the low-GT grains are gelatinized completely at this temperatures (Webb and Stermer, 1972).

iii. Solids lost in cooking water Solids lost in cooking water are determined by drying an aliquot of the cooking water in a tared evaporating dish (Juliano, 1985b).

For rice samples with less than 25% amylose, the amount of amylose extracted by heating a milled rice flour in hot water for 15 min in a boiling water bath was proportional to the amylose content (Juliano et al., 1968). Some high-amylose samples had a low concentration of soluble amylose, which was shown to be caused by *in situ* retrogradation of amylose in the gelatinized starch granule (Juliano, 1979b).

Priestley (1977b) further measured the 'apparent solubility' of the starch that is released after the cooked grains are macerated, in addition to measuring the solids lost in cooking-water, to permit estimation of 'soluble' and 'insoluble' amylose and amylopectin. There was a highly significant negative correlation ($r=-0.82^{**}$, $n=48$) between amylose content of the rice starch and 'soluble' amylopectin in the cooked kernel. This relationship was thought to be due to both the inherent compositions of the starch and the amount of complexed amylose present which caused insolubilization of the branched component by a

process of molecular entanglement. The insoluble material was found to show a V-type diffraction pattern, indicating that this material was rich in a helical complex of amylose and fatty acids. As the content of complexed amylose increased, a greater proportion of the amylopectin may be insolubilized by molecular entanglement with the complexed linear fraction. Since rice varieties of similar amylose contents may contain widely different amounts of free fatty acids, they could also be expected to differ in extent of amylose complex formation and hence the 'soluble' amylopectin content of the cooked rice kernels. This may account for the different rice cooking and eating qualities within the similar range of amylose content in all other reported studies. The stickiness of cooked rice may be primarily dependent on the content of 'soluble' starch and, in particular, 'soluble' amylopectin.

Bhattacharya et al. (1978) reported on the importance of hot-water insoluble amylose content, calculated from total amylose and soluble amylose at 100°C, as a determinant of rice quality; he considered that total amylose alone is not enough to explain the differences of cooked rice texture. High-amylose rices (>26%) are classified into three types based on insoluble amylose of >15%, 12.5-15%, and <12.5%. This division correlates with increasing amylograph breakdown, increasing stickiness, and decreasing consistency (hardness) of cooked rice (Bhattacharya et al., 1982). Juliano (1985b) suggested that because of the small differences involved in hot water insoluble amylose, differentiation by gel consistency of milled rice flour (Juliano, 1979a) is more sensitive

as a screening procedure than is insoluble amylose at 100°C (Juliano and Bechtel, 1985).

Juliano and Pascual (1980) reported that gel consistency of milled rice flour (Juliano, 1979a) correlated negatively with amylograph setback (r=-0.58**) and amylograph consistency (r=-0.60**) of milled rice flour for 302 samples and with cooked rice Instron hardness (r=-0.63**, n=266) and positively with cooked rice stickiness (r=0.40**, n=268).

iv. Cooking time Differences in the starch gelatinization temperature may be reflected in the differences in cooking time of milled rice, which is measured as the minimum time for the core of the grain to become translucent or gelatinized when rice grains are dropped in boiling water (Juliano and Perez, 1983). Samples with higher gelatinization temperature require a few more minutes to cook than those with low gelatinization temperature, which provably reflects the relative porosity of the whole endosperm, as evident in the use of the extent of grain dispersion in the alkali test to index the gelatinization temperature. For example, Century Patna 231 with high gelatinization temperature in the alkali digestibility test takes a longer time to cook than typical long-grain varieties with intermediate gelatinization temperature (Juliano et al., 1964a). Nagato and Kono (cited in Juliano and Bechtel, 1985) showed the greatest endosperm hardness distribution in Century Patna 231. Hardness distribution by Vickers microhardness values was determined in kilograms per square millimeters along the dorsiventral and lateral lines crossing at the

central point on the cross section of the caryopsis (refer to cross sectional view of rice grain in Figures 69 and 70).

The cooking time tends to be longer for higher protein rices (Juliano, 1979a). The nature and amount of the nonstarch constituents are important because these materials act as a physical barrier to the swelling of the starch granules on cooking (Juliano et al., 1964a).

b. Eating quality Amylose content is correlated negatively with tenderness, stickiness, color (whiteness) and gloss, and positively with aroma of cooked rice. Among these attributes, tenderness (hardness) and stickiness (cohesiveness) are commonly determined. The same relationship of tenderness and stickiness to amylose content is obtained regardless of whether the cooking is done at the same rice/water ratio or at optimum rice/water ratio (Juliano, 1979a).

Stickiness of cooked rice determined with an Instron Universal tester correlated negatively with amylose content ($r=-0.92^{**}$, n=34), and a wider spreading values were obtained for hardness ($r=0.77^{**}$, n=27) compared to stickiness of cooked rice (Perez and Juliano, 1979).

Among high-amylose rices, differences in hardness of cooked rice are related to differences in gel consistency of milled rice flour (Cagampang et al., 1973). Samples with hard gel consistency gave a harder cooked rice and had a very high amylograph setback of milled rice flour (Perez and Juliano, 1979).

Among intermediate-amylose rices, differences in hardness of cooked rice were related to differences in either gel consistency of milled

rice flour or final gelatinization temperature (Perez and Juliano, 1979).

Among low-amylose rices, hardness of cooked rice was also related to differences in modified gel consistency of milled rice flour (120 mg flour/ 2 mL of 0.2 N KOH) and amylograph consistency of 12% milled rice flour (Perez and Juliano, 1979).

C. Gelatinization *in situ*

Most of the studies on starch gelatinization phenomena have been conducted on isolated starch granules. However, most rices are consumed as boiled, milled rice. *In situ* gelatinization (e.g., during parboiling or cooking of rice) is a more complex process which involves not only starch but also other components such as protein or lipids (Gariboldi, 1974).

Knowledge of the structure and composition of the rice grain is important to understanding the starch gelatinization phenomena during cooking of milled rice.

1. Structure and composition of rice grain

The gross structure of the mature rice grain has been described by many investigators (Little and Dawson, 1960; Juliano, 1972a, 1980a, 1984; Juliano and Bechtel, 1985; Bechtel and Pomeranz, 1980).

The mature rice grain is harvested as a covered grain (rough rice or paddy) as shown in Figure 12. Generally, a rice grain can be

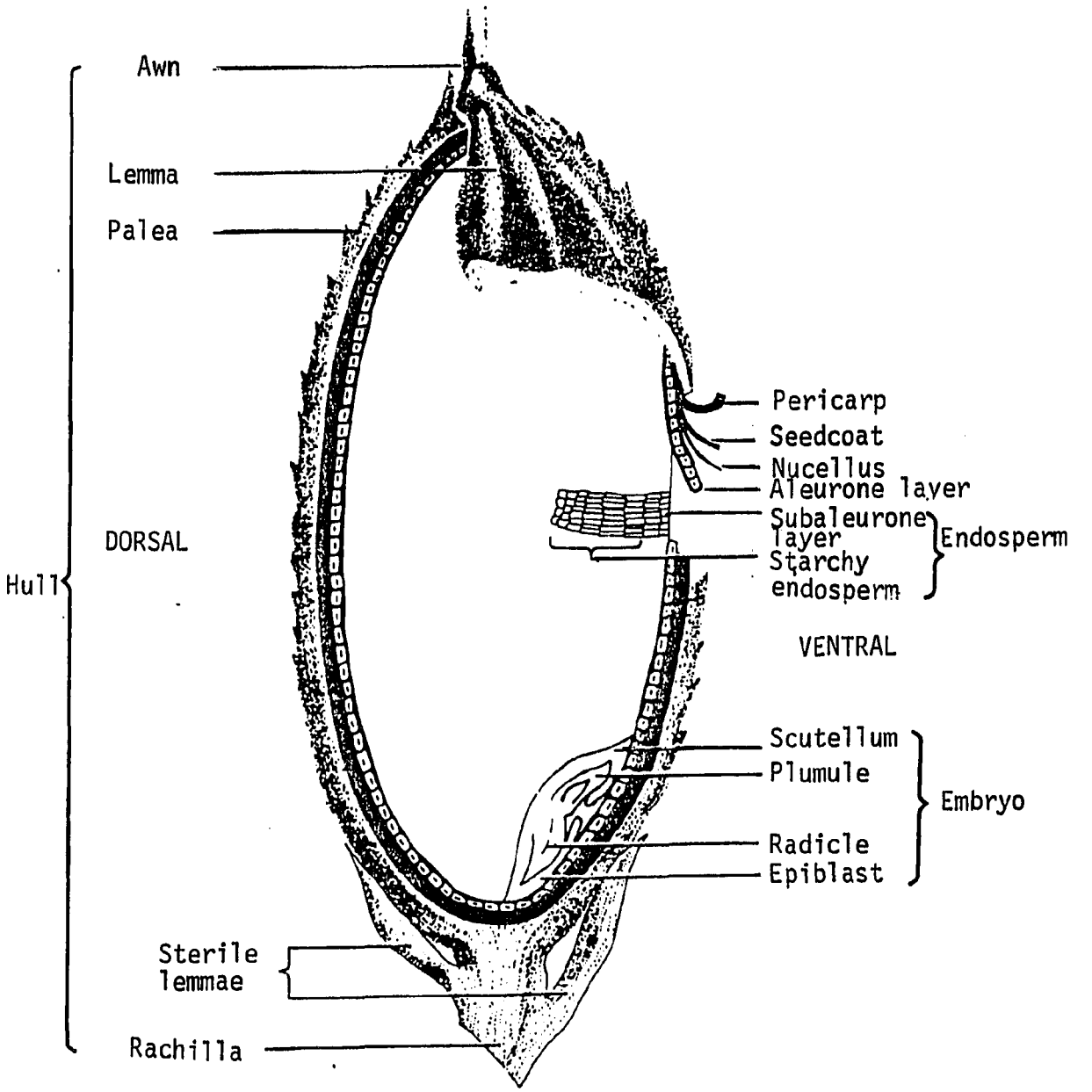


Figure 12. Structure of the rice grain (adapted from Juliano and Bechtel, 1985)

separated into four major parts: hull (husk), bran, germ and starchy endosperm (Little and Dawson, 1960).

The hull is the outermost part of a rice grain, composed of two modified leaves, the palea and the larger lemma. The weight of hull ranges from 16 to 28% (avg. 20%) of the rough rice (Juliano, 1972a). The primary function of the husk is to provide resistance to insect infestation due to the high content of silica (ca. 15% of the weight of the husk). According to Bechtel and Pomeranz (1978c), since the moisture content of the husk was low (ca. 13.9%), the husk provides protection against fungi and rancidity during storage of the paddy.

Rice bran is approximately 6-11% by weight of the brown rice (hulled rice grain). As shown in Figure 12, the rice bran consists of four different tissues: pericarp, seed coat, nucellus and aleurone layer (Bechtel and Pomeranz, 1978c). Other investigators considered the seed coat and nucellus as one group called the "testa layer" (Little and Dawson, 1960). The bran is high in protein (11.3-14.9%) and lipid (15.0-19.7%) which provide nourishment to insects and fungi (Juliano and Bechtel, 1985). Thus, brown rice is highly susceptible to deterioration. Also the bran tissues offer little resistance to infestation and penetration into the endosperm by insects or fungi because they are relatively thin (Bechtel and Pomeranz, 1978c). Individually, each layer of the bran tissues can be characterized by its resistance to moisture migration. The pericarp consists of several layers of crushed parenchyma cells that probably act as a sponge and readily absorb water (Bechtel and Pomeranz, 1978c). The cell walls of

the pericarp reacted positively for protein, pectin, hemicellulose and cellulose; the seed coat, nucellus, and the aleurone layer give a positive reaction for lipid. Therefore, these tissues act as a water barrier (Little and Dawson, 1960). Prevention of water diffusion might also be due to the presence of cuticle in the pericarp, seed coat and nucellus (Barber, 1972; Houston, 1972). The aleurone layer, the outermost layer of endosperm tissue, may be one to seven cells thick and is thicker on the dorsal (back) than along the lateral (side) and ventral (front, embryo side) surfaces (Juliano, 1972a; Watson and Dikeman, 1977). Bechtel and Pomeranz (1977) differentiated between two types of aleurone cells, one type around the starch endosperm and the other around the embryo. The parenchyma cells surrounding the starchy endosperm are cuboidal, and have densely packed cytoplasm and two prominent storage structures: aleurone grains (protein bodies) and lipid bodies. The second type of aleurone cells around the embryo (modified aleurone layer) is rectangular, has less densely packed cytoplasm, has fewer and smaller lipid bodies, and lacks aleurone grains.

The germ (embryo) is extremely small and located on the ventral side at the base of the grain; it contributes about 2-3% of the weight of brown rice (Juliano and Bechtel, 1985). It contains embryonic leaves (plumule), root (radicle) and stem (hypocotyl), and is connected to the endosperm by the scutellum (cotyledon). The scutellum serves as an absorbing and conducting organ for nutrients carried from the endosperm to the embryo during germination (Danjo and Inosaka cited in Juliano and

Bechtel, 1985). Bechtel and Pomeranz (1978a, 1980) observed that the germ is high in protein (14.1-20.6%) and lipid bodies (16.6-20.5%). During abrasive milling, the germ is easily removed with bran tissues due to the fact that the germ is not well bound to the endosperm. In addition, the endosperm in this region does not have well-defined walls, thus providing a structural defect that allows easy removal of the germ (Bechtel and Pomeranz, 1978a).

The portion of the rice grain which is involved in the gelatinization process during cooking of the milled rice is the starchy endosperm. Based on the size distribution of starch granule and the type of protein bodies, the starchy endosperm is divided into two regions: 1) the subaleurone layer, the two outermost layers of cells located just beneath the aleurone layer; and 2) the central region consisting of the rest of the starchy endosperm (Bechtel and Pomeranz, 1980). Bechtel and Pomeranz (1978b) found three types of membrane-bound protein bodies in the subaleurone layer: large spherical (1-2 μm in diameter), small spherical (0.5-0.75 μm in diameter), and crystalline protein bodies (2-3.5 μm in diameter); however, in the central region of the mature rice, only the large spherical protein bodies were present. Since the subaleurone layer is only two cells thick and lies directly below the aleurone layer, it is removed with relative ease during milling (Bechtel and Pomeranz, 1978c). The starch granules in the subaleurone layer are small (2-4 μm) and usually form tiny clusters surrounded by crowded protein bodies (Little and Dawson, 1960). The central region is composed of large, polygonal compound starch granules

surrounded by proteinaceous material. The protein is found between each of the starch granules as well as around the entire group of compound granules (Bechtel and Pomeranz, 1978b). Little and Dawson (1960) reported that the size of starch granules is between 2 and 10 μm, forming closely packed group, and there were several groups in each cell. The cluster of starch granules within an amyloplast is of varying size from 7 to 39 μm in diameter. Each amyloplast contains 20 to 60 small polyhedral granules, covered by a thin electron-dense matrix that is in contact with proteinlike bodies (Juliano and Bechtel, 1985) The pits on the surface of the individual granules are presumably formed by the removal of protein bodies (Evers and Juliano, 1976; Hayakawa et al. cited in Juliano and Bechtel, 1985).

2. Studies of gelatinization in situ

Viscosity measurement by the Brabender amylograph, x-ray diffraction pattern, polarizing and light microscopy, and scanning electron microscopy have provided qualitative information on gelatinization in situ (Little and Dawson, 1960; Kongseree and Juliano, 1972; Priestley, 1975, 1976a, 1976b, 1977a, 1977b; Watson and Dikeman, 1977; Bechtel and Pomeranz, 1980; Damir, 1985).

Most of these studies were done on gelatinization which occurred during parboiling. Studies about in situ gelatinization and further swelling of starch during cooking of boiled rice are not available in the literature.

III. MATERIALS AND METHODS

A. Materials

Twelve rice varieties including long-, medium-, and short-grain types produced in the United States were studied. The rice varieties included the 6 long-grain, 4 medium-grain, and 2 short-grain types listed in Table 4. All varieties except Kokuho Rose were obtained from the National Rice Quality Laboratory, Agricultural Research Service, U.S. Department of Agriculture, Beaumont, TX in 1983. Kokuho Rose was obtained from the local oriental store, Ames, IA in 1983.

Milled rices were ground to flours in a Burr mill type grain grinder attached to multi-function mixer (Kitchenaid Div., Hobart Co., Troy, OH) and passed through a No. 70 sieve (212 μm). Immediately after grinding, the flours were sealed tightly in plastic containers and stored in a freezer (-20°±0.5°C).

Rice starches were isolated by alkali extraction of the protein using cold 0.2% sodium hydroxide solution (H. Fuwa, Department of Food and Nutrition, Osaka City University, Japan, personal communication). Milled rice was steeped in 5-6 volumes of cold 0.2% sodium hydroxide solution at 0°-4°C for 24 hours to soften the endosperm. The steep liquor was drained off, and the endosperms were pressed and ground lightly in successive small fractions with a mortar and pestle. The slurry was then diluted to 12-15 volumes with cold 0.2% sodium hydroxide solution. The mixture was stirred for 30 min and allowed to settle overnight at 0°-4°C. The cloudy supernatant was discarded. The

Table 4. Varieties and sources of rices studied

Grain type	Variety	Source
Long-grain	Newrex	National Rice Quality Lab., Beaumont, TX
	Lebonnet	National Rice Quality Lab., Beaumont, TX
	Bellemont	National Rice Quality Lab., Beaumont, TX
	Labelle	National Rice Quality Lab., Beaumont, TX
	Lemont	National Rice Quality Lab., Beaumont, TX
	Century Patna 231	National Rice Quality Lab., Beaumont, TX
Medium-grain	Pecos	National Rice Quality Lab., Beaumont, TX
	Brazos	National Rice Quality Lab., Beaumont, TX
	Vista	National Rice Quality Lab., Beaumont, TX
	Kokuho Rose	Local oriental store, Ames, IA (produced and distributed by Nomura and Co., Inc., San Francisco, CA)
Short-grain	S-6	National Rice Quality Lab., Beaumont, TX
	Early Colusa	National Rice Quality Lab., Beaumont, TX

sediment was ground with a mortar and pestle until the resulting mixture could be passed through a No. 200 sieve (57 μm). It was diluted to 5-6 volumes with cold 0.2% sodium hydroxide solution, stirred, and allowed to settle. This sedimentation process was repeated several times. The starch layer was then collected by centrifugation at 1,600 x g for 15 min. A thin yellowish surface layer was scraped off. This centrifugation process was repeated until the supernatant gave a negative reaction to the biuret test for protein. The starch was suspended in cold deionized water and repeatedly washed with water until the supernatant gave a pH value below 7.0 with the pH meter. The starch was collected by centrifugation and air-dried. After being dried, the starch was passed through a No. 70 sieve (212 μm). The whole process took 30-40 days. The average yield of starches from the milled rices was 68±5%.

B. Methods

Twelve different varieties of rices were examined for the physicochemical characteristics which have been thought to be related to the cooking and eating quality of rice and with the SEM after heating to different temperatures to observe the changes during cooking. For isolated starches, tests included amylose content, gelatinization temperature range and BEPT, granule size distribution, relative crystallinity, swelling power and solubility throughout the pasting range (65°-95°C), amylographic viscosity (7%, d.b.) and SEM. For milled rice, tests included crude fat content, protein content, water uptake

and solids lost in cooking-water at 75° and 95°C, Amylographic viscosity (10%, as-is basis), cooked milled rice stickiness and SEM.

1. Determination of moisture content

Moisture content of rice starch and milled rice were measured by a vacuum oven drying method described by Smith (1964). For rice starch, approximately 2 g were heated at 120°C under 29 mm Hg absolute pressure for four hours. During the drying period, a slight stream of dried air was passed through the oven. Samples were allowed to cool in the desiccator. Moisture contents were determined by weight differences and expressed as percent (%) of original weight of sample. All measurements were conducted in triplicate. A similar procedure was used to determine moisture content of milled rice. Prior to moisture determination, however, milled rices were ground to flours.

2. Determination of protein content

Protein content of milled rice was measured according to the AOAC procedures (1980) using a Macro-Kjeldahl apparatus.

Approximately 1 g of rice flour was conditioned with 2 Keltabs (0.3 g K_2SO_4 + 0.175 g HgO per tablet) and 15 mL sulfuric acid overnight to prevent foaming during digestion. Samples were digested until solutions became clear, cooled to room temperature and 75 mL distilled water were slowly added. Forty mL of sodium hydroxide-sodium thiosulfate solution (25 mL 25% $Na_2S_2O_3 \cdot 5H_2O$ in 100 mL 50% NaOH) were added and samples were distilled using Kjeltec System 1003 Distillation Unit (Tecator, Höganäs, Sweden). The distillates were received in a

250-mL Erlenmeyer flask which contained 25 mL 4% boric acid to which 1-2 drops of Tashiro's indicator (0.375 g methyl red and 0.250 mL methylene blue in 300 mL of 95% ethanol) had been added. The distillate mixture was titrated with standardized 0.1 N hydrochloric acid. The end-point was a blue-gray color.

Protein content was calculated from Kjeldahl nitrogen multiplied by the factor 5.95, and expressed as percent dry weight basis (%, d.b.). This factor is based on the nitrogen content of the major rice protein (glutelin) of 16.8% (Juliano, 1972a). All measurements were conducted in triplicate.

3. Determination of crude fat content

Crude fat content of milled rice was measured according to AOAC procedures (1980) using a Goldfish apparatus. Approximately 2 g of rice flour were wrapped in filter paper according to the method described by Pomeranz and Meloan (1978) and exhaustively extracted with petroleum ether (Skellysolve B, b.p. 69°-70°C) for 4 hours. Extracted solvent was evaporated in a hood overnight and dried at 100°C for 30 min.

Crude fat contents were determined by weight differences and expressed as percent dry weight basis (%, d.b.). All measurements were conducted in triplicate.

4. Determination of amylose content

Amylose content of rice starch was measured by the potentiometric iodine titration method described by Schoch (1964a).

Before evaluation of iodine binding capacity, the starch samples were thoroughly defatted with 95% ethanol and moisture contents of defatted starches were previously measured by a vacuum oven drying method (Smith, 1964).

Approximately 100 mg of rice starch were transferred to a 250-mL beaker, previously tared to 0.1 g. Approximately 1 mL of water and 5 mL of 1.0 N potassium hydroxide were added. The mixture was placed in a refrigerator (4°±0.5°C) overnight until a perfectly clear solution was effected. It was then neutralized to pH 7 with 0.5 N hydrochloric acid; 10 mL of 0.5 N potassium iodide solution and sufficient water at 30°C were added to give a total weight of 100.9 g and a total volume of 100 mL at 30°C. It was then potentiometrically titrated with iodine solution (0.1996 N; standardized with standard sodium thiosulfate solution (Fisher Scientific, Fair Lawn, NJ) at 30.0°±0.1°C with continuous mechanical agitation.

A digital pH/mV meter (Orion Research model 701A with 0.1 mV precision) was connected to bright platinum (+) and calomel (-) electrodes. This was used to take millivolt readings at some 10 to 15 points between 230 and 280 mV with a wait of 2 min after each addition of iodine. From the millivolt readings, the amount of free iodine in solution was calculated by using a calibration curve (Figure 13). The amount of bound iodine in solution was estimated from the total amount of iodine added to the solution and the amount of free iodine found at each point of millivolt reading. Bound iodine (Y) was plotted against

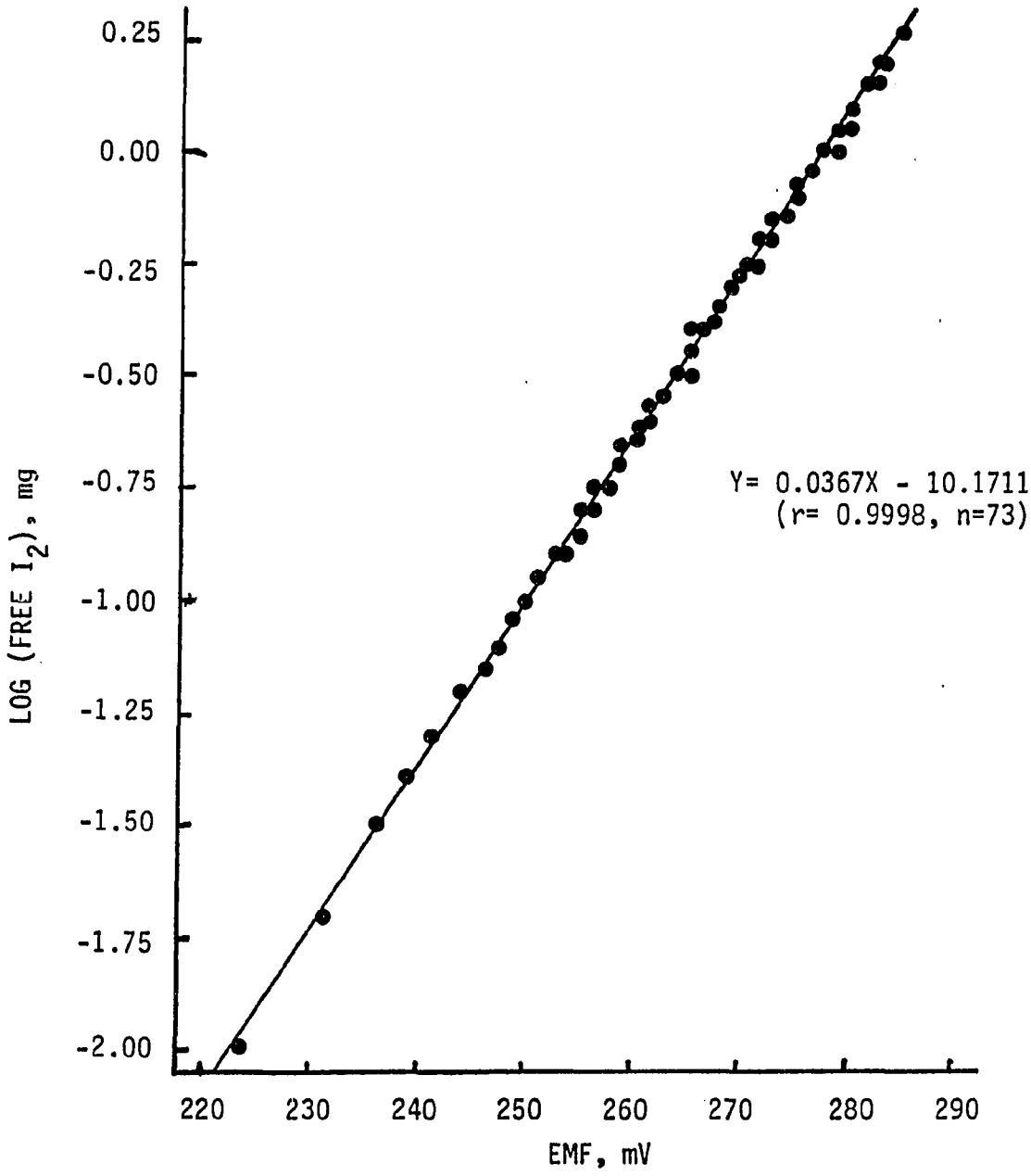


Figure 13. Calibration curve for determination of amylose content

free iodine (X) and a regression line was calculated using the upper linear portion of this curve.

The iodine binding capacity (IBC) was calculated by the amount of bound iodine (mg) at the zero intercept of this regression line and expressed as percent dry weight basis (%, d.b.). Amylose content was calculated based on the typical IBC of rice amylose (19.0%) (Juliano, 1984). All measurements were conducted in triplicate.

$$\% \text{ IBC} = \frac{\text{mg of bound iodine at zero intercept X 100}}{\text{mg of sample weight (on dry basis)}}$$

$$\% \text{ amylose} = \frac{\text{IBC of starch sample X 100}}{\text{IBC of rice amylose}}$$

5. Determination of gelatinization temperature range

The gelatinization temperature range was determined by measuring the percent loss of birefringence with an electrically-heated microscopic hot stage and a polarizing microscope (Leitz Wetzlar, Germany) using the method described by Watson (1964).

Approximately 0.1% aqueous starch suspension was prepared and a small drop of this suspension was spotted on a microscope slide and surrounded by a continuous ring of high viscosity petroleum jelly. A cover glass was placed on the drop in such a way that air bubbles were excluded. A uniformly distributed field of about 100 to 200 granules was observed at magnification of 125 X during heating (2°C/min). The gelatinization temperature range is defined as the temperature range between the point at which the first 2% of granules in the field lose

birefringence and the point at which 98% of the granules have lost their birefringence. The 98% loss-point is taken as the birefringence end-point temperature (BEPT). All measurements were conducted in triplicate.

6. Determination of swelling power and solubility

Swelling power and solubility of rice starch were measured by the method described by Schoch (1964b).

Five grams (as-is basis) of starch were suspended in 180 mL deionized water in a preweighed 250-mL centrifuge bottle. Moisture content of starch was previously measured. The suspension was stirred thoroughly by a magnetic stirrer and placed in a constant temperature water bath (Blue M Electric Co., Blue Island, IL, ±0.2°C). Stirring of 4 different samples heated simultaneously was induced by a group of magnets attached to the stirring shaft of a variable-speed stirrer placed in the water bath between the bottles. A slow constant speed was used to keep the starch slurry suspended. After 30 min heating, the bottles were removed, stirrer was removed and rinsed into the bottle with sufficient deionized water to bring the total amount of water present to 200.0 g, including the original moisture in the starch sample. The bottle was mixed gently, and centrifuged for 20 min in a swinging bucket rotor centrifuge (International Equipment Co., Meedham Hts., MA) at 2,200 rpm. The supernatant was drawn off by suction, a 50-mL aliquot was concentrated on a steam bath and the solubles present determined by drying in a vacuum oven (Smith, 1964). For a full

characterization of the starch, the starch suspension was heated at 5°C intervals over the entire pasting range (65°-95°C). The swelling power of the starch was expressed as the weight of sedimented paste per gram undissolved starch dry matter. The solubility was expressed as the percentile of soluble starch per gram starch dry matter. All measurements were conducted in duplicate.

$$\%\ \text{Solubles (on dry basis)} = \frac{\text{Weight of soluble starch X 400}}{\text{Weight of sample on dry basis}}$$

$$\text{Swelling power (corrected)} = \frac{\text{Weight of sedimented paste X 100}}{\text{Weight of sample on dry basis X (100 - \% solubles)}}$$

7. Determination of water uptake and solids lost in cooking-water of milled rice

Water uptake and solids lost in cooking-water of milled rice during cooking was determined basically in the same way that was used to measure swelling power and solubility of starch (Schoch, 1964b).

Approximately 2.5 g of milled rice (as-is basis) were added to 100 mL of deionized water held in a constant temperature water bath (Blue M Electric Co., Blue Island, IL, ±0.2°C), and heated for 30 min. After the desired heating period, the rice was collected on a wire-gauze (1.6 mm), held for 3 min, placed on a paper towel for 30 sec and weighed. Solids lost in cooking-water was determined from a 25-mL aliquot collected in a beaker. These procedures were done at 75° and 95°C. The water uptake of milled rice was expressed as the weight of water absorbed per gram milled rice dry matter. Solids lost in cooking-water

was expressed as the percentile of soluble material per gram milled rice dry matter. All measurements were conducted in duplicate.

8. Determination of granule size distribution

The granule size distribution of the rice starch was determined by photomicrography. Instead of light micrographs, scanning electron micrographs were used for this purpose because starch granules were separated and recognized better in scanning electron micrographs than in light micrographs.

From the scanning electron micrograph, circumference of each starch granule was measured and then converted into area automatically using a graphic tablet connected to an Apple IIe computer. The diameter (D) of each starch was calculated from the area (A) by assuming that each starch granule is basically a circle.

$$D = 2\sqrt{\frac{A}{\pi}}$$

where

A = area of starch granule

D = diameter of starch granule

Many starch granules in the field (n=102-140) were counted because the accuracy of granule size data is dependent upon number of granules counted (Snyder, 1984).

9. X-ray diffraction

X-ray diffraction data was collected on native rice starches. Isolated rice starch samples were ground and sieved through a No. 200 screen (57 μm) after air-drying process. Powdered starches were equilibrated overnight at 25°C and a relative humidity of 100% to maintain moisture content to 20.08±0.23%. For x-ray diffraction, samples were filled into a sample holder and packed as densely as possible with the edge and face of a microscope slide. The finished surface was smoothed and made flush with the face of the sample holder (Zobel, 1964; Nara et al., 1978). Copper K_α radiation (λ=0.154 nm, 50 KV, 14 MA) was generated by a Picker 2 Theta-Theta diffractometer (Picker X-ray Co., Cleveland, OH) with a Ni beta filter. The scan was made from a diffraction angle (2θ) of 4° to 36°, using a time constant of 2 sec, scanning angular velocity of 0.05°. This diffractometer was interfaced to a DEC VAX 11/730 computer. All numerical calculations and plotting were done with a DEC VAX 11/780 computer. An estimate of theta zero was obtained by adding a small amount of NBS Al_2O_3 (corundum) to one of the samples (Figure 14) and all sets of data were then normalized to this set of data. The data were smoothed using a 7-point digital filter, and peak positions were obtained using the second derivative of the data after theta zero correction had been made.

The relative crystallinity of starch was measured on the basis of the theory of Hermans and Weidinger (1948, 1949). Herman's theory was shown in the following equation:

$$a_c = xA_c \qquad (1)$$

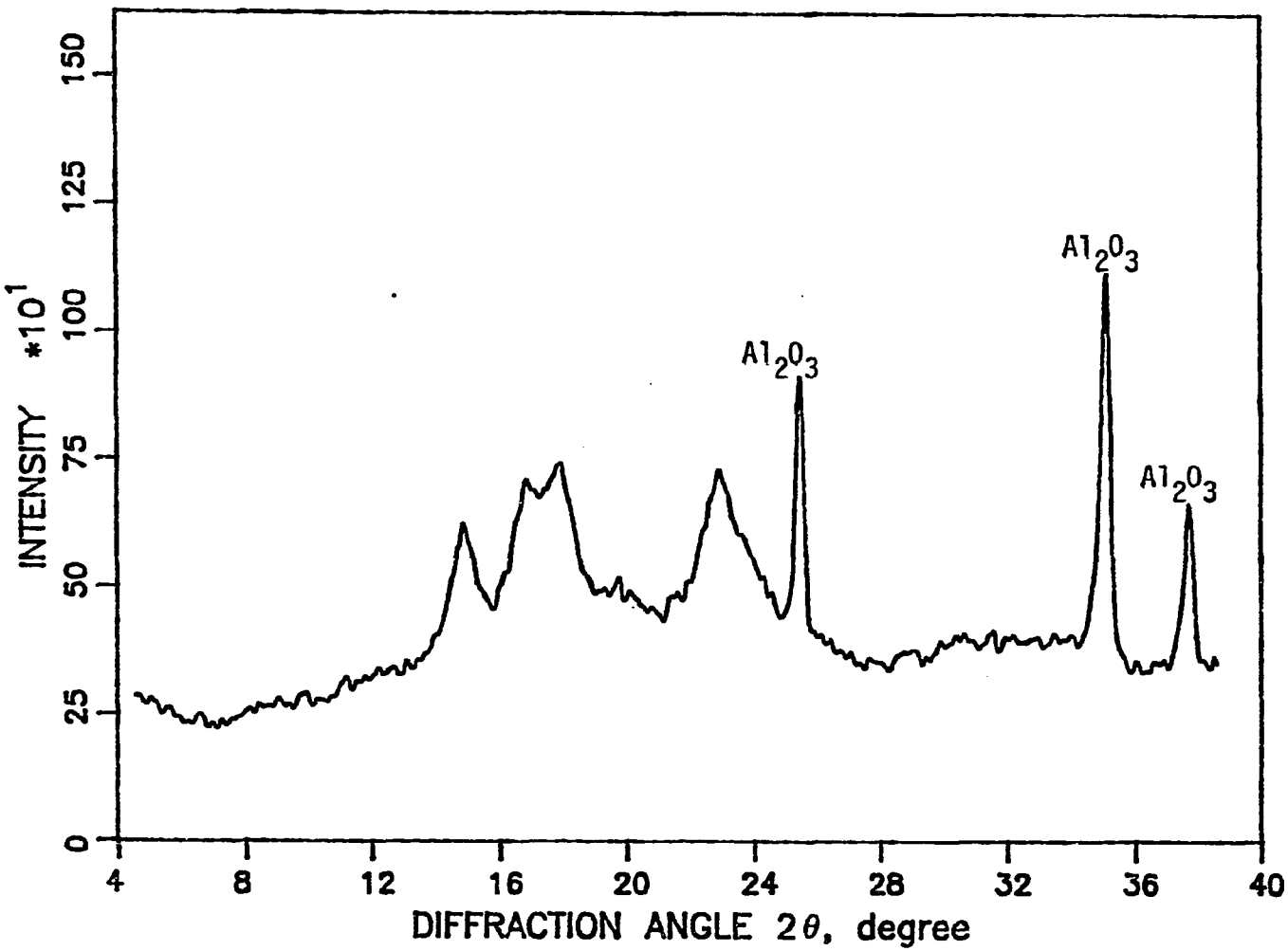


Figure 14. Estimation of theta zero in x-ray diffraction pattern

$$a_c = (1 - x)A_a$$

$$= (1 - \frac{a_c}{A_c})\ A_a \qquad (2)$$

$$= A_a - \frac{A_a}{A_c}\ a_c$$

or

$$i_a = (1 - x)\ I_a$$

$$= (1 - \frac{a_c}{A_c})\ I_a \qquad (3)$$

$$= I_a - \frac{I_a}{A_c}\ a_c$$

where

A_a = diffraction area of 100% amorphous substance

a_a = area of amorphous fraction of sample

A_c = diffraction area of 100% crystalline substance

a_c = area of crystalline fraction of sample

I_a = diffraction intensity of 100% amorphous substance

i_a = maximum intensity in the amorphous fraction of sample

x = degree of crystallinity of sample

The background (primarily due to the amorphous fraction) was estimated by connecting each point of minimum intensity far apart by a smooth curve, but when any points of minimum intensity were adjacent to each other, some of the points were not joined by a smooth curve (Figure 15). The upper region (a_c) above the middle dashed line was the area of the crystalline fraction; the lower (a_a) was that of the amorphous fraction; and i_a was maximum intensity in the amorphous fraction. Ac

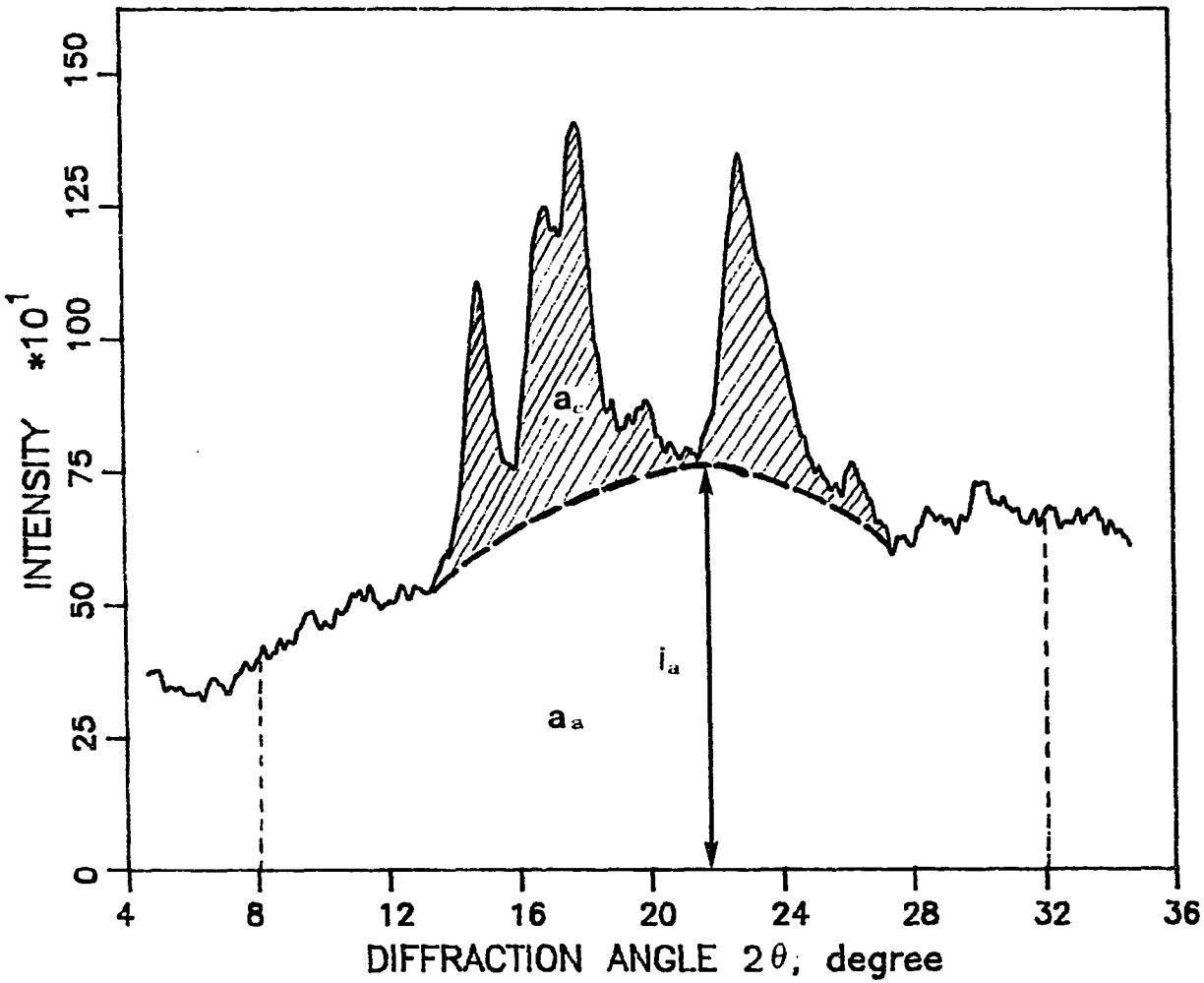


Figure 15. X-ray diffraction pattern of rice starch

was the diffraction area for 100% crystalline substance; A_a and I_a were the diffraction area and intensity, respectively, for 100% amorphous substance; and x was degree of crystallinity of sample. The areas of the crystalline fraction (a_c) and the amorphous fraction (a_a) were measured with a planimeter. The ratio of the area of the crystalline fraction to that of total (a_c+a_a) was calculated to offset the differences in the amount of sample used and served as the measure of degree of crystallinity. Relative crystallinity was indicated as the ratio of the degree of crystallinity of the sample to that of Bellemont which has the highest degree of crystallinity.

10. Determination of amylograph viscosity pattern

The viscosity pattern of a 7% w/v (on dry basis) starch suspension was determined using the Brabender Visco/amylo/Graph (C.W. Brabender Instruments, Inc., South Hackensack, NJ) as described by Tipples (1982) in The Amylograph Handbook.

Starch (35 g, d.b.) was accurately weighed to 0.1 g in a 600-mL beaker which was previously tared. About 300 mL of distilled water were added to the starch sample and mixed thoroughly to obtain a homogeneous suspension by stirring with a magnetic stirrer for 5 min. Then pH of the dispersion was adjusted to pH 6. The dispersion was transferred to a 500-mL volumetric flask and diluted to volume with distilled water at 25°C. The dispersion was transferred to the sample cup in the amylograph with a 700-cm·g sensitivity cartridge. It was heated from

30° to 95°C at 1.5°C/min, held for 15 min at 95°C and then cooled down to 50°C at 1.5°C/min with constant stirring at 75 rpm.

If the viscosity was recorded over 1,000 B.U. (Brabender Unit), it was adjusted by adding weight to suppress the zero value.

To determine the viscosity pattern of milled rice flours, 10% w/w (as-is basis) rice flour suspension was used. Fifty grams (as-is basis) of rice flour were suspended in 450 g of distilled water. The viscosity pattern was determined in the same way with rice starch.

11. Scanning electron microscopy

For observation with a scanning electron microscope, several drops were removed from a 2.5% w/v (as-is basis) starch suspension heated up to one of the various temperatures used for swelling power measurement. The drops were frozen quickly by immersion in melting trichlorodifluoromethane (Freon 113, TED Pella, Inc., Tustin, CA) cooled in liquid nitrogen (m.p. -195.8°C). This way avoids the insulation effect which results from nitrogen bubbles when samples are dropped directly into liquid nitrogen. Each frozen sample was freeze-dried overnight. The powdery granules were sprinkled sparsely on specimen support stubs covered with metal tape and coated with a layer of gold-palladium (20-80%) 200-300 Å thick in a Polaron E5100 sputter coater (Polaron Instruments Inc., Hartfield, PA). The granules were examined using an acceleration voltage of 15 kV with a JSM-35 scanning electron microscope (Jeol Ltd., Tokyo, Japan) and photographed with Polaroid P/N type 665 black and white land pack film (Polaroid Co., Cambridge, MA).

For milled rice samples, milled rices were cooked to various temperatures in a Brabender Visco/amylo/Graph to control the heating rate (1.5°C/min). The cooked rice grains were taken out at each temperature, frozen quickly in the same way as the starch suspension. Frozen whole milled rice was removed and freeze-fractured transversely with a precooled sharp razor blade in liquid nitrogen and then freeze-dried, sputter-coated and observed in the same manner as the rice starch samples. For milled rice samples, however, silver paint (TED Pella, Inc., Tustin, CA) was used to stick each large chunk onto the stub.

12. Determination of stickiness of cooked milled rice

Stickiness of cooked milled rice was determined with the Instron Universal Testing Instrument, model 1122 (Instron Engineering Co., Quincy, MA) based on the method described by Mossman et al. (1983).

Eight grams of milled rice (as-is basis) were placed in a 30-mL beaker to which 12 mL of distilled water (a ratio of 1.50 water to rice) were added, since that amount of water was completely absorbed by rice during cooking. The beaker was then covered with a watch glass and a practical limit of six beakers were placed equidistant from the center of a screen in a covered pan 25 cm in diameter and 15 cm deep. The level of water was adjusted not to touch the bottom of beakers during heating. The heating rate was controlled to increase the temperature of the 12 mL of water in each covered beaker above 95°C within 5 min of the start of steaming. After steaming 20 min, the pan was removed from the heat and the samples were held in the pan an additional 10 min. Each

beaker was then removed and inverted on its cover glass (to prevent condensate drip) to cool for 40 min at room temperature before testing. Without mixing, 4 g of rice were taken from the center of the rice for testing on the Instron. The content of the pan (six beakers in a pan) was run as a set, with the order of presentation to the Instron randomized.

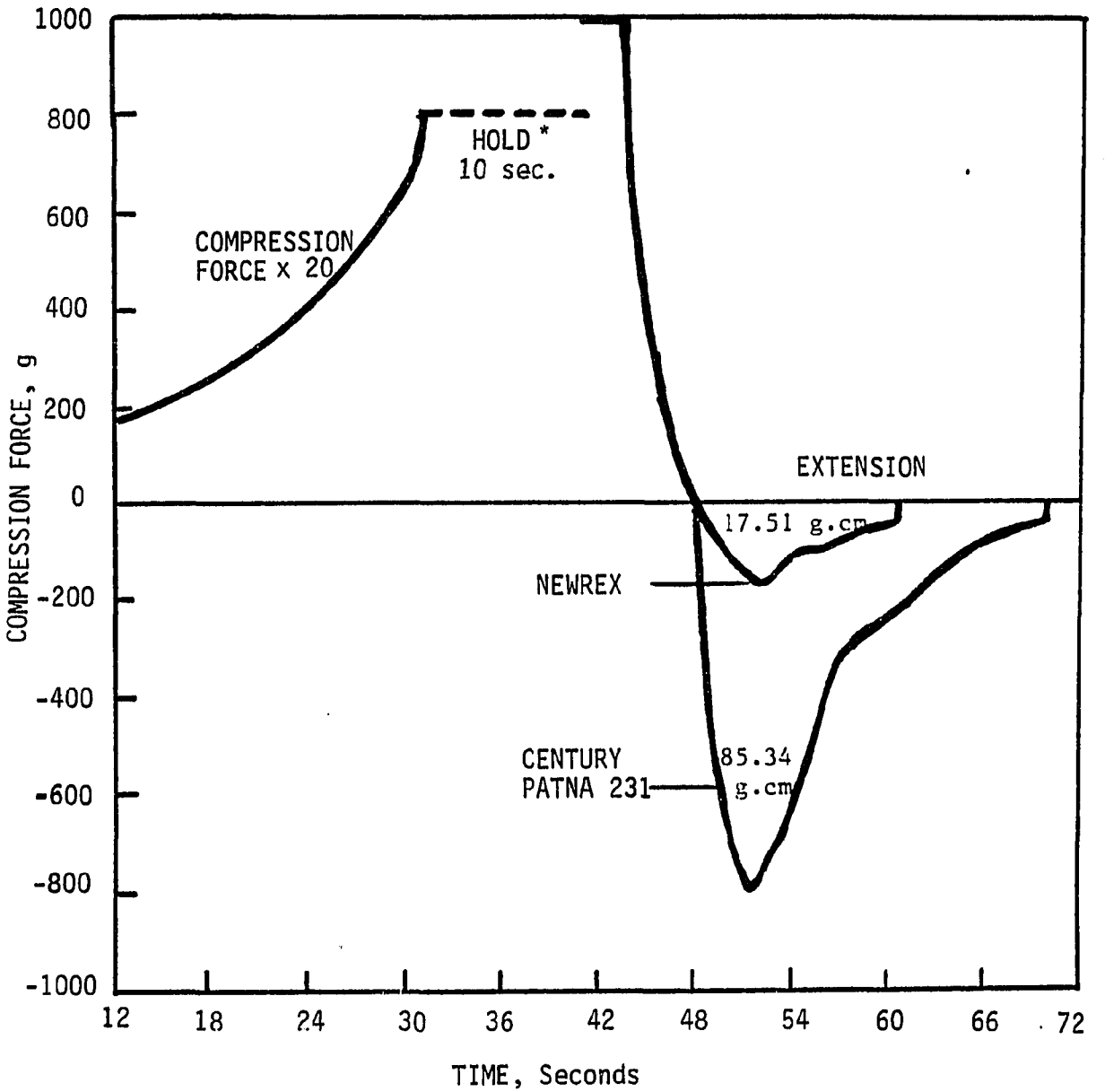
The Instron tester consists of two horizontal, parallel, stainless steel plates (attachment for compression): the top one is movable up or down at a constant rate, and the bottom one is stationary. A 500 kg Tension/Compression cell is the moving crosshead to which top plate is attached. Before the test, the instrument was zeroed at the center of the recorder chart, and the full-scale deflection was calibrated. For testing, the empty platform was balanced to zero, and a 4 g sample of cooked rice was piled on the bottom plate as high as possible without packing. The crosshead was lowered at 5 mm/min, while the recorder chart moved at 200 mm/min. As pressure on the rice increased, the pen moved in the positive direction. At 16 kg of pressure (80% of full scale at sensitivity 2) the crosshead movement was stopped for exactly 10 sec, during which time the sensitivity was increased to maximum (sensitivity 0.1), causing the pen to move off-scale. After the 10 sec, the crosshead was moved upward at the same speed, causing the pen to cross the zero line to the negative field and return. When it recrossed the negative 20 g line on the return, the test was stopped. A line was dropped from this crossing point to zero, the long tail on the curve was thus cut off, and the total negative area was taken as representing the

stickiness value (Figure 16). The planimeter was used to measure the area. The stickiness values are the area units converted to work units (g·cm, grams adhesive force and centimeter crosshead movement) by multiplying by the appropriate factor. All measurements were repeated four times.

13. Statistical analysis

Analysis of variance (SAS, 1985) was used (general linear model, PROC GLM) to test the effect of variety (12) for amylose content, BEPT, mean granule size, protein content, crude fat content and stickiness. When F-values were significant, least significant differences (LSD) at a 5% level of significance were calculated.

Pearson correlation coefficients (SAS, 1985) were used (PROC CORR) to measure the degree to which variables vary together. When Pearson correlation coefficients (r) were close to 1, regression equations were calculated (PROC REG).



*Sensitivity changed from 2 to 0.1 during the holding period.

Figure 16. Instron stickiness curve for cooked rice

IV. RESULTS AND DISCUSSION

A. Starch

Physicochemical properties of starches from twelve different varieties are presented in Table 5.

1. Amylose

Amylose content ranges from 10.4 to 27.8 % among the twelve varieties studied (Table 5). To analyze the varietal difference on amylose content, one-way analysis of variance method was used as shown in Appendix A. Amylose contents were significantly different among the varieties studied (α=0.01).

According to the IRRI classification (Juliano, 1979a), Newrex can be classified as high-amylose; Lebonnet, Bellemont, Labelle and Pecos as intermediate-amylose; and Lemont, Century Patna 231, S-6, Kokuho Rose, Brazos, Early Colusa and Vista as low-amylose types. Newrex was developed to satisfy the rice industry's need for a drier and fluffier table rice with superior cooking and processing properties (Bollich et al., 1980). Newrex is characterized by an amylose content 2-4% higher than that of the typical long-grain type (23-26%).

2. Gelatinization temperature (GT) range

Birefringence-end point temperature (BEPT) ranges 64.7° to 78.8°C among the twelve varieties studied (Table 6). BEPTs varied significantly among the varieties studied (α=0.01, Appendix A).

Table 5. Physicochemical properties of starches[a]

Grain type	Variety	Amylose[b] %, d.b.	BEPT[c] °C	Granule size, μm	Rel. crystallinity	Swelling Power[d] 75°C	Swelling Power[d] 95°C
Long	Newrex	27.8 (H)	74.8 (H)	4.49	0.85	7.60	19.65
	Lebonnet	23.2 (I)	74.7 (H)	4.66	0.87	9.82	30.69
	Bellemont	21.2 (I)	75.1 (H)	4.46	1.00	9.55	23.93
	Labelle	20.5 (I)	75.8 (H)	4.95	0.97	9.60	41.79
	Lemont	14.1 (L)	74.0 (I)	4.80	0.95	9.93	38.93
	Century Patna 231	10.4 (L)	78.8 (H)	4.94	1.00	4.95	53.96
Short & Medium	Pecos	23.0 (I)	67.3 (L)	4.85	0.92	10.60	38.42
	S-6	19.7 (L)	64.7 (L)	5.03	0.81	13.52	26.28
	Kokuho Rose	18.2 (L)	73.5 (I)	5.02	0.87	9.83	22.89
	Brazos	15.2 (L)	68.0 (L)	4.57	0.86	10.99	29.60
	Early Colusa	12.8 (L)	68.8 (L)	4.74	0.83	10.71	23.00
	Vista	11.2 (L)	71.2 (I)	5.69	0.84	11.32	40.31
LSD (α=0.05)		0.42	0.95	0.29	-	-	-

[a]Mean value of replicates.
[b]In ( ), amylose type; H=high, I=intermediate, L=low.
[c]In ( ), GT type; H=high, I=intermediate, L=low.
[d]Unit; g/g, d.b.

Table 5. (Continued)

Grain type	Variety	Solubility, %, d.b.		Amylograph viscosity[e], B.U.			
		75°C	95°C	Peak	Breakdown	Setback	Consistency
Long	Newrex	4.16	15.41	485	25	285	310
	Lebonnet	4.34	24.01	565	75	45	120
	Bellemont	4.23	20.82	640	90	85	175
	Labelle	4.53	28.92	675	110	0	110
	Lemont	4.29	28.53	875	345	-35	310
	Century Patna 231	7.17	45.09	695	280	-55	225
Short & Medium	Pecos	2.89	24.76	590	150	170	320
	S-6	8.38	22.54	520	35	80	115
	Kokuho Rose	4.82	14.68	535	60	75	135
	Brazos	4.05	17.67	735	85	20	105
	Early Colusa	3.49	10.79	840	285	0	285
	Vista	2.99	18.97	960	400	-220	180
LSD (α=0.05)		-	-	-	-	-	-

[e]35 g (d.b.) / 500 mL (7%) paste.

Table 6. Gelatinization temperature range and granule size range of starch

Grain type	Variety	GT range[a] °C	BEPT[b] °C	Granule size range, μm	Mean granule[c] size, μm
Long	Newrex	61.5-74.8	74.8±0.3	2.32-7.27	4.49±0.09
	Lebonnet	60.5-74.7	74.7±0.6	2.51-7.53	4.66±0.11
	Bellemont	58.5-75.1	75.1±0.6	1.99-6.55	4.46±0.11
	Labelle	59.3-75.8	75.8±0.3	2.24-7.87	4.95±0.10
	Lemont	61.2-74.0	74.0±0.5	2.34-8.18	4.80±0.10
	Century Patna 231	65.2-78.8	78.8±0.3	2.23-8.49	4.94±0.13
Short & Medium	Pecos	55.7-67.3	67.3±0.8	3.05-7.53	4.85±0.09
	S-6	55.0-64.7	64.7±0.3	2.44-8.20	5.03±0.11
	Kokuho Rose	55.0-73.5	73.5±0.5	2.29-8.69	5.02±0.10
	Brazos	58.0-68.0	68.0±0.0	2.42-7.28	4.57±0.11
	Early Colusa	56.2-68.8	68.8±0.3	2.99-9.24	4.74±0.09
	Vista	59.7-71.2	71.2±1.2	3.03-9.65	5.69±0.12

[a]2% loss of birefringence - 98% loss of birefringence.
[b]Mean ± standard deviation (n=3).
[c]Mean ± standard error (n=102-140).

According to the IRRI classification (Juliano, 1979a), Newrex, Lebonnet, Bellemont, Labelle and Century Patna 231 can be classified as high-GT; Lemont, Kokuho Rose and Vista as intermediate-GT; and Pecos, S-6, Brazos and Early Colusa as low-GT types.

Century Patna 231 has a much higher gelatinization temperature than the typical U.S. long-grain type (71°-74°C). Century Patna 231 has been known to have an extremely high gelatinization temperature and a low amylose content, producing poor cooking and eating characteristics (Juliano et al., 1964a). Kokuho Rose and Vista also show a little higher gelatinization temperature than the typical U.S. medium-grain type (65°-68°C). Final gelatinization temperature may vary more than 10°C within a cultivar depending on the ambient temperature during grain development (Resurreccion et al. cited in Juliano and Bechtel, 1985). A high ambient temperature tends to increase gelatinization temperature of the starch. A low ambient temperature has the opposite effect. Thus, Vista grown in Texas may be expected to have higher final gelatinization temperature than that in California.

Gelatinization of starch usually occurs over a 10°C temperature range. Gelatinization temperatures of rice starches range from 9.7° to 18.5°C (Table 6), indicating that some granules in a sample exhibit different gelatinization temperatures (Schoch and Maywald, 1956). The Narrower gelatinization temperature range of the S-6 may reflect the lower heterogeneity of molecular bonding forces from granule to granule than found in the Kokuho Rose which has wider gelatinization temperature range.

3. Granule size

Diameters of individual starch granules ranges from 1.99 to 9.65 μm with an average of 4.85 μm (Appendix B, n=1387), regardless of variety (Table 6). This agrees very well with other reported data about granule size of rice determined by various methods (Little and Dawson, 1960; Briones et al., 1968; Juliano, 1985a)

The granular starch samples showed significant varietal differences in their mean sizes (α=0.01, Appendix A), which ranged from 4.46 μm for Bellemont to 5.69 μm for Vista (Tables 5 and 6). A histogram of granule size distribution was close to normal distribution; values from large groups of granules are concentrated near the mean value of 4.85 μm (Appendix B). Therefore, comparison with mean granule size is justified.

Methods for the measurement of particle size distribution include those using a microscope, sedimentation balance, Whitby centrifuge, micromerograph, photodensitometer, and Fisher subsieve sizing apparatus. Recently, an automated procedure using a Coulter counter and an image analyzer has been used for measuring particle sizes of flours and starches (Williams, 1970). Instead of these rather simple and rapid automated procedures, the microscopic method, which is somewhat tedious and subject to sampling error, was chosen for the measurement of granule size distribution of rice starches. Since rice starch has the smallest granules of the cereal starches, and is frequently aggregated into large clusters in solution, the Coulter counter method did not give a reliable result. The Image analyzer was not good enough for the measurement of

granule size distribution of rice starch because the instrument cannot separate the starch granules aggregated into large clusters. To minimize sampling error in the microscopic method, as many starch granules as were recognized as whole entities in the photomicrograph field were counted (n=102-140).

4. X-ray diffraction

The x-ray diffraction patterns of starch from twelve different varieties are presented in Figures 17-19. They exhibited the A-type diffraction pattern characteristic of most cereal starches (Zobel, 1964). The principal indices of the pattern were at diffraction angles (2θ) of 15.3°(s), 17.1°(s), 18.2°(s), 20.3°(m), 23.5°(s), and 27.0°(w^+). These peaks corresponded to interplanar Ångstrom spacings of 5.78, 5.17, 4.86, 4.37, 3.78, and 3.30, respectively.

Relative crystallinity varied slightly among the starches from the twelve different varieties (Table 5). Differences in crystallinity of starch from different varieties of rice have been reported by Lugay and Juliano (1965).

Because the crystallites in starch granules are very small (100-150 Å), estimates of the degree of crystallinity cannot be rigorously or unambiguously assigned. The theory of x-ray diffraction indicates that very small or imperfect crystals give broadened diffractions. At the border of a crystallite, there is a zone in which the crystallinity changes from a high degree of perfection to a totally disordered

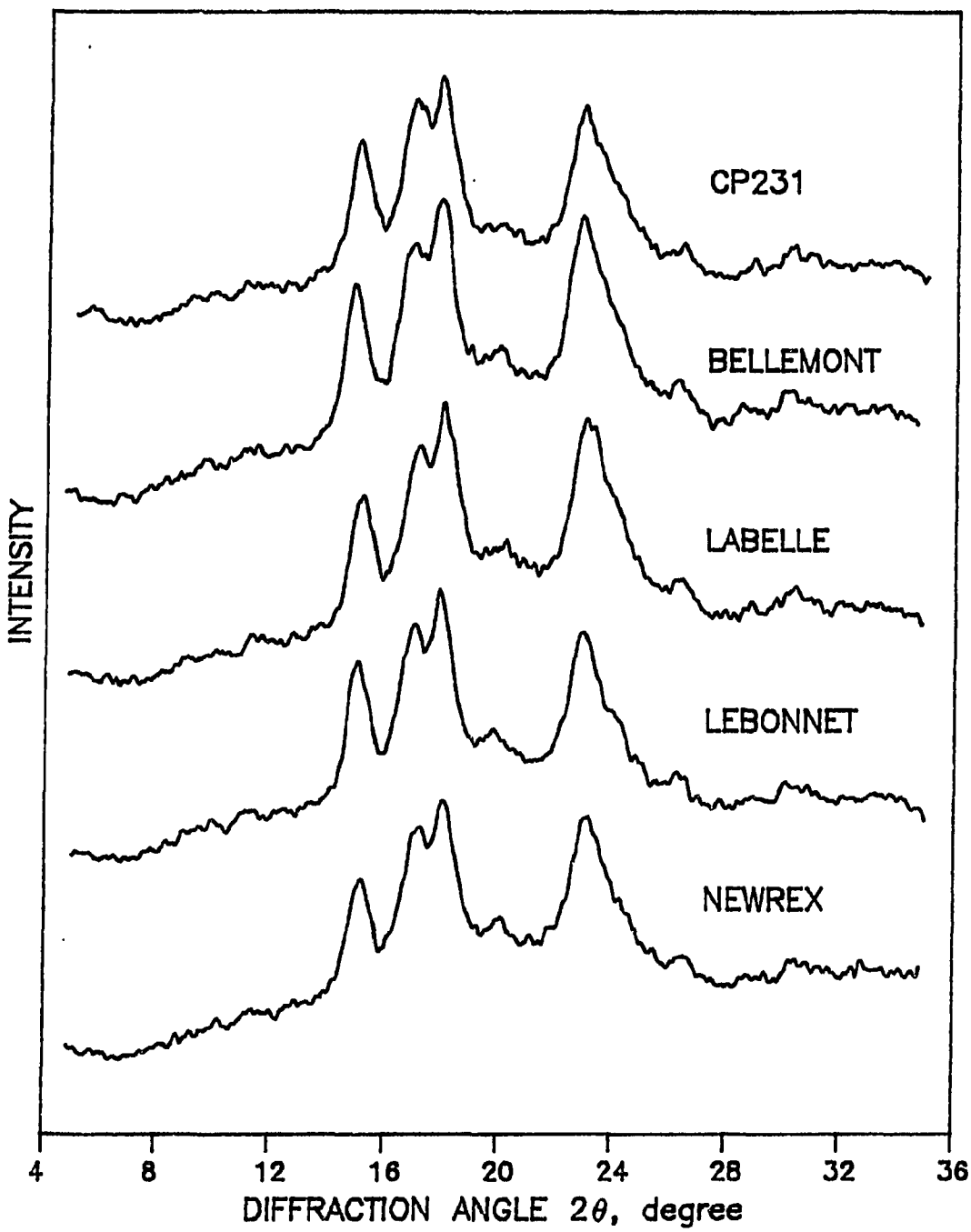


Figure 17. X-ray diffraction patterns of high gelatinization temperature rices

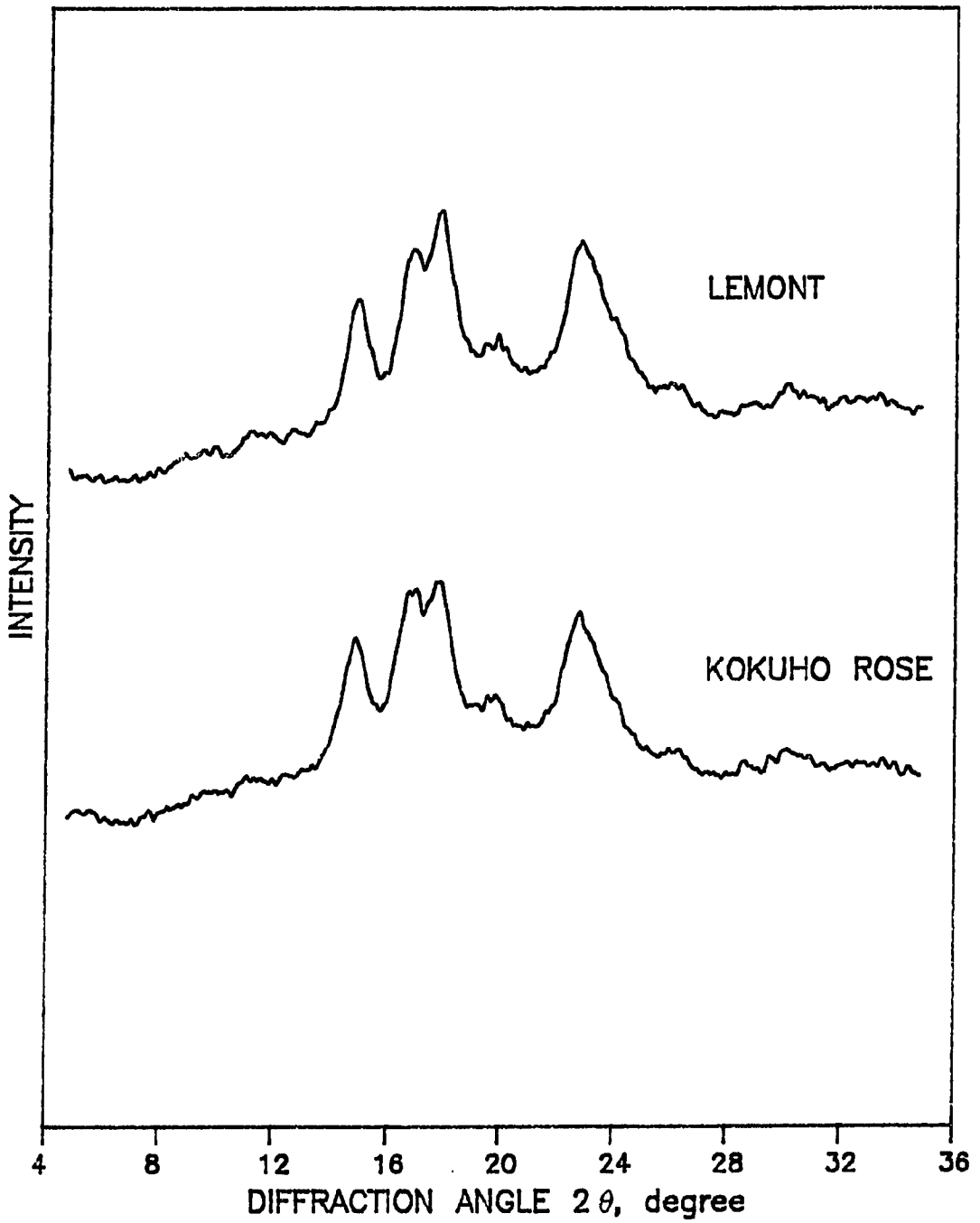


Figure 18. X-ray diffraction patterns of intermediate gelatinization temperature rices

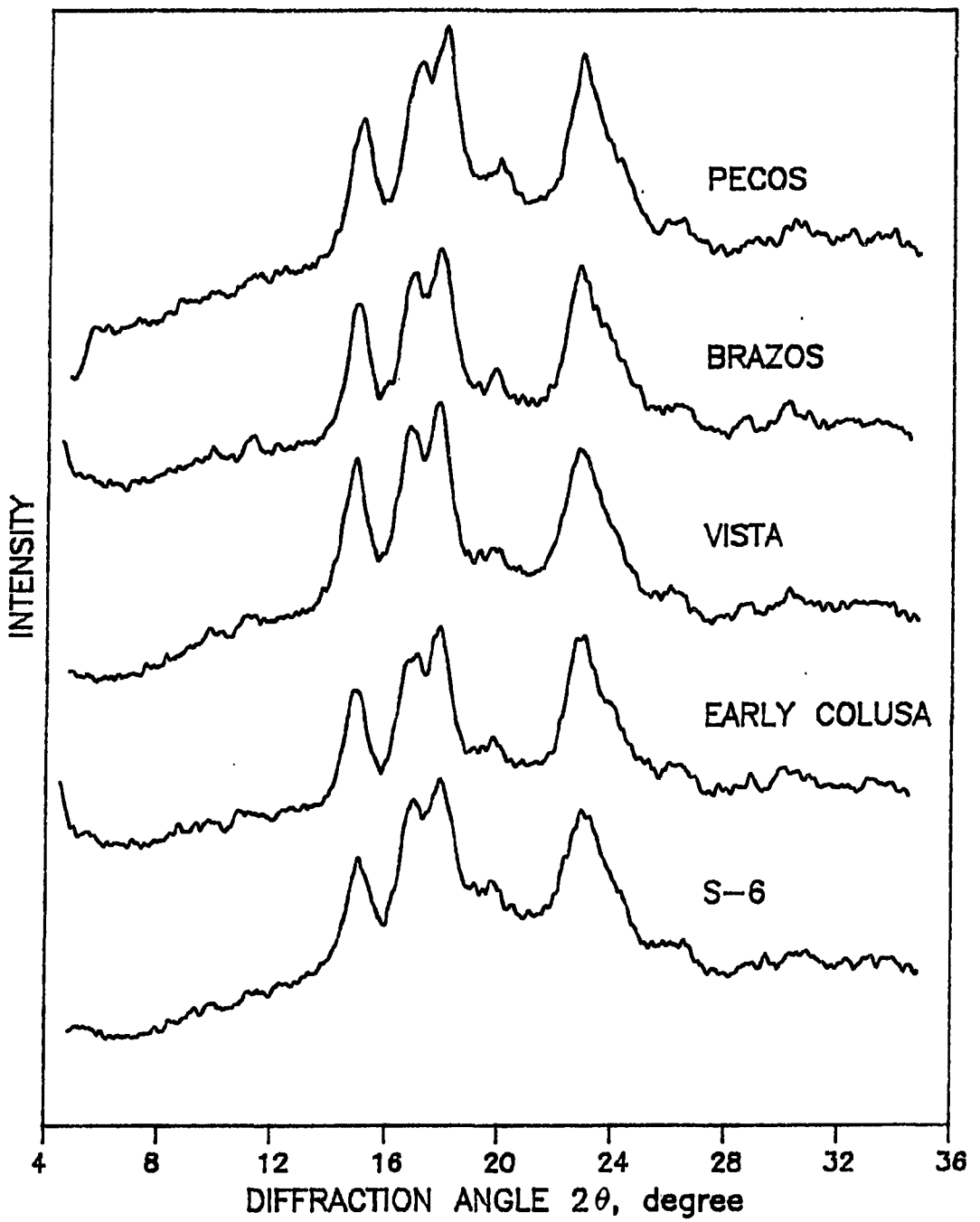


Figure 19. X-ray diffraction patterns of low gelatinization temperature rices

structure characteristic of a liquid or amorphous arrangement (French, 1984).

5. Swelling power and solubility

The primary event during starch gelatinization in an aqueous medium is granule swelling. Swelling power of starch granules increases with temperature. Only representative swelling power patterns are presented in Figure 20. As a direct result of granule swelling, there is a parallel increase in starch solubility (Figure 21).

Rice starch exhibited a two-stage swelling and solubility pattern like any other cereal starches. Leach (1965) explained this phenomenon by suggesting the presence of two different internal bonding forces in the highly organized and amorphous areas of the granule.

Generally, until the temperature reached the gelatinization temperature of each starch, limited swelling and solubilization occurred. However, solubility of Century Patna 231 below its gelatinization temperature was much higher than expected from its limited swelling power at this region (Figure 22). This is clearly shown (Figure 48) in that more exudate leached out from the granules even as swelling barely started at 65°C when compared to the other varieties. As temperature increased above gelatinization temperature, rapid increase in swelling power and solubility were observed in all starches, which was accompanied by the severe tangential expansion of starch granules (Figures 53-60). Swelling at the higher temperatures varied among the starches (Table 5), with Century Patna 231 showing the

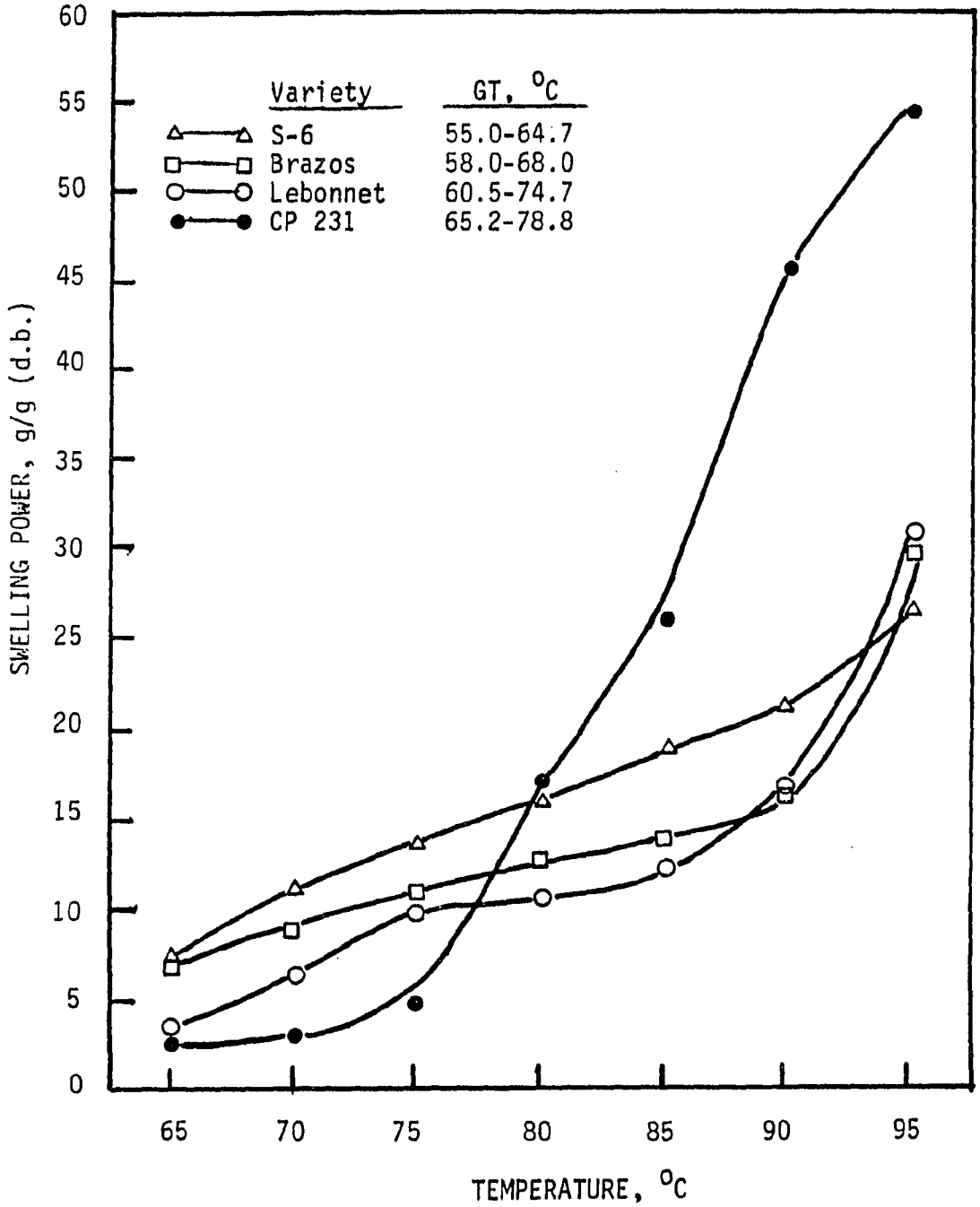


Figure 20. Representative swelling power patterns of starch from different varieties of rice

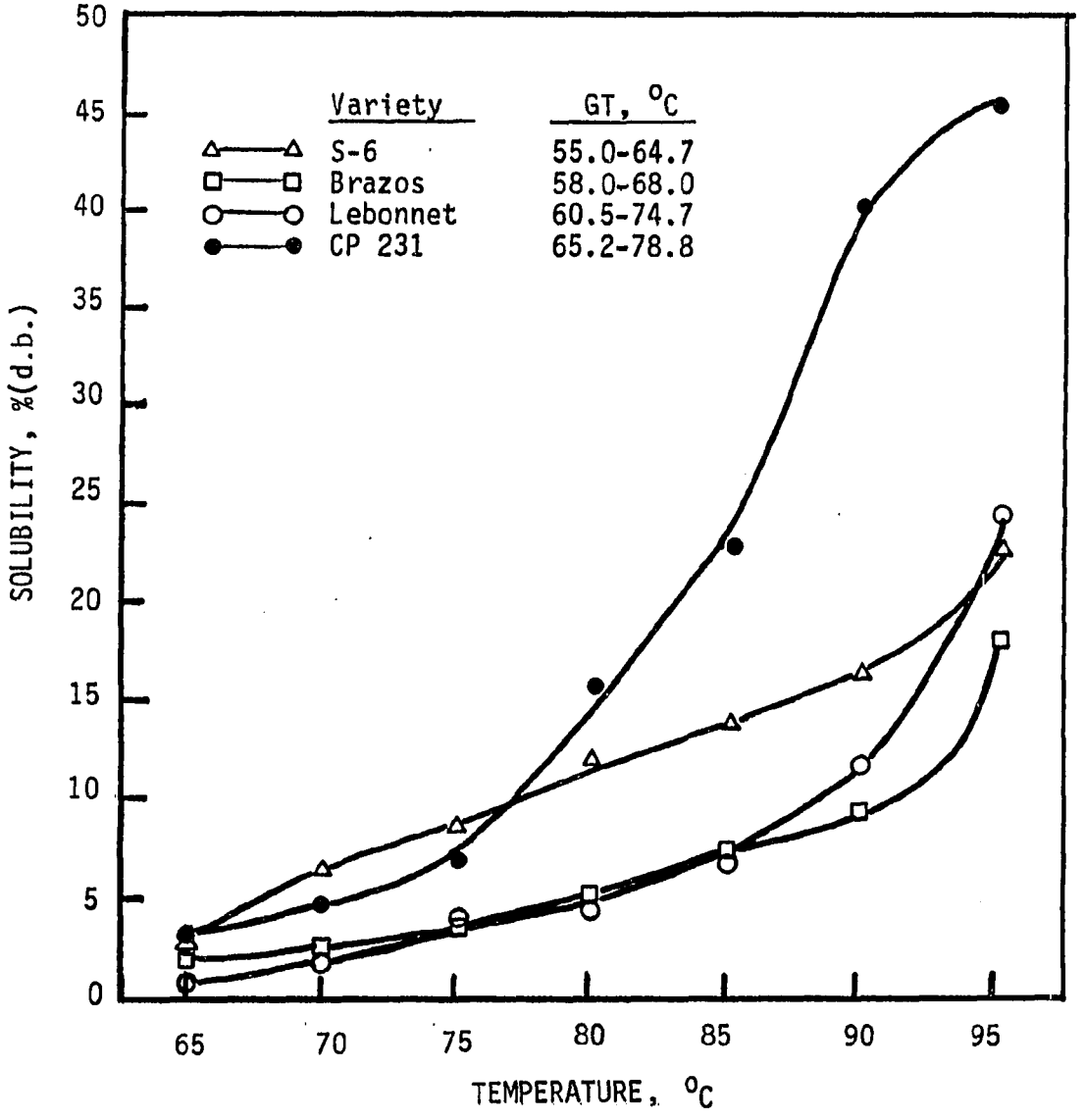


Figure 21. Representative solubility patterns of starch from different varieties of rice

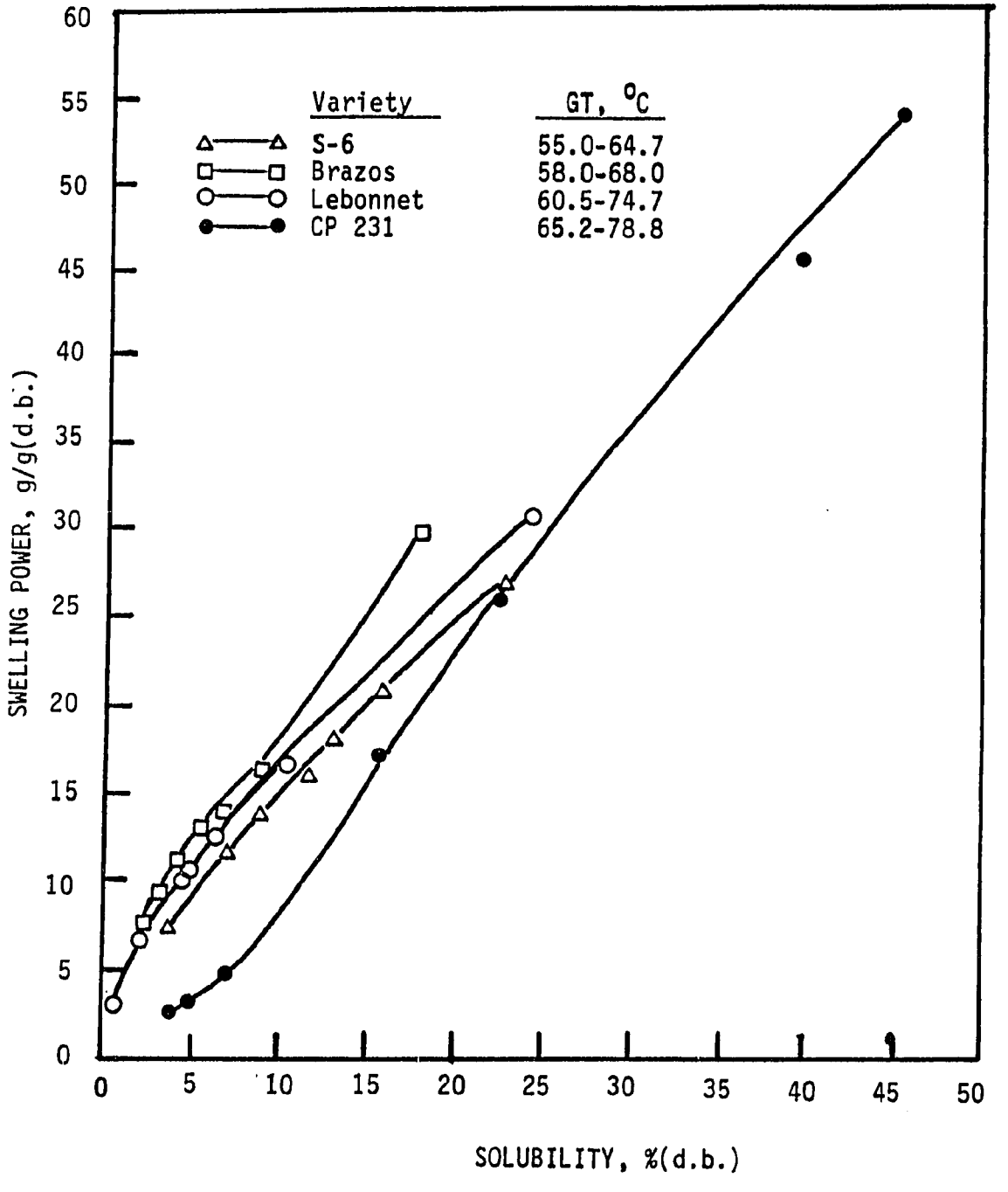


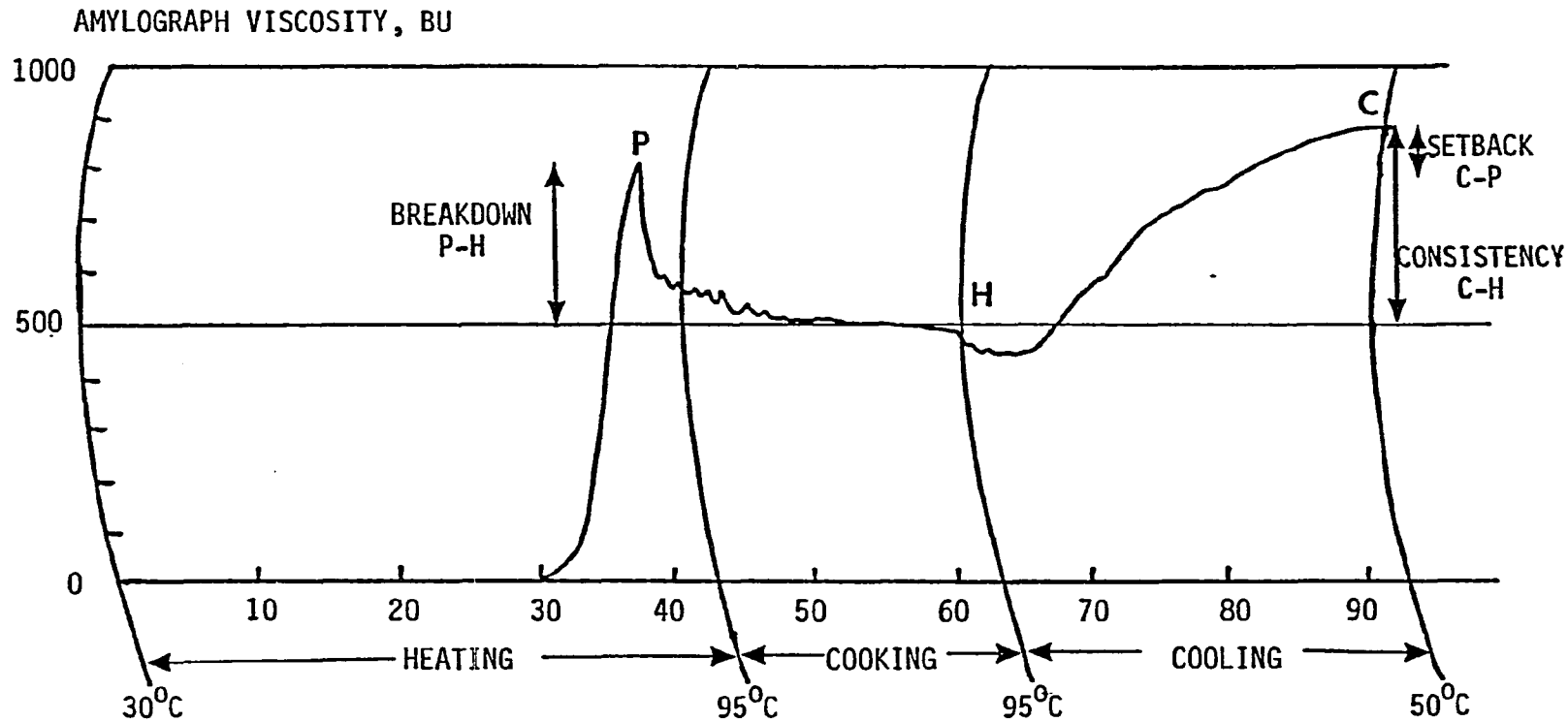
Figure 22. Representative presentation of the relationship between solubility and swelling power of starch from different varieties of rice

greatest increase in both swelling power and solubility. Leach (1965) reported that normal corn, rice and sorghum starches showed restricted swelling when compared to their waxy counterparts. Schoch (1967) reported the swelling power of waxy rice at 95°C as 55, close to that found in this study for Century Patna 231 (Table 5). This greater increase in both swelling power and solubility of Century Patna 231 may be due to its lower amylose content than the other starches studied.

The differences between low and high gelatinization temperature samples in swelling power and solubility were mainly below 75°C (Figures 20 and 21).

6. Amylography

Data of interest in amylography are peak viscosity (P), final viscosity after cooking at 95°C (H), and viscosity after cooling to 50°C (C), all in Brabender Units (B.U.). From these values, breakdown, setback, and consistency may be calculated. Breakdown is the decrease in viscosity between the peak and the end of 95°C holding period (P-H); setback is cooled paste viscosity to 50°C minus peak viscosity (C-P); and consistency is cooled paste viscosity to 50°C minus final cooking viscosity at 95°C (C-H) (Figure 23) (Perez and Juliano, 1979; Merca and Juliano, 1981). Breakdown indexes fragility and solubility of swollen granules, whereas setback and consistency measure the tendency of association and retrogradation of elements in the hot paste (swollen granules, fragments of swollen granules, colloidally and molecularly dispersed starch granules) during cooling (Perez and Juliano, 1979;



P = Peak viscosity
H = Final viscosity at 95°C
C = Viscosity when cooled to 50°C

Figure 23. Representation of an amylogram of milled rice flour and viscosity values (adapted from Juliano, 1985b)

Vladimir, 1982; Zobel, 1984). Amylograph consistency in rice research is synonymous with the term "setback on cooling" which is generally used by most starch chemists. Amylograph setback is completely different from the term "setback on cooling" and is used by only rice chemists. Another properties of interest are pasting temperature (temperature at which initial viscosity increases), temperature at peak viscosity and 'gelatinization time' (from onset of viscosity increase to peak viscosity) (Mazurs et al., 1957; Halick and Kelly, 1959; Zobel, 1984).

Amylograph gelatinization and pasting characteristics of rice starches are tabulated in Table 7 and amylograph peak viscosity, breakdown, setback, and consistency of starch in Table 5. Representative amylograph curves from different varieties are presented in Figure 24. In general, amylograph curves shown by the tested rice varieties were typical of those of other cereal starches, but they gave appreciable differences among the varieties that are different in amylose content and BEPT. Size of peak viscosity, breakdown, setback and consistency were determined primarily by the ratio of amylose and amylopectin and their correlation with amylose content will be discussed further later. Shape of the amylograph curve was dependent upon both BEPT and amylose content. 'Gelatinization time' was shortest for Century Patna 231 (Table 7), because its higher gelatinization temperature delayed the onset of viscosity increase and its lower amylose content hastened the viscosity increase to a greater extent compared to the others (Figure 24). The S-6, which had the lowest gelatinization temperature, showed longest 'gelatinization time,' which

Table 7. Amylograph gelatinization and pasting characteristics of rice starches[a]

Variety	Amylose[b]	BEPT[c]	Pasting temperature	Temperature at peak viscosity	Gelatinization time[d]	Amylograph viscosity, BU		
	%, d.b.	°C	°C	°C + min	min	Peak	95°C hold	50°C
Newrex	27.8(H)	74.8(H)	78.0	95.0 + 4.7	16.0	485	460	770
Lebonnet	23.2(I)	74.7(H)	73.5	95.0 + 3.7	18.0	565	490	610
Pecos	23.0(I)	67.3(L)	72.0	95.0 + 2.2	17.5	590	440	760
Bellemont	21.2(I)	75.1(H)	73.5	95.0 + 3.7	18.0	640	550	725
Labelle	20.5(I)	75.8(H)	73.1	95.0 + 2.7	17.3	675	565	675
S-6	19.7(L)	64.7(L)	66.8	95.0 + 6.2	25.0	520	485	600
Kokuho Rose	18.2(L)	73.5(I)	70.5	95.0 + 3.7	20.0	535	475	610
Brazos	15.2(L)	68.0(L)	69.0	95.0 + 4.2	21.5	735	650	755
Lemont	14.1(L)	74.0(I)	69.0	95.0 + 2.2	19.5	875	530	840
Early Colusa	12.8(L)	68.8(L)	70.5	94.5	19.0	840	555	840
Vista	11.2(L)	71.2(I)	69.0	95.0 + 2.2	19.5	960	560	740
Century Patna 231	10.4(L)	78.8(H)	75.0	94.5	13.0	695	415	640

[a]35 g (d.b.) / 500 mL (7%) paste; 1.5°C/min heating and cooling rate.
[b]In ( ), amylose type; H=high, I=intermediate, L=low.
[c]In ( ), GT type; H=high, I=intermediate, L=low.
[d]Time from onset of viscosity increase to peak viscosity.

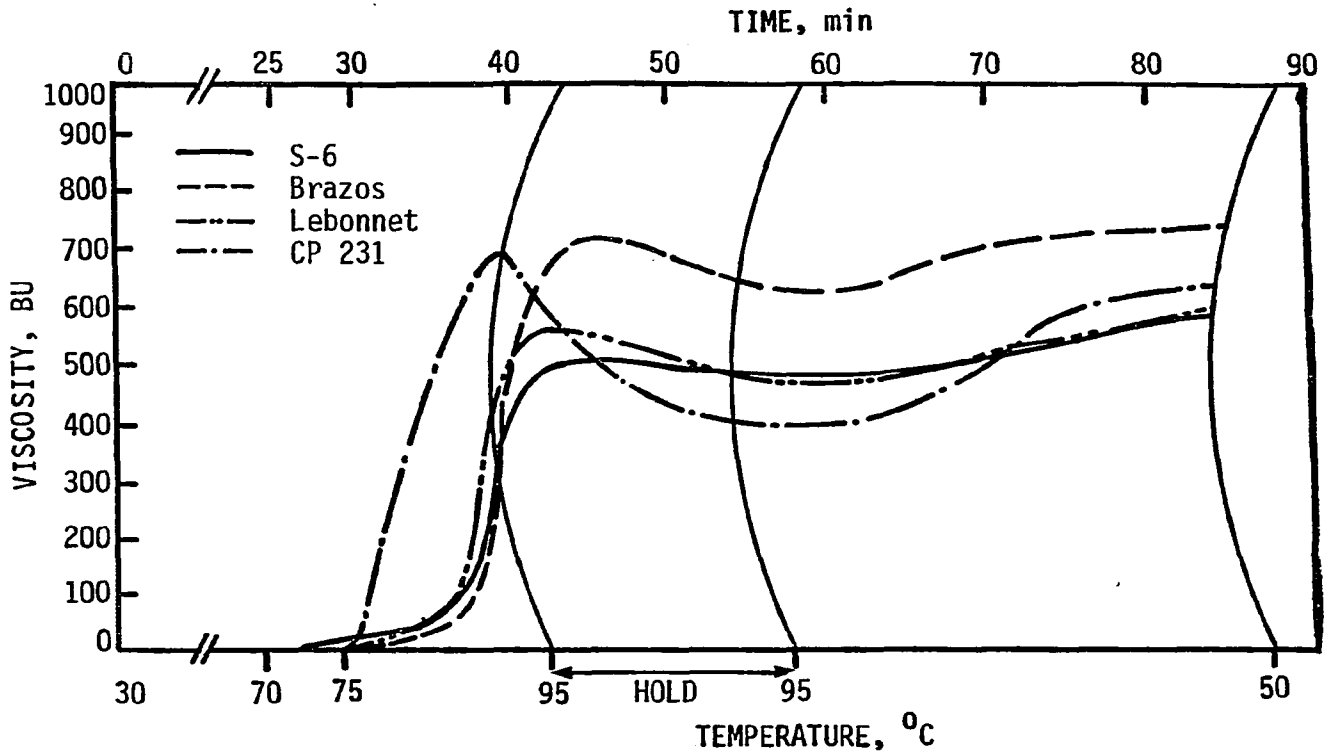


Figure 24. Representative amylograph viscosity patterns of starch (7%, d.b.) from different varieties of rice

must be due to earlier onset of viscosity increase than the others. Even though low amylose content and high gelatinization temperature tend to shorten 'gelatinization time,' their effects are complicated.

B. Milled Rice

Physicochemical properties of milled rices from twelve different varieties are presented in Table 8.

1. Protein

Protein contents of milled rice ranges from 6.68 to 10.48% (Table 8) and varied significantly among the samples tested (α=0.01, Appendix A). These levels were of the same order of magnitude as levels reported for milled rice samples by several researchers from different countries, which ranged from 5.6 to 13.3% as reviewed by Juliano (1972a). Protein content has been shown to vary according to location and among crops grown in the same field (Gomez, 1979).

2. Crude fat

Crude fat contents of milled rice ranges from 0.14 to 0.29% (Table 8) and showed significant differences among varieties tested (α=0.01, Appendix A). These crude fat values were in the range which had been reported for milled rice (Juliano, 1972a).

3. Cooked rice stickiness

Instron cooked rice stickiness ranges from 17.51 to 85.34 g.cm (Table 8), and showed significant varietal differences (α=0.01, Appendix

Table 8. Physicochemical properties of milled rices[a]

Grain type	Variety	Amylose[b] %, d.b.	Protein %, d.b.	Crude fat %, d.b.	Stickiness g·cm	Water uptake[c] 75°C	Water uptake[c] 95°C
Long	Newrex	27.8 (H)	8.92	0.18	17.51	0.37	3.89
	Lebonnet	23.2 (I)	10.16	0.24	28.22	0.51	3.44
	Bellemont	21.2 (I)	8.62	0.22	21.70	0.39	3.73
	Labelle	20.5 (I)	7.76	0.17	35.53	0.35	3.79
	Lemont	14.1 (L)	10.48	0.20	25.13	0.38	3.58
	Century Patna 231	10.4 (L)	6.68	0.21	85.34	0.38	3.85
Short & Medium	Pecos	23.0 (I)	7.83	0.18	69.73	0.85	3.86
	S-6	19.7 (L)	8.42	0.21	42.64	1.15	3.56
	Kokuho Rose	28.2 (L)	7.12	0.25	54.35	1.14	-
	Brazos	15.2 (L)	8.21	0.14	65.07	0.64	3.58
	Early Colusa	12.8 (L)	8.45	0.29	44.96	0.71	3.48
	Vista	11.2 (L)	8.32	0.18	61.29	0.51	3.39
LSD (α=0.05)		0.42	0.16	0.04	11.65	-	-

[a]Mean value of replicates.
[b]In ( ), amylose type; H=high, I=intermediate, L=low.
[c]Unit; g/g, d.b.

Table 8. (Continued)

Grain type	Variety	Loss to cooking-water[d]		Amylograph viscosity[e], B.U.			
		75°C	95°C	Peak	Breakdown	Setback	Consistency
Long	Newrex	0.68	6.36	850	105	570	675
	Lebonnet	0.48	5.09	735	215	415	630
	Bellemont	0.93	5.95	695	175	395	570
	Labelle	1.13	5.36	975	400	145	545
	Lemont	1.27	6.09	710	195	465	660
	Century Patna 231	2.17	10.68	1150	650	-400	250
Short & Medium	Pecos	3.70	7.52	1000	390	60	450
	S-6	3.59	8.03	770	305	130	435
	Kokuho Rose	5.32	9.53	765	275	155	430
	Brazos	1.49	6.30	1045	495	-65	430
	Early Colusa	1.75	5.31	990	470	10	480
	Vista	1.22	5.81	1210	560	-90	470
LSD (α=0.05)		-	-	-	-	-	-

[d]Unit; %, d.b.
[e]50 g (as-is basis) / 450 g (10%) paste.

A). Generally, short- and medium-grain types were stickier than the long-grain type except Century Patna 231.

Because changes in stickiness due to aging of the rough paddy rice are detectable even at 2°C, these values should not be considered absolute for these varieties (Fellers et al., 1983). In addition, samples of the same variety can be expected to vary, depending on differences in sample histories. Fellers and Deissinger (1983) reported that degree of milling is also critical to the stickiness values determined by the Instron method.

Various methods for assessment of the texture of cooked rice have been reviewed (Juliano, 1982). In recent years, instruments have been used for the measurement of texture as a final indicator of the eating quality of a rice sample. They include the Instron food tester (Blakeney, 1979; Perez and Juliano, 1979; Mossman et al., 1983), the Texturometer (Okabe, 1979; Suzuki, 1979), the Viscoelastograph (Laignelet and Feillet, 1979) and Tensipresser (Tsuji, 1981). Aside from the use of various instruments, different cells and methods have been employed. The results of international cooperative studies demonstrated that instrumental methods are generally more sensitive than sensory analysis in measuring stickiness of rice cooked by the same method (Juliano et al., 1981). Therefore, the Instron Universal Testing Instrument with attachment for compression (Mossman et al., 1983) was chosen for this study. The following modifications were made based on suggestions by Mossman et al. (1983) and the results from preliminary examination: increase the water to rice ratio from 1.25 to 1.5;

increase the size of the test sample from 2 g to 4 g; use a constant pressure of 16 kg and holding period of 20 sec instead of 640 g and 10 sec, respectively, because of the different sensitivity of the instrument.

Although stickiness values among various instrumental methods were significantly correlated, data obtained on bulk samples instead of on individual grains were more reproducible because of the wide variation of properties among individual grains (Juliano et al., 1981; Juliano et al., 1984).

Because of the changes in texture of cooked rice during cooling and storage, the handling of cooked rice was standardized to reduce further variables in the assessment. The cooked rice was covered during cooling to minimize water loss. Cooked rice has usually been assessed within 1hr of cooking (Juliano, 1982). Okabe (1979) reported a holding time of 1 hr at 18°-24°C or 1.5 hr above 25°C ambient temperature. In this study, cooked rices were cooled for 40 min at room temperature. This is important because poor thermal equilibration of the cooked rice will cause poor reproducibility of texture measurements, especially of stickiness.

Stickiness is the tendency of the cooked rice to adhere to itself and to other objects. In objective terms, it was the force of the rice pulling against the crosshead measured throughout the crosshead movement. Since work is obviously done on the rice by the crosshead anvil during compression, expressing the reverse adhesive resistance in work (force X distance) units seems appropriate.

The clearance between the two horizontal plates at constant pressure varies with hardness of the rice. It must vary if the cut-off force is fixed and the sample resistance varies. That is, the force and clearance cannot then both be constant. With bulk samples, Instron stickiness was more sensitive when measured after compression to constant pressure than after compression to constant clearance (IRRI, 1983). Indeed, hardness of cooked rice influences the stickiness value obtained. Juliano et al. (1981) reported that stickiness indices showed significant negative correlation with hardness indices.

4. Water uptake and solids lost in cooking-water

Water uptake and solids lost in cooking-water were determined as an indication of cooking quality.

Water uptake at 95°C ranges from 3.39 to 3.89 g/g (d.b.) and solids lost in cooking-water at 95°C from 5.09 to 10.68% (d.b.) (Table 8). Water uptake at 75°C ranges from 0.37 to 1.15 g/g (d.b.) and solids lost in cooking-water at 75°C from 0.48 to 5.32% (d.b.) (Table 8). Their correlation with other physicochemical properties will be discussed later.

Water uptake values have several sources of error: 1) approximation of values because of solids lost in cooking water in the excess water method; 2) blotting step to remove free water; and 3) inclusion of adsorbed water to the cooked grain in addition to absorbed water (Juliano, 1985b).

5. Amylography

Amylography is viewed as a measure of cooking characteristics of rice (Juliano et al., 1985).

Amylograph gelatinization and pasting characteristics of milled rice flours are tabulated in Table 9 and amylograph peak viscosity, breakdown, setback and consistency of milled rice flour in Table 8. Correlation between these values with properties of milled rice will be discussed later. Representative amylograph curves of milled rice flour from different varieties, which are different in amylose content, protein content and BEPT, are presented in Figure 25.

'Gelatinization time' of milled rice flour was shortest for Century Patna 231 (9.8 min) followed by the high-GT (12.5-14.5 min), intermediate-GT (15.0-15.5 min), and low-GT (17.0-21.0 min) varieties (Table 9). The short 'gelatinization time' for Century Patna 231 may be due to its higher gelatinization temperature and lower amylose content compared to the other varieties. Halick and Kelly (1959) found that 'gelatinization time' was associated with grain type; long-grain type (11-14 min) was shorter compared to the short- and medium-grain types (15-18 min). Association of 'gelatinization time' with grain type may be interpreted on the basis of gelatinization temperature rather than grain type, as gelatinization temperature type in commercially produced U.S. varieties is highly correlated with grain type.

Juliano et al. (1985) reported that 'gelatinization time' was shortest for waxy rice (6.5-9.8 min) followed by the intermediate-GT

Table 9. Amylograph gelatinization and pasting characteristics of milled rice flours[a]

Variety	Amylose[b]	BEPT[c]	Pasting temperature	Temperature at peak viscosity	Gelatinization time[d]	Amylograph viscosity, BU		
	%, d.b.	°C	°C	°C + min	min	Peak	95°C hold	50°C
Newrex	27.8(H)	74.8(H)	76.5	95.0 + 0.2	12.5	850	745	1420
Lebonnet	23.2(I)	74.7(H)	75.0	95.0 + 1.2	14.5	735	520	1150
Pecos	23.0(I)	67.3(L)	69.0	95.0 + 0.7	18.0	1000	610	1060
Bellemont	21.2(I)	75.1(H)	73.5	95.0 + 0.2	14.5	695	520	1090
Labelle	20.5(I)	75.8(H)	73.5	93.8	13.5	975	575	1120
S-6	19.7(L)	64.7(L)	64.5	95.0 + 0.7	21.0	770	465	900
Kokuho Rose	18.2(L)	73.5(I)	72.0	94.5	15.0	765	490	920
Brazos	15.2(L)	68.0(L)	67.5	95.0 + 1.7	20.0	1045	550	980
Lemont	14.1(L)	74.0(I)	72.0	95.0 + 0.2	15.5	710	515	1175
Early Colusa	12.8(L)	68.7(L)	69.0	95.0 + 0.7	18.0	990	520	1000
Vista	11.2(L)	71.2(I)	71.3	95.0 + 1.2	17.0	1210	650	1120
Century Patna 231	10.4(L)	78.8(H)	78.3	93.0	9.8	1150	500	750

[a]50 g (as-is basis) / 450 g (10%) paste; 1.5°C/min heating and cooling rate.
[b]In ( ), amylose type; H=high, I=intermediate, L=low.
[c]In ( ), GT type; H=high, I=intermediate, L=low.
[d]Time from onset of viscosity increase to peak viscosity.

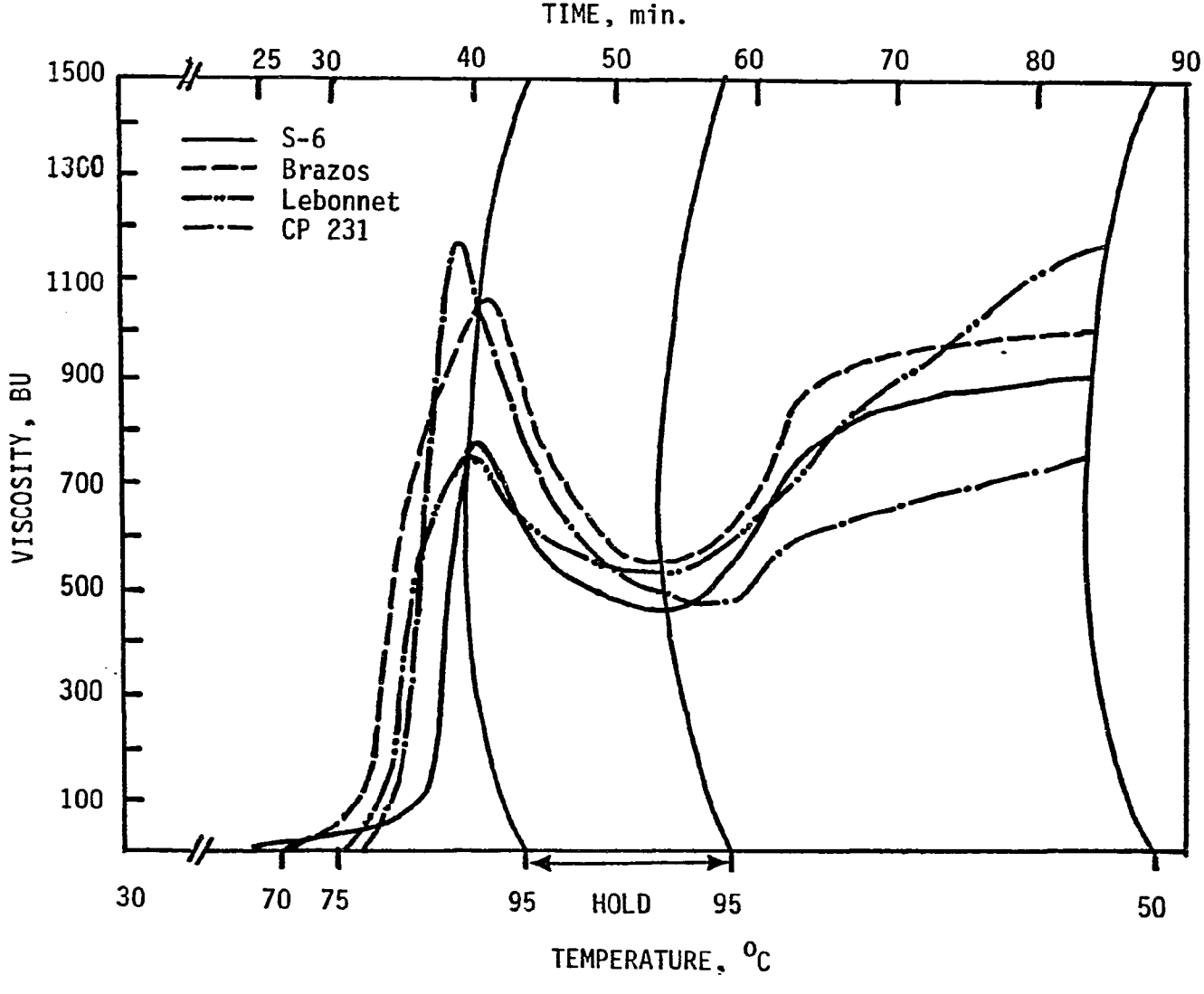


Figure 25. Representative amylograph viscosity patterns of milled rice flour (10%, as-is basis) from different varieties

nonwaxy rice and low-GT nonwaxy rices. Mean 'gelatinization time' for three nonwaxy rices ranged from 13.9 to 18.9 min.

In a 1981 survey conducted by the International Association for Cereal Chemistry (ICC) Working Group 21/II "Tests Methods for Rice Cooking Properties" (Juliano, 1982), 12 out of 41 scientists reported routinely running 10% milled rice amylograms (Halick and Kelly, 1959) to evaluate cooking and eating quality of milled rice. Perez and Juliano (1979) indicated that a 10% paste effectively distinguishes among high-amylose rices but provides little distinction among low- and intermediate-amylose rices. Therefore, they suggested that use of higher paste concentration of 11-12% was better suited for differentiating among intermediate- and low-amylose rices.

C. Correlations of Milled Rice and Starch Properties with Cooking and Eating Qualities

Tests of nonwaxy varieties with diverse and extreme characteristic were involved in this study to obtain a clearer understanding of the physicochemical basis of rice quality. Correlation coefficients were obtained among possible variables of twelve varieties of nonwaxy rices which significantly differ in their physicochemical properties (Table 10).

1. Correlations between amylose content, protein content, crude fat content and BEPT

There was no correlation between amylose content and other constituents of milled rice (protein and crude fat) and final

Table 10. Correlation coefficients of milled rice and starch properties with cooking and eating quality indices among nonwaxy rices (n=12)

Property	Amylose	Protein	Crude fat	Stickiness	BEPT
Milled rice					
Amylose	1.00				
Protein	0.25	1.00			
Crude fat	-0.12	0.07	1.00		
Cooked rice stickiness	-0.58*	-0.72**	-0.18	1.00	
Water uptake at 75°C	0.04	-0.31	0.28	0.29	-0.69**
Water uptake at 95°C[a]	0.42	-0.47	-0.36	0.08	0.35
Cook-water loss at 75°C	-0.06	-0.56*	0.21	0.47	-0.38
Cook-water loss at 95°C	-0.23	-0.68**	0.04	0.62*	0.12
Amylograph Peak	-0.55	-0.55	-0.35	0.75**	-0.06
Breakdown	-0.76**	-0.61*	-0.15	0.87**	-0.10
Setback	0.71**	0.74**	0.09	-0.93**	0.13
Consistency	0.58*	0.83**	0.00	-0.91**	0.15
Starch					
BEPT	-0.00	-0.04	0.07	-0.18	1.00
Granule size	-0.52	-0.29	-0.06	0.45	-0.14
Crystallinity	-0.05	-0.16	-0.17	0.03	0.67**
Swelling power at 75°C	0.05	0.27	0.02	-0.15	-0.84**
Swelling power at 95°C	-0.50	-0.27	-0.35	0.57*	0.35
Solubility at 75°C	-0.10	-0.25	0.07	0.13	0.02
Solubility at 95°C	-0.26	-0.21	-0.26	0.36	0.50
Amylograph Peak	-0.79**	0.15	-0.04	0.21	-0.01
Breakdown	-0.79**	0.07	0.08	0.32	0.11
Setback	0.85**	0.06	-0.03	-0.38	-0.10
Consistency	0.03	0.19	0.09	0.05	0.04

[a]n=11 (values for Kokuho Rose were excluded).
* $P \leq 0.05$.
** $P \leq 0.01$.

gelatinization temperature (BEPT) determined by the loss of birefringence (Table 10).

Amylose content and BEPT are known to be independent properties of rice starch and are affected by environmental factors, mainly by temperature during grain ripening (Gomez, 1979; Juliano, 1984). Halick and Kelly (1959) found no correlation between gelatinization temperature and amylose content of varieties in the United States. However, high-amylose varieties are usually high in BEPT and protein content in the typical U.S. long-grain type and vice versa in the typical U.S. short- and medium-grain types, which occur strictly as a result of planned breeding (Webb, 1985). This implies that kernel dimensions are not useful indexes of the chemical composition of rice grain.

Crude fat content was not correlated with any other physicochemical properties of starch and/or milled rice (Table 10). Therefore, crude fat content of milled rice does not important to explain any varietal differences of cooking and eating characteristics.

2. Factors affecting gelatinization temperature of starch

Gelatinization temperature is one of the most important starch characteristics. Although gelatinization temperature seems to have little relation to the palatability characteristics of table rice (Juliano et al., 1965), it may have some influence on the cooking quality of rice (i.e., cooking time), and on the processing quality of rice. Beachell and Stansel (1963) noted that varieties suitable for parboiling and canning and for quick-cooking processing have an

intermediate gelatinization temperature; varieties with low gelatinization temperature, regardless of their amylose content and setback viscosity, are considered unsuitable. Low-GT rices are preferred by brewers and cereal manufacturers using diastatic digestion in their process. A low gelatinization temperature allows complete liquefaction of starch before thermal inactivation of the enzyme can occur (El-Seid et al., 1979). Also, gelatinization temperature seems to have some relation to the palatability characteristics of products made from waxy rice, such as rice cakes made in Japan and in the Philippines (Perdon and Juliano, 1975). Therefore, it is interesting to understand which factors affect the gelatinization temperature of starch.

The granular starch samples differed significantly in their mean sizes (Table 5). Mean granule sizes and BEPTs of the samples, however, were not correlated (Table 10), nor were their gelatinization temperature ranges measured by the loss of birefringence correlated with their granule size ranges (Table 6). The histogram of granule size distribution (Appendix B) and SEM (Figures 32 and 36) confirmed no correlation between granule size and gelatinization temperature.

From microscopic observation, Banks and Greenwood (1959) suggested that, in any one population, the larger granules appear to be the most susceptible to gelatinization and vice versa. Similar observations were reported by other investigators (Radley, 1960; Stevens and Elton, 1971; Rockland et al., 1977). However, these observations were made on single sample.

On the contrary, DSC study by Wirakartakusumah (1981) showed that larger rice starch granules in one sample were more resistant to gelatinization. Merca and Juliano (1981) also reported that samples with high gelatinization temperature had a larger mean granule sizes than those with low gelatinization temperature among waxy and intermediate-amylose rices.

Another group of investigators (Reyes et al., 1965; Goering et al., 1974; Goering, 1978; Dengate et al., 1979) reported no significant effect of granule size on the gelatinization temperature. Goering et al. (1974) observed that it appeared as if the large granules were first to lose polarization crosses followed by the medium size granules and finally the small granules, because with the former, loss of contrast was very evident and in many cases it appeared that the granule was swelling and expanding in size. By careful observation at high magnification, however, both large and small granules are seen to lose polarization crosses simultaneously.

Within a single type of starch (i.e., wheat starch) the size of the granules varies from 2 μm to approximately 35 μm. In addition, the distribution of granule size in wheat starch shows a bimodal population of the granules with approximately the same number of granules in each size. Unlike wheat starch, the range of granule size in rice starch is narrow (2-10 μm) and the distribution is close to the normal distribution. Even though there might be a difference in the susceptibility to gelatinization due to the granule size, varietal difference in granule size may be considered relatively minor compared

to the other factors affecting varietal difference in gelatinization temperature of rice starch.

Crystallinity of starch was significantly correlated with BEPT (r=0.67**) (Table 10). Similar observations were made by Reyes et al. (1965), Lugay and Juliano (1965), and Juliano et al. (1969). Studies with Lintnerized starch supported this relationship between crystallinity of starch and BEPT (Kongseree and Juliano, 1972; Evers and Juliano, 1976; Maniñgat and Juliano, 1979). Lintnerized starch had sharper x-ray diffraction peaks than native starch. BEPT values of starch were shown to be negatively correlated with the amounts of dry substance lost during Lintnerization (Lintnerization loss), regardless of amylose contents. This correlation between crystallinity of starch and BEPT is not surprising theoretically since the starch granule is generally considered as a semicrystalline polymer which contains both crystalline and amorphous regions. The BEPT is thus a measure of the degree of orderliness of the granule organization by the loss of birefringent characteristics of starch granules. The micellar structure of the molecules in the starch granule seems to be the main factor determining the varietal differences in BEPT.

BEPT was not affected by the amylose content at all (Table 10). It has been known that BEPT and amylose content are independent properties of starch and are affected by environmental factors, mostly the ambient temperature during grain development. Although the intermediate-GT type is rare in waxy and low-amylose rices and the high-GT type is rare for intermediate- and high-amylose rices, whether this limited occurrence of

the gelatinization temperature type and the amylose type of rices is due to genetic coincidence is still unknown at this time.

3. Correlations of water absorption and solids lost in cooking-water of milled rice, and swelling power and solubility of starch with other properties

BEPT of starch was significantly correlated with water uptake of milled rice at 75°C (r=-0.69**) and swelling power of starch at 75°C (r=-0.84**) (Table 10). Swelling power of starch at 75°C differentiated gelatinization temperature better than water uptake of milled rice at 75°C because BEPT and swelling power measurements involve only starch and water without the possible effect of all the other components and structure of rice grain and the accuracy of method is better for swelling power measurement than water uptake measurement. Water uptake measurement, however, takes less time than swelling power measurement because it does not need the preparation of starch. Therefore, many rice researchers used water uptake below boiling temperature (75°, 77°, or 80°C) to distinguish between low-GT and intermediate-GT rices since only the low-GT grains are completely gelatinized at these temperatures (Halick and Kelly, 1959; Bhattacharya and Sowbhagya, 1971; Webb, 1975). For this purpose, Bhattacharya et al. (1972) proposed the use of water uptake ratio between 80° and 96°C to eliminate the effect of differences in surface area and various other interfering factors among varieties.

Water uptake of milled rice at 95°C was not correlated with amylose content (Table 10). A higher amylose content improves the capacity of the starch granule to absorb water and expand in volume without

collapsing, because of the greater capacity of amylose to hydrogen-bond or retrograde (Juliano, 1985a), but at higher temperature, water uptake may become a function of surface area of the grain, dependent on size and shape, and varietal differences in composition might then be masked. Batcher et al. (1957) reported that long-grain types absorbed more water than the short- and medium-grain types. The surface area of long-grain types are more than that of short- and medium-grain types. The larger surface area and the higher amylose content tend to increase the water uptake during cooking, and outweigh the tendency of the higher protein content to decrease it. Rices with high amylose content generally absorb more water than rices with low amylose content. The question can be asked as to why swelling power of starch at 95°C tends to be higher in lower amylose rices even though higher amylose content improves the capacity of starch granule to absorb water. This can be explained clearly with SEM (compare Figure 20 and Figures 53-60). Swelling power of starch increased rapidly after the loss of original granular structure and severe tangential expansion. At 95°C, swelling power seems to depend on the exposure of surface area of starch material as thin filaments (Figures 65-68). The lower the amylose content, the more tangential expansion into thin filaments of swollen granules occurred and the more surface area of swollen granules were exposed. The positive correlation between swelling power at 95°C and cooked rice stickiness may be interpreted more on the basis of amylopectin than on swelling power itself, since cooked rice stickiness is more attributable to amylopectin than to amylose (Table 10).

Solids lost in cooking-water at 95°C was negatively correlated with protein content of milled rice (r=-0.68**) and positively correlated to the cooked rice stickiness. Solids lost in cooking-water measures not only the solubles, but also the fragments lost into cooking-water because the outer region of each grain disintegrated severely during cooking. Rice grains with low protein content are the ones deformed and chipped out most (Figures 101 and 102). Therefore, protein may affect the solids lost in cooking-water and cooked rice stickiness by acting as a barrier for water diffusion and swelling because the starch granule is encased in a proteinaceous matrix in the starchy endosperm and the proteinaceous matrix forms a barrier in the outermost subaleurone layer.

4. Correlations of amylograph viscosities with other properties

Pasting characteristics of milled rice flour have been correlated to the cooking quality of rice (Halick and Kelly, 1959; Beachell and Stansel, 1963).

Correlation coefficients suggested that amylograph peak viscosity of milled rice flour was slightly affected by amylose and protein content, even though they were were not significantly correlated with amylose (r=-0.55, p=0.07) and protein content (r=-0.55, p=0.06) (Table 10).

Negative correlation between peak viscosity and protein content was found previously in other studies, too (Juliano et al., 1964a, 1964b; El-Seid et at., 1979; Juliano and Pascual, 1980). The effect of protein on peak viscosity may be due to suppressing starch swelling, as the

starch granules are encased in a protein matrix (Little and Dawson, 1960; Figures 75-78). Competition for water between starch and protein is probably not one of the reasons why protein suppresses starch swelling. Protein bodies and cell matrix remain intact after milled rice grains are heated to 85°C (Figures 94 and 95) and 95°C (Figures 99 and 100), while starch granules inside the cell matrix are already gelatinized and cooked (compare the size of protein bodies in Figures 77 and 78 with that in Figures 94 and 95; 99 and 100).

Conflicting reports of correlation between peak viscosity of milled rice flour and amylose content have been made (Halick and Kelly, 1959; Juliano et al., 1964a, 1964b; El-Seid et al., 1979; Juliano and Pascual, 1980). Juliano et al. (1964b) tried to interpret the negative correlation between peak viscosity of milled rice flour and amylose content, as observed by Halick and Kelly (1959), on the basis of protein rather than amylose content, as the high-amylose U.S. varieties, such as Rexoro, are usually high in protein content. But this interpretation does not apply to this study, because there was no correlation between amylose content and protein content in the samples studied. However, the strong correlation between peak viscosity of starch and amylose content ($r=0.79^{**}$, Table 10) suggested that the presence of protein in milled rice actually weakened the effect of amylose content on peak viscosity.

Amylograph breakdown of milled rice flour during cooking was significantly correlated with amylose content ($r=-0.76^{**}$) and protein content ($r=-0.61^{*}$) (Table 10). Merca and Juliano (1981) reported

similar results with 12% milled rice flour: negative correlation with amylose content (r=-0.62*) with intermediate-amylose rices (n=14). Juliano et al. (1964b) previously reported a negative correlation with amylose content (r=-0.74**, n=51) but no correlation with protein content.

Starch showed negative correlation between amylose content and amylograph breakdown viscosity, also (r=-0.79**, Table 10). Thus, resistance to disintegration of starch during cooking might be related to amylose content. This observation can be explained clearly in Figures 61-64. Starch granules with high amylose content tend to hold their granular structure better. The lack of change in viscosity through the 95°C holding period is attributed to retardation of swelling caused by a strengthening of the swollen starch granules with high amylose content by complex formation between the amylose fraction and lipids present in these starches (Zobel, 1984). MacMaster and Wolff (1959) demonstrated the in situ formation of such complexes both within and outside starch granules by tempering pastes for several days at 80°-90°C and observing spherocrystal formation microscopically. Priestley (1975, 1976a, 1976b, 1977a) has shown by x-ray diffraction that solubility and amylograph viscosities for rice starch decrease as complex formation increases.

Amylograph setback and consistency reflects the degree of retrogradation during cooling. Generally, both setback and consistency of milled rice flour were positively correlated with amylose content (r=0.71**, r=0.58**, respectively) and protein content (r=0.74**,

r=0.83**, respectively) (Table 10). A similar observation was reported by Merca and Juliano (1981). Conflicting reports have been made on the correlation of protein content with amylograph breakdown, setback and consistency (Juliano et al., 1964a, 1964b; El-Seid et al., 1979; Juliano and Pascual, 1980). The presence of correlation between amylograph viscosities and protein content often seems to be masked due to the wider range of amylose content compared to the range of protein content used for the studies. Juliano et al. (1964b) did not show any correlation of protein content with breakdown viscosity and setback when they employed the samples with amylose content ranged from 2.8 to 31.2% (n=51). But Merca and Juliano (1981) reported the influence of protein on amylograph viscosities with intermediate-amylose rices (21.8-25.5%, n=14). The effect of protein content on peak viscosity, breakdown, setback and consistency became clear when comparison was made among samples of similar amylose content.

The ratio of amylose to amylopectin is the major factor affecting amylograph viscosities, but protein might become an important factor among varieties with a narrow range of amylose content by acting as a barrier for water diffusion and starch swelling.

5. Correlations of cooked rice stickiness with other properties

Cooked rice stickiness was significantly affected by protein content (r=-0.72**) and amylose content (r=-0.58**) among samples tested (Table 10).

It has been known for a long time that the ratio of amylose and amylopectin is the major factor governing the eating quality of milled rice (Juliano, 1979a). But there have been contradictory results about the effect of protein on cooked rice stickiness. Generally, when samples with a wide range of amylose content were employed, the effect of protein content seemed to be outweighed because the difference in amylose content was far larger than that of protein content.

For example, Juliano and Pascual (1980) reported that cooked rice stickiness was significantly correlated with amylose content ($r=-0.82^{**}$, $n=268$) and not significantly correlated with protein content. In this study, protein content ranged from 4 to 14% at 14% moisture, and amylose content ranged from 0.0 to 32.8% on dry weight basis. Juliano et al. (1981) also reported that the cooked rice stickiness measured with various instruments and sensory evaluation was significantly correlated with amylose content ($r=-0.82^{**}$ to -0.98^{**}) and not significantly correlated with protein content ($r=-0.04$ to -0.38). Ten milled rice samples were employed for this study with amylose contents from 1.5 to 27.9% on dry weight basis and protein contents from 5.8 to 10.0% at 12% moisture.

When Merca and Juliano (1981) used only nonwaxy rices with intermediate-amylose content (21.8-25.5%), cooked rice stickiness was significantly correlated with both amylose content ($r=-0.69^{**}$, $n=14$) and protein content ($r=-0.72^{**}$, $n=14$), which compared well with this study.

From these comparisons, it might be concluded that the ratio of amylose to amylopectin is the primary factor affecting the cooked rice

stickiness, but the effect of protein on the cooked rice stickiness becomes more apparent among the rices of narrow ranges of amylose content.

Cooked rice stickiness was significantly correlated with amylograph viscosities of milled rice, but not with those of starch (Table 10). Especially, cooked rice stickiness showed strong correlation with amylograph breakdown (r=0.74**), setback (r=-0.93**) and consistency (r=-0.91**) of milled rice flour. Merca and Juliano (1981) showed high correlation of cooked rice stickiness with amylograph breakdown (r=0.74**), setback (r=-0.83**) and consistency (r=-0.80**) of milled rice flour with intermediate-amylose nonwaxy rices (21.8-25.5%, n=14). However, the correlations of cooked rice stickiness with setback (r=-0.38**) and consistency (r=-0.48**) of milled rice were not strong enough when diverse samples in amylose content (0.0-32.8%, n=236) were used. Therefore, the milled rice flour amylograph viscosities can be used as good indexes to differentiate among rices within narrow range of amylose content. The regression plots and equations between cooked rice stickiness and amylograph viscosities are presented in Figures 26-28.

D. Scanning Electron Microscopy

1. Starch

a. Size and shape of starch granule Rice starch has the smallest granules among common starches; diameter ranged from 2 to 10 μm. Scanning electron micrographs emphasize the sharp, angular nature

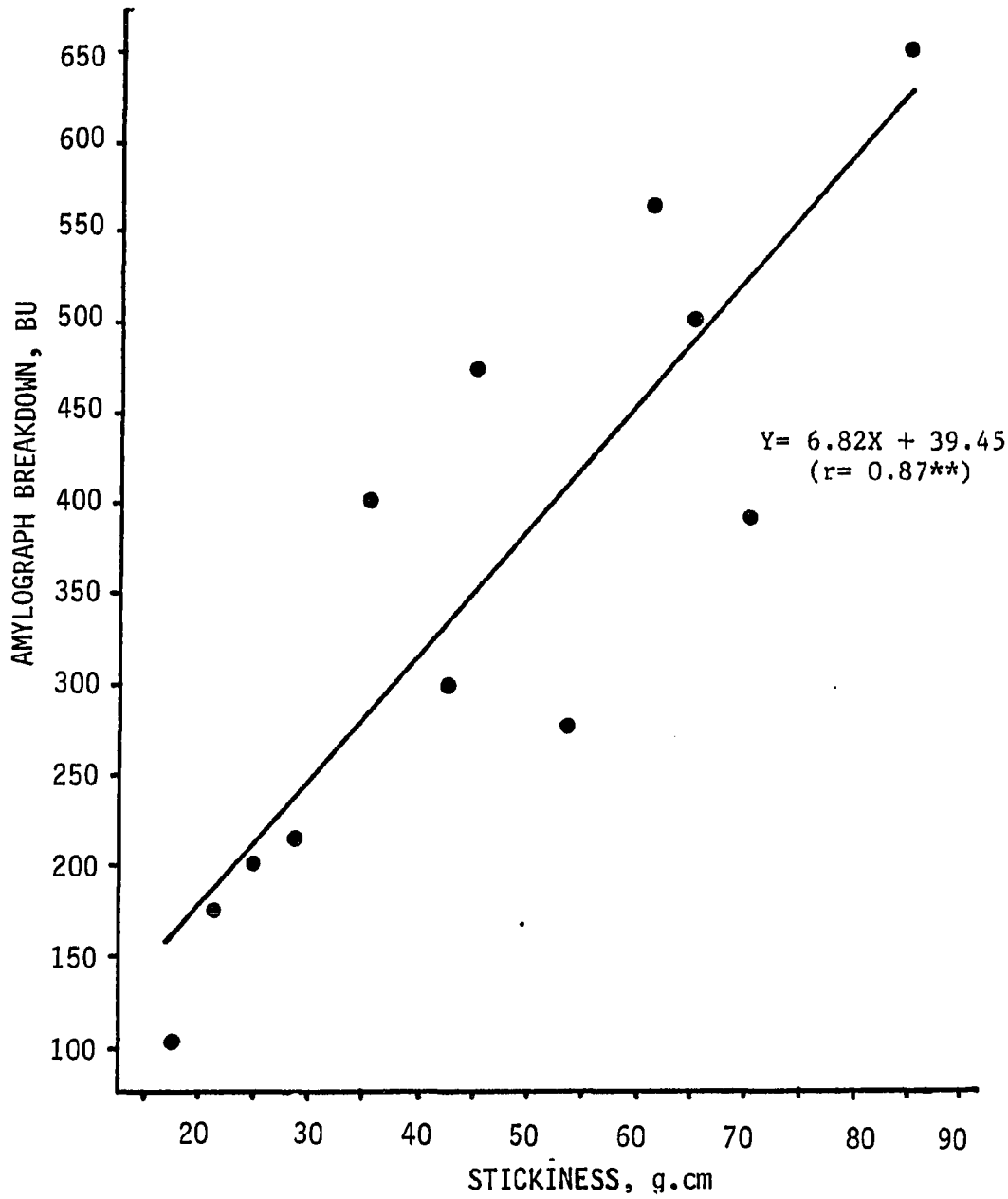


Figure 26. Relationship between cooked rice stickiness and amylograph breakdown values of 12 nonwaxy milled rice flours (10%, as-is basis)

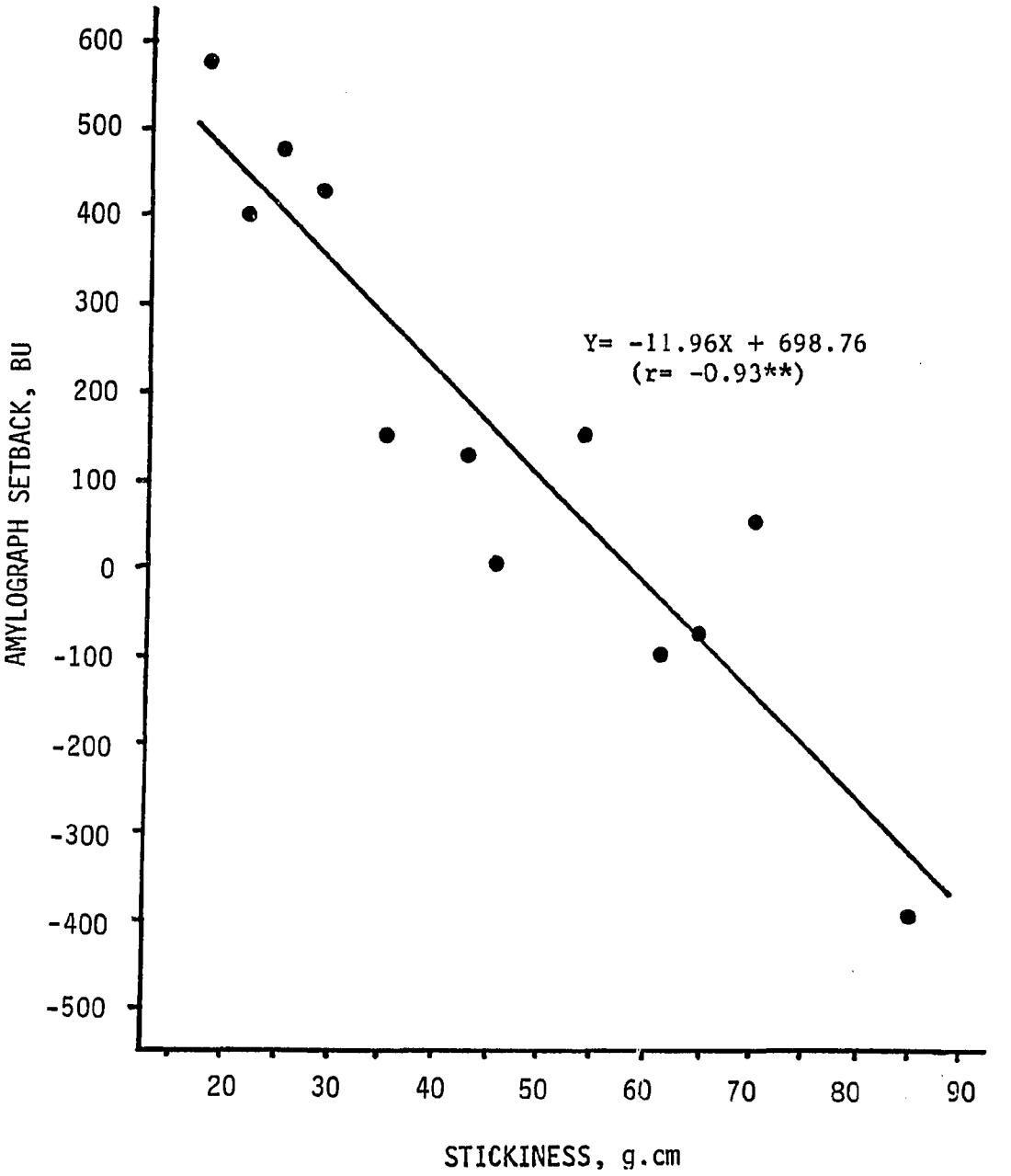


Figure 27. Relationship between cooked rice stickiness and amylograph setback values of 12 nonwaxy milled rice flours (10%, as-is basis)

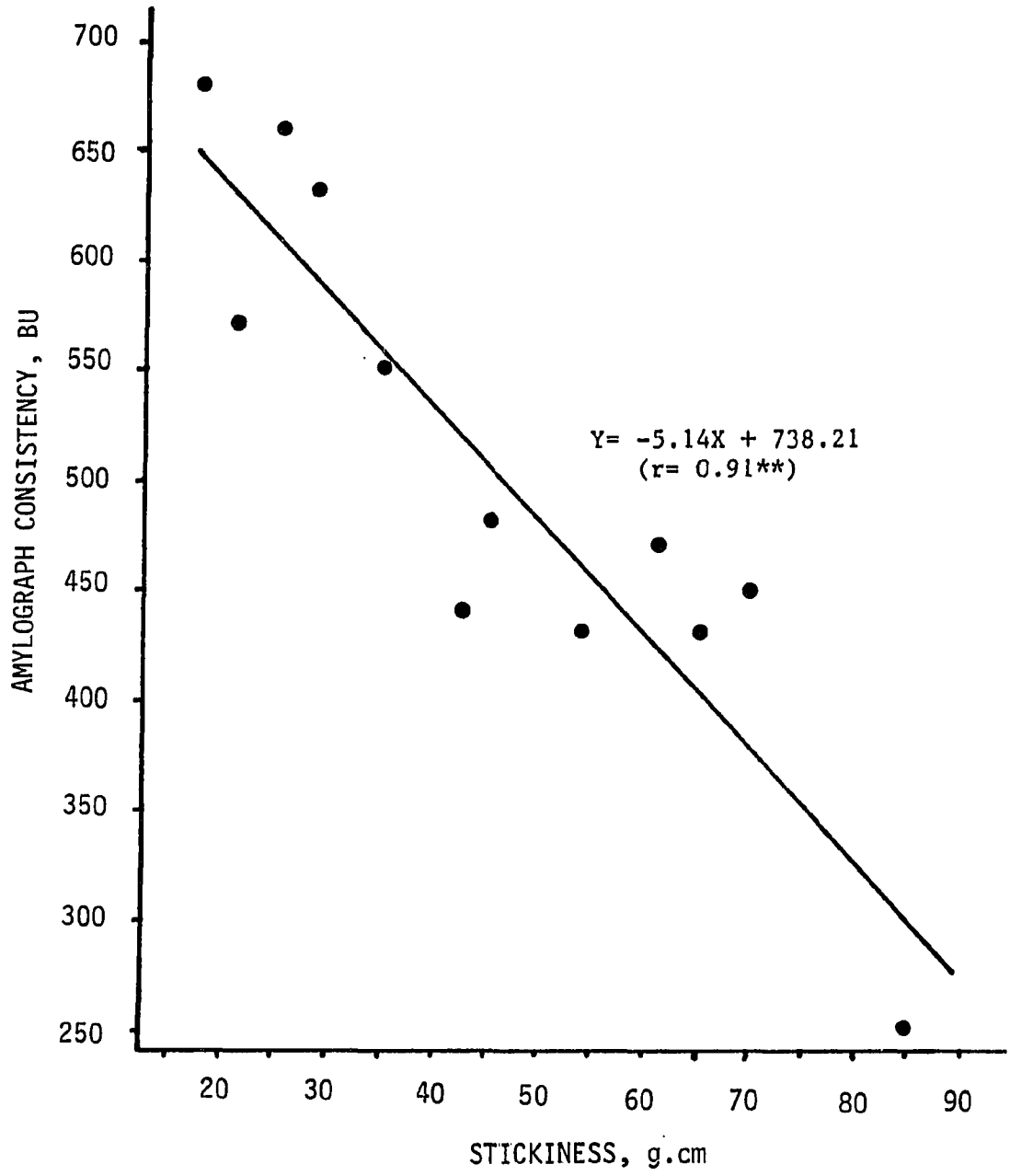


Figure 28. Relationship between cooked rice stickiness and amylograph consistency values of 12 nonwaxy milled rice flours (10%, as-is basis)

of the granules and the irregular, layered appearance of the surfaces (Figures 29-36). Some starch granules had indentations on their surfaces probably from the pressure of protein bodies on the developing granules (Evers and Juliano, 1976; Figures 77 and 78).

There have been several observations about the relationship between size and shape and amylose content. According to Greenwood (1979), the granule size and shape dependent on the apparent amylose content of the parent starch. This behavior was exemplified by maize starch where the typical angular granule of normal maize (25% amylose) becomes more rounded as the amylose content of 70% was reached, very bizarre sausage-like granules appear. However, Hood (1982) indicated that granule shape and size were not well correlated with amylose content because tapioca, corn, wheat and potato starches all have 15-25% amylose but have very different granule morphologies. Even though waxy corn and normal corn, waxy rice and nonwaxy rice have very different amylose contents, it is impossible to distinguish between them by their granule size and shape. At the inception of growth in the plant cell, all granules have the same shape. Characteristic shapes develop as the granule grows by apposition at its surface.

Contradictory observations have been reported about the relationship between the granule size and gelatinization temperature as previously described (Banks and Greenwood, 1959; Reyes et al., 1965; Stevens and Elton, 1971; Goering et al., 1974; Rockland et al., 1977; Goering, 1978; Dengate et al., 1979; Merca and Juliano, 1981; Wirakartakusumah, 1981).

Evers and Juliano (1976) reported that starch granules of high protein rice had more indentations than those from low protein rice.

This study showed that starch granules cannot be differentiated visually by their size and shape among rices studied, regardless of amylose content, protein content and gelatinization temperature (Figures 31-36). Newrex has the highest amylose content; Century Patna 231 has the lowest amylose content, the highest gelatinization temperature and the lowest protein content; Lemont and Lebonnet has high protein content, Kokuho Rose has low protein content; S-6 has the lowest gelatinization temperature among samples studied (Tables 5 and 8).

Even though mean granule size showed varietal differences statistically (Table 5), Vista with the largest mean granule size (5.69 μm) did not show any visual difference with Bellemont with the smallest mean granule size (4.46 μm) (Figures 29 and 30).

b. Morphological changes of starch granules during heating SEM studies were carried out on the raw starches (25°C) and on starch dispersions heated (65°-95°C at 5°C intervals) at low concentration (2.5%, w/v) for 30 min with minimum stirring. This low starch concentration and minimum stirring minimize the viscosity development and the shear stress placed on granules during heating.

All the samples studied showed similar patterns of morphological changes of starch granules during heating, regardless of variety. The variations were when and to what extent the starch granules deform, which may depend on gelatinization temperature of starch and the ratio

of amylose to amylopectin of starch. Therefore, only micrographs of one representative variety are presented here (Figures 37-44).

At 65°C, very little swelling of starch granules occurred when compared to raw starch granules, even though starch granules absorb water about 2 times of their weight (swelling power = 2.94). Allen et al. (1977) studied tapioca starch granules during gelatinization using the freeze-etching technique. They observed that water infiltrated into the central region of the granule first and formed pockets enclosed by starch, leaving the outer region relatively unaffected until the granule center was markedly altered. Granule swelling occurred as the outer regions of the granules were affected by water. The diameter of the granules increased as both central and outer regions were hydrated and severely altered; the characteristic raw starch granule shape was lost. In agreement with their views, it appears that most of the water infiltrated into starch granules at 65°C might be restricted in the central region of the granule.

At 70°C, the sizes of the granules increased and started to produce thick ridges at the surface as more water was absorbed (swelling power = 5.25). These granules were heated to the midpoint of gelatinization temperature range. These progressive shape changes can also be seen with light microscope. Therefore, these morphological changes cannot be considered as artifacts of freeze-drying. Sterling (1978) postulated that the molecular organization of radially elongated molecules of both the branched and unbranched components is responsible for radial contraction and tangential expansion during gelatinization. In

agreement with his view, it appears that different portions of the granule swell differently depending on the molecular ordering of the starch molecules within the granule.

These ridges became thinner and more numerous and then started to collapse as further heating and hydration weaken the granule structure at 75°C, where all the granules lost their birefringent characteristics.

At 80°C, the granules appeared to go through a transition of melting or softening, which is even more evident at 85°C. During this transition, the swelling power and solubility had been forced to increase rapidly because of loss of granular structure. As temperature was raised to 90°C, the melted granules stretched into threads by tangential expansion and fused together to form a three-dimensional network.

At 95°C, they produced thinner filaments and relatively homogeneous matrix structure, which can hold water inside. Therefore, swelling power at 95°C seems to depend on the water holding capacity of matrix structure as well as the water binding capacity of starch molecules by hydrogen bonding.

The morphological changes observed in rice starch granules are unlike those occurring with lenticular wheat starch (Figure 7), but are more close to those with corn starch (Christianson et al., 1982). At a comparable stage of gelatinization, swelling of lenticular wheat starch granules is maximized in a single direction tangentially, thus, the granules form a flat disk which later folds and refolds until a complex puckered structure is developed above 80°C. On the other hand, corn

starch and rice starch granules swell in an irregular fashion, and develop structures similar to those of puckered wheat starch granules at a much lower temperature. It is apparent from these results that the molecular organization of amylose and amylopectin in the rice starch granule differs from that of the lenticular wheat starch granule and more similar to that of the corn starch granule.

To show the variations in morphological changes among varieties which are related to the differences in swelling power, solubility and amylograph viscosities, representative SEMs of starches with different amylose content and gelatinization temperature range are presented (Table 11 and Figures 45-60).

At 65°C, starch granules of S-6 and Brazos with low gelatinization temperature have already swelled and started to collapse, whereas those of Lebonnet and Century Patna 231 showed little swelling and still maintained their characteristic granular shape (Figures 45-48). Susceptibility of the granule to change as a result of heat and moisture treatment is dependent on the degree of crystallinity of starch granule. Especially, Century Patna 231 showed some extragranular material solubilized from starch granules without any swelling of starch granules themselves. This observation is well correlated with the higher solubility value compared to swelling power of Century Patna 231 at this temperature (Figure 22).

As the temperature was increased to 75°C (Figures 49-52), S-6 and Brazos granules underwent progressive changes in their configuration. By this temperature, however, Lebonnet granules had lost nearly all

Table 11. Amylose content and gelatinization temperature (GT) range of representative varieties

Grain type	Variety	Amylose %, d.b.	GT range[a] °C	BEPT °C
Short	S-6	19.7	55.0-64.7	64.7
Medium	Brazos	15.2	58.0-68.0	68.0
Long	Lebonnet	23.1	60.5-74.7	74.7
Long	Century Patna 231	10.4	65.2-78.8	78.8

[a]2% loss of birefringence - 98% loss of birefringence.

their original shape, which agreed with the loss of their birefringences. In the case of Century Patna 231, about half of the granules still maintained their shape and showed little swelling, but the rest underwent some melting. This observation confirmed that 75°C is about the midpoint of the gelatinization temperature range of Century Patna 231.

This abrupt change in the structure of Century Patna 231 granules is related to the rapid increase of amylograph viscosity (Figures 24 and 25) after all the starch granules swell to collapse. Once starch granules start to lose their original shape and collapse, the rate seems to be affected primarily by amylose content (Figures 53-56 and Figures 61-64). At 85°C, Century Patna 231 granules, with low amylose content, melt faster and produce thinner filaments more quickly than any others. This correlates well with their rapid increase in swelling power (Figure 20), solubility (Figure 21), and amylograph peak viscosity (Figures 24 and 25).

At 95°C, a thinner and more extensive filamentous network structure was developed with increased hydrothermal stress (Figures 57-60). The more fragile and lacy appearance of Century Patna 231 at 95°C explains why, with the shearing force of the amylograph, the swollen granules were broken down more rapidly than those of the other varieties, causing a greater decrease in viscosity (Figures 24 and 25).

The amylograph viscosity curves have been explained by the morphological changes that occurred during heating. Schoch (1969) proposed the theory that viscosity developed as a result of the swollen

granules restricting the flow of the suspension. However, this does not take into account the extensive extragranular starch network which was observed in SEM studies (Miller et al., 1973; Allen et al., 1977; Holmes and Soeldner, 1981). Miller et al. (1973) demonstrated the extent of this extragranular network at low starch concentrations (0.25%) and postulated that it was responsible for viscosity development in low starch concentrations. However, Allen et al. (1977) indicated that neither of the latter two theories was sufficient to explain the situation in higher starch concentrations. They postulated that the development of viscosity was a result of the interaction of the swollen granules and the extragranular network, since the final image at peak viscosity does not show any identifiable granules. This study supports the result of Allen et al. (1977).

2. Milled rice

a. Ultrastructure of milled rice grain The starchy endosperm consists of thin walled parenchyma cells which are elongated radially on cross-sectional view and filled with compound starch granules and some protein bodies (Figures 69 and 70).

Little and Dawson (1960) observed the thin section of rice grain with a light microscope and indicated that cells of the center were nearly isodiametric and small in size from 45 X 50 to 80 X 105 μm; the cells toward the flattened or lateral sides were either isodiametric or slightly elongated in shape; those in the dorsiventral direction were greatly elongated; and cells adjacent to the periphery were smaller and

many were flattened radially. Same observations were made from the transversely fractured surface of rice grain with SEM in this study.

Two types of cleavage planes were present at the fractured surface: intercellular, in which the cleavage planes coincided with cell boundaries; and intracellular, in which the cleavage planes occurred through cells in directions independent of cell boundaries. The nature of compound starch granules was seen through intracellular cleavage. The two types of planes were seen in all the grains studied but to different degrees. Generally, in short- and medium-grain types, cleavage occurred mainly along the cell boundaries but some intracellular cleavage planes were noted in both the central and peripheral regions; in long-grain type, intracellular cleavages were dominant for the entire fracture surface. In Japonica rices, which are similar to U.S. short- and medium-grain rices, the core and the peripheral cells are reported to be softer than the rest of the endosperm (Evers and Juliano, 1976; Nagato and Kono cited in Juliano and Bechtel, 1985). However, the mode of cleavage seems to be related to the state of cell packing in endosperm rather than the hardness distribution.

The fracture faces of crumbly or soft-endosperm nonwaxy rice showed mainly intercellular cleavage. The cell boundaries in crumbly rices were relatively rough in appearance, indicating the presence of less matrix material between compound starch granules and parenchyma cells (Figure 71). The cell walls were composed of cellulose microfibrils, a matrix phase of hemicellulose, pectic substances and 3% protein

(Juliano, 1985a). In the center, individual starch granules were shown through intracellular cleavage and the loose packing among individual starch granules was most marked.

The fracture faces of hard-endosperm nonwaxy rice, mostly long-grain type, showed mainly intracellular cleavage. The cell boundaries were smooth, and angular and starch granules in parenchyma cells compact, and the demarcation between individual granules and compound granules were not apparent (Figure 72).

In the endosperm, the compound nature of the rice starch granule was evident and well defined (Figures 73 and 74). Generally, compound granules were polygonal in shape and were composed of small individual starch granules with intact walls, shown when the compound granules were fractured by pressure. Juliano (1972a), reviewing earlier work of others, reported that rice starch granules are polygonal and composed with the structure of a pentagonal dodecahedron, and suggested that the polyhedral form might be caused by the compression of starch granules during development. However, the extent of compression seems to be dependent upon the state of packing. For example, compound granules from loosely-packed rices were less polygonal and rather more round than those from compactly-packed rices. This difference in packing state affected the shape of compound granule markedly, and also that of individual granules; some of the starch granules from loosely-packed rices had one or more faces well rounded.

Starch granules in the peripheral cells of the endosperm were smaller than those in the major central portion, confirming previous

observations made by Little and Dawson (1960). The compound granules in the peripheral cells were separated by electron-dense proteinaceous material (Little and Dawson, 1960; Juliano, 1985a), whereas those in the central portion were closely packed without any apparent intervening material (Figures 75 and 76).

In the peripheral cells of endosperm, the presence of protein bodies was evident (Figures 77 and 78). Bechtel and Pomeranz (1978b) found three types of membrane-bound protein bodies in the subaleurone region, large spherical, small spherical and crystalline protein bodies, but only large spherical bodies in the central region of endosperm were seen using transmission electron microscopy. But all the protein bodies are shown as spherical and types of protein bodies cannot be differentiated from these micrographs because only the surface characteristics are shown in SEM.

Some of the individual starch granules had indentations on their surface (Figures 29-36 and Figures 77 and 78). These indentations were probably from pressure of protein bodies on the developing starch granules (Rosario et al., 1968; Evers and Juliano, 1976). Robutti et al. (1974) suggested that the dents on the surface of corn starch granules result from pressure of protein bodies.

b. Changes in ultrastructure during heating All the rice samples studied showed a similar pattern of structural changes during heating, regardless of variety. The variations were dependent upon the rate of water and heat diffusion, properties of starch (amylose content and BEPT) and protein content of the milled rice. Progressive changes

from the periphery toward the center of the endosperm were evident in both sticky and less sticky rices (Figures 79-86).

In the central portion of crumbly rices, where loose packing was evident, the cell matrix material is solubilized and loosened up, resulting in the separation between compound granules and of compound granules into individual granules during soaking in water for 30 min at room temperature (Figures 87 and 88). Therefore, the soaking process assists the gelatinization of starch and reduces the cooking time.

The same effect as soaking can be seen during cooking. The time until the temperature of the cooking water reaches gelatinization temperature of starch will serve as soaking time at elevated temperature. It is well acknowledged that water of high temperature decreases the soaking time significantly (Gariboldi, 1974). The water diffusion rate seems to be affected greatly by the packing state of rice grain during this time lapse. At the same temperature and time, water diffused into the central portion more easily in loosely packed rices than in compact ones (Figures 89 and 90). After starch absorbed enough water and heat to gelatinize, the changes in the ultrastructure of cooked grain might be affected by starch properties - i.e., amylose content and BEPT.

One representative sample is presented here to show more in detail the in situ gelatinization and swelling of starch during heating of various rice samples studied (Figures 91-93). Unlike the starch suspensions with excess water, amount of water and space for gelatinization and further swelling are limited in rice grains. The

parenchyma cell and starches in the central region of the grain underwent little change, even though the modification was extensive within about one-fourth to one-third the distance from the outer layer toward the center of grain. As water and heat penetrated into this region with temperature increase, the cell matrix started to loosen up, admitting enough water and heat for gelatinization of starch. Above the gelatinization temperature, starch granules gradually started to gelatinize and swell further without losing their shape. At this time, cell matrix materials and protein bodies have not been affected by heat and water even though the starch granules have already started to gelatinize (Figures 94 and 95). Bechtel and Pomeranz (1980) observed a similar pattern of structural changes in parboiled rice where starch in the central endosperm may be modified little, if at all, while the protein bodies in the endosperm were apparently not affected; the structure and the crystal lattice and rings of the protein bodies were unchanged, according to examination by TEM. As more water is absorbed, the size of parenchyma cells increased markedly and starch granules lost their original shape and structure. The resistance to loss of structure may be dependent on amylose content, as previously shown in starch suspensions (Figures 62-64).

After being heated for 10 min at 95°C, starch granules were fully gelatinized and milled rice grains were fully cooked (Figures 96-98). The fractured surface showed starch gelatinization <u>in situ</u> was somewhat limited inside the cell and cell boundaries were still maintained (Figure 97 and 98). The enlarged view of the fully cooked rice grain

showed the homogeneous gel matrix structure with cell boundaries (Figure 97 and 98).

Separation of the subaleurone layer from starchy endosperm occurred during heating (Figures 99 and 100). Once this outermost layer of endosperm was separated from starchy endosperm and even removed, water and heat penetration and solids lost in cooking-water could be increased rapidly, and this assisted gelatinization of starches to a great extent. This fragmentation of the outer layers of grain seems to be greater in low-protein rices (Figures 101 and 102). This suggested that protein may act as a barrier for water diffusion from the subaleurone layer toward the center of starchy endosperm. Increase in solids lost in cooking-water by separation of the subaleurone layer and/or fragmentation may affect the stickiness of cooked rice. This is supported by the correlation coefficients between solids lost in cooking-water at 95°C and protein content ($r=-0.68^{**}$), solids lost in cooking-water at 95°C and stickiness ($r=0.62^{*}$), and protein content and stickiness ($r=-0.72^{**}$) (Table 10).

So far, the effect of the physical structure of milled rice and the role of protein on the cooking and eating qualities of rice have been underestimated. This study suggests that differences in cooking and eating qualities of rice seem to be due to several factors: endosperm cell arrangement and protein content of milled rice, and gelatinization temperature range and amylose content of starch.

V. CONCLUSIONS

A. Effect of the Physicochemical Properties of Rice Starch and Milled Rice on the Cooking and Eating Qualities of Rice

The physicochemical properties of isolated rice starch and milled rice from twelve varieties of nonwaxy rice with diverse and extreme characteristics were examined to obtain a clearer understanding of causes of cooking and eating qualities of rice.

The stickiness of cooked rice was moderately correlated with amylose content ($r=-0.58^{*}$), but was relatively more correlated with protein content ($r=-0.72^{**}$) among nonwaxy rices, whose amylose content ranged from 10.4 to 27.8%. Amylograph breakdown ($r=0.87^{**}$), setback ($r=-0.93^{**}$) and consistency ($r=-0.91^{**}$) values of milled rice flour (10%, as-is basis) showed strong correlation with cooked rice stickiness, and these can be used as good predictors of cooked rice stickiness, especially among nonwaxy rices with narrow ranges of amylose content.

Starch granules are generally considered as spherocrystals with amorphous and crystalline regions. Susceptibility of the granule to gelatinization is dependent mainly on the degree of crystallinity, as indicated by the significant positive correlation between BEPT and the relative crystallinity ($r=0.67^{**}$). Granule size distribution does not affect the gelatinization temperature range, nor does amylose content.

B. Morphological Changes of Rice Starch Granules during Heating

Rice starch granules from the twelve varieties of nonwaxy rice were dispersed in water at 2.5% w/v concentration and heated for 30 min at a certain temperature in the range of 65°-95°C. Morphological changes of starch granule were examined by scanning electron microscopy (SEM).

Rice starch granules proceed through a similar pattern of progressive morphological changes during heating, regardless of variety. These morphological changes differ from those observed in the lenticular granules of wheat starch (Bowler et al., 1980) and are similar to those in the corn starch granules (Christianson et al., 1982). This may indicate that granule shape reflects the molecular organization of amylose and amylopectin chains within the granule.

Rice starch granules begin to swell radially below their gelatinization temperature, and then undergo radial contraction and random tangential expansion to form complex structures while within the gelatinization temperature range. When the temperature reaches the birefringence end-point temperature (BEPT) of the starch, the granules have undergone swelling to many times their original size and have lost their original molecular orientation. At higher temperatures, starch granules soften and melt into thin flat disks, and then stretch into thin filaments to form three-dimensional networks.

These progressive morphological changes are reflected in the changes of swelling power, solubility and amylograph viscosity of starch. During the transition of melting or softening, rapid increases

of swelling power, solubility and amylograph viscosity take place. Starches yielding a thinner and more extensive filamentous network, like Century Patna 231, are characterized by very high swelling power and high amylograph peak viscosity. They are also less resistant to amylograph breakdown and hence exhibit significant viscosity decreases after reaching the maximum value.

The time of loss of granular structure of starch during initial swelling occurs throughout the gelatinization temperature range. The ratio of amylose to amylopectin is largely responsible for the rate of melting or softening and the fineness of a three-dimensional filamentous network during the latter stage of swelling. Therefore, both the gelatinization temperature range and amylose content of starch affect the rate of cooking, and amylose content of starch affects the final texture of cooked starch paste.

C. Structural Changes of Milled Rice during Heating

Milled rice grains were heated in large excess water at the rate of 1.5°C/min in the temperature range of 65°-95°C and the structural changes were observed by scanning electron microscopy (SEM).

Milled rice grains undergo a similar pattern of structural changes, regardless of variety. These structural changes occur from the periphery toward the center of the endosperm along the direction of water diffusion.

Differences in cell arrangement in the endosperm of different varieties were observed; some had loosely packed endosperm with many air

spaces and a crumbly appearance, whereas others had compactly packed endosperm with a smooth and angular appearance. The more extensive separation and fragmentation of the outermost layers of the endosperm were observed in low-protein rices. The rate of water diffusion, therefore, appears to be dependent on the cell arrangement in the endosperm and the protein content of milled rice. Once water and heat reach the starch granules, the rate of in situ gelatinization of starches appears to be dependent on their own gelatinization temperature range and amylose content as demonstrated with the isolated starch suspensions. Protein acts as a barrier for the swelling of starch and water diffusion in two ways: 1) by encasing starch granules in the starchy endosperm, and 2) by forming a barrier between the subaleurone layer and the starchy endosperm. Therefore, the separation and fragmentation of the outermost layers of the endosperm occurred more easily in the low-protein content rices, and was associated with increases of solids lost in cooking-water at 95°C and stickiness of cooked rice.

From the analysis of physicochemical properties of rice starch and milled rice and the SEM study of the structural changes of rice starch and milled rice whose amylose content ranges from 10.4 to 27.8%, it is concluded that protein content and endosperm cell arrangement of milled rice, along with amylose content and gelatinization temperature type of starch, are important factors that affect cooking and eating qualities of rice.

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VIII. APPENDIX A: ANALYSIS OF VARIANCE

Analysis of variance for amylose content data

Source	DF	Sum of squares	Mean square	F
Variety	11	826.82	75.17	1503.40**
Error	21	1.13	0.05	
Total	32	827.95		

Analysis of variance for protein content data

Source	DF	Sum of squares	Mean square	F
Variety	11	36.17	3.29	329.00**
Error	22	0.18	0.01	
Total	33	36.35		

Analysis of variance for BEPT data

Source	DF	Sum of squares	Mean square	F
Variety	11	580.39	52.76	164.88**
Error	24	7.57	0.32	
Total	35	587.96		

**$\alpha = 0.01$.

Analysis of variance for granule size data

Source	DF	Sum of squares	Mean square	F
Variety	11	135.27	12.30	9.76**
Error	1375	1738.59	1.26	
Total	1386	1873.86		

Analysis of variance for crude fat data

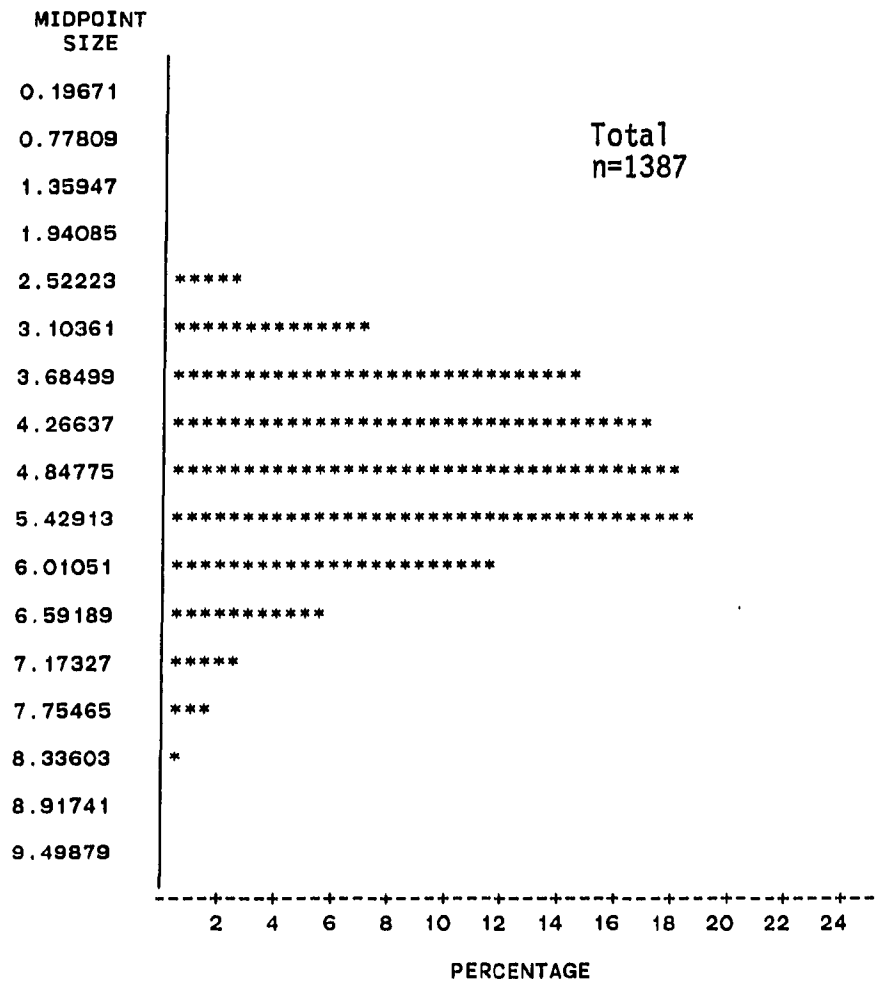
Source	DF	Sum of squares	Mean square	F
Variety	11	0.0550	0.0050	8.33**
Error	24	0.0132	0.0006	
Total	35			

Analysis of variance for cooked rice stickiness data

Source	DF	Sum of squares	Mean square	F
Variety	11	16354.17	1486.74	22.80**
Error	31	2021.72	65.22	
Total	42			

**α = 0.01.

IX. APPENDIX B: HISTOGRAM OF GRANULE SIZE DISTRIBUTION



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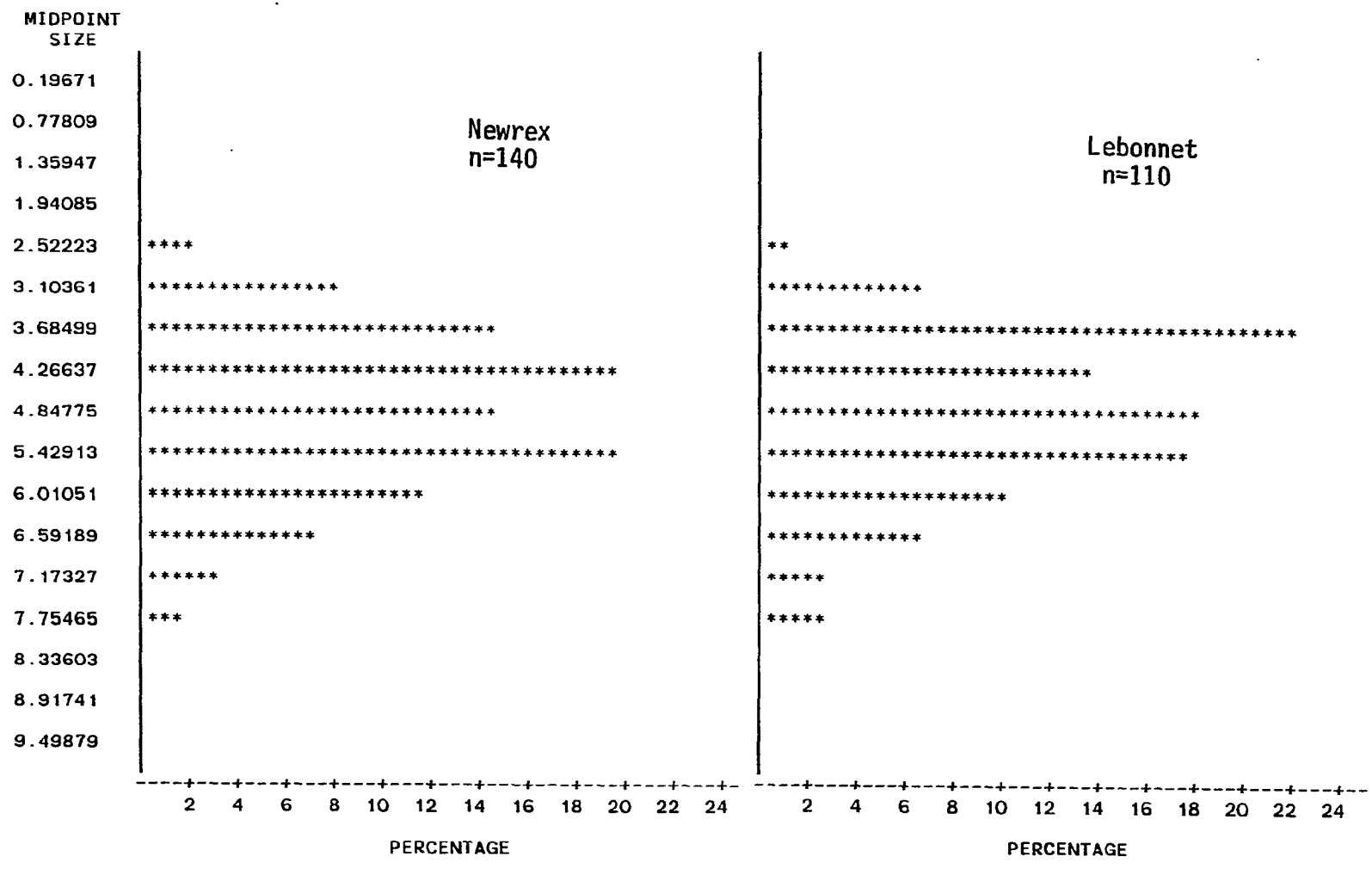

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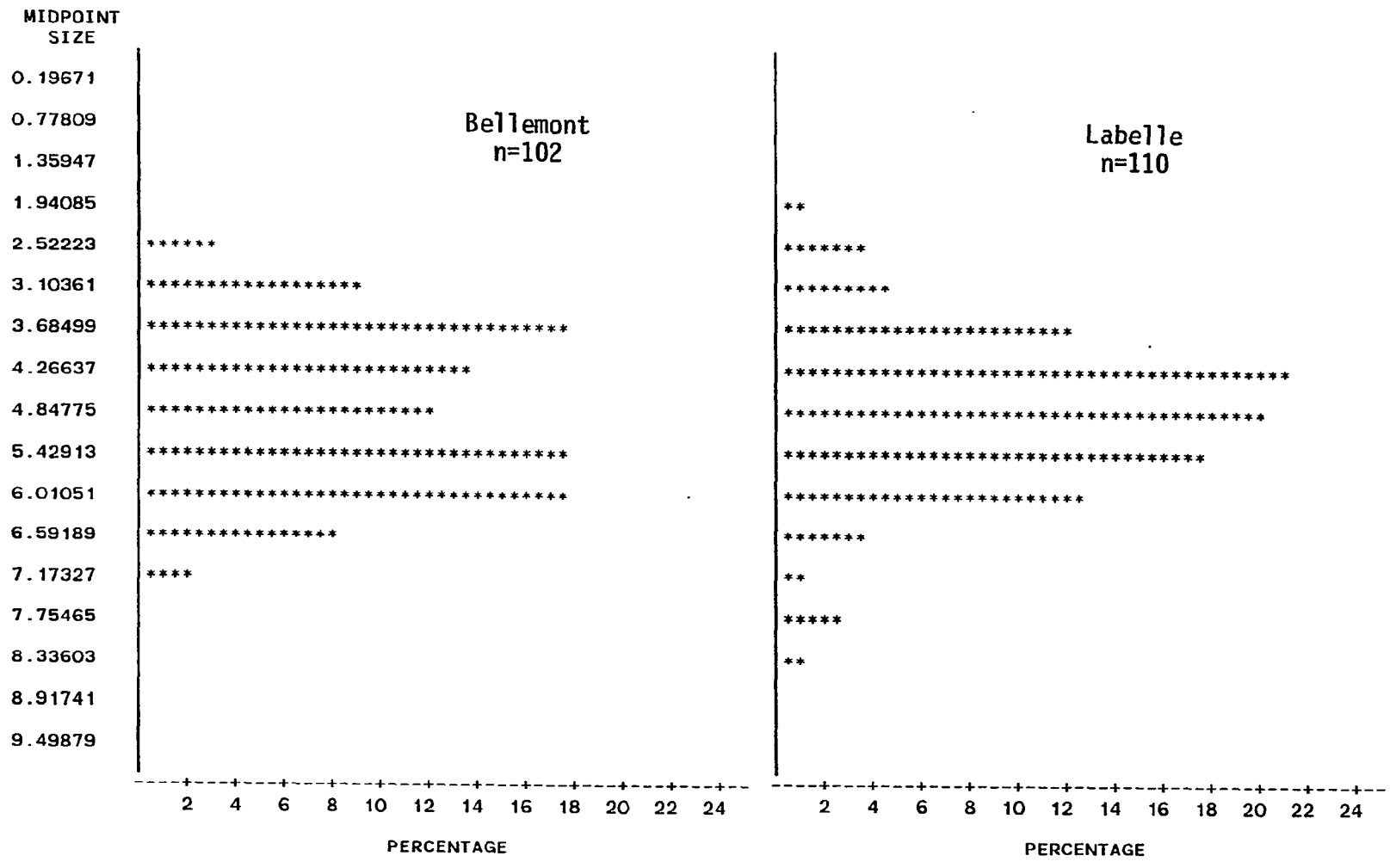

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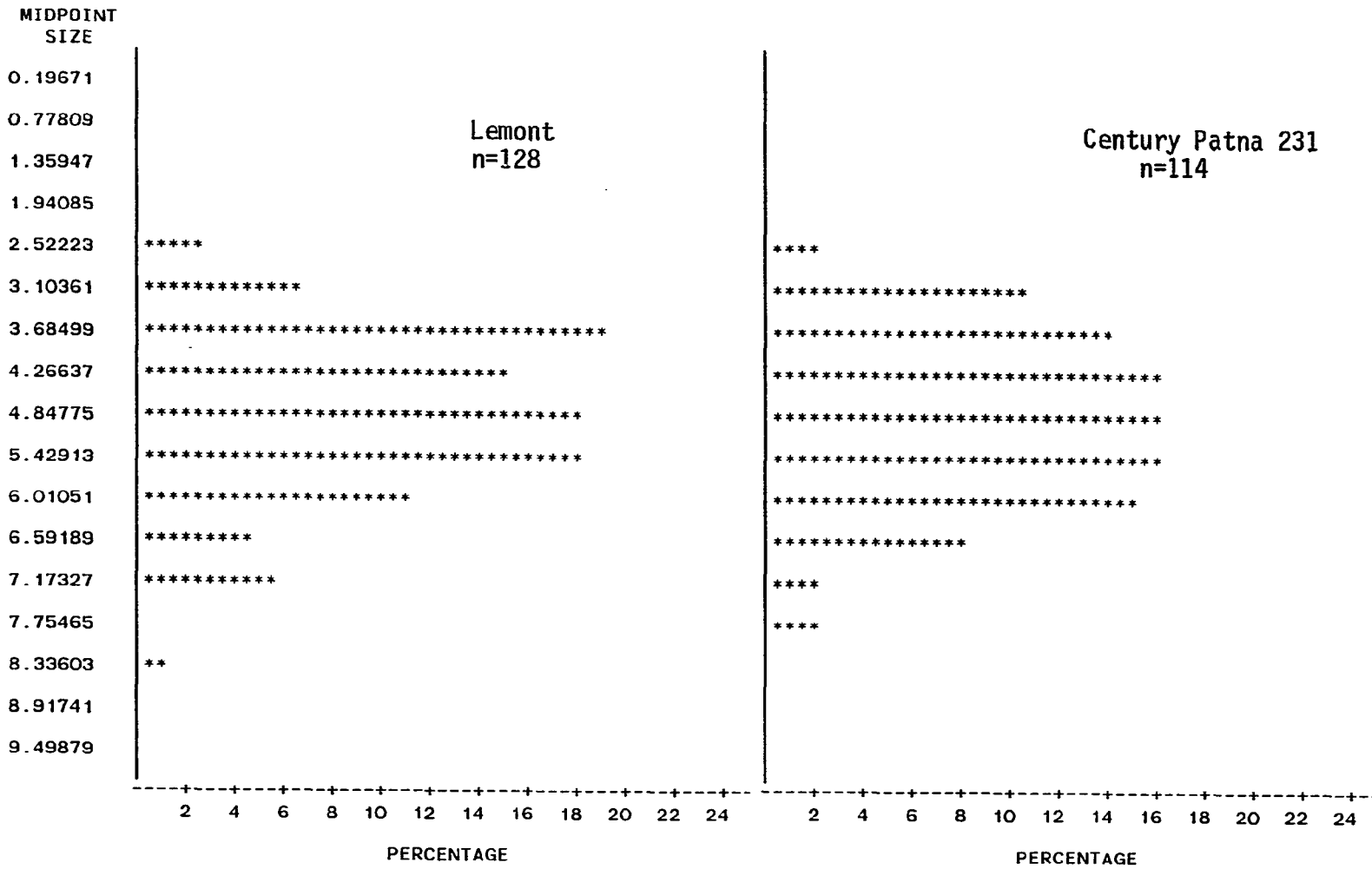

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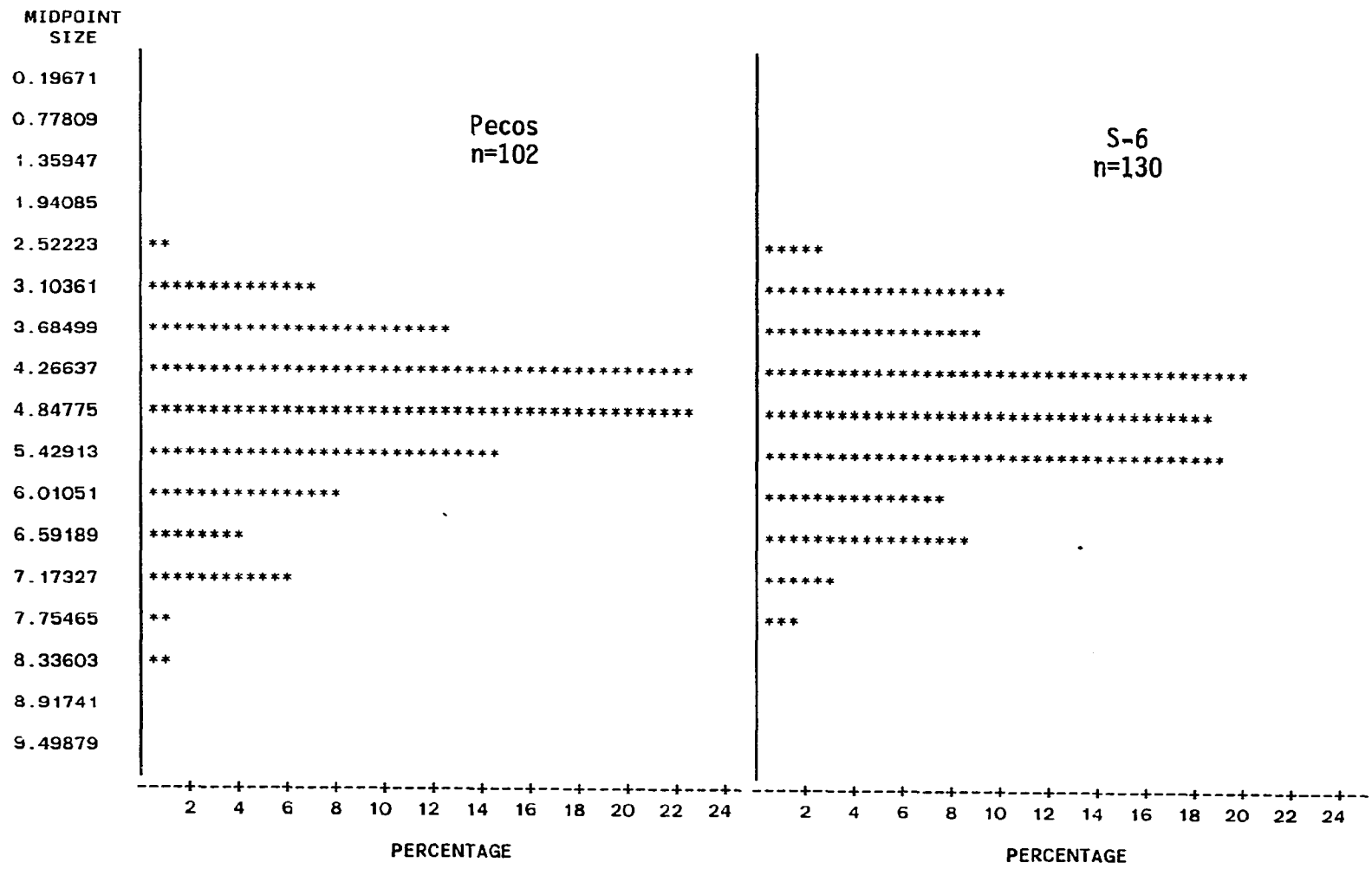

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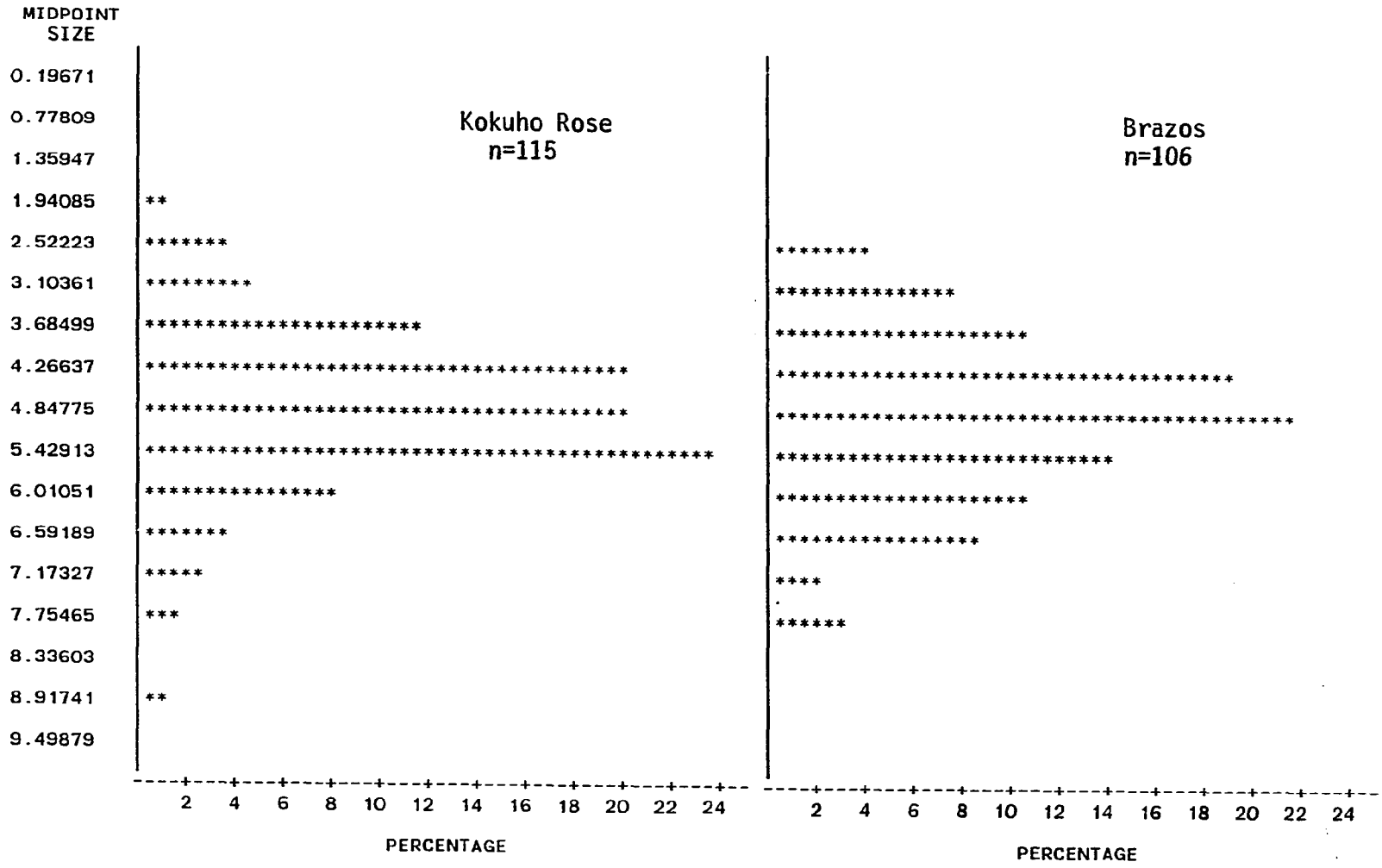

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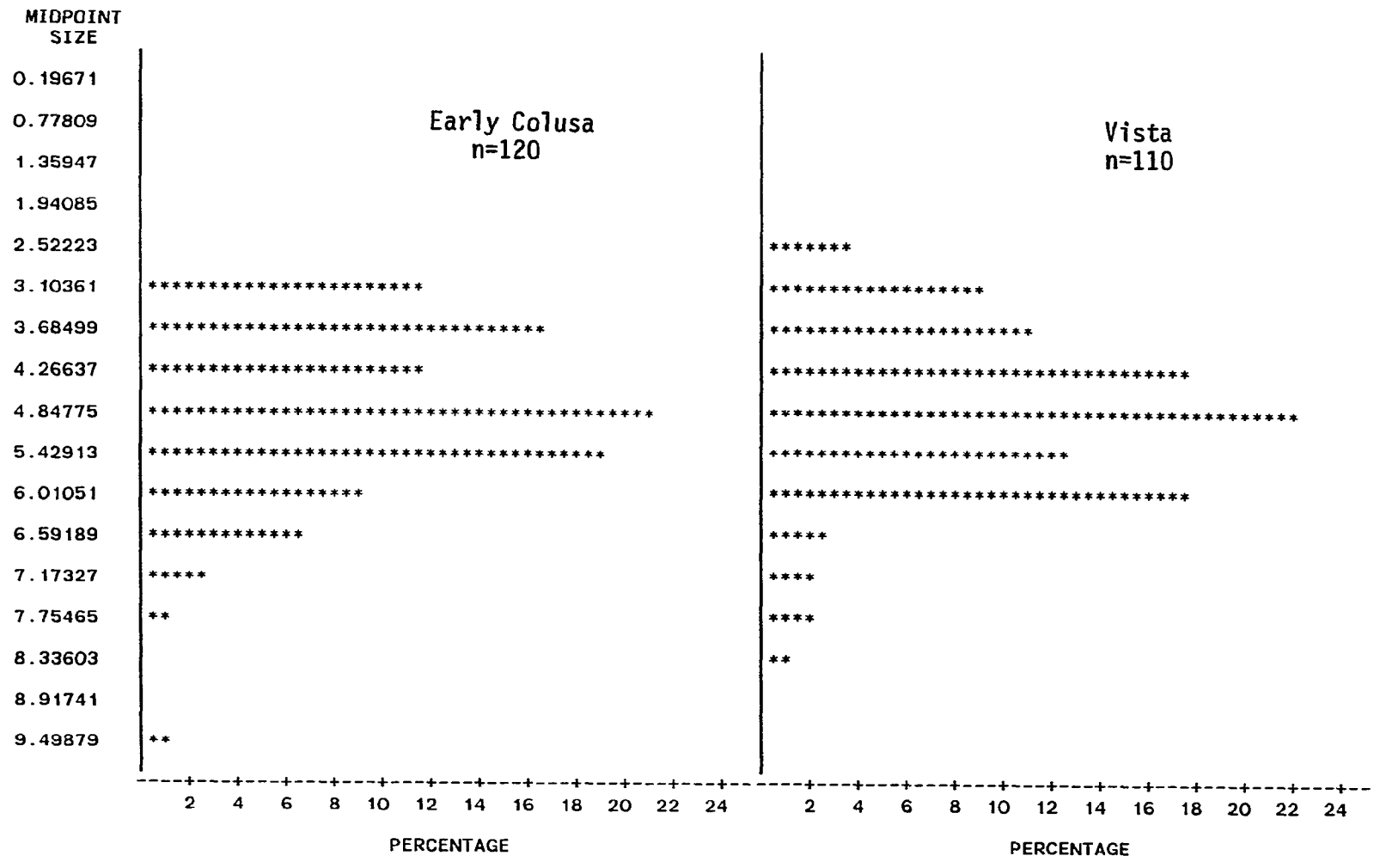

Based on standardized data
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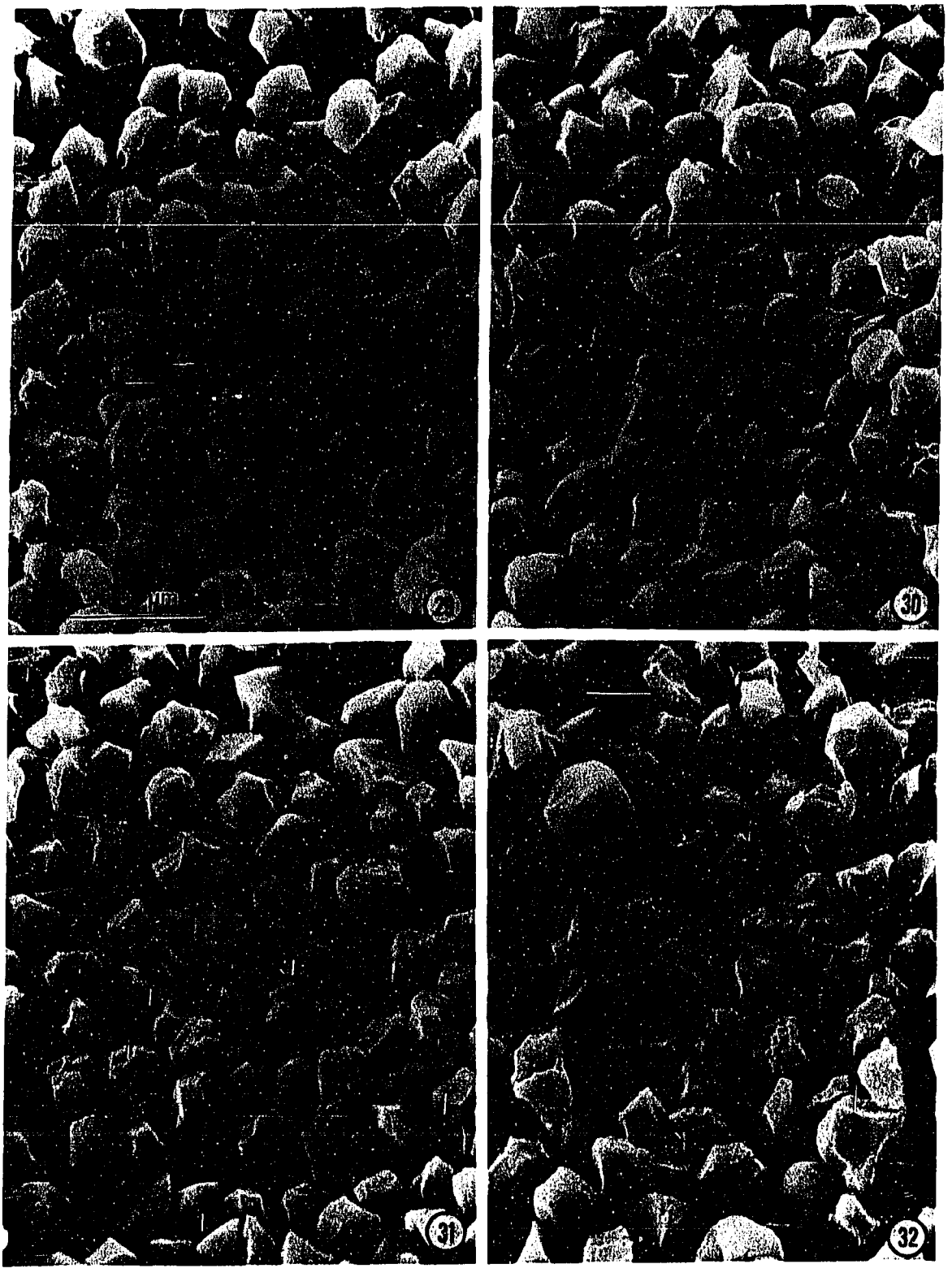
X. APPENDIX C: SCANNING ELECTRON MICROGRAPHS

keys to symbols

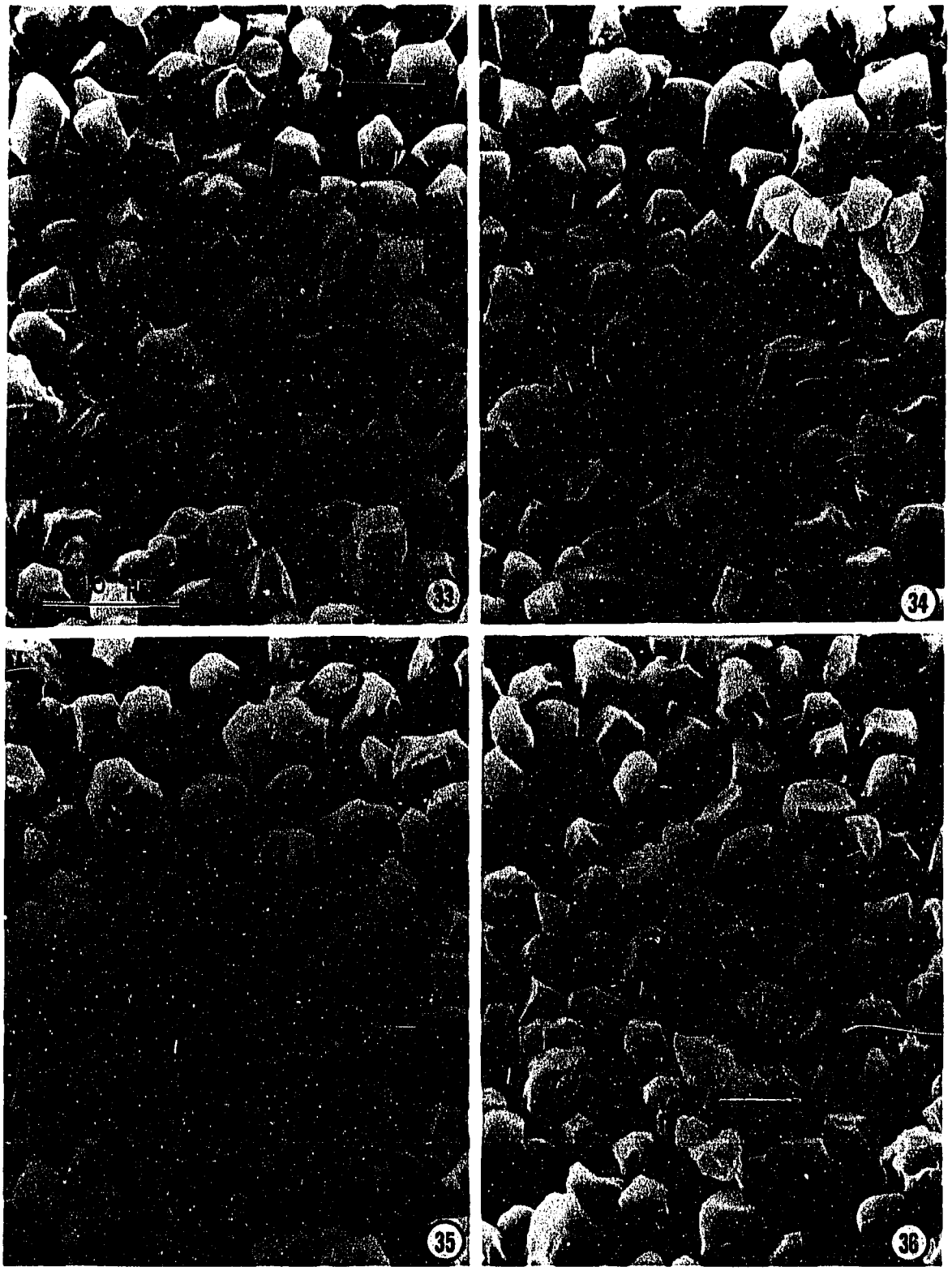
CM	Cell matrix
CS	Compound starch granule
D	Dorsal side
DM	Demarcation
E	Starchy endosperm
I	Indentation
IS	Individual starch granule
L	Lateral side
M	Missing individual starch granule
P	Protein body
S	Subaleurone layer
V	Ventral side

Figures 29-32. Sizes and shapes of rice starch granules

29. Vista has the largest mean granule size (5.69 μm).
30. Bellemont has the smallest mean granule size (4.46 μm).
31. Newrex has the highest amylose content (27.8%).
32. Century Patna 231 has the lowest amylose content (10.4%), the highest BEPT (78.8°C) and the lowest protein content (6.68%).


30
31
32

Figures 33-36. Sizes and shapes of rice starch granules
33. Lemont has the highest protein content (10.48%).
34. Lebonnet has high protein content (10.16%).
35. Kokuho Rose has low protein content (7.12%).
36. S-6 has the lowest BEPT (64.7°C).


33
34
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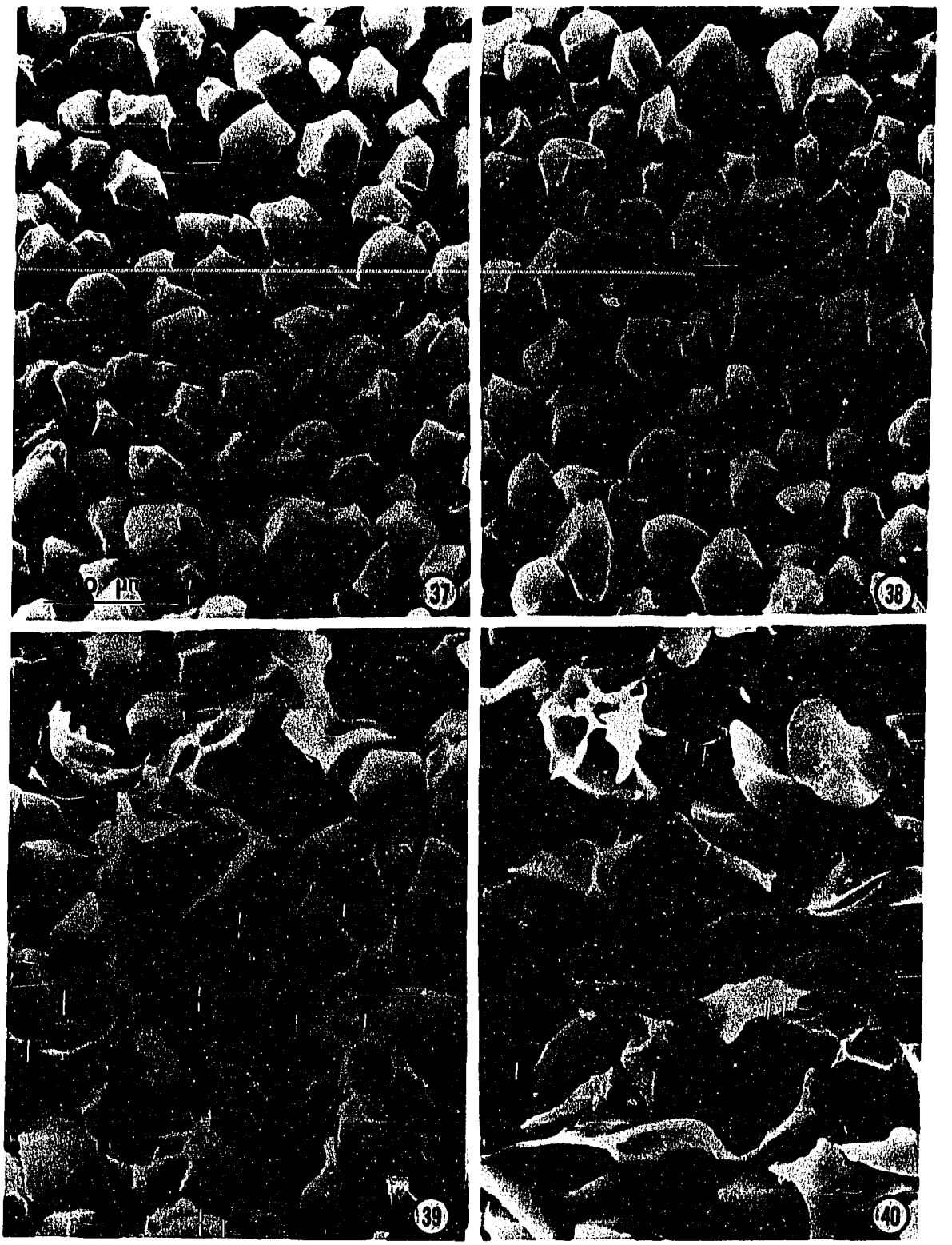
36

Figures 37-40. Representative morphological changes of rice starch granules during heating (Labelle, amylose content = 20.5%, GT range = 59.3°-75.8°C; 2.5% (w/v), 30 min)
37. 25°C
38. 65°C
39. 70°C
40. 75°C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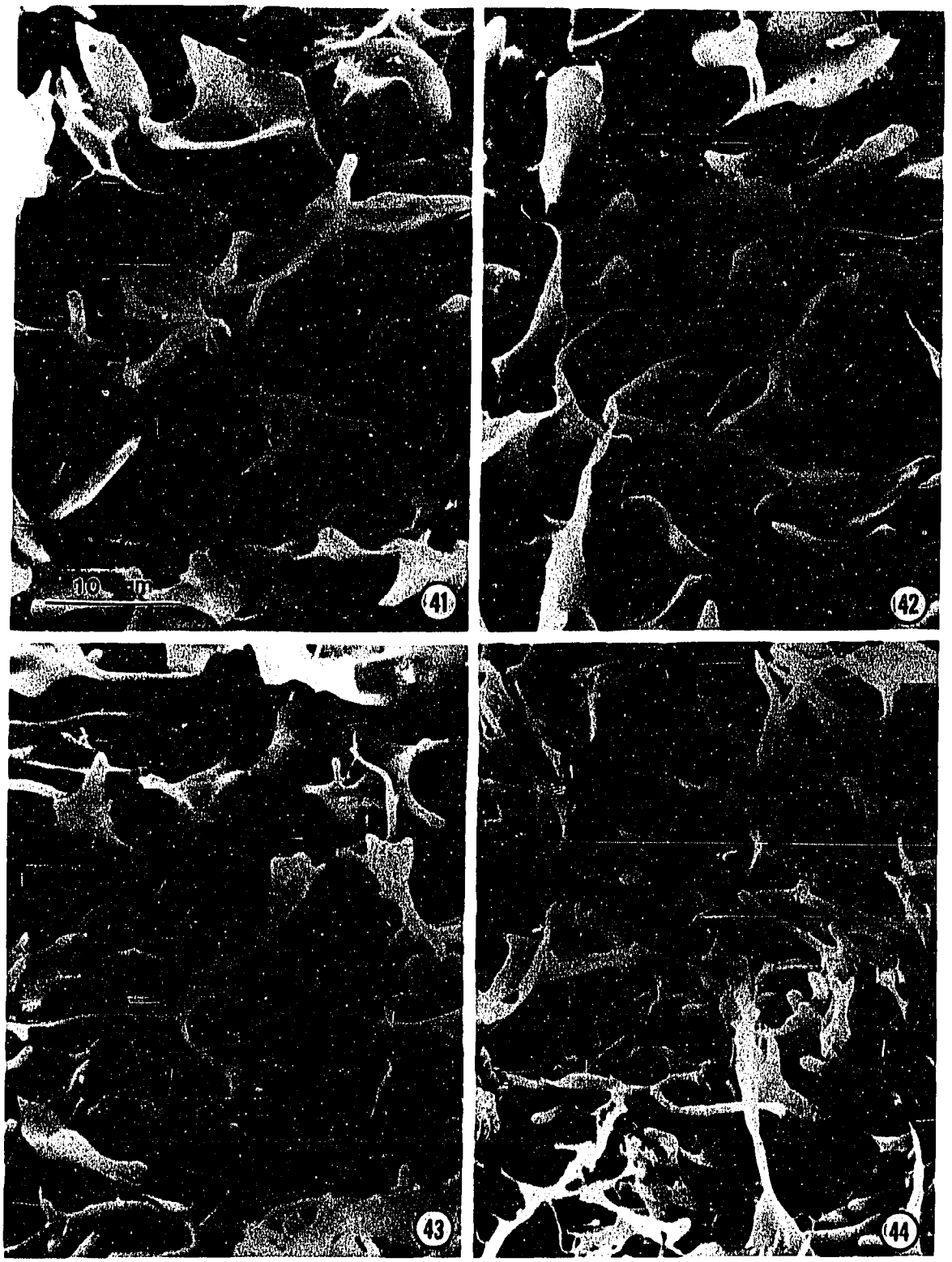
Figures 41-44. Representative morphological changes of rice starch granules during heating (Labelle, amylose content = 20.5%, GT range = 59.3°-75.8°C; 2.5% (w/v), 30 min)
41. 80°C
42. 85°C
43. 90°C
44. 95°C


10 μ
41
42
43
44

Figures 45-48. Representative morphological changes of starch granules at 65°C from different varieties of rice (2.5% (w/v), 30 min)

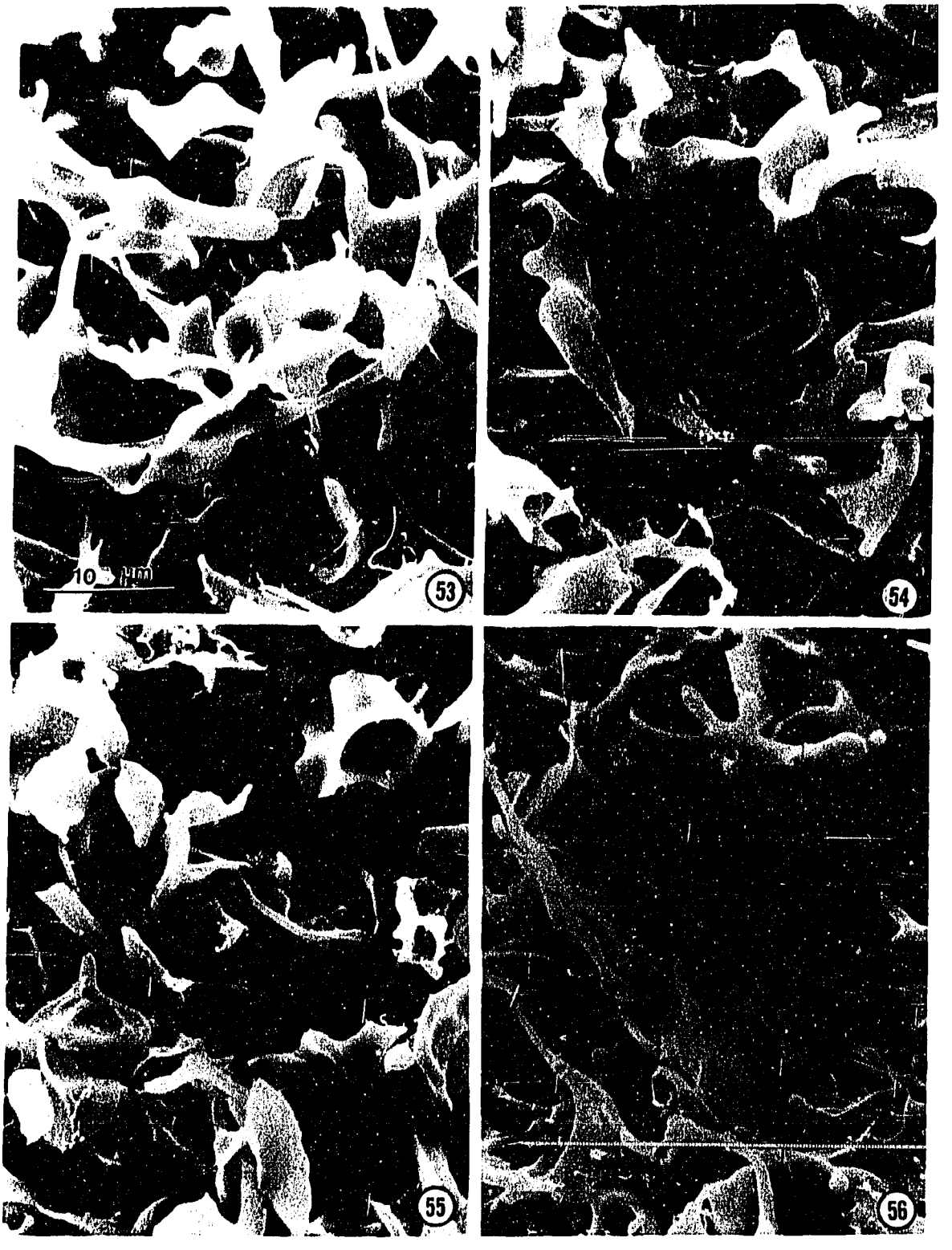
45. S-6: amylose content = 19.7%, GT range = 55.0°-64.7°C
46. Brazos: amylose content = 15.2%, GT range = 58.0°-68.0°C
47. Lebonnet: amylose content = 23.1%, GT range = 60.5°-74.7°C
48. Century Patna 231: amylose content = 10.4%, GT range = 65.2°-78.8°C


45
46
47
48

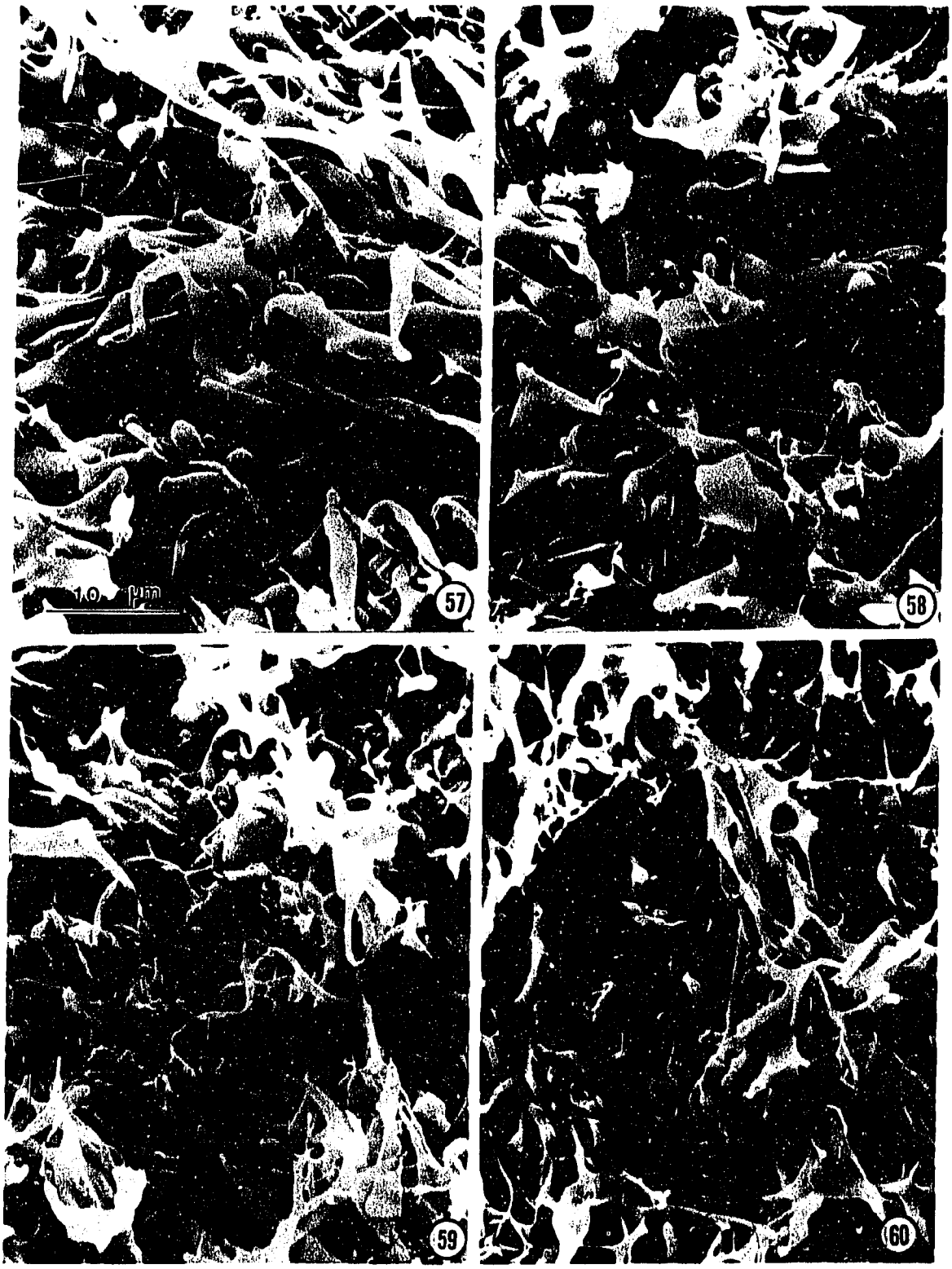
Figures 49-52. Representative morphological changes of starch granules at 75°C from different varieties of rice (2.5% (w/v), 30 min)
49. S-6
50. Brazos
51. Lebonnet
52. Century Patna 231


10 µm
49
50
51
52

Figures 53-56. Representative morphological changes of starch granules at 85°C from different varieties of rice (2.5% (w/v), 30 min)
53. S-6
54. Brazos
55. Lebonnet
56. Century Patna 231

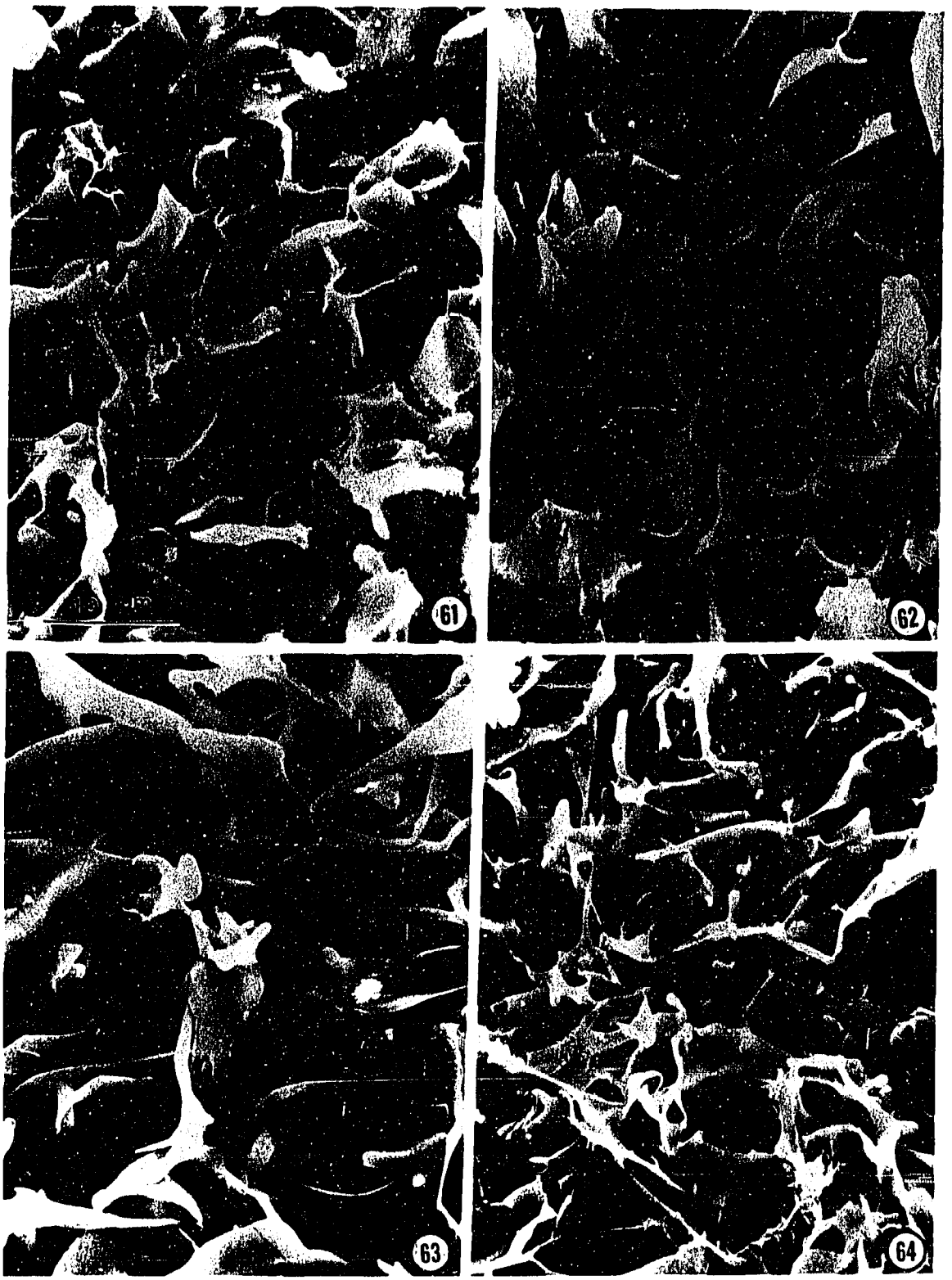

10 µm
53
54
55
56

Figures 57-60. Representative morphological changes of starch granules at 95°C from different varieties of rice (2.5% (w/v), 30 min)
57. S-6
58. Brazos
59. Lebonnet
60. Century Patna 231

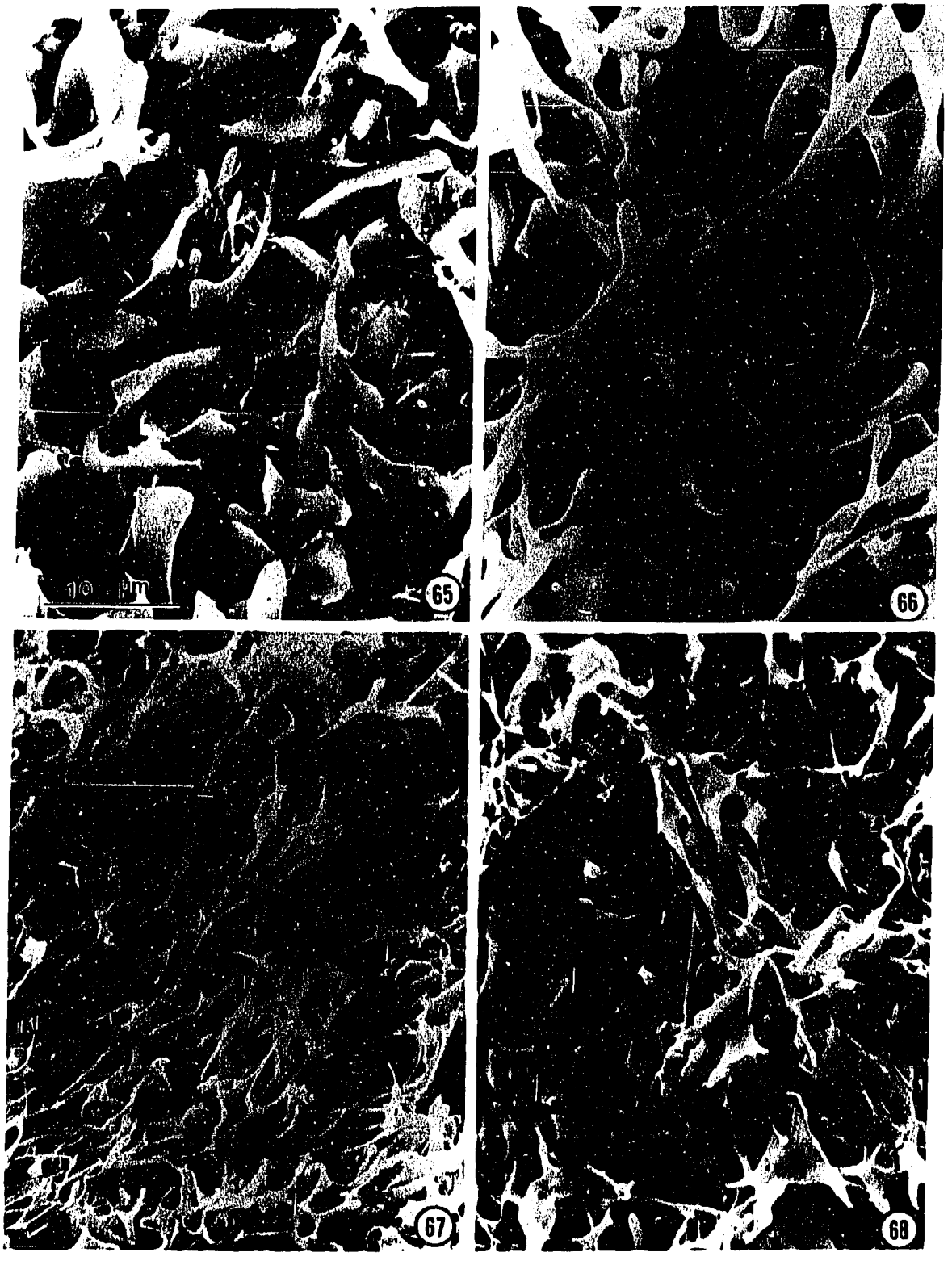

1.0 μm
57
58
59
60

Figures 61-64. Effect of amylose content on the morphological changes of starch granules at 80° and 90°C (2.5% (w/v), 30 min)

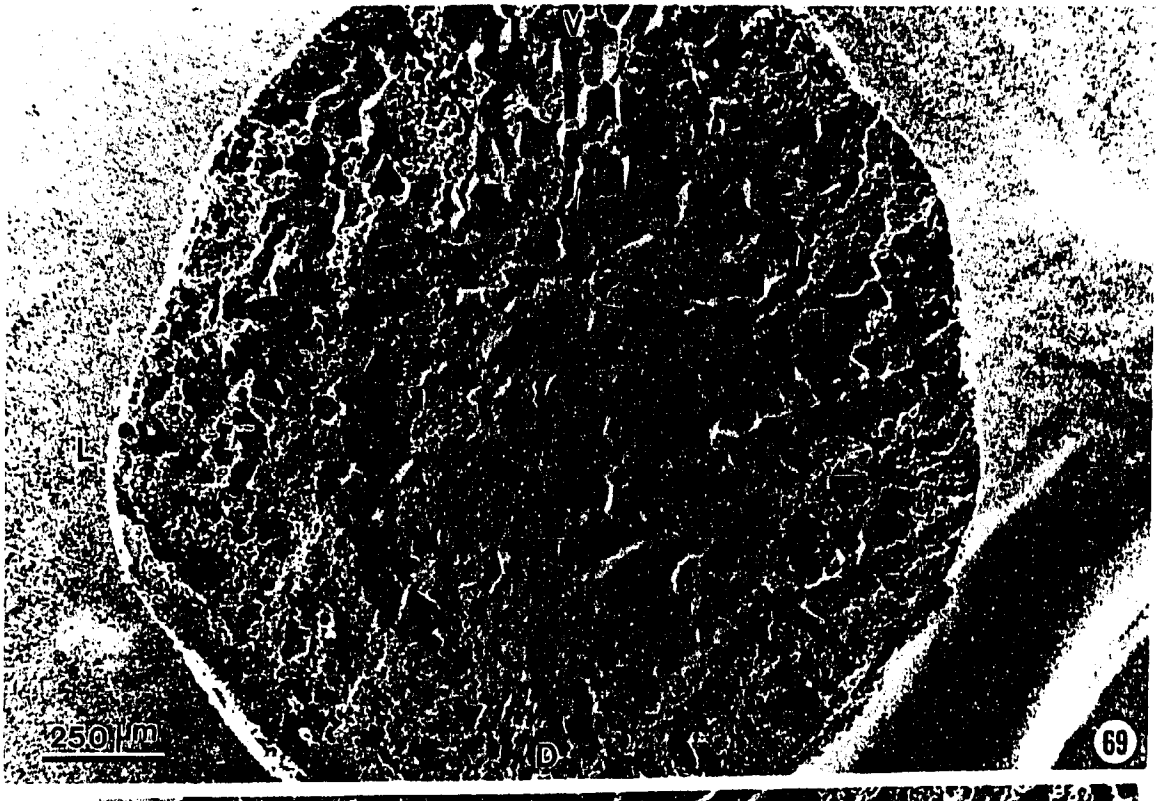
61. Newrex: amylose content = 27.8%, 80°C
62. Newrex: amylose content = 27.8%, 90°C
63. Vista: amylose content = 11.2%, 80°C
64. Vista: amylose content = 11.2%, 90°C

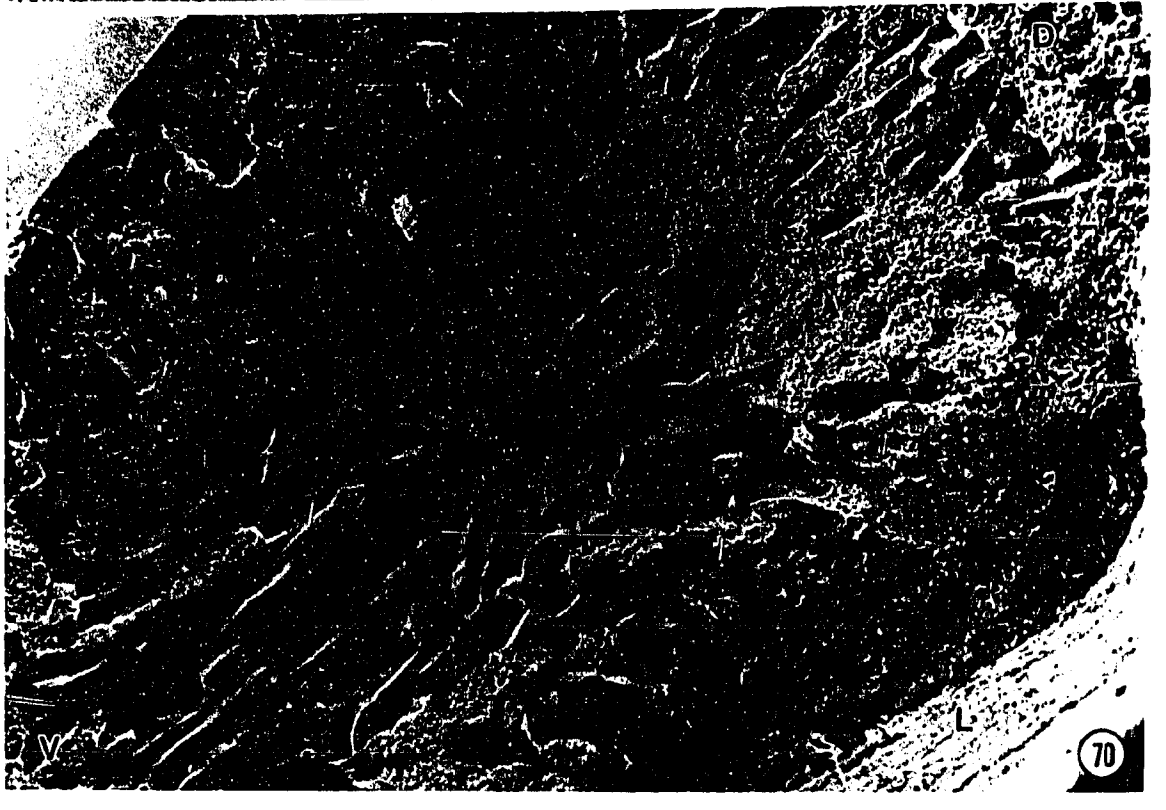

61
62
63
64

Figures 65-68. Correlation between morphological changes of starch granules and swelling powers (SP) at 95°C (2.5% (w/v), 30 min)
65. Newrex (SP=19.65)
66. Early Colusa (SP=23.00)
67. Vista (SP=40.31)
68. Century Patna 231 (SP=53.96)

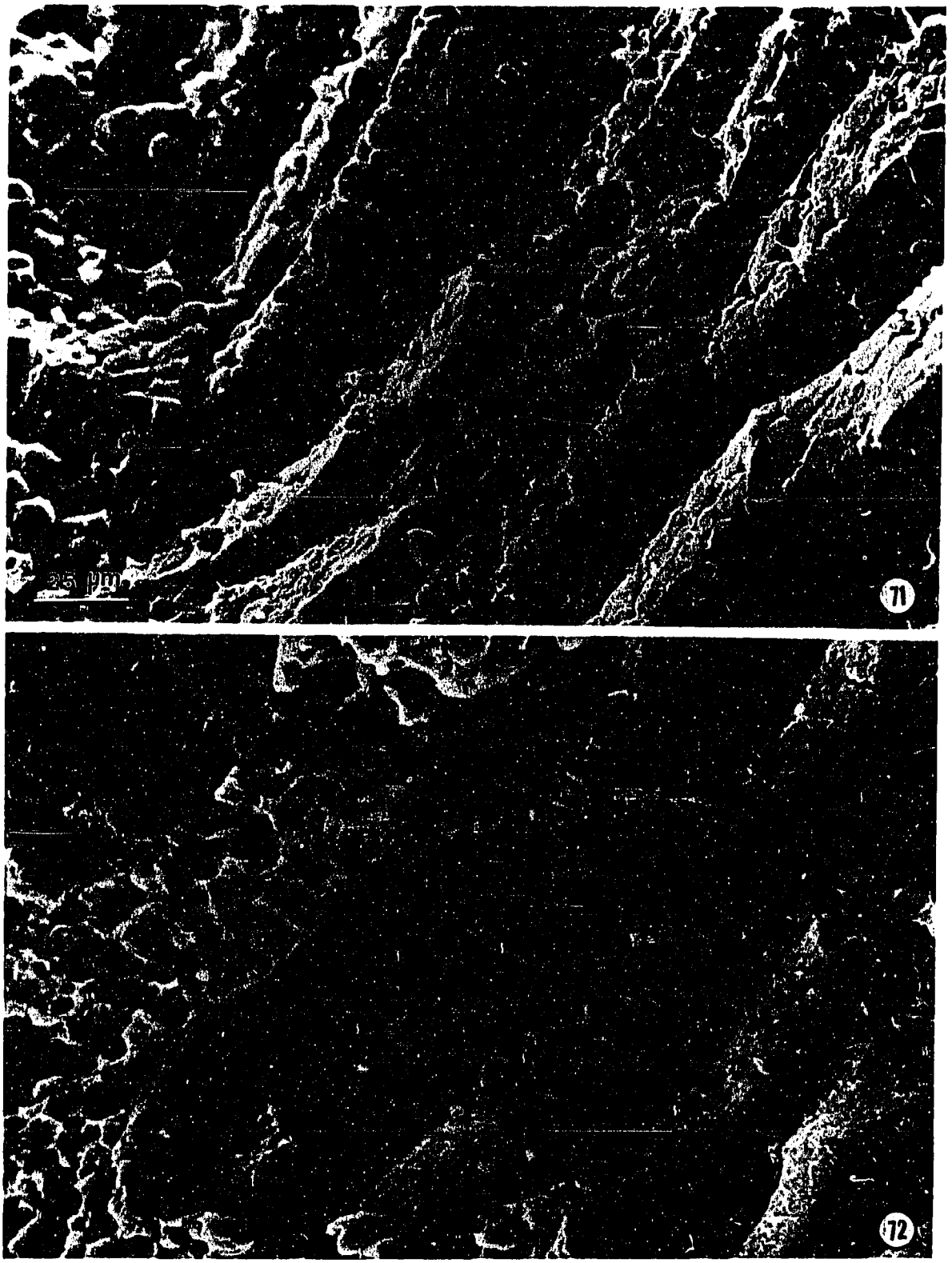

10 µm
65
66
67
68

Figures 69-70. Entire fracture face of rice grain of long- and short-grain types, showing variation in cell arrangement
69. Newrex (Long)
70. S-6 (Short)


V
L
250 µm
D
69

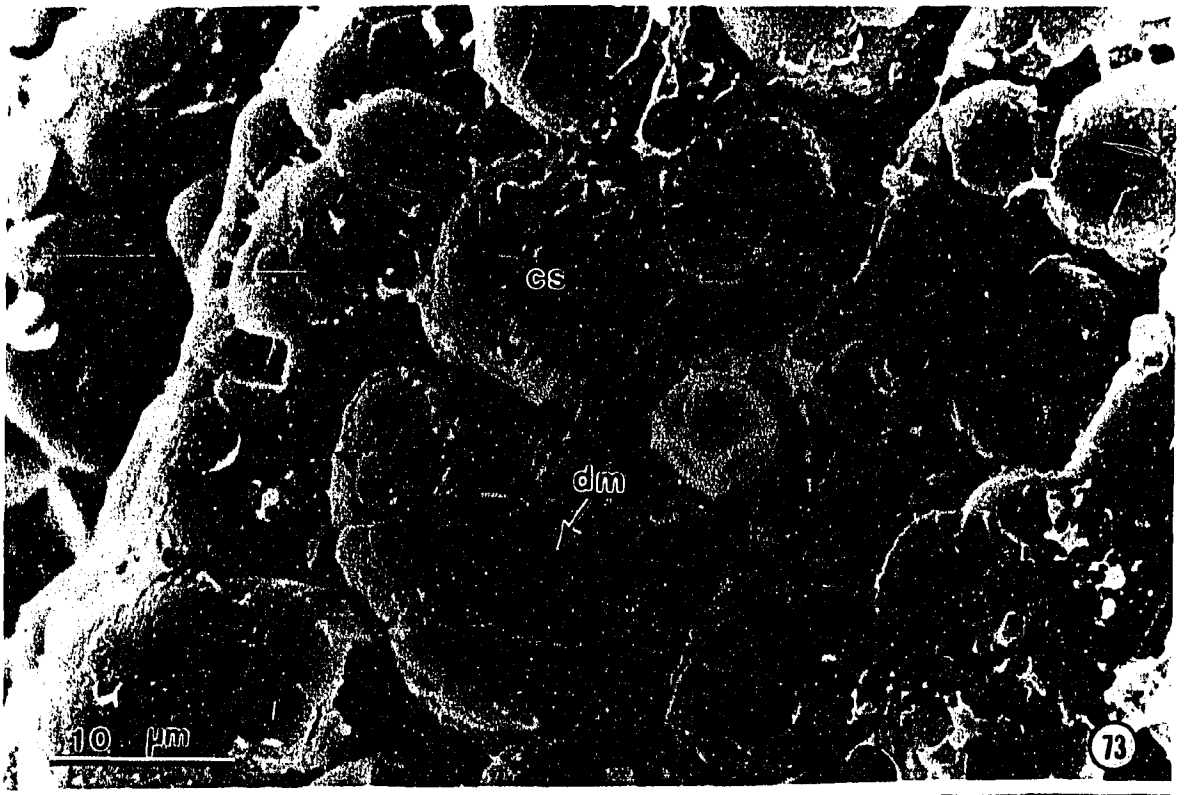

D
V
L
70

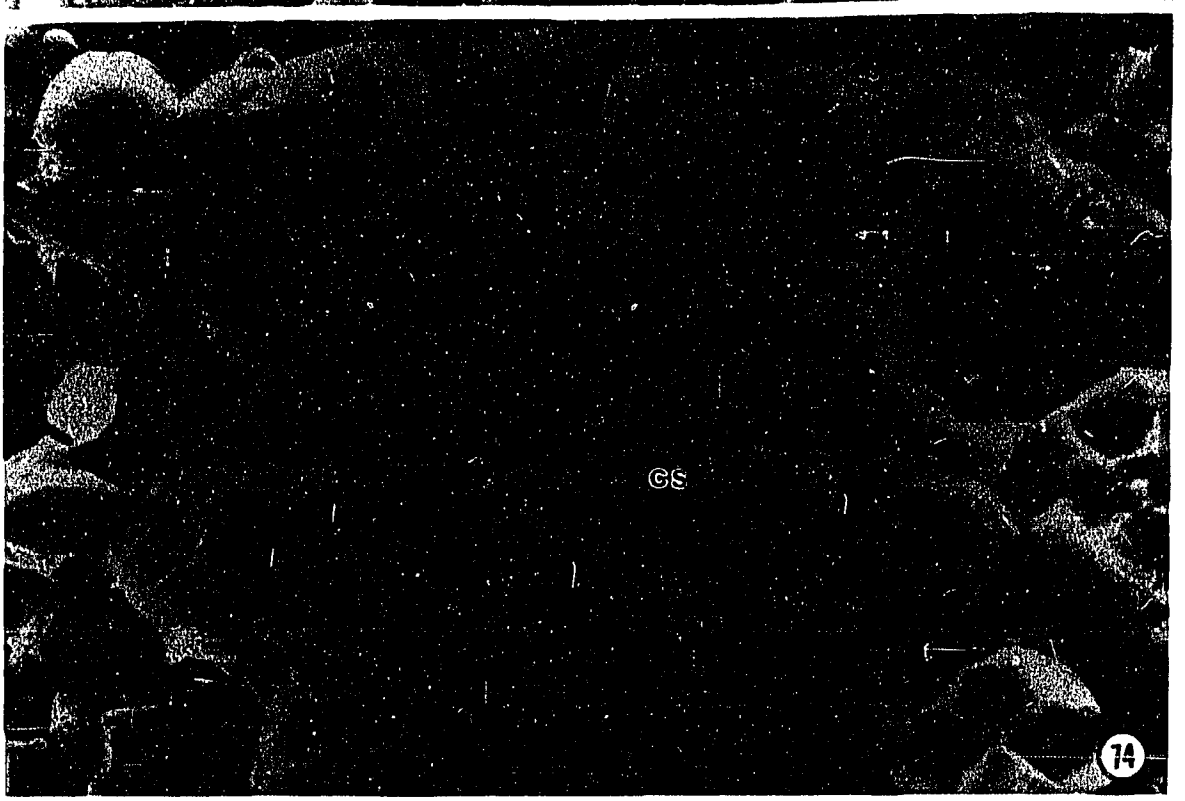
Figures 71-72. Cell surfaces in the endosperm of rice grain
71. Early Colusa, with loose packing, many air spaces, and crumbly surface
72. Lebonnet, with compact packing, smooth and angular surface


25 μm
71
72

Figures 73-74. Compound starch granules of rice

73. Early Colusa, with rather round compound granules and definite demarcation between individual starch granules
74. Lebonnet, with polygonal compound granules and no definite demarcation between individual starch granules

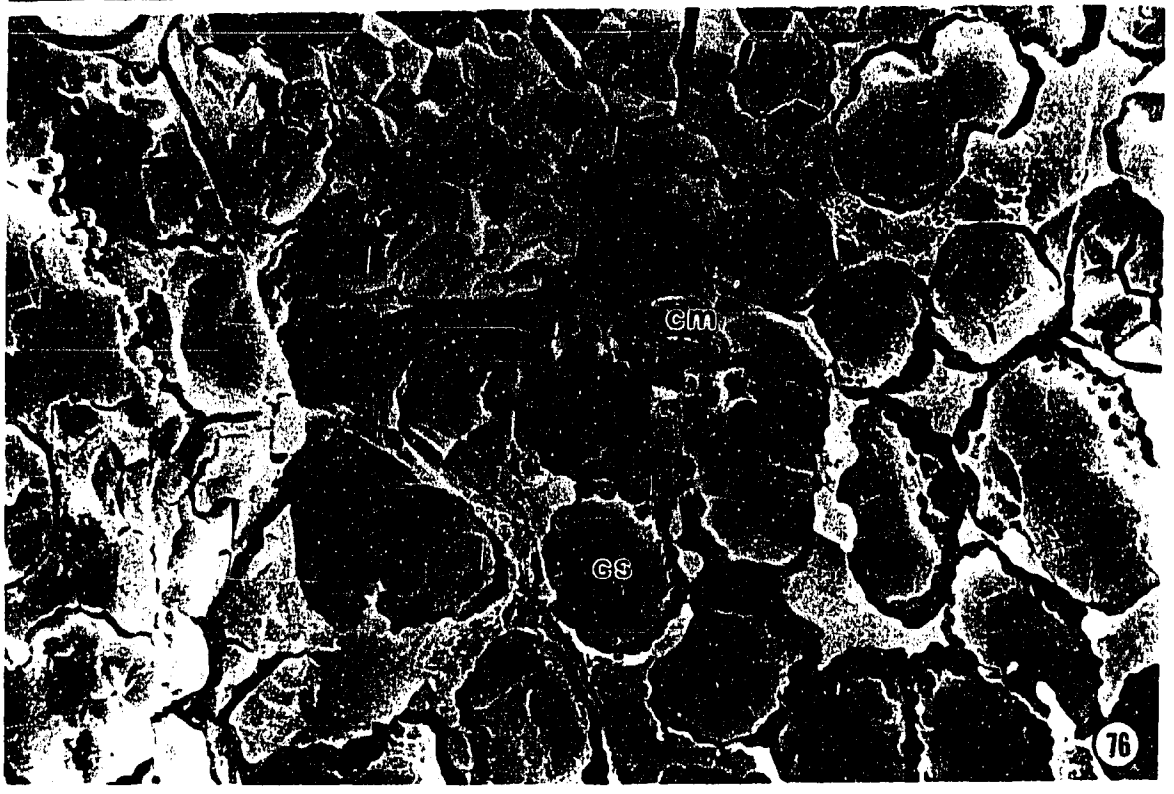

cs
dm
10 µm
73


cs
74

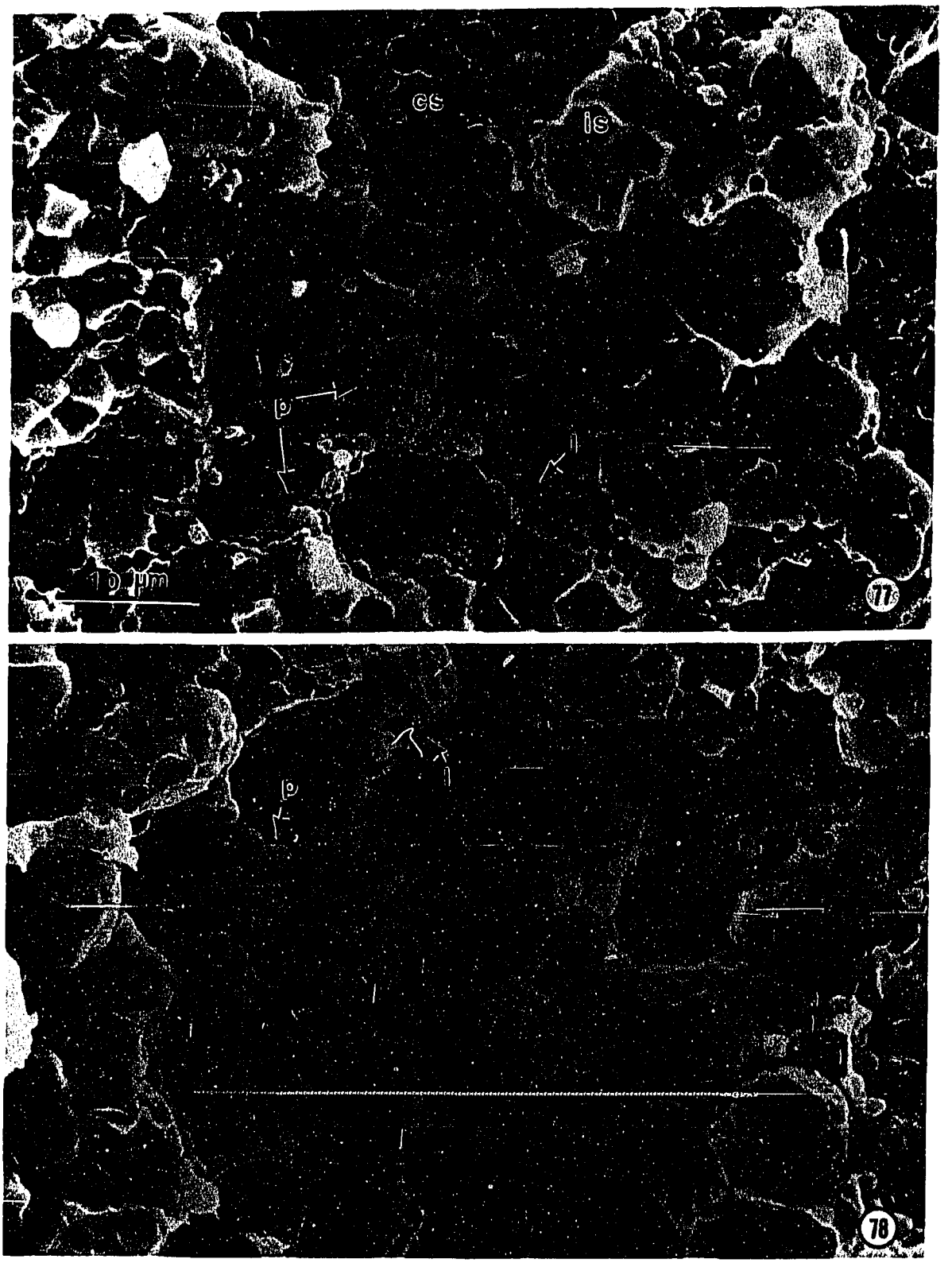
Figures 75-76. Starch granules in the center and the peripheral cells of the endosperm of rice grain

75. Starch granules are closely packed without any intervening cell matrix materials in the center of the endosperm.
76. Starch granules in the periphery of the endosperm are separated by electron-dense proteinaceous materials.

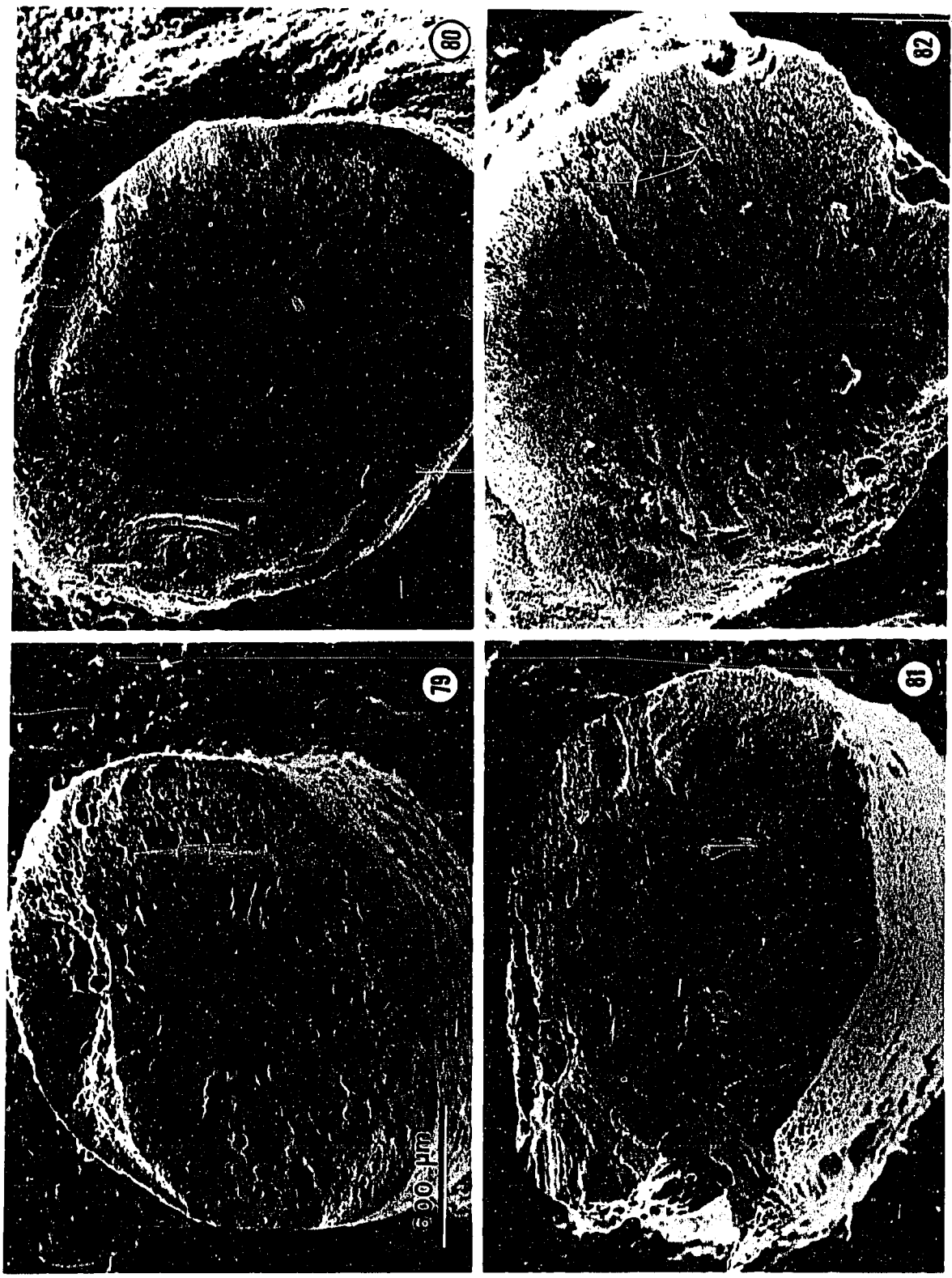

p
cm
is
cs
1.0 µm
75


cm
cs
76

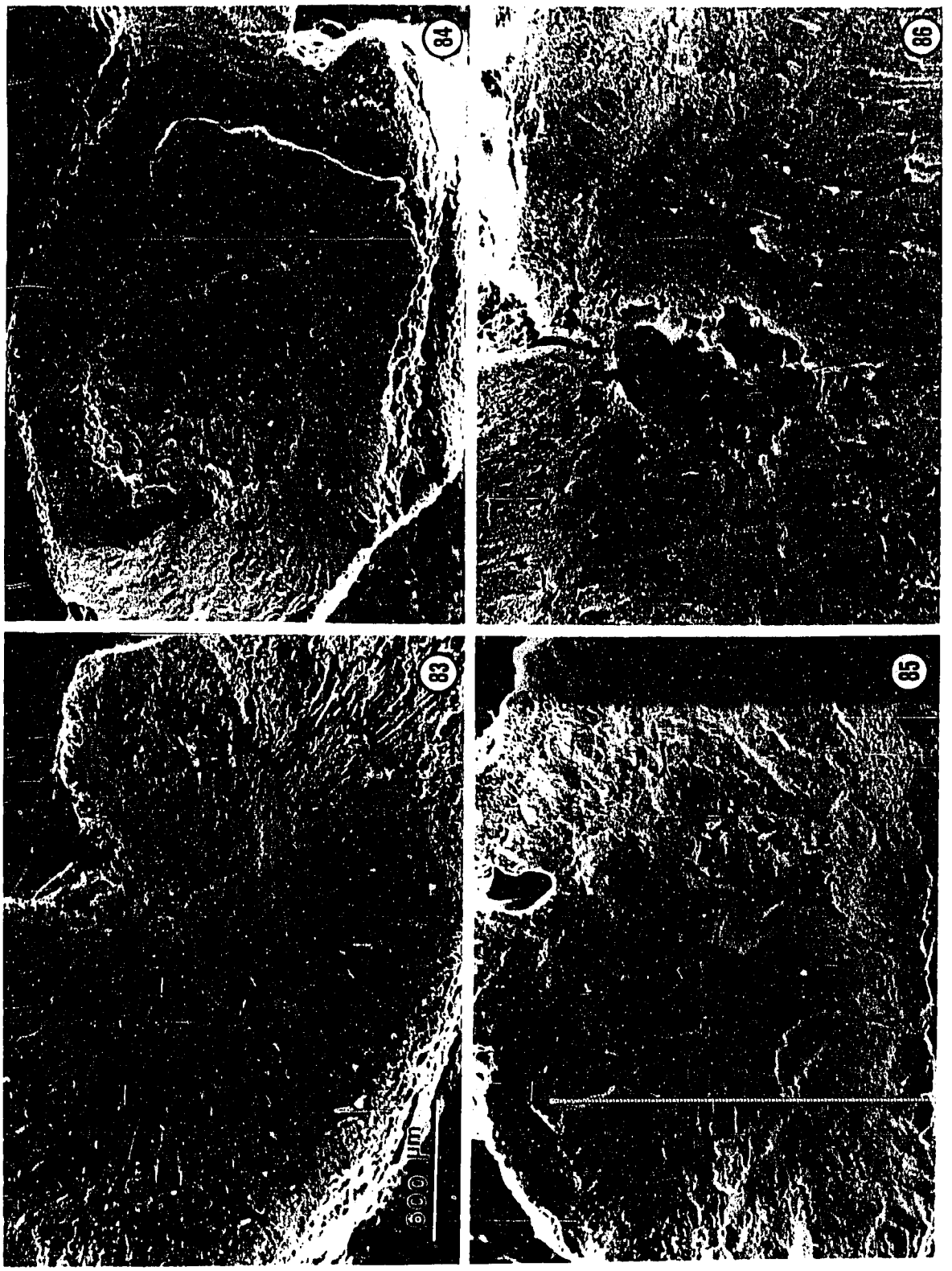
Figures 77-78. Indentations on starch granule from the pressure of protein bodies during developing grain


cs
is
p
l
10 µm
77
p
l
78

Figures 79-82. Structural changes of transversely fractured surface of less sticky rice during heating (Labelle); progressive changes from the periphery toward the center of the endosperm with increase in temperature
79. 75°C
80. 85°C
81. 95°C
82. 95°C, 10 min

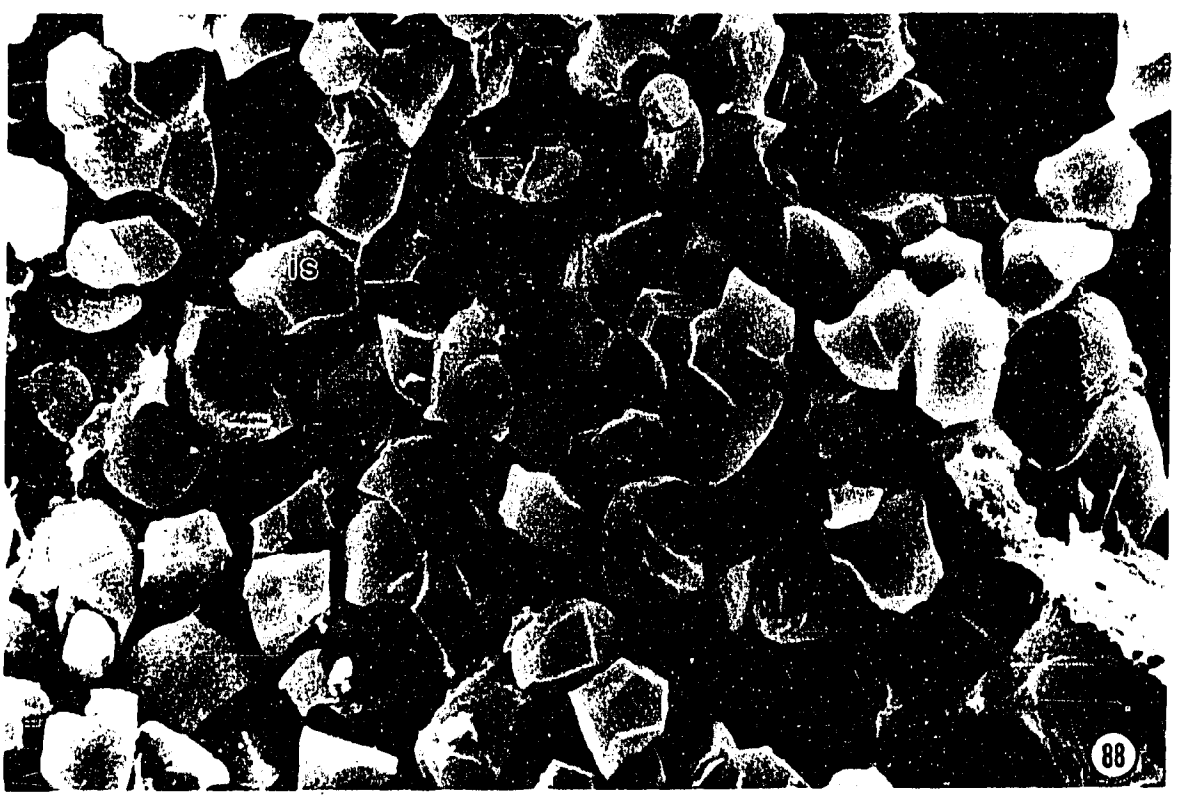

80
82
78
100 µm
76

Figures 83-86. Structural changes of transversely fractured surface of sticky rice during cooking (Pecos); progressive changes from the periphery toward the center of the endosperm with the increase in temperature
83. 75°C
84. 85°C
85. 95°C
86. 95°C, 10 min


84
86
83
85
0.0.9 µm

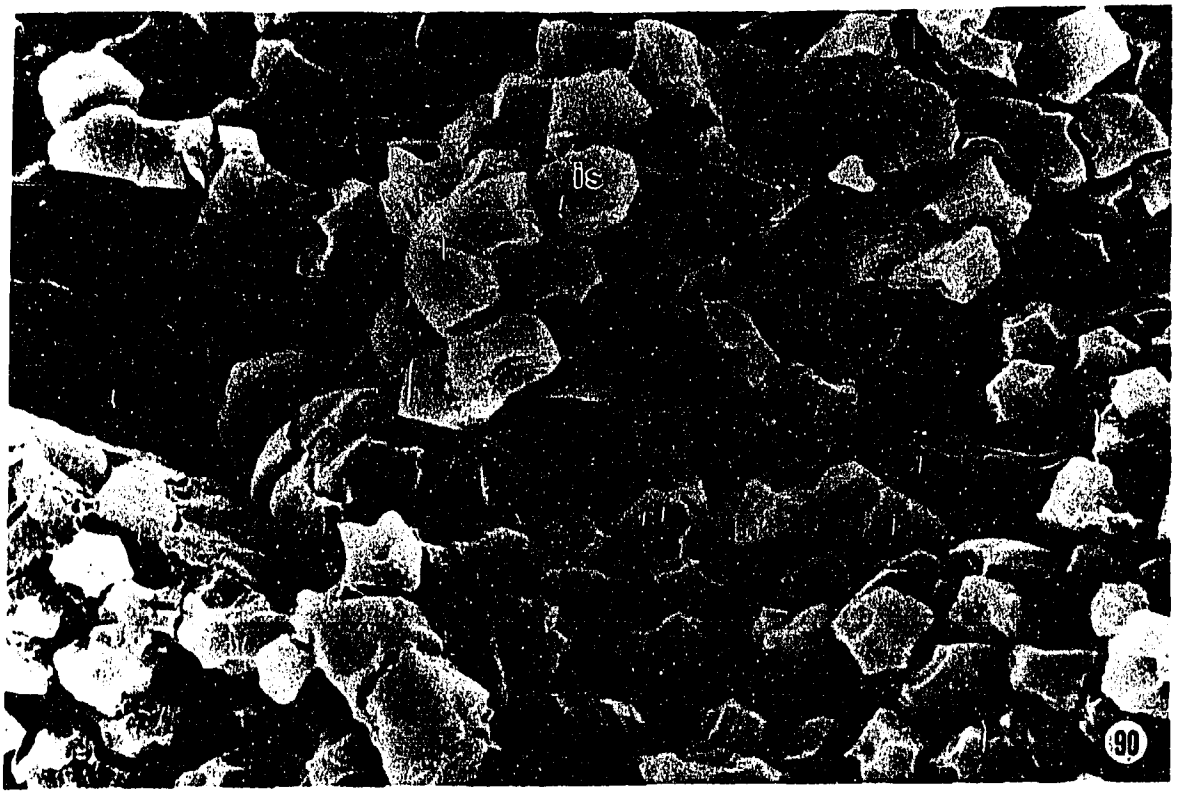
Figures 87-88. Solubilization of cell matrix materials during soaking in water for 30 min at 25°C


cm
cs
10 µm
87

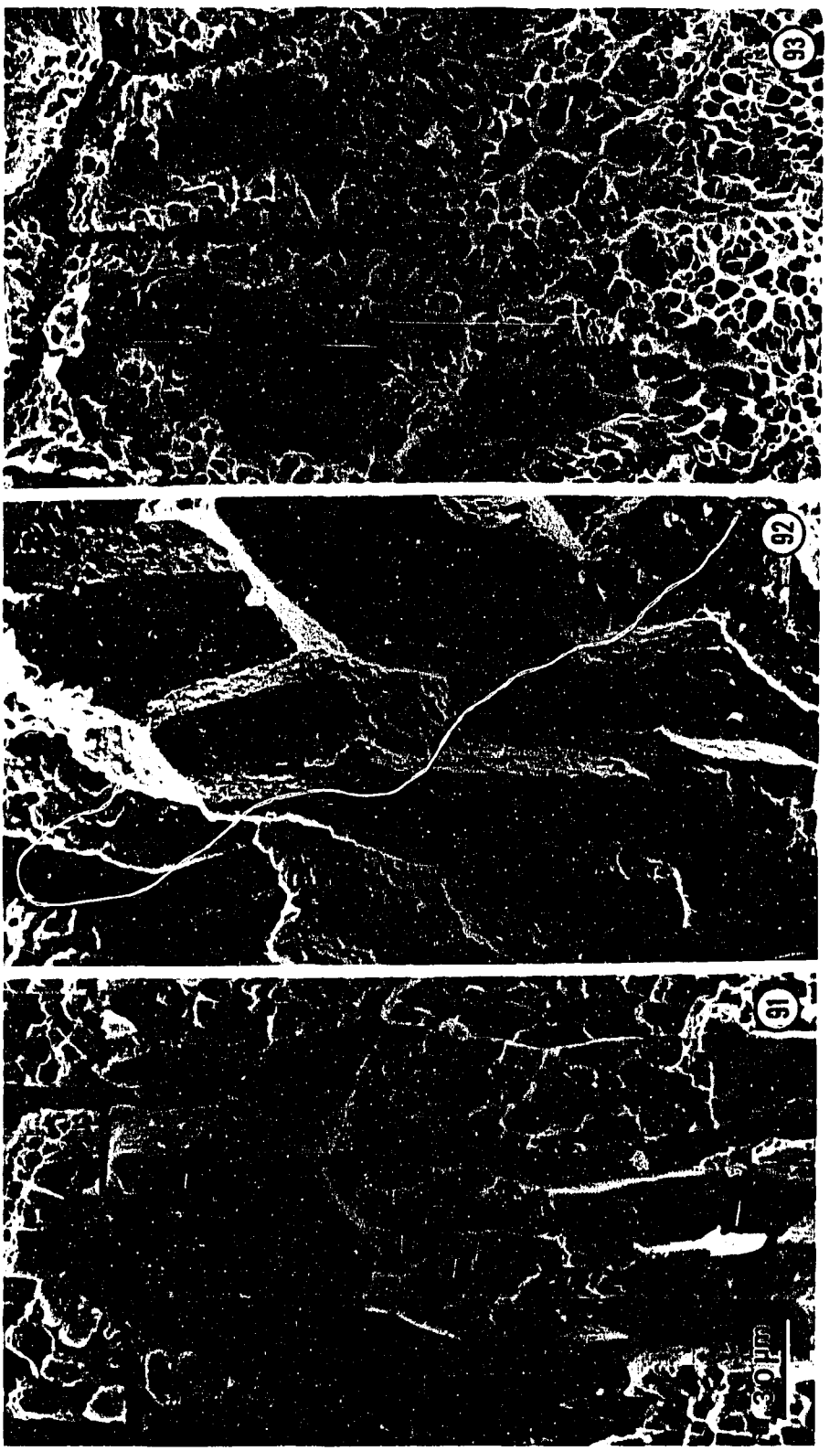

is
88

Figures 89-90. Differences in water diffusion rate between compactly-packed and loosely-packed endosperm (75°C)
89. Lebonnet has compactly-packed endosperm.
90. Brazos has loosely-packed endosperm.

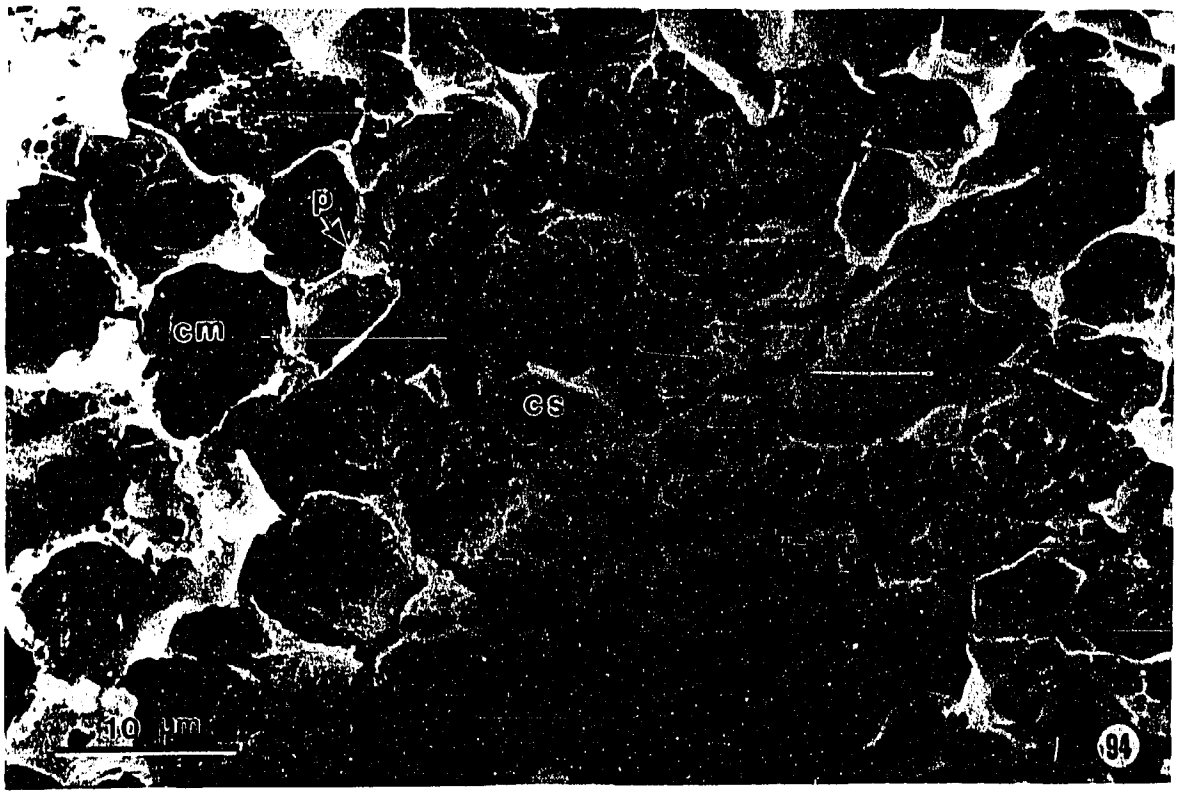

is
cs
m
10 µm
89

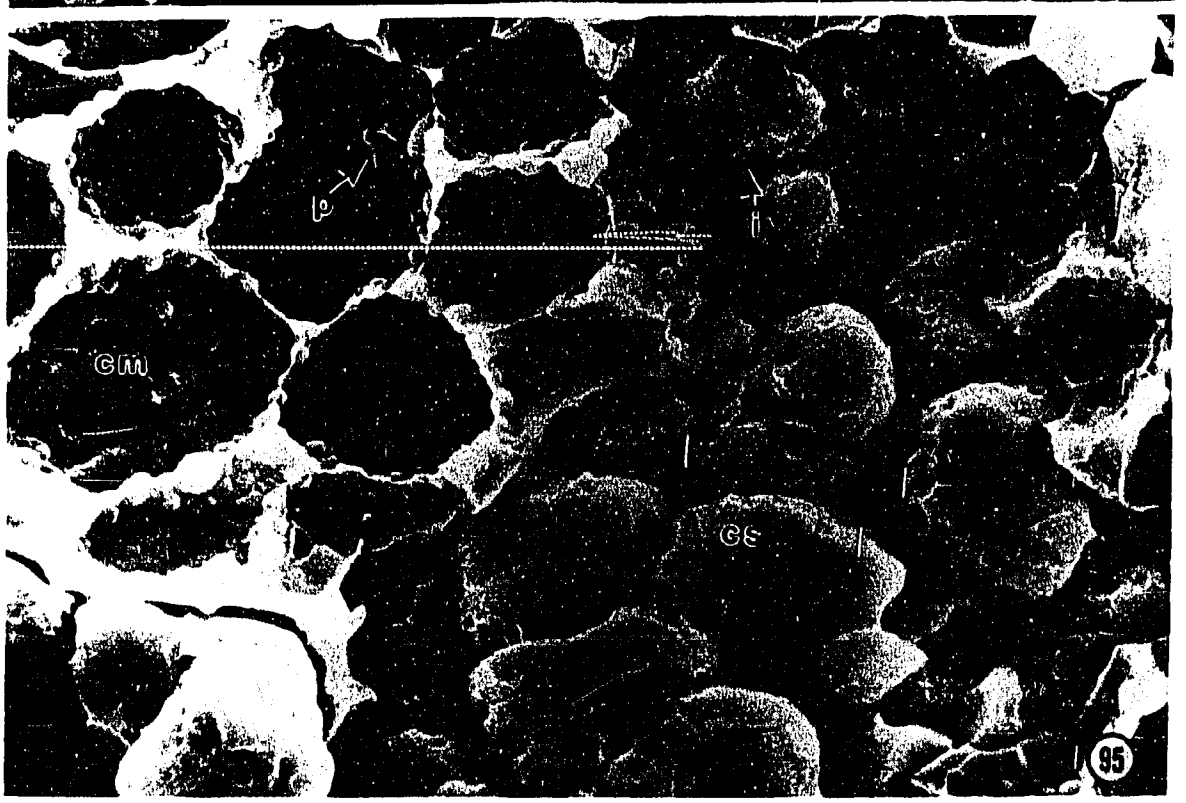

is
90

Figures 91-93. Structural changes of parenchyma cells in the endosperm during heating (Newrex)
91. 65°C
92. 75°C
93. 95°C


91
92
93
μm 10

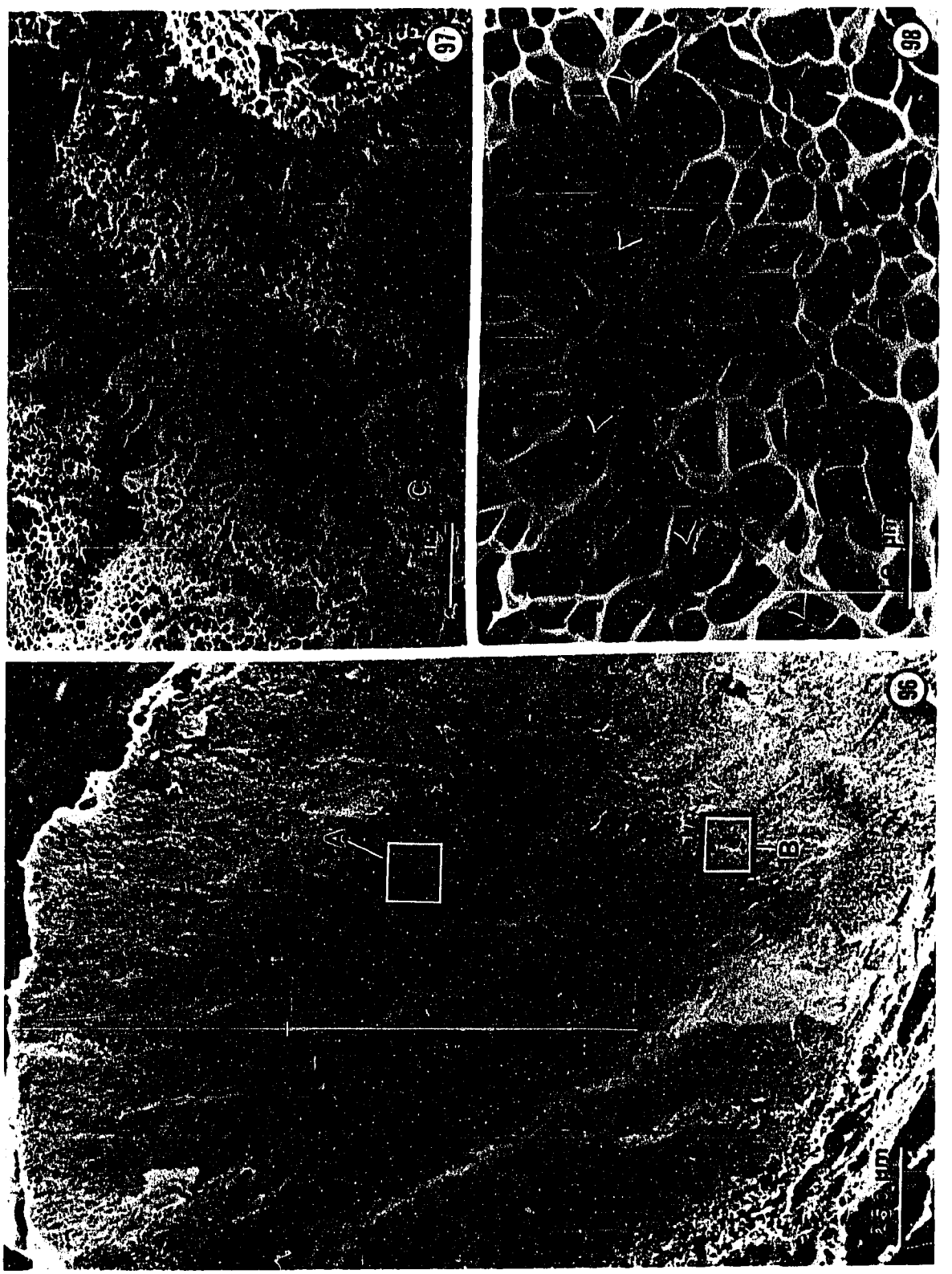
Figures 94-95. Morphological changes of compound granules at 85°C during heating; starch granules inside the cell are gelatinized without changes of cell matrix materials and protein bodies
94. Early Colusa
95. Newrex


p
cm
cs
10 µm
94

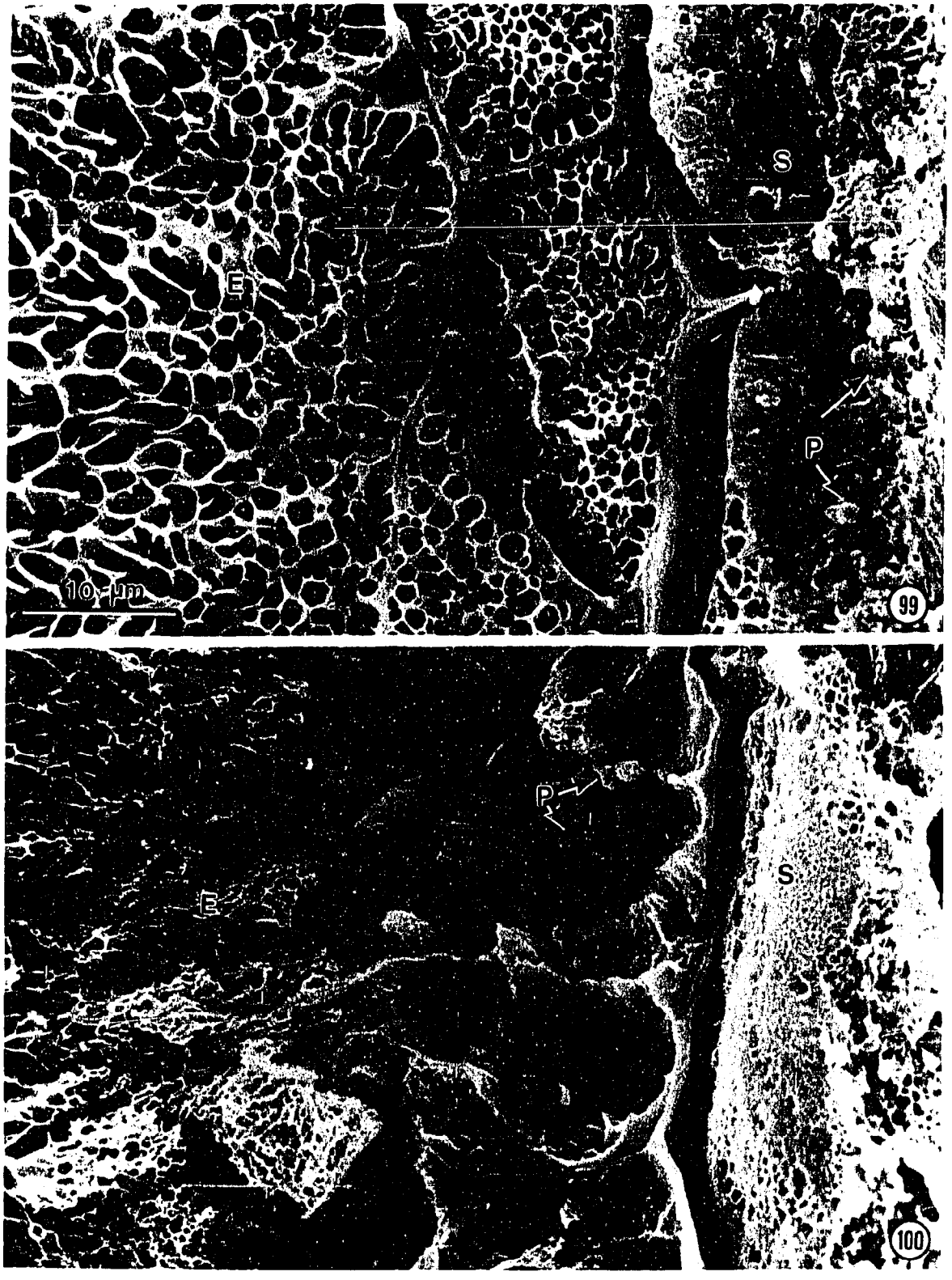

p
i
cm
cs
95

Figures 96-98. Fractured surface of fully cooked rice grain (Lemont, 95°C, 10 min)

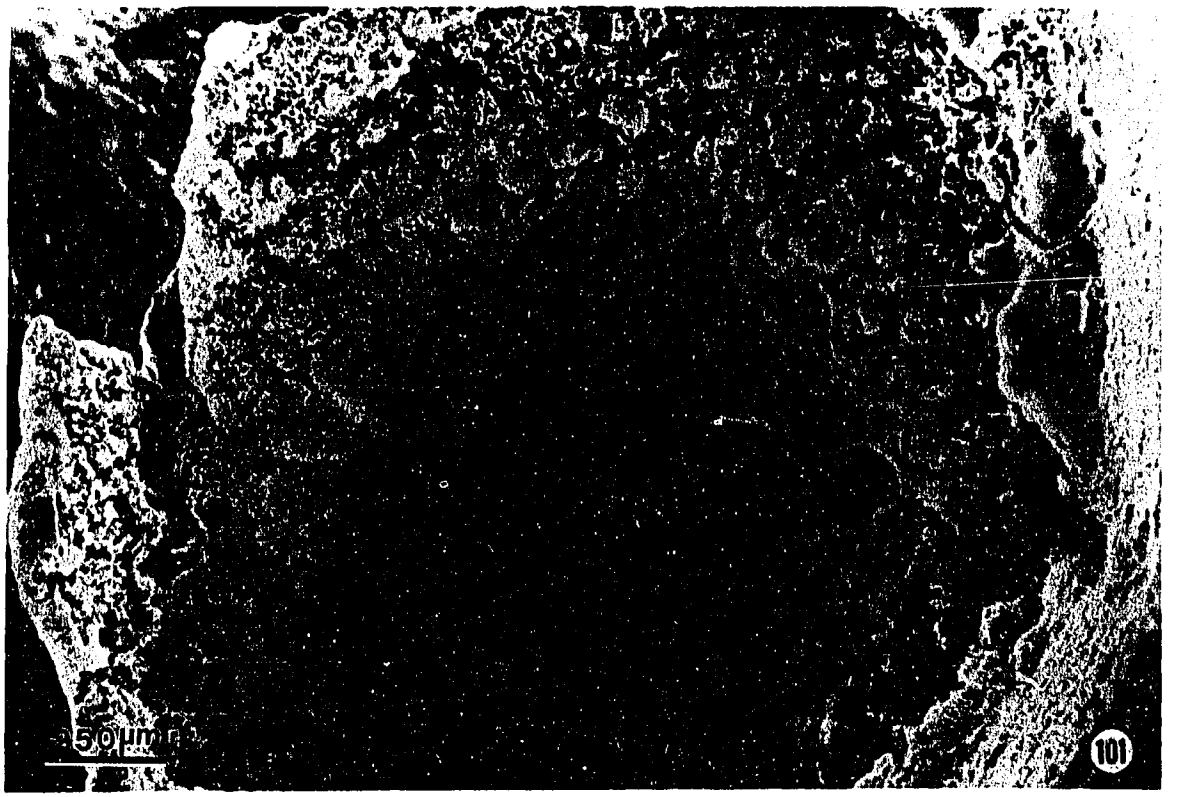
96. Entire fractured surface through middle of fully cooked rice grain
97. Enlarged view of region A of Figure 96, showing hollow center with whole parenchyma cells which are fully cooked
98. Enlarged view of region B of Figure 96, showing fully cooked rice grain with outline of cell boundaries (see arrowheads)


97
98
96
B
C
μm

Figures 99-100. Separation of the subaleurone layer of rice grain at 95°C during heating
99. Century Patna 231
100. S-6


S
E
P
10 µm
99
P
E
S
100

Figures 101-102. Fragmentation of the outer layer of grain during heating in low-protein rices (95°C, 10 min)
101. Century Patna 231
102. Kokuho Rose


50μm
101


102