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EFFECT OF MONOGLYCERIDES ON SOME CHARACTERISTICS OF POTATO GRANULES

BY

RATNAJOTHI HOOVER

A THESIS

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The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research, for acceptance, a thesis entitled EFFECT OF MONOGLYCERIDES ON SOME CHARACTERISTICS OF POTATO GRANULES submitted by RATNAJOTHI HOOVER in partial fulfilment of the requirement for the degree of Doctor of Philosophy.

Supervisor

External Examiner

Date 16th APRIL 1982

ABSTRACT

Native potato starch grains and those complexed below the gelatinization temperature with 1-monoglycerides (C_8 to C_{18}) were compared for solubility, swelling power (SP), viscosity, heat stability and water binding capacity (WBC). X-ray diffraction analysis proved that complexes were true clathrates. Clathrate stability was a function of monoglyceride chain length. The presence of clathrates in grains decreased solubility by up to twice and SP up to 10 times, while WBC dropped from 0.39 to 0.25 g water/g starch. Endotherm characteristics were determined for gelatinization, most perfect crystallites and clathrate fusions. Enthalpies of 15.4 Kcal/mole for native starch and 27.5 for clathrate were obtained irrespective of monoglyceride chain length.

Palmitic and stearic acid types of monoglycerides were assessed for their ability to complex amylose in a simulated Add-Back (A-B) potato granule process. Monoglycerides applied as hydrated gels (pH 2.3 - 7.1) and microbead powders, had α and β crystal forms, respectively, as proved by X-ray diffraction and infrared spectroscopy. The α form and the palmitic acid type of monoglyceride were superior for amylose insolubilization. Scanning electron microscopy (SEM) was used to determine the effect of added monoglycerides on the extent of amylose leaching from potato granules and heated starch grains.

Monoglyceride incorporation in an A-B or Freeze-Thaw (F-T) process decreased the potato granules Blue Value Index (BVI), SP, rehydration rate and WBC, and increased the intact sound cell count. With 0.2% monoglyceride, SP, WBC and rehydration rate of A-B granules

were 8.4, 6.7 and 6.4%, respectively, lower than F-T granules; while the BVI of A-B granules was 25.3% higher. Monoglyceride levels above 0.2% caused negligible changes. The impact sound cell count was higher when a precooking step was applied. The porous F-T and compact A-B granule structures partially accounted for differing water penetration rates. X-ray analysis revealed a weak monoglyceride - starch interaction during the granule process.

The SP, WBC and rate of rehydration of granules (complexed with 0.2% monoglyceride) decreased during the initial 14 weeks by an average of 25.5 (F-T) and 27.3% (A-B) at 4°C and by 11.1 (F-T) and 12.0% (A-B) at 25°C. However, the moisture content showed an opposite trend, increasing by 5.9 (F-T) and 7.5% (A-B) at 4°C and by 3.6 (F-T) and 4.9% (A-B) at 25°C. Storage beyond 14 weeks at 4°C resulted in increases in SP, WBC and rate of rehydration and decreases in moisture content. However, such a trend was not observed at 25°C.

The percentage decreases in SP (during the initial 14 weeks) of treated granules (A-B and F-T) were lower than those of untreated granules by an average of 11.0% at 4°C and 10.5% at 25°C.

The extent of starch matrix - cell wall separation and the intensity of the "V" diffraction pattern of an X-ray analysis increased during storage, with greater increases being found at 4°C.

Viscosity and differential scanning calorimetry studies showed the inability of monoglyceride to complex potato pectin.

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I. INTRODUCTION

Potato granules are a dehydrated convenience food. They consist largely of separated, whole tissue cells which are reconstituted easily by the addition of hot water to form a product that ideally, closely resembles freshly mashed potatoes in color, flavor and texture. The only process at the present time for commercial production of potato granules is the Add-Back (A-B) process (Boyle, 1967). A Freeze-Thaw (F-T) process for the production of potato granules was recently developed by Ooraikul (1977) to eliminate or minimize some of the major problems which have been plaguing the A-B process. Perhaps the biggest advantage of the F-T process lies in the fact that the process is "straight through", one in which no recycling of the dry granules is necessary. Nevertheless, the process has not yet been commercially applied. The granules obtained by these two processes differ in their physicochemical characteristics (Moledina et al., 1978).

In manufacturing dehydrated mashed potatoes, prevention of excessive release of amylose from intact and ruptured cells is of great importance to ensure an acceptable textural quality of the reconstituted product. Less starch is extruded from such cells when a preheating and cooling step is used. Processes based on the above observations have been patented in which cooked and mashed potatoes are freed from stickiness, pastiness or glueyness (Cording and Willard, 1957; Sullivan et al., 1961). The leached-out amylose content in mashed potatoes is reduced further in additional steps of processing. Retrogradation of amylose in predrying, low temperature conditioning or tempering steps of an A-B process (Olson and Harrington, 1955) or the freezing step of

an F-T process (Ooraikul, 1977) are two such examples. The undesirable effect of amylose may also be avoided by mashing at a temperature close to that of cooking, which keeps cell rupture low, and/or by tying up the amylose by incorporating monoglycerides at this step. In addition, monoglycerides also affect the end product swelling (Swelling Power, SP), Water binding capacity (WBC) and/or rate of rehydration, i.e. a set of parameters which affects mixing and handling properties of reconstituted mash and also extrusion properties of the dough during manufacture of French-fries.

Granules exhibiting rehydration rates in the region of 5.9×10^{-2} sec^{-1} have been found ideal for French-fry production. However, such rates are only achieved by the addition of Ca^{+2} to precooking water, or by storage at room temperature for 6 months (Ooraikul and Moledina, 1980). Prolonged storage in commercial production is impractical and also brings about the additional problem of end-product rancidity.

1. OBJECTIVES OF THE INVESTIGATIONS

Presently, the Alberta processors export their dehydrated mashed potato granules to Europe and Japan. A number of properties of the granules are needed to be improved. The most important ones are: (1) increase in the number of granules with intact cell wall; (2) decrease the rate of water uptake; (3) reduce the high swelling test values; and (4) to reduce the unsatisfactory soluble amylose values. The main objective of the present work was aimed at solving these problems. In order to achieve this, a detailed study was needed on the effect of monoglyceride on potato tissue and particularly, its starch content.

1.1. Characterization of Potato Starch and its Monoglyceride Complexes.

Industry experience and some published data strongly suggest that quality parameters like SP, WBC and rate of rehydration involve mostly starch and starch-lipid interaction products (Hadziyev and Steele, 1979). Hence, a study was initiated to determine the properties of potato starch and its monoglyceride interaction products. Native starch was reacted with 1-monoglycerides (C_8 to C_{18}) and the product, a true starch-lipid complex as proved by X-ray diffraction, was then investigated for heat stability, SP, amylose leaching and WBC. Evidence was provided for the ability of each monoglyceride to tailor these properties of native starch.

1.2. Effect of Monoglycerides on Amylose Complexing During a Potato Granules Process.

The superiority of the α-crystalline form of a monoglyceride

over that of β in complexing amylose was reported by Krog and Nybo Jensen (1970). However, the possible advantage of using either α- or β-crystalline forms in a granule process has not been reported. The present work determined the extent of amylose complexing with commercially available monoglycerides, one with palmitic and the other with stearic acid being predominant, and both being applied in crystalline states which corresponded to powder (β) and gel (α) forms. Potato starch model systems and whole potato tissues were put through semi-pilot scale or simulated steps of an A-B granule process. Since in this process the duration and temperature of the mash-mixing step, and concentration of added monoglyceride, appear to be chosen by industry somewhat arbitrarily, the effects of changes in these parameters on amylose complexing were also studied in detail.

1.3. Effect of Monoglyceride on some Rehydrating Properties of Potato Granules.

Presently, monoglyceride is added at a level of 0.3-0.5% (with some processors up to about 1%) during the mash-mixing step of a granule process. However, the effect of different concentrations of monoglycerides on rehydration quality parameters has not been determined. Therefore, the influence monopalmitin-type monoglyceride at various levels on SP, WBC, extent of amylose leaching, and count of intact sound cells was determined and the optimum concentrations for industry suggested. Simultaneously the formation of an inclusion complex between starch and monoglyceride in the granule process was confirmed by X-ray diffraction analysis.

1.4. Effect of Storage Temperature on some Rehydrating Properties of Potato Granules.

A systematic study has not been made on the influence of different storage temperatures on the rehydration properties of granules. Ooraikul and Moledina (1980) observed that an increase in starch retrogradation caused a decrease in rehydration rate. This observation, together with those of Katz and Reinstma (1930) and Whistler (1954), who observed an acceleration of starch retrogradation with decrease of temperature, led to a comparative study of the effect of storage temperatures (4 and 25^{o}C) on WBC, SP, starch matrix-cell wall separation, and crystallinity degree of F-T and A-B granules.

1.5. Pectin-Monoglyceride Interaction.

An interaction between citrus pectin and monoglyceride was reported by Ooraikul and Hadziyev (1974). To verify these observations and to clarify the possible role of pectin as an extracellular binder in a granule process, a study was designed which involved an attempt to react monoglyceride with potato pectin and citrus pectin (of various degree of esterification). The product so formed was examined by viscometry and differential scanning calorimetry.

II. REVIEW OF THE LITERATURE

1. PROCESSING OF POTATO GRANULES.

The potato (Solanum tuberosum, L.) is an annual herbaceous dicotyledonous plant belonging to the family solanaceae. Currently, 35% of the potatoes produced in Alberta are consumed as fresh table potatoes, 5% are used for seed production and 60% are processed into dehydrated granules, chips or French-fries (Chung and Hadziyev, 1980). Processing of potatoes into dehydrated granules or flakes is perhaps the most satisfactory method of creating a product that is not only nutritionally and organoleptically adequate but remains so over an extended period of time.

Early development of dehydrated mashed potato was reviewed by Olson and Harrington (1955). Recent patents were reviewed by Torrey (1974), Hanson (1975) and Hadziyev and Steele (1979). Basic information related to potato dehydration was given by Feustel et al.(1964).

The earliest attempt to produce dehydrated granules involved spray drying (Heirmerdinger, 1926), which was modified later by Bowen (1931) and Burton (1944). Other methods which followed were the "Freeze and Squeeze" method (Greene et al ., 1947; Hall, 1953). A method that has been widely investigated for the reduction of moisture content of cooked potatoes to approximately 40% is addition of an appropriate amount of previously dried material. This is called the Add-Back (A-B) process, and early developments of this method were described by Volpertas (1939), Rivoche (1948, 1950) and Rendle (1943).

Willard (1966) developed a modified A-B process with minimum recycling. The process involved admixing cooked mashed potatoes with

dehydrated granules in an amount sufficient to produce a moist, friable mixture having a moisture content of about 35 to 45%, permitting the mixture to equilibrate its moisture content for 20 min, remixing and then drying to the desired final moisture content. Homogeneous mixing of the moist and dry components was accomplished with the aid of monoglyceride. Willard (1967) introduced a process in which potatoes were cooked and mashed at the same time in a combination unit which continuously removed the cooked exterior portions of the potatoes. In this manner, over-cooking of the outer portions of the potatoes was eliminated, and mechanical damage to the cells of inner portions of the potatoes, which require longer cooking, was minimized.

Precooking and cooling steps were omitted in a process developed by Shatila and Terrel (1976). Partially mashed steam-cooked potatoes were riced in the presence of glycerol monostearate. The subsequent steps were predrying, granulation and fluidized bed drying.

Ooraikul (1977, 1978) developed the Freeze-Thaw (F-T) process, which also omitted the precooking and cooling steps. Mashed potatoes frozen overnight in an air-blast freezer at -29°C were thawed to 5°C before being subjected to predrying, granulation and final drying. Most of the granules (85%) so produced were smaller than 60 mesh and the broken cell count was not more than 6%.

In a similar process Shub and Bogdanova (1976) subjected the mashed potatoes to temperatures of -10 to -40°C for 2-15 min before fluidized bed drying.

1.1. Add-Back Process.

At present the only significantly successful commercial process for potato granule manufacture in Canada and the U.S.A is the A-B process. Because of this fact, some of the details of this process will be elaborated in this review.

The basic features of the A-B process are: peeling, slicing, precooking and water cooling; followed by steam-cooking, mash-mixing (with about 2 parts of recycled granules), conditioning, remixing, air-lift drying, fluidized bed drying,and cooling and sieving. The rationale for the sequence of processing steps described above has been reviewed by Hadziyev and Steele (1979).

Though the A-B process has been improved, its major disadvantage still remains: 1/10 to 1/6 of the solid material handled is the end product, while the remainder stays in the system by recycling. This has a bearing on operating costs. In addition, granule quality can be reduced because undesirable characteristics, once developed, remain in the system in appreciable percentage even after several recycles of continuous production.

1.2. Freeze-Thaw Process.

Ooraikul (1973) introduced the F-T technique for granule production in order to overcome some of the drawbacks of the A-B process.

The F-T process consists of peeling, cooking, mashing, freezing and thawing, predrying, granulation, drying and sifting.

Precooking and cooling were avoided in this process, since

introduction of these two steps contributed to tissue strengthening, which in turn required greater mechanical shearing, resulting in excessive cell damage and a more gluey mash (Moledina et al., 1978).

The biggest advantage of the F-T process lies in the fact that the process is a "straight-through" one in which no recycling of the dry granules is necessary (Ooraikul, 1978). The A-B conditioning step is replaced by the freezing and thawing steps. The major advantage of freezing temperatures is the minimization of microbial growth. In addition freezing temperatures provide better retention of ascorbic acid (Jadhav et al., 1975). However, the F-T process might have a great disadvantage due to its high energy demand and capital expenditure. The latter economical parameters have not yet been reported for F-T process.

2. EFFECT OF PROCESSING ON POTATOES.

2.1. Cooking (Precooking and Steam Cooking)

Potato slices subjected to the A-B granule process are usually precooked in water at 65-80^{o}C for 20-30 min and cooled before further processing (Olson and Harrington, 1955; Cording and Willard, 1957). Precooking serves to solubilize pectic substances, gelatinize starch grains (Kinter and Tweedy, 1967) and strengthen potato cells (Bartolome and Hoff, 1972; Moledina et al., 1981). Omission of precooking results in mechanical damage to the potato cells during mash-mixing, causing the release of free starch and resulting in a texturally inferior product (Cording and Willard, 1957). Thus, precooking plays an important part in determining the physical properties of A-B granules (Olson and Harrington, 1955). Steam-cooking brings about final softening of the tissue.

2.1.1. Effect of Cooking on Pectic Substances and Textural Quality.

Pectic substances in the cell wall (CW) and middle lamella (ML) have been found to influence the textural properties of potato granules. Solubilization of pectin and loss of cellular cohesion occurs during cooking.

A mechanism for the degradation and solubilization of pectic substances during cooking was presented by Keijbets et al. (1976). These authors showed that depolymerization of pectic galacturonan by β or trans-elimination was possible at the natural pH of potato tissue (5.5-6.5), and that the extent of depolymerization increased with increase of pH. The mechanism of this β-elimination was clarified by Neukom and Deuel (1958) and Albersheim et al. (1960). At 100°C, cations such as Ca^{+2}, K^{+} and Mg^{+2} and anions such as phytate and chloride were found to enhance depolymerization by β-elimination. The nature, rather than the concentration of the ions, was found to be the predominant factor (Keijbets and Pilnik, 1974; Keijbets et al., 1976).

Bartolome and Hoff (1972), Hoff (1972) and Moledina et al. (1981) showed that firming during precooking was due to de-esterification of CW pectin by potato pectin methyl esterase (PME). Firming occurred by metal bridge formation between the freed COOH groups and Ca^{+2} and Mg^{+2} diffused from the cell interior. This would increase the matrix viscosity, thus causing an increase in cell cohesion (Warren and Woodman, 1974).

Pectin solubilization during cooking was found to be retarded by Ca^{+2} but not by Mg^{+2} (Keijbets et al., 1976). Haydar et al. (1980) and Moledina et al. (1981) reported similar findings at precooking temperatures. These authors showed that tissue firming in the presence

of divalent cations involved both CW and starch. Ca^{+2} firmed both starch and CW, while Mg^{+2} firmed only starch. The firmness of potato tissue precooked and cooked in deionized water without cooling was found to be equal to that of tissue straight-cooked or precooked, cooled and cooked in deionized water. In the presence of Ca^{+2}, only the latter steps brought about firming (Haydar et al., 1980).

Moledina et al. (1981) found that Ca^{+2} but not Mg^{+2}, supplied as Ca(Mg) starches, retard pectin solubilization, while cooling following precooking resulted in a higher uptake of Ca by retained pectin. The firming effect was attributed to Ca release from gelatinized starch during precooking, and to stabilization of Ca bridges with free COO^- groups of cell wall pectin during cooking. The role of pectin methyl esterase (PME) in causing firming was de-emphasised, since the PME level in potato tissue permitted only a maximum of 11.3% demethylation.

2.1.2. Effect of Cooking on Starch and Textural Quality.

During precooking and steam-cooking, starch grains lose their crystalline structure and become hydrated, swollen and gelatinized. The swollen gel occupies almost the entire cell volume in the cortex, but only partially fills the pith cell. Fedec et al. (1977) attributed this finding to the smaller size and lower number of starch grains per pith cell.

Amylose leaching occurs during starch gelation. The extent of leaching was found to be greater at 82.2^{o} than at $65.5^{o}C$ (Reeve, 1963). Precooking a starch suspension at $65^{o}C$ followed by steam-cooking at $100^{o}C$ resulted in a decrease in dissolved starch content (Potter et al.,

1959). An increase in precooking time resulted in greater decreases, suggesting that starch retrogradation occurs during precooking. However, the extent of retrogradation was even greater when cooling followed precooking (Potter, 1954; Reeve, 1954 a,b; Harrington et al., 1959). Minimal extrusion of gelatinized starch occurs only when tubers are cooked after a preheating and cooling steps. This results in mealiness, a required feature of good quality mashed potatoes (Cording and Willard, 1957; Sullivan et al., 1961).

Microscopic observations by Reeve (1954a) done during the cooking of potato tissue, have shown that cell separation is accompanied by "rounding off" of the cells, so that walls of adjacent cells are pushed apart. Other observations showed the "rounding off" to be the result of swelling of gelatinized starch. Hoff (1972) and Warren et al. (1975) disputed the existence of such a "swelling pressure", and suggested that the texture of cooked potatoes was only related to the factors that influence the strength of CW and ML. These are cell size, cell surface, starch content, amylose/amylopectin ratio, specific gravity, total solids, Ca^{+2} and organic acid contents, age and storage time of the tuber, and starch retrogradation (Hoff, 1972). Warren et al. (1975) suggested that sloughing or mealiness of cooked potato tissue was due to extensive hydration of CW. Cell separation was favoured by high levels of phytate and polyuronides and low levels of polyvalent cations in the CW.

The controversial nature of the texture of cooked potato is, thus, obvious.

2.2. Mashing.

Mashing of cooked potatoes is a critical operation in the production of high quality granules. The individual tissue cells should be separated by the application of compressive and shear forces but should remain whole, with CW's enveloping the swollen, heat-gelatinized starch (Olson and Harrington, 1955).

The quality of potatoes, temperature of mashing, and the type of mixer used determine the success of the mashing step (Olson and Harrington, 1955; Ooraikul, 1974). The cells in potatoes mashed at a temperature close to that of cooking are easily separated with little cell damage. However, as the mashing temperature is decreased, the percentage of broken cells increases (Ooraikul et al., 1974). Therefore, mashing at "high" temperature immediately after cooking is desirable.

The amount of cell rupture correlates with the pastiness of the end product and the amount of released free amylose and its Blue Value Index (BVI). Rehydrated potato granules with 20% broken cells are designated as pasty, while those with 10-12% broken cells are average and those with 6% or less are superior (Greene et al., 1949; Reeve and Notter, 1959). Good quality dehydrated mashed potatoes have a BVI of 92-182 (Hadziyev and Steele, 1979).

In the F-T process best results are obtained by mashing for about 2 min, at a temperature of 70^{o}C or above, in a Hobart mixer equipped with a flat beater.

In the A-B process, cell separation is achieved by hot mashing at or above 60^{o}C of the cooked tissue with dry granules. This results in a decrease in the moisture content of cooked potatoes to a level where cell separation can be achieved without rupture (Severson et al., 1955).

High temperature mashing enables uniform distribution of additives (monoglycerides, antioxidants, sodium acid pyrophosphate) throughout the whole mash. Thus, F-T granules would exhibit more uniformity in their properties between individual granules, while A-B granules would provide a better uniformity based on bulk sample granules. Effective cell separation in the F-T process would enable quick water removal in the predrying step (Moledina et al., 1978).

2.3. Freezing and Thawing.

Freezing and thawing of cooked potatoes reduces the swelling power of their gelled starch and influences the textural properties of frozen potato products (Reeve, 1967). Freezing strengthens the CW (Greene et al., 1948) making possible predrying of the mash at an elevated temperature in a stirred bed dryer and granulation with only minimum damage to the potato cells (Ooraikul and Hadziyev, 1974). By freezing and thawing, the resulting product is made more granular and less gelatinous in texture (Rendle, 1945). Granules prepared from potatoes of different varieties or dry matter content were found to have consistent water reabsorption capacity (Ooraikul, 1978). This could be attributed to acceleration of starch gel retrogradation to near completion at freezing temperatures (French, 1950).

The thawed mash should not be higher than $5^{o}C$ when predrying begins, or the benefit of freezing will be lost through reabsorption of water and softening of CW's (Moledina, 1978).

2.4. Conditioning.

Changes undergone by A-B granule during conditioning are similar to those observed during the freezing and thawing steps of a F-T process.

Conditioning for 30-60 min at 40-50°C results in retrogradation of gelatinized starch, resulting in improved cell separation in the subsequent steps of fluff-mixing (Potter, 1954; Ooraikul, 1978) and improved textural quality of the reconstituted granules (Severson et al., 1955).

2.5. Predrying and Granulation.

Predrying and granulation are well covered by the literature (Rendle, 1945; Rivoche, 1950; Cooley et al., 1954; Potter, 1954; Severson et al., 1955; Olson and Harrington, 1955; Ooraikul, 1973). In predrying, the moisture content of the cooked potatoes is reduced to a critical range of 35-45% in the F-T process (Ooraikul, 1978) and 30-35% in the A-B process (Harrington et al., 1959). Within this range, potato cells are more resistant to mechanical damage, friable and easily handled (Olson et al., 1953). Predrying and granulation in the A-B process are achieved during mash-mixing. Fluff-mixing also ensures a more complete separation of cell aggregates into individual cells (Severson et al., 1955).

Predrying in the F-T process takes place rapidly under a long constant-rate period (Ooraikul, 1978). The heat and mass transfer rates in the bed are sufficiently high so that the temperature of the potatoes is kept low (no more than 45°C). Granulation, which follows predrying is carried out quickly using a high rate of stirring and a low air velocity. This ensures that the particles remain within the crit range of moisture content. The granules, after the granulation step, usually consist of more than 85% fine powder of smaller than 60 mesh, with less than 1% discard (Ooraikul, 1977). Predrying and granulation determine

the amount of fine granules in the final product, the extent of cell damage, and the amount of discard.

2.6. Final Drying.

This is carried out in the F-T process in a batch fluidized bed drier (Ooraikul, 1977). Drying takes place in only 10-15 min under relatively high air temperature and velocity. In the A-B process, granulated potatoes are dried in an air lift drier to about 12% moisture and finally dried to 6% moisture in a fluidized bed drier. Drying occurs during the 10-30 min residence time. The inlet air temperature can be quite high without scorching the product because transfer of heat occurs so rapidly that none of the granules is exposed to overly high temperature.

3. POTATO STARCH AND ITS CHARACTERISTICS AS RELATED TO GRANULE PROCESSING.

3.1. Starch Grain Distribution in Potato Tuber.

Scanning electron microscopy studies by Fedec et al. (1977) revealed the presence of starch grains in storage parenchyma cells adjacent to the vascular tissue, cortex, internal phloem and pith, and the absence in cork cells or periderm. Internal phloem and cortical cells were found to contain grains of similar size varying from 4.3-18.6 μm in outer and 20 x 38-50 x 86 μm in inner cells of the cortex. Storage parenchyma cells adjacent to the vascular tissue contained grains which were small and round. Spherical and oval-shaped grains in pith ranged in size from 4.5-18.2 μm and 24 x 32-38 x 50 μm,

respectively. Johnston et al. (1970) and Chung and Hadziyev (1980) reported the predominance of the 38-53 and < 38 μm grain size fractions in potato tubers.

Putz et al. (1978) and Chung and Hadziyev (1980) found a significant influence of year and location on starch grain size. The latter authors and Johnston et al. (1968) showed the dependency of amylose content on grain size. Larger grains were found to have a slightly higher percentage of amylose. Starch grains from southern and central Alberta tubers, regardless of tuber weight, had a higher population of larger grains, hence, higher amylose content than those from northern Alberta (Chung and Hadziyev, 1980).

Reeve (1967) reported the influence of storage temperature on size distribution. Smaller grains were found to be digested more rapidly than larger ones at high storage temperatures. However, Mica (1975) found that larger grains were degraded to smaller ones in European potatoes stored for 6 months at 2 and 10°C. Johnston et al. (1968) found that storage of "Netted Gem" potatoes at 4°C for up to 6 months had no influence on grain size distribution.

3.2. Molecular Structure of the Starch Grain.

Plants elaborate their starch in the form of microscopically small grains (Sterling, 1968; Badenhuizen, 1969) in which the molecules of starch lie with their long axes radial to (Kreger, 1951; Meyer, 1895) or, more exactly, perpendicular to the grain surface at which they are laid down (Badenhuizen, 1969; French, 1972; Sterling, 1977). Gruber et al. (1973) claimed that swelling of potato starch grains in water involves, firstly, an inner "core". In other reagents an outer "mantle"

will first swell. They believed that this behavior lends support to the idea that the starch grain consists of blocklets, crystalline isodiametric micelles of folded molecules, which are mostly amylose in the core. The amylose micelles form radial fibrillar domains (Gruber, 1972). Outside the core, a mantle of isodiametric fringed micelles of folded amylopectin molecules is said to be formed in tangentially cohesive layers. Mühlethaler (1965) and Holzl (1973) were also in favor of viewing the starch grain as composed of isodiametric micelles of folded molecules of both amylose and amylopectin. The evidence for this concept is as follows: the granular surface of freeze-fractured starch grains (Mühlethaler, 1965), a lamellar periodicity of 80 to 100 nm (lamellar thickness 40-50 nm) seen upon digestion with acid (Frey-Wyssling and Buttrose, 1961), and crystallization of long molecules of amylose (in platelets 7.5-10 nm thick) from butanol (Yamashita, 1965).

By subjecting potato starch grains to differential swelling in water, Sterling (1974, 1976), showed the presence of radially coursing fibrils of variable diameter (0.1 to 10 μm), radiating from the hilum and traversing the concentric lamellations of the starch. The molecules in the fibril were shown to be connected by covalent bonds in the radial direction. Sterling (1977) showed that the major lines of weakness occur between radial fibrillar units rather than between concentric tangential shells.

The above fibrillar structure implies the presence of pores on the surface of starch grains. The pore sizes in wet swollen potato starch were determined by precipitating crystals of silver within the grain and measuring their diameters (Sterling, 1973). Diameters ranged from 0.5-75 nm. Large pores were concentrated in the interlamellar

regions and small pores (0.5-2.0 nm) in the intermolecular and intermicellar spaces within the lamella.

Native starch grains are semicrystalline and exhibit two different X-ray diffraction patterns, the so-called A- and B-patterns, depending on the source of starch (Katz and Van Itallie, 1930). The former is characteristic of cereal starches, while the latter is predominantly found in tuber and leguminous starch. A third type, the C-pattern, is thought to be a mixture of A- and B-patterns, and is found in banana (Sterling, 1968). Interaction exists between these crystalline forms. For example, heat/moisture treatment will convert the B-pattern of potato starch to an A-type, with corresponding changes in the physical properties of the grains. Controlled drying of a heated starch gel can produce depending on the temperature, any of the crystalline forms.

In general, it is now apparent that crystallinity is due to the amylopectin component (Banks and Greenwood, 1975).

A number of different unit cells and structure have been proposed for both A- and B-starches, but none has been completely correct. French (1972) postulated that none of the alternative models provide a structure capable of explaining X-ray observations without distorting bond lengths and bond angles, or introducing into the unit cell unacceptably high amounts of water of crystallization. French (1972) suggested that, since none of the single-stranded helical models for the starch chain is satisfactory, attention should be given to double-stranded helix formation, even in the amylopectin component.

The crystal structures of A-, B- and C-polymorphs of amylose have been determined through a combination of fiber X-ray diffraction analysis and computer-based structure refinement (Sarko and Wu, 1978).

These authors showed that the three structures correspond to the naturally occuring A-, B- and C-starches, and all three are based on double-stranded helices. Both A- and B-amylose are virtually identical in conformation: both are right-handed, parallel-stranded helices. However, the A- and B-structures differ in the crystalline packing of the helices and the water content. The A-amylose crystallizes in an orthogonal unit cell with slightly distorted hexagonal packing and with eight water molecules per unit cell. The B-amylose crystallizes in a hexagonal unit cell with a much more open hexagonal packing and 36 water molecules per unit cell. The C-structure is a mixture of A- and B-unit cells, and is, therefore, intermediate between the A- and B-forms in packing density.

3.3. Starch Components.

3.3.1. Amylose.

3.3.1.1. General Characteristics.

Amylose, a linear α-1, 4D-glucan, comprises 21.2% of potato starch (Chung and Hadziyev, 1980). Amylose isolated from mature tubers has a iodine binding capacity of 19.5%, a B-amylolysis limit of 76% and a limiting viscosity value ($[\eta]$) in 1 M KOH of 410 ml/g (Greenwood and Thomson, 1962).

3.3.1.2. Conformation and Behaviour of Amylose in Solution.

The conformation of the amylose chain depends on the ring conformation of the glucose residue (Rao et al., 1967). Hollo et al. (1961) concluded from models that amylose would exist as a flexible

ring if the ring conformation were either B1 or C1, whereas the 3B conformation could lead only to an extended chain. Rao and Foster (1963, 1965) showed from NMR studies of polymers of D-glucose that all the glucose units exist only in the C1 conformation. This is supported by the X-ray crystallographic studies of Hybl et al. (1965), which revealed that all six glucose units in cyclohexa-amylose potassium acetate complex are in the C1 conformation. Rao et al. (1967) showed (from calculations of potential energy of non bonded interactions) that out of 8 probable conformations (2 chair and 6 boat forms) for α-D glucopyranoside, the C1 (chair) conformation had the lowest energy. Thus, the boat forms are ruled out as possible ring conformations for all the units in amylose, since all the glucose residues in the C1 configuration can be linked through α 1-4 linkages without any steric strain.

The configuration and behavior of amylose in aqueous solution has been the subject of much controversy, as can be seen from the models that have been proposed. They are: the Hollo-Szejtli tight helix model, the Banks-Greenwood random coil model, and the Senior-Hamori extended helix model.

Hollo and Szejtli (1961) proposed an interrupted, tightly-wound helix for the structure of the amylose chain. Amylose was depicted as a molecule composed of helical segments, with the helical regions stabilized by intermolecular hydrogen bonds, each segment consisting of about 120 glucose units, with limited regions of random coil interspaced between the segments.

Banks and Greenwood (1971) observed a large decrease in the viscosity number (i.e. a decrease in hydrodynamic volume) on the addition of iodine and n-butanol to amylose in neutral aqueous solution. Therefore,

they postulated that amylose possesses no helical character in neutral aqueous salt solution, and that the helical configuration is forced upon amylose by the addition of complexing agents.

Senior and Hamori (1973) disagreed with the Hollo-Szejtli model for the following reasons. They observed intrinsic viscosity changes even near the zero value of iodine binding, suggesting that there is a conformational change (due to a contraction of the linear dimension of the polysaccharide chain) accompanying the binding of even the first few iodine molecules. Such a change would not occur in the presence of tight helical segments. Although the Banks-Greenwood model explained the above changes, it did not explain the kinetic results of Senior and Hamori (1973), who observed that addition of iodine to already formed iodine-amylose complex resulted in fresh nucleation and rapid growth of newly complexed regions, rather than in growth of existing polyiodine chains. They interpreted that there were alternating sections on the amylose molecule, one kind of which was suitable and other kinds of which were not suitable for a rapid complexation reaction. These authors proposed a conformation for amylose which involves regions of loose and extended helices which alternate with shorter random coil sections. Based on this model, the formation of the amylose/iodine complex can be visualized as the entrapment of iodine atoms by the contraction of the loose helical regions of the macromolecule into tight helices of the "V" amylose. This model would also be compatible with the pronounced decrease in the intrinsic viscosity of aqueous amylose solution around pH 12 (Erlander, 1968; Erlander and Purvinas, 1968). Such a decrease was attributed to the destruction of the loose helical regions as a result of electrostatic repulsion arising from dissociated hydroxyl groups.

3.3.1.3. Formation of Monoglyceride Inclusion Complexes.

Starch, especially the amylose fraction, combines with a variety of compounds like iodine, aliphatic alcohols, cyclic and aliphatic hydrocarbons, long chain fatty acids and monoglycerides to form so-called inclusion compounds which are insoluble at room temperature. Inclusion compounds are not the result of chemical interactions, but have been defined rather as addition compounds in which one entity (guest) fits into and is surrounded by the lattice of the other (host). The bonds involved in inclusion compounds are primarily Van der Waals attractive forces which are quite weak but sufficient to provide the formation of stable complexes when all molecules are close together (Osman-Ismail, 1972).

The structure of the amylose molecule in suspension can be represented as a chain with 10-12 helices, each containing a mean of 12 windings of six glucose units (length of winding: 8 Å). It follows that every helix binds at least one and, in many cases, two molecules of glyceryl monopalmitate (GMP) during complex formation. The length of the GMP molecule is about 22 Å. If a helix with 12 windings forms an inclusion compound with 2 moles GMP, the free space is 50 Å and, consequently, consists of about 6 windings or about 35 glucose units (Lagendijk and Penings, 1970).

The inside diameter of the amylose helix is 4.5-6.0 Å, depending on the number of glucose units per turn, which varies from six to eight (Krog, 1977). Straight hydrocarbon chains, such as saturated monoglycerides, can very easily be enclosed in the helical core, but the presence of a double bond in unsaturated monoglycerides gives a bend to the fatty acid chain, making it impossible for such monoglycerides to

penetrate as readily into the amylose helix. The difficulty is compounded even more in the case of cis-isomerism (Birnbaum, 1971).

In the helical form the interior surface is built up by C-H groups and glycosidic oxygen atoms forming a lipophilic core, while all the polar hydroxyl groups are positioned on the outer surface of the helix (Banks and Greenwood. 1972). Carlson et al. (1979) have shown that the hydrocarbon chain conformation inside the helix seems to be ordered as in the crystalline state and their results indicate that the polar group is not included in the helix.

X-ray powder diffraction of amylose-monoglyceride complexes (of different chain lengths) has shown that they have the same diffraction patterns as described by Zobel (1964) for the so-called "V" form of amylose, indicating that all monoglycerides, irrespective of chain length, form the same type of inclusion compounds with amylose but to a different extent (Krog, 1971).

Complex formation between corn starch and fatty acids was first reported by Schoch et al. (1944). A few years later Mikus (1946) showed that the complexing agent was entrapped within the helical chain.

Osman et al. (1961) demonstrated a method to evaluate food-grade surface active agents with respect to their amylose complexing ability. This method was based on potentiometric measurements of the reduction of the iodine affinity of the amylose. All materials used, with the exception of diglycerides and triglycerides of soybean oil, greatly reduced the iodine affinity of the amylose but in no case was it reduced to zero. They also found that the reduction of the affinity was directly related to the percentage of monoglyceride added.

Lagendijk and Penings (1970) studied the relationship between

the complex formation of starch with monoglycerides and the firmness of bread. Using pure amylose and amylopectin, isolated from potato starch, they gelatinized the starch fractions in the presence of relatively pure (95%) monoglycerides with varying fatty acid moieties. They found that monoglycerides formed complexes with both amylose and amylopectin but did so to a much greater extent with amylose. The optimum complexing effect was found with glyceryl monopalmitate.

Krog (1971) observed optimum complexing with glyceryl monomyristate. He also found that mono- and diglyceride blends of 45% monoester content did not provide expected complexing at monoester levels equivalent to the distilled monoglycerides of 95% monoester content. This anomaly was attributed to the formation of an emulsion, with the di- and triglycerides present binding the monoglycerides at the oil/water interface.

The molecular conformation of amylose in the presence of surfactants was studied by measuring viscosity (Kim and Robinson, 1979). The intrinsic viscosity of neutral, aqueous salt amylose solutions decreased slightly upon complexing with surfactants, indicating that surfactants enter into the already existing helical cavity of amylose molecules.

The complex formation between monoglycerides and amylose has found extensive application in the production of dehydrated mashed potatoes (Gutterson, 1971). Harrington et al. (1960) reported that the addition of monoglyceride either during the A-B process or in the dry granule reduces the stickiness of gelled starch extruded from ruptured or intact cells. A similar observation was made by Severson et al. (1955).

Ooraikul and Hadziyev (1974) found that a blend of monoglycerides was superior to that of a single monoglyceride in controlling the texture

of reconstituted granules. These authors found that the addition of Myvatex (a blend of glyceryl monostearate and propylene glycol monostearate) to a mash with an average broken cell count of 2% gave the best results at a concentration of 0.2%, against 0.3% when glyceryl monostearate alone was used.

In potato granule processing the significance of this complex formation is in the possibility of partially removing the free starch from potato cell binding matrix into a clathrate complex using monoglyceride alone or in combination. The freezing step of the (F-T process) or the conditioning step of the (A-B process) cause retrogradation of an additional amount of free starch, resulting in further reduction of the cementing ability of the matrix.

3.3.2. Amylopectin.

3.3.2.1. Fine Structure.

Amylopectin has been shown to consist of a large number of chains, each containing an average of 20-25 α-(1-4)-linked glucose residues. The individual chains, which vary considerably in length from about 10 to more than 100 glucose residues, are interlinked by α-(1-6)-glucosidic linkages. Although these interchain linkages amount to only 4-5% of the total, they have a profound effect on the molecular shape and properties of amylopectin (Wolfrom and Khadem, 1965).

Three classical models have been proposed for amylopectin: (1) the laminated structure of Haworth et al. (1937); (2) the herringbone structure of Staundinger and Huseman (1937); and (3) the randomly-branched structure of Meyer and Bernfeld (1940). In each three types of chains can be distinguished (Peat et al., 1952): A-chains, which are linked to the

molecule by only a single linkage from the potential reducing group; B-chains, which carry one or more A-chains and are themselves linked to an adjacent chain by the potential reducing group; and a single C-chain, which carries the only reducing end group in the molecule.

The three models can be thought of as structures with ratios of A- to B-chains close to zero, infinity and one, respectively.

Gunja-Smith et al. (1970) have revised the Meyer model based on the inability of Cytophaga isoamylase to remove branch-linkages joining maltosyl units to the main chain. Although this model still has the A:B chain ratio of unity, it differs from Meyer's model in having only half of the B-chains bearing substituent A-chains, while half have their nonreducing chains within the molecule.

Marshall and Whelan (1974) have shown that the A:B chain ratio is not the unity of the Meyer model but lies in the range of 1.5-2.6. Their ratio was calculated from the reducing power liberated from isoamylose and isoamylose-pullulanase incubated B-limit dextrins.

The contradictory results for the A:B chain ratio may be due to the type of amylopectin analysed, and also to errors in measuring reducing power (Altwell et al., 1980). French (1972) suggested a racemose form for amylopectin, which appears to account adequately for most of the known properties of amylopectin. Robin et al. (1974), using enzymatic debranching techniques to elucidate the structure of lintnerized potato starch, proposed a potato amylopectin structure consisting of alternating compact crystalline areas of chain clusters with a degree of polymerization of 15, and less compact intercrystalline areas rich in α 1-6 linkages.

3.3.2.2. General Characteristics.

Molecular weight values reported in the literature for amylopectin vary from 10-500 x 10^6, depending on the botanical origin, method of starch fractionation, and method of molecular weight determination (Manners, 1978). The molecular weight of potato amylopectin has been shown to be 30 x 10^6 (Witnauer et al., 1955) and 50 x 10^7 (Greenwood, (1960).

The phosphorus (P) in potato starch occurs in the form of orthophosphate (30-175 mg % P) esterified with the C_6-hydroxyl group of amylopectin (Posternak, 1951; Palasinski, 1980). The ester phosphate confers on the amylopectin the properties of a polyelectrolyte. Furthermore, the limited degree of branching confers considerable flexibility on the molecule and enables it to respond to its solvent environment by changing the volume it occupies (Banks and Greenwood, 1975).

3.4. Gelatinization and Swelling Characteristics of Starch Grains.

Starch grains heated in the presence of sufficient water exhibit an order-disorder phase transition called gelatinization, which results in near solubilization of the starch. Minimally, gelatinization entails: (1) diffusion of water into the grain, resulting in hydration of the starch, accompanied by granule swelling; (2) hydration - facilitated helix-coil transition which is a melting process; and (3) the loss of crystallinity of the granule as measured by loss of birefringence and its X-ray diffraction pattern.

Various methods have been used to study gelatinization. These include viscosity methods such as amylography (Bean and Osman, 1959;

Dahle, 1971), optical methods such as photopastegraphy (Seidmann, 1967; Kainuma et al., 1968), and microscopic examinations of morphological and polarizing pattern changes (Watson, 1964; Miller, 1973). These methods, however, are limited by certain parameters such as concentration change (due to water evaporation), water measurement, starch/water ratio and inability of measuring gelatinization at temperatures above 100°C (Wada et al., 1979).

Differential scanning calorimetry (DSC) is well suited to investigate the phase transitions of starch water systems (Donovan, 1979; Donovan and Mapes, 1980; Biliaderis et al., 1980) because it allows: (1) study of starch gelatinization over a wide range of starch/water ratios; (2) determination of gelatinization temperatures above 100°C; and (3) estimation of transition temperatures.

Starch grains heated with water to temperatures slightly lower than the gelatinization temperature undergo some physical changes associated with gelatinization. Thus, grains swell but birefringence is retained (Gough and Pybus, 1971). Marchant and Blanshard (1978), using a small-angle light scattering apparatus, have shown by means of temperature-jump experiments, that two processes in which birefringence is lost can occur simultaneously, but at different rates, and that the stability of the crystalline regions depends on the conformation of starch chains in the amorphous regions. DSC studies on potato starch (Donovan, 1979) showed that two mechanisms govern the loss of structure of the ordered regions of the grains on heating: (1) in the presence of excess water, swelling of the amorphous regions of the grain "strips" starch chains from the ordered crystallites in the process known as gelatinization; and (2) at lower water content, the crystallites

melt at a higher temperature, the melting temperature being a function of water content.

Wootton and Bamunuarachchi (1979), Donovan (1979) and Biliaderis (1980) have shown that decreases in gelatinization enthalpies (ΔH) occur in the presence of limited amounts of water. A lower degree of disorder achieved by the starch during gelatinization of concentrated starch/water systems was proposed as the reason for the decreased ΔH values (Stevens and Elton, 1971). Donovan (1979) has further suggested that at low water content the ΔH value mainly represents the enthalpy of melting of the starch crystallites. At high water levels, however, the ΔH value can account for grain swelling, crystallite melting and hydration of the starch molecules. Gelatinization temperature is altered by the addition of certain chemicals, some of which accelerate the disruption of hydrogen bonds to increase gelatinization temperature, whereas others inhibit gelatinization by acting as desolvating agents (Leach, 1965). Repression of gelatinization can be achieved by the addition of sodium sulphate, whereas sodium nitrate or urea lower the gelatinization temperature. Esterification or etherification lower gelatinization temperatures and increase grain swelling. However, cross-linkage reinforces the strength of internal bonding, as evidenced by marked inhibition in grain swelling and solubilization (Leach, 1965).

Polyhydric alcohols and methanol were found to decrease the gelatinization temperature of potato starch. This was attributed to the lessened tendency of the medium to rupture hydrogen bonds (Gerlsma, 1970). Monohydric alcohols at lower concentrations decreased the gelatinization temperatures, however, at higher concentration an increase was observed. The lowering effect was attributed to the lessened

tendency of the medium to rupture hydrogen bonds and the increase to an association of solute molecules.

Sodium chloride has been shown to control starch swelling. Ganz (1965) associated the effect of salt with the presence of crystalline regions in the starch grain which have binding forces of varying strengths or different accessibilities. In the 60-70°C range, NaCl seemed primarily to affect the weak forces or readily accessible regions involved in swelling. The author assumed that NaCl inhibited the "opening" of these regions.

Bean and Osman (1959) showed that sugars delay gelatinization by tying up water molecules, making them unavailable for starch. Gray and Schoch (1962) and Longley and Miller (1971) observed that polar surfactants (e.g. higher fatty acids, monoglycerides), which complex strongly with the linear fraction, restrict the swelling and solubilization of corn, potato and even waxy sorghum starches over the pasting range of 60-95°C. The degree to which this effect was noted differed depending upon the chemical composition of the surfactant, the length of the chain, and the degree of saturation of the lipophilic parts.

Gelatinization temperatures have been found to be dependent on starch grain size. The microscopic sequence of events in gelatinization was followed by Sterling (1974, 1976) and Chung and Hadziyev (1980). Larger grains were found to undergo rapid gelatinization. The latter authors observed that potato starch grains less than or equal to 30 μm in diameter remained intact even at 66°C. However, complete gelatinization was evident at 70°C.

The swelling power of starch is a function of temperature and genetic origin. Potato starch swells more and at a lower temperature

than sorghum, but it is much less soluble at equivalent degrees of swelling (Leach et al., 1959). Starches of high amylose content are gelatinized only with great difficulty, so that birefringent, ungelatinized grains may be found even after 30 min at 95°C (Leach et al., 1959). It can, therefore, be presumed that swelling is particularly related to the quantity of branched molecules (Waldt and Kehoe, 1959).

The presence of ionizable esterified phosphate groups in potato starch has been held partly responsible for its high swelling power (Leach, 1965).

3.5. Starch Retrogradation.

The phenomenon of retrogradation of starch refers to the aging event in which there is a decreased SP, WBC, digestibility by acids or hydrolysing enzymes, iodine affinity and cold water solubility of the gel framework (Katz, 1928, 1930; Volz and Ramstad, 1952; Sterling, 1957). As time goes on, the gel shrinks, becomes more opaque and more rigid, and often may exude moisture (Sterling, 1960). Retrograded starch cannot be gelatinized, although it can be resolubilized by heating to higher temerature. Retrogradation is due to parallel association of starch molecules (Hellman et al., 1954; Hellendoorn, 1971), in which hydrogen bonds are formed between hydroxyl groups of starch molecules (Collison, 1968).

Katz and Van Itallie (1930) revealed that retrograded gel always displays the "B"-pattern regardless of the initial crystalline pattern of the native starch. Katz (1930) and Bear (1942) showed that freshly prepared corn starch displays a "V"-pattern when precipitated with alcohol. During retrogradation, the alcohol-precipitated paste

gradually shows an increasing intensity of the "B"-pattern (Katz, 1930) and a decreasing intensity of the "V"-pattern. However, Zobel (1973) reported that freshly-baked bread, without added surfactants, shows only "V"-crystallinity due to amylose reacting with the naturally occuring fatty acids in wheat flour. During retrogradation, the amorphous starch crystallizes ("B"-type), while the intensity of amylose complex ("V"-type) remains virtually unchanged. However, bread with added surfactants showed increases in intensity of "V"-lines during retrogradation. The higher "V" intensities confirmed that complex formation takes place between these surfactants and the amylose fraction.

The rate and extent of retrogradation are found to be influenced by a number of factors, such as chain length (Whistler, 1965), linearity of chains (Lampitt et al., I948), esterification and etherification of starch (Greenwood and Hourston, 1967), temperature (Katz, 1928; Sterling, 1960; Colwell, 1969; Kalb and Sterling, 1961b), time (Brenan and Sodah-Ayernor, 1973; Knightly, 1977; McIver et al., 1968), surfactants (Zobel, 1973), temperature of gelatinization (Kalb and Sterling, 1961a), moisture content (Hellendoorn, 1971), cations and anions (Ciacco and Fernandes, 1979), type of starch (Loewus and Briggs, 1957), molecular weight of amylose (Lansky et al., 1949) and pH (Kalb and Sterling, 1961b).

The optimum chain length for retrogradation corresponds to reduced viscosities of 0.45-0.56 for potato amylose (Whistler, 1965). Molecules smaller or bigger than this do not associate as completely.

In contrast to amylose, amylopectin retrogrades very slowly. Molecules of amylopectin, because of their branched nature, can associate

only with difficulty (Lampitt et al., 1948). In a normal starch dispersion the retrogradation of amylose is retarded by amylopectin. The rate and extent of retrogradation of any particular amylose-amylopectin mixture varies in direct ratio with the amount of amylose present (Radley, 1953).

Modification of native starch through esterification or etherification has been shown to prevent excessive parallel alignment of amylose chains due to steric hindrance imposed by their bulky groups (Greenwood and Hourston, 1967).

The association of starch molecules in retrogradation has been found to be temperature dependent. A maximum rate is reached at -2°C, (Katz, 1928; Sterling, 1960). Retrogradation is minimal at or above 60°C or below -20°C (Sterling, 1960). However, Lampitt et al. (1948) showed that retrogradation is the same at 37°C as at 62°C in 2% pastes of corn and potato starch. Sterling (1960) reported that 13% starch gel at 70°C became less dispersible than that held at room temperature. Thus, discrepancies exist in the effect of storage temperature on retrogradation.

The rate of retrogradation continually decreases with time. McIver et al. (1968) stated that the kinetics of retrogradation could be represented by the theory of Avrami (1939, 1940). The Avrami theory applies most accurately to the initial stage of the crystallization when the nuclei are forming and growing.

The Avrami equation is expressed as: $\theta = \exp(-Kt^n)$

where θ represents a noncrystalline portion of a material after a time "t"; "k" is a parameter designating crystal growth; and "n" is the characteristic of nucleation that produces a new phase change and can be

expressed by integers from 1-4. The Avrami exponent (n) indicates various types of nucleation and growth of a system. Since n values obtained by various workers (Colwell et al., 1969; Axford and Colwell, 1967; Willoft, 1971) are essentially equal, retrogradation of starch gels apparently involves instantaneous nucleation followed by the rod-like growth of crystals.

Surfactants reduce the rate of retrogradation by reducing the hydrophilic characteristics of the starch so that the normal molecular alignment of starch chains with each other and with water fails to occur (Zobel, 1973).

Kalb and Sterling (1961a) found that the higher the temperature to which starch is heated during gelatinization (greater the dispersal of starch molecules), the slower is the rate of retrogradation.

Hellendoorn (1971) showed that in dry mashed potato products the rate of retrogradation increases rapidly with decreasing moisture content and reaches a maximum at a moisture content of approximately 30%. The absolute minimum of retrogradation is reached when only a monomolecular layer is retained, e.g. at a moisture content of 7% (Duckworth and Smith, 1963).

The effect of various ions on the mode and kinetics of retrogradation of concentrated wheat starch gel was studied by Ciacco and Fernandes (1979). The retrogradation rate for the halogen anions increased in the following order: I^-, Br^-, Cl^- and F^-. The retrogradation rates for cations increased in the following order: K^+, Li^+ and Na^+. The results obtained were dependent on the charge distribution of the anions studied.

Kalb and Sterling (1961b) showed that the effect of pH on

retrogradation rates depended on time of pH adjustment. Adjustment of pH before gelatinization resulted in maximum rates of retrogradation at pH 5.0, in agreement with Hollo's (1960 a,b) findings on butanol precipitated starch. However, adjustment after gelatinization resulted in maximum rates being shown at pH 1.3-2.2, in agreement with Schoch (1941).

Retrogradation of starch, which occurs during precooking, cooling and conditioning steps (A-B process) and during the freezing step (F-T process), reduces water absorbance and, therefore, the swelling capacity of the gel. This limits the degree to which tissue cells are distended and separated, resulting in greater firmness and reduced sloughing of cooked potatoes (Potter et al., 1959).

4. PECTIC SUBSTANCES.

Pectic substances are polygalacturonides with non-uronide carbohydrates covalently bound to an unbranched chain of 1-4 linked α-galacturonic acid units. The carboxyl groups of the galacturonic acid are partly esterified, while free groups are more or less neutralized. The monomer is thought to have the C1 conformation. The glycosidic bonds are, therefore, of the axial-axial type, which causes the polymer chain to have a screw-like axis with a tendency to coil (Pilnik and Voragen, 1970).

Discrepancies appear in the literature with respect to the amount of pectic substances in raw tubers. On a dry weight basis, reported amounts are 0.7-1.5% (Potter and McComb, 1957) 4.5-4.8% (Jaswal, 1969) and 2.4-3.9% (Hoff and Castro, 1969). Discrepancies can be explained as being due to differences between analytical techniques

applied as well as between samples.

Pectic substances in raw tuber exist in the form of protopectin, the water insoluble parent substance, and pectin, which is composed of water-soluble pectinic acids. The ratio of protopectin to pectin was found to change with storage temperature (Sharma et al., 1959) and maturity, variety and cultural practise (Bettelheim and Sterling, 1955; Linehan and Hughes, 1969). Raw potatoes were found to be low in pectic substances in both water-soluble and calgon soluble fractions (Ooraikul et al., 1974). The water-soluble fraction appeared to be higher than the calgon soluble fraction. Furthermore, cooking was found to considerably increase the apparent total (water + calgon soluble fractions). These observations led to a suggestion that ionic bonds are not important in the structure of protopectin. Thus, it appears that, as suggested by Doesburg (1965), physical enmeshing of the polyuronides in the cellulosic fibres of the CW's, and other bonds existing in CW's and ML are more important. This fraction of enmeshed polyuronides was found to be solubilized by HCl (Bettelheim and Sterling, 1955; Ooraikul et al., 1974).

Hoff and Castro (1969) showed that only one half of the pectic substances isolated from potato CW were polyuronide compounds. The remainder was found to be sugars, mainly galactose.

5. MONOGLYCERIDES.

5.1. Preparation and Uses of Monoglycerides and Their Derivatives.

Monoglycerides have been used in the food industry since 1921. Today the industry annually uses approximately 100,000 tons of fat-derived

surfactants, of which monoglycerides and their derivatives total about 75% on a volume basis (Krog, 1981).

Most monoglycerides are prepared by the base-catalyzed interesterification reaction of excess glycerol directly with a triglyceride at a temperature of 200°C (Lauridsen, 1976). Up to about 65% monoglyceride can be obtained by using a reasonable excess of glycerol and carefully controlling the reaction conditions. At the end of the ester interchange, the catalyst is neutralized and the excess glycerol removed by vacuum stripping (Pitt, 1971). To obtain higher concentrations, the mono- and diglyceride mixture is distilled under high vacuum (0.001 mm Hg) in centrifugal molecular stills. The resulting distilled monoglyceride consists of about 92-95% total monoglyceride, with the remainder being principally diglyceride (Lauridsen, 1976).

Monoglyceride consist of a hydrophobic fatty acid chain esterified to the hydroxyl group of glycerol. Industrially used monoglycerides possess fatty acids with chain lengths varying from C_{12} to C_{18}. Both the fatty acid chain length and degree of unsaturation are important for the functional properties of monoglycerides (Krog, 1981). The surface activity of monoglycerides is closely related to their chemical structure. The hydrophilic/lipophilic balance (HLB) of a monoglyceride depends on hydrophilicity of the polar group in relation to the lipophilicity of the fatty acid group (Krog, 1981). Although monoglycerides function as excellent softening and staling retardant agents (Knightly, 1968), their low HLB value (Del Vecchio, 1975) makes them ineffective as dough strengtheners. However, this limitation has been overcome by ethoxylation and succinylation or by reaction of monoglycerides with diacetyl tartaric acid (Pitt, 1971).

5.2. Crystalline Behaviour and Lyotropic Mesophases.

Molecules in a monoglyceride crystal are arranged in such a manner that the terminal methyl groups of the hydrocarbon chains make up the surface layer, while the hydroxyl groups are within the interior of the unit cell. This is the so-called β-crystalline form (Birnbaum, 1971). When monoglyceride crystals are mixed with water and heated at a temperature close to the melting point, the hydrocarbon chains become liquid, and at the same time water penetrates between the polar groups and a liquid crystalline mesophase is formed. If the temperature is increased further, the lamellar structure may breakdown, resulting in the formation of hexagonal or cubic structures (Krog, 1981). On cooling below the melting point, the hydrocarbon chains crystallize again, normally in the α-crystalline form. In this form the hydroxyl groups make up the surface layer while the hydrocarbon moiety is within the interior of the unit cell. The same volume of water may still be located between the lipid bilayers, and a gel-structure consisting of bimolecular lipid layers alternating with water layers is formed. In this physical state monoglycerides react optimally with amylose (Wren, 1968; Krog and Jensen, 1970). The mesomorphic behavior of monoglycerides in water has also been investigated by Lutton (1965), Larrson (1967) and Krog and Lauridsen (1976).

5.3. Physical State and Functionality.

Wren (1968) and Krog and Jensen (1970) found that the most effective monoglycerides in breadmaking exhibit α-crystallinity. Their results demonstrated the need for hydration of the monoglycerides prior to use. By making such a product, the specific surface of the

monoglycerides is increased about 700-times compared to a normal powdered product (Krog, 1977). An alternative for hydration would be to allow the monoglycerides (which exist normally in the β-form) to crystallize in α-crystallinity form in the presence of propylene glycol monostearate (Birnbaum, 1978).

Evidence has been provided to the effect that a multicomponent monoglyceride system performs better than any of its individual components, and these improved results are obtained at equivalent HLB values (Knightly, 1968; Ooraikul and Hadziyev, 1974). According to Knightly (1968), this might be due to the formation of stronger monoglyceride micelle films, since it is conceivable that several surfactants may fit together more intimately because of structural configuration and form a more closely packed layer on micelle surfaces, with fewer interstitial voids.

III. EXPERIMENTAL

1. POTATOES.

Potatoes used were cv.Russet Burbank ("Netted Gem") with specific gravity of 1.096 ± 0.002 (corresponding to a dry matter content of 25.0%) grown under irrigation in Southern Alberta.

The tubers were stored at 4°C and were reconditioned at 24°C for 10 days before use. Proximate analysis gave the following percentages on a dry matter basis of peeled tubers: crude protein 8.8; fat, oil 0.5; crude fiber 2.5; ash 4.0; and starch 75.0. Amylose content of the starch was 21.2% as determined by potentiometric titration with iodine (Chung and Hadziyev, 1980).

2. CHEMICALS.

1-monoglycerides with fatty acid chain lengths of C_8-C_{18}; 99% purity and only traces of the 2-isomer were obtained from Sigma Chemical Co., St.Louis, MO. Fatty acids of chain length C_8-C_{20} and 95-98% purity were from Eastman Kodak Co., Rochester, NY. The C_{16}-emulsifier, containing at least 90% distilled monoglycerides (derived from hydrogenated palm oil which had been enriched with palmitic acid), was from Vauxhall Foods Ltd, Vauxhall, Alberta.

The C_{18}-emulsifier, also containing at least 90% distilled monoglycerides (derived from hydrogenated soybean oil which had been partially enriched with palmitic acid), was from Eastman Kodak Co., Rochester, NY. Glutaraldehyde and osmium tetroxide (EM grade) were from Polysciences, Inc; Warrington, PA and Stevens Metallurgical, New York, NY. respectively. Citrus pectins (of varying degrees of esterification)

were from Frank Dempsey and Sons; Québec, Canada. All other chemicals used in this study were of reagent grade and were supplied by Fisher Scientific Co.

3. EQUIPMENT.

Centrifuges used were: Beckman Centrifuge Model J 21 B, JA-14 rotor (Beckman Instr. Inc, Palo Alto, CA), and International Centrifuge, size 2 (International Equipment Co; Boston, MA).

Starch grain size distribution was analysed with a Coulter Counter Model T using a counter tube of 280 μm aperture diameter.

Viscosity measurements were done using the NV sensor system of a Haake Rotovisco Model RV-3 (Haake, Karlsruhe, Germany).

X-ray diffraction patterns were recorded on a Philips Model PW-1011-60 diffractometer equipped with a curved crystal AMR monochromator. Colorimetric measurements were made with a Unicam SP 1800 Spectrophotometer (Pye-Unicam Ltd, Cambridge, U.K.).

Gelatinization and other phase transitions were recorded on a Du Pont Model 990 differential scanning calorimeter (DSC) with a 910 cell base (Du Pont Co, Wilmington, DE).

An Olympus Model EHA microscope equipped with a camera (Olympus Optical Co, Ltd, Tokyo, Japan) was used to determine the count of intact sound cells.

The Electron microscope used was a Stereoscan 150 scanning electron microscope (Cambridge Scientific Instruments Ltd, Cambridge, England). The freeze dryer used in SEM work was an Edwards-Pearse Tissue Dryer from Edwards High Vacuum Mfg, Crawley, Sussex, U.K.

Infrared spectra of the emulsifiers were recorded in Nujol by

using a Nicolet series 7000 Fourier transform IR spectrophotometer (Nicolet Inst. Co, Madison, WI).

The fatty acid methyl esters of the C_{16} and C_{18}-emulsifiers were separated on a Hewlett-packard M 7620 gas chromatograph equipped with FID detectors and dual 1.5 m x 4mm I.D.glass columns packed with 8% SP-2340 cyanopropyl silicone on Gas Chrom Q 80/100 mesh (Supelco Inc, Bellefonte, PA).

Equipment used during processing of potato granules was: abrasive potato peeler, Model 6115; vegetable slicer, Model H 4212; Kitchen Aid mixer equipped with a flat beater, all from Hobart Mfg. Co; Don Mills, Ontario; stainless steel trays (60 x 46 cm); air blast freezer with minimum air temperature of $-29^{o}C$ and air velocity of 1.42 m^3s^{-1}; Manesty Petrie fluid-bed dryer, Model MP.10.E., equipped with a stirrer as designed by Ooraikul (1973), from Manesty Machines Ltd., Speke, Liverpool, England; speedomax 12 point temperature recorder (Leeds Northrup, Canada Ltd); Canadian standard sieve series and portable sieve shaker (W.S.Tyler Co, Canada Ltd., St.Catherines, Ont).

Other equipment used was forced draft iso-temp oven and serological bath, both from Fisher Scientific Co., Ltd; Caframo type RZR 1-64 stirrer (Caframo Ltd, Wiarton, Ont); Lo Temptrol Water Bath (Precision Scientific, Chicago, IL); vacuum oven (National Appliance Co, Spokie, IL); Bell-stir heavy duty magnetic stirrer (Bellco Glass Inc, Vineland, NJ); wrist-action shaker (Burrel Co, Pittsburgh, PA); Buhler Tissue Disintegrator (Edward Buhler and Co, Tubingen, Germany); Buchi Rotavapor (Buchi Glasapparate Fabrik, Flawil, Switzerland).

4. METHODS.

4.1. Characterization of Potato Starch and Its Monoglyceride Complexes.

4.1.1. Isolation of Native Starch Grains from Whole Tuber.

The washed and diced tubers were dipped in ice-cold water containing 100 ppm $NaHSO_3$ and homogenized at low speed in a waring blender. The slurry was squeezed through a 100-mesh polyester sieve cloth and the filtrate centrifuged at 700 x g for 15 min. The supernatant and the amber-brown layer of protein atop the starch layer were removed by suction. Further purification was achieved by repeated suspension in water, centrifugation and removal of contaminating proteins and cell debris. The purified nondefatted starch was dried overnight at 30°C in a vacuum oven to a moisture content of 12.5% and then kept in a desiccator over P_2O_5. Before analysis the residual moisture content was determined by heating at 130°C for 1 h.

4.1.2. Starch Grain Size Distribution Within Potato Tuber.

The procedure used was as outlined by Williams (1970). A 5% (w/w) solution of NH_4SCN in isopropanol was used as the electrolyte for dispersing the starch grains. Prior to use, the electrolyte was filtered through Millipore filter pads (type AA) with a stated porosity of 0.8 µ. The aperture diameter of the counter tube was 280 µm.

4.1.3. Solubilization.

The lintner standard method for soluble starch preparation was followed. Potato starch was treated for 3 days at 40°C with 1.5-times its volume of 7.5% HCl, after which it was thoroughly washed and dried in a desiccator.

4.1.4. Starch-Fatty Acid Complex Preparation.

Equimolar weights (1.0 mmole) of 1-monoglycerides were dispersed in 20 ml water preheated at 65°C, and stirred for 15 min, after which 3.5% (w/w) of the translucent emulsion was added to 5 g dry starch suspended in 100 ml water and heated at 50°C with gentle stirring for 12 h (final concentration of the monoglyceride was 0.7 mmole per 100 g starch dry matter). The suspension was centrifuged at 20000 x g for 15 min, then the sedimented complex was washed with water and dried in a vacuum oven at 30°C. The complexes were stored in a desiccator over P_2O_5. The residual moisture content was determined by heating at 130°C for 1 h.

Complexes were also prepared from fatty acid K-salts. The fatty acids were neutralized with alcoholic 1 N KOH. The alcohol - water mixture was then removed by distillation under vacuum. Equimolar, 1.0 mmole amounts of salts were dispersed in 20 ml water and heated at 70°C for 25 min. The emulsion was added to an aqueous starch suspension (0.7 mmole per 100 g starch dry matter) and heated at 50°C with gentle stirring for 12 h. The suspension was adjusted to pH 4.5 with 2 N HCl and filtered on a Buchner funnel. The retained complex was thoroughly washed with deionized water and then dried in a vacuum oven at 30°C.

4.1.5. Starch Swelling Power and Solubility.

The procedure used was as outlined by Schoch (1964a) with slight modifications. A single point characterization was done at 85°C. A starch sample of 0.5 g was suspended in 180 ml deionized water in a preweighed centrifuge bottle and stirred at 200 rpm with a 1.98 x 3.8 cm rectangular

stainless steel paddle, initially for 3 min at 24°C and then for 30 min at 85.0 ± 0.1°C. The content was then adjusted with water to 100 ml, mixed gently and centrifuged for 15 min in a swinging bucket rotor at 1200 x g. The supernatant was removed by suction, and the solubles present determined from a 50 ml aliquot. The swelling power (SP) of the starch grains, expressed as the weight of sedimented paste per g starch (dry matter), after correcting for the soluble starch, was calculated as follows:

$$SP = \frac{\text{Wt of Sedimented paste, g} \times 100}{\text{Wt of Sample, g} \times (100 - \% \text{ solubles, dry basis})}$$

4.1.6. Starch Viscosity.

Viscosity measurements were done at a 0.3% (w/v) optimal starch gel concentration using the NV sensor system of the Haake Rotoviscometer at a rotor speed of 90.5 rpm. Starch suspensions were heated in a water bath for 30 min at 50, 60, 70 and 80°C, and 20 ml aliquots were taken for assay. The sensor system and the cup were kept at the same temperature. Viscosity was recorded for 3 min and was expressed in centipoise (Cp).

4.1.7. X-ray Diffraction.

X-ray diffraction patterns of powdered starch samples were recorded using copper Kα radiation (1.5418 Å) with a time constant of 4 sec scanning angular velocity of 1° 2θ and a chart speed of 1 cm/min. Samples were densely packed in an Al-holder, with precautions taken against granule damage.

4.1.8. Turbidimetric Measurements.

Starch samples suspended in deionized water (0.1% starch dry matter per 100 ml water) were heated at 80.0 ± 0.1°C for 30 min. The percent transmittance at 520 nm was read in 1 cm cells at 80°C or, after cooling, at 25°C.

4.1.9. Differential Scanning Calorimetry.

4.1.9.1. Gelatinization and Phase Transition Temperatures.

Water was added with a micro syringe to native starch (2.15 mg) and complexed starch samples (1.75 mg) in DSC pans, then the pans were sealed, reweighed and allowed to stand for 3 h at room temperature. The amount of water added was expressed as the volume fraction of water, v_1, which equaled the total volume of added water (density 1.00) divided by the total volume of starch (density 1.55) plus water. The analyses were performed at a heating rate of 5 C°/min, using equal amounts of water or empty pans as a reference.

The cell calibration coefficient was determined from the known heat of indium fusion (6.79 mcal/mg) and from specific heat vs temperature of a sapphire standard.

Transition temperatures were recorded from a plot of heat flow vs temperature (30-140°C). The onset (t_o), peak (t_p) and end of transition (t_m) were given in °C. The gelatinization temperature recorded in the presence of excess water was designated as G, while that of the most perfect crystallites was M_1 and of starch-monoglyceride complex, M_2.

The experimental data for variations in transition temperature

T_m (^oK) with ν_1 were plotted according to the Flory-Huggins equation (1):

$$\frac{1}{T_m} - \frac{1}{T_m^0} = (R/\Delta H_u)\ (V_u/V_1)\ (\nu_1 - X_1\nu_1^2) \quad (1)$$

$$\frac{1}{T_m} - \frac{1}{T_m^0} = (R/\Delta H_u)\ (V_u/V_1)\ (1 - \nu_1) \quad (2)$$

ν_1, volume fraction
R, gas constant
ΔH_u, enthalpy of fusion per repeating unit
V_u/V_1, ratio of the molar volume of the repeating unit to the molar volume of the diluent
X_1, Flory-Huggins polymer-diluent interaction parameter
T_m, transition temperature
T_m^0, melting point of the most perfect crystallites

while the enthalpy of fusion per repeating glucose unit of starch, ΔH_u, was derived from form (2) of the same equation. Eq (1) gives a linear relationship between $1/T_m$ and ν_1, hence, when $X_1=0$, the intercept at $\nu_1=0$ gives the reciprocal of the transition temperature of the most perfect crystallites, $1/T^o_m$. A plot of the left-hand side of Eq (2) against ν_1 provided the ΔH_u in Kcal/mole D-glucose unit.

The percent of bound amylose in starch-monoglyceride complexes was determined at $\nu_1=0.85$ from the endotherm centered at 104^oC. The enthalpy of fusion of the complex was taken as 7.4 cal/g amylose, as suggested by Kugimiya et al. (1980). The amylose content of the cv. Netted Gem potato starch, 21.5%, was determined potentiometrically from the content of iodine bound to starch by extrapolation to the zero level of free I_2 (Schoch, 1964b).

4.1.9.2. Water Binding Capacity.

A DSC method was applied in order to measure the freezable water in a starch-water slurry. The fraction of water that is not frozen when the slurry is cooled down to -50^oC is defined as bound water (Wootton and Bamunuarachchi, 1978). A 5-20 mg aliquot of starch-water slurry, equilibrated overnight, was sealed in a DSC-pan, cooled with liquid N_2

at the cell platform, allowed to equilibrate 3 min, then heated to 40°C at 10 C°/min. Endotherm areas of ice fusion were integrated and compared with those of known weights of water. From the results of at least 4 runs at different free vs total water contents, the amount of bound water per g of starch or its complex was equated to the total water content extrapolated to the zero free-water level.

4.1.10. Scanning Electron Microscopy.

One drop of heated starch suspension was placed on a microscope slide and frozen in liquid Freon 12 cooled with liquid N_2. The sample was then freeze dried at -80°C, mounted on Al stubs with silver paste, coated with 20 nm of gold and examined at an accelerating potential of 10 KV. Amylose was revealed by iodine staining as observed in light microscopy. In a similar procedure, the liquid N_2 freezing step was replaced by drying the drop of starch suspension overnight on a microscope slide or Al-stub at room temperature in a desiccator over P_2O_5.

4.2. The Effect of Monoglycerides on Amylose Complexing During a Potato Granule Process.

4.2.1. Determination of the Fatty Acid Composition of C_{16}- and C_{18}-type Monoglycerides.

The monoglycerides were saponified with 50% ethanolic KOH under reflux for 2 h. The reaction mixture was then acidified with 10 N H_2SO_4, the free fatty acids extracted by hexane, the extract dried over Na_2SO_4, and then the hexane was evaporated under vacuum and N_2. The residual acid was dissolved in excess methanol and refluxed for 2 h in the presence

of 1% sulfuric acid. The fatty acid methyl esters were taken up in pet ether, then washed and recovered. The esters were separated on a gas chromatograph. The carrier gas was N_2, 50 ml/min. The initial temperature was held at 50°C for 5 min, followed by a 4°/min increase to 200°C.

4.2.2. Monoglyceride Gel Preparation.

4.2.2.1. C_{16}-type Gel (pH 2.3).

A dispersion containing 15 parts of C_{16}-emulsifier in 85 parts of deionized water was heated at 65°C until a translucent homogenous emulsion was obtained. It was then cooled to 24°C in order to form a plastic semi-translucent gel.

4.2.2.2. C_{18}-type Gel (pH 3.5).

C_{18}-emulsifier (15 parts) was mixed with 74 parts of deionized water and heated at 65°C until a clear emulsion was formed. Then 1 part of propionic acid was added and the mixture stirred while cooling to 24°C.

4.2.2.3. Gel of pH 6.5.

Emulsifier (15 parts) was added to 85 parts of deionized water and heated to 65°C until a translucent emulsion was obtained. It was then cooled to 24°C to form a plastic gel.

4.2.2.4. Gel of pH 7.1.

The gel of pH 7.1 was prepared in a similar manner to the pH 6.5 gel, except that 0.3% K-stearate was added to the emulsion while it was being heated.

A semi-solid gel was formed after cooling to 24°C.

4.2.3. Extent of Amylose Complexing with Monoglyceride.

The ability of monoglyceride to complex starch was followed by determining the Amylose Complexing Index of model systems consisting of undamaged, nongelatinized starch grains, solubilized starch grains, solubilized starch, and whole potato tissue slices precooked, cooled, steam-cooked and mashed as in an A-B granule process. The Complexing Index is defined as $(A_{control} - A_{sample} / A_{control}) \times 100$, where A is the absorbance of the amylose - iodine complex at 680 nm.

4.2.3.1. Complexing with Soluble Starch.

Additional solubilization of lintnerized starch was needed. A soluble starch suspension was treated with 1 N KOH and kept at 0°C for 30 min, with occasional stirring, neutralized with 0.5 N HCl and then adjusted to a 0.1% solution by adding deionized water. Emulsifier was added in a range of 0.1-3.5%, as calculated on a starch dry weight basis, and the mixture heated to 60°C and kept at that temperature for 5-35 min. The reaction mixture was cooled to 24°C and centrifuged at 20,000 x g for 25 min. A 5 ml aliquot of the clear supernatant was diluted with an equal volume of water and 1 ml was used for blue color development with iodine as described by Gilbert and Spragg (1964). Their method was as follows: To 1 ml of the clear solution obtained above was added 0.5 ml of N. NaOH. This mixture was warmed for 3 min in a boiling water bath. After cooling, an equivalent amount of approximately 1 N HCl was added, followed by 0.1 g potassium hydrogen

tartarate, 45 ml distilled water and 0.5 ml of iodine solution (2 mg of iodine/ml, 20 ml of KI/ml). The solution was then made up to 50 ml, mixed and allowed to stand for 20 min at room temperature. The absorbance was read at 680 nm using a 1 cm cell.

4.2.3.2. Complexing with Gelatinized Starch Grains.

Batches of 5-100 g potato starch were slurried in 3 parts water and heated at 70°C for 30 min. The slurry was cooled to 25°C over a period of 25 min and then steam-cooked for 30 min. The steamed starch was cooled to 50, 60 or 70°C, and 0.5% emulsifier was added, again calculated on a starch dry weight basis. At intervals of 5-35 min, 2 ml aliquots were taken, diluted with 20 ml water, cooled to 24°C and then clarified by centrifugation as above. A 5 ml volume of supernatant was diluted to 30 ml with water and 1 ml used for amylose-iodine color development.

4.2.3.3. Complexing with Mashed Potatoes.

Peeled potato slices 6.4 mm thick were immersed in 0.5% $NaHSO_3$ and then precooked at 70°C for 30 min in a 1:3 (w/w) ratio of tap water, cooled to 24°C, and steam-cooked. The cooked slices were mashed at 50, 60 or 70°C and emulsifiers were added at a level of 0.75% calculated on a tuber dry weight basis. Samples of 10 g taken from the mixed mash at 5-35 min intervals were suspended in 100 ml water, cooled to 24°C and clarified by high speed centrifugation as above. A 5 ml aliquot of clarified supernatant was used to determine the Amylose Complexing Index.

4.2.4. X-ray Diffraction.

The powder X-ray diffraction technique for microbead and hydrated forms of emulsifiers was applied, in both cases with samples densely-packed into an Al-sample holder. The operating conditions were as described in section 4.1.7.

4.2.5. Infrared Spectrophotometry.

The infrared spectra for microbead and hydrated forms of emulsifiers were recorded in Nujol.

4.2.6. Scanning Electron Microscopy.

For scanning electron microscopy (SEM), several procedures were applied for sample preparation.

4.2.6.1. Starch Suspensions.

Starch suspensions, 0.1% in water were heated at 70 and 80°C for 10-30 min. One drop of the suspension was placed on a circular microscope cover glass that had been cleaned thoroughly with chromic acid. The glass was then immersed at an angle in liquid Freon 12 cooled with liquid-N_2, and kept in this position for 10 s or until boiling ceased. The sample was then freeze-dried overnight at -80°C, mounted on Al-stubs with silver paste and coated with 20 nm of gold.

4.2.6.2. Starch-Monoglyceride Complex Suspensions.

Starch-monoglyceride complexes were formed from monoglyceride previously dispersed in water at 65°C for 15 min at a concentration of

1.8%. This emulsion was then added to 5 g of starch suspended in 100 ml water in amounts corresponding to 0.25 or 1.0% of pure monoglycerides per 100 g starch on a dry weight basis. The complex was formed by gently stirring the suspension at a temperature below that of starch gelatinization, i.e, 50°C for 12 h. Then the suspension was centrifuged at 20,000 x g for 15 min, washed with water, dried in a vacuum oven at 50°C, and stored in a desiccator over P_2O_5. Before SEM study, a 0.1% suspension of starch emulsifier complex in water was heated for 5-30 min at the starch gelatinization temperature of 80°C. Further preparation of the sample followed the procedure given above.

4.2.6.3. Starch Suspensions Subjected to Drying over P_2O_5.

The procedure under 4.2.6.1. was repeated, however, the liquid-N_2 freezing step was replaced by drying of the starch suspensions, either on the circular microscope cover glass or directly on Al-stubs, at 24°C over P_2O_5 in a desiccator.

4.2.6.4. Monoglyceride Microbeads and Gels.

The above microbeads or gels were freeze-dried at -80°C and coated with 15 nm of gold for 1.5 min, using the Peltier effect cooling device in order to avoid heat-induced crystallinity structure deformation.

4.3. Effect of Monoglyceride and Storage Temperature on some Rehydrating Properties of Potato Granules.

4.3.1. Granule Preparation.

The F-T granules were prepared as follows: potato slices

(6.4 mm thick) were steam-cooked at atmospheric pressure and then mashed at or above 75°C with 0.1-0.5% (w/w) of a C_{16}-type monoglyceride (composition 73% C_{16}- and 22% C_{18}-monoglycerides). The mash was then processed by steps which involved freezing, thawing, predrying, granulation, drying and sifting. The A-B granules were prepared by precooking the slices at 70°C for 30 min in 3 parts by weight of tap water. These slices were then mashed at 75°C in the presence of monoglyceride and processed into granules by omitting the freeze-thaw steps of the F-T process. The granules were dried in a Manesty-petri fluid bed dryer. Some of the granules so prepared were stored in brown bottles at 4 and 25°C.

4.3.2. Amylose Leaching.

A granule sample of 2 g and 25 ml water were thoroughly blended for 30 min at 18±1°C in a Buhler tissue disintegrator containing about 25 glass beads. The homogenate was transferred into a 250 ml volumetric flask, made up to the mark with water, then stirred at 25°C for 1 h. A 10 ml aliquot was centrifuged at 2500 x g for 30 min. The supernatant contained soluble starch, 2.5 ml of which were mixed with 7.5 ml water, vortexed for 15 sec, heated at 100°C for 10 min and then cooled to 24°C. Then it was mixed with 0.2 ml standard iodine solution (0.02 N KI_3), left to stand for 10 min and the absorbance read at 640 nm. The soluble starch content was expressed as absorbance units per g dry matter (BVI).

4.3.3. Swelling Power.

The method described by Potter (1954) as modified by Ooraikul and Moledina (1980), was used to determine [illegible] of potato granules.

Samples of 2.5 g were placed in 50 ml graduated centrifuge tubes and mixed with water at 25°C to make 25 ml of homogeneous slurry. The tubes were agitated at 25°C for 1 h with a wrist-action shaker and then centrifuged at 1000 x g for 15 min. The supernatant was swiftly decanted, then 10 ml water were carefully pipetted onto the sediment and the total volume determined. The volume of the swollen material (SP), on a basis of 10 g dry solids was calculated from (total volume - 10) x 4.

4.3.4. Water Binding Capacity.

The operating parameters for the determination of WBC of granules using the differential scanning calorimeter was the same as that described under 4.1.9.2. However, in this case a 6-35 mg aliquot of granule-water slurry equilibriated overnight was used in the determinations.

4.3.5. X-ray Diffraction.

The operating parameters for the X-ray diffraction patterns of granules were as described under 4.1.7.

4.3.6. Microscopy.

4.3.6.1. Scanning Electron Microscopy.

The precooked and/or cooked and mashed samples were fixed for 12 h at 4°C in 3% glutaraldehyde in 0.1 M K-phosphate buffer pH 7.0. After rinsing in buffer, the fixed sections were treated overnight at 4°C in 2% OsO_4 in the same buffer. The samples were once again rinsed in buffer and then dehydrated by successive treatments at 30 min

intervals at 25°C in 50, 70, 90 % and twice, absolute ethanol. The samples were transferred into brass boats which were then immersed in liquid Freon 12 that had been cooled with liquid-N_2. The samples were freeze-dried overnight at -80°C, mounted on Al-stubs with silver paste and coated with 20 nm of gold.

The end product granules were examined without any treatment prior to gold coating, while a portion of the slurry of the water-reconstituted fresh and stored granules (1 g/10 ml deionized water, gently stirred for 1 min and then left to stand for 2 h) was freeze-dried and examined as with the mash.

4.3.6.2. Light Microscopy.

Potato granules were also examined with a light microscope in order to obtain the count of intact sound cells. Granules (1 g) were suspended in 20 ml of deionized water with gentle stirring for 1 min, and left to stand 2 h. A drop was spotted on a microscope slide, stained with a drop of 0.1% aqueous methylene blue and viewed at 50-100 x magnification using a phase-contrast microscope.

4.3.7. Rehydration Rate.

The method of Tamura and Packer (1976) was used to determine the rehydration rate of A-B and F-T granules (fresh & stored). A 30 g sample of granules was gravitationally fed through a 8.5 cm glass funnel with its opening adjusted by means of a flexible tube and a clamp to allow all the granules to pass through in 12 sec. The granules dropped into a beaker of 9 cm diameter containing 63 ml of tap water (18±1°C) vigorously stirred with a magnetic stirrer. The magnetic bar was

1 x 7.5 cm, and the stirrer speed was set at 4.5 on the speed dial. The time in sec was taken from the first contact of granules with water until the magnet stopped moving due to the "setting" of the slurry into a firm dough. The relative rehydration rate (sec^{-1}) was an average of three determinations.

4.3.8. Extraction of Lipids.

4.3.8.1. Free Lipids.

Fresh and stored (6 months at 25°C) granules, 16 g, were extracted three times with 75 ml petroleum ether (b.p. 40-60°C) each time for 3 h in a Soxhlet extractor at a condensation rate of 3-4 drops/sec. The combined extracts were pooled and evaporated at 40°C in a vacuum flash rotary evaporator. The remaining 15 ml solvent was removed under N_2.

4.3.8.2. Bound Lipids.

The above petroleum ether-extracted granules were subjected to extraction with water-saturated n-butanol (WSB; Morrison et al., 1975) 3 x 75 ml for 3 h at 90-100°C with occasional shaking, and the extracts centrifuged and filtered through a medium porosity sintered glass under reduced pressure. The combined extracts were then concentrated as described above.

The dried extracts (free and bound lipids) were redissolved in diethyl ether, and the volume made up to 10 ml. The lipid yields were determined from 20 µl aliquots that were dried in a stream of nitrogen at room temperature in Al-foil cups and weighed on an Cahn-gram micro electrobalance.

4.3.8.3. Total Lipids.

Fresh and stored granules were stirred under nitrogen with a magnetic stirrer for 3 h with a solvent consisting of chloroform-methanol (2:1 v/v). The solution was filtered through sintered glass and the residue taken up in fresh solvent and stirred again for 2 h and filtered. This extraction was repeated several times. For the first extraction, 10 ml of solvent per gram of sample were used and for subsequent extractions, 5 ml per gram. The combined filtrates were evaporated as described earlier. The crude lipid residue was redissolved in 150 ml of the chloroform-methanol solvent, and nonlipid impurities were removed by shaking the solution with one-fifth of its volume of 0.58% aqueous sodium chloride, and leaving it to equilibrate overnight at 4°C (Folch et al., 1957). The upper phase was removed by a Pasteur pipet, and the remaining interface impurities were rinsed twice with small amounts of pure upper phase solvent. The lower phase, containing the purified lipids, was taken to dryness under vacuum. It was redissolved in anhydrous, ethanol-free chloroform. Approximately 0.5 mg of BHT was then added and the volume made up to 10 ml. The lipid yields were determined from 20 µl aliquots of lipid solutions that were dried in a stream of nitrogen at room temperature in Al-foil cups and weighed on a Cahn-gram micro electrobalance.

4.3.9. Lipid Fractionation by Silicic Acid Chromatography.

Column chromatography was used to separate the neutral lipid fraction (obtained by extraction with ether and WSB) from other lipid constituents. Silicic acid was washed with hot methanol, followed with hot acetone, and then dried at 105°C for 2 h. Celite was also treated

in a similar manner. The absorbent (3 g silicic acid + 1 g celite) was packed in a slurry of diethyl ether and was allowed to settle in a 30 cm x 8 mm i.d. glass column with gentle tapping. Lipid extracts were redissolved in 1 ml of diethyl ether, and applied to the column. The neutral lipid fraction was removed from the column by eluting with 80 ml of diethyl ether. The eluent containing the neutral lipid fraction was then evaporated. The dried extracts were redissolved and made up to a volume of 10 ml with diethyl ether. The lipid yields were determined from 20 µl aliquots that were dried in a stream of nitrogen at room temperature.

4.3.10. Thin-Layer Chromatography.

The neutral lipids were analysed by thin-layer chromatography on 20 x 20 cm glass plates coated with 0.3 mm activated MN-Kieselgel N (without binder). Freeman and West's (1966) system was used for the separation of neutral lipids. The first development was in a solvent mixture of diethyl ether:benzene:ethanol:acetic acid (40:50:2:0.2 v/v) and the second in diethyl ether-hexane (6:94, v/v).

The lipids were detected by spraying with 50% H_2SO_4, followed by charring for 20 min at 170°C. The R_f value of the monoglyceride spot was noted.

Preparative thin-layer chromatography was performed by repeating the above experiment and omitting the spraying step. The spots containing monoglyceride were located by their R_f values, and were recovered from the plates by scraping off equal areas of the spots into funnels plugged at the end of the stem with glass wool and eluting with 20 ml diethyl ether. The extracts were then centrifuged at 250 x g for 10 min and evaporated to dryness under nitrogen. The dried extracts

were then redissolved in diethyl ether, and the volume made up to 10 ml. The monoglyceride yields were determined from 20 µl aliquots that were dried in a stream of nitrogen at room temperature.

4.3.11. Gas-Liquid Chromatography.

Transesterification procedures were used to obtain fatty acid methyl esters of the monoglyceride fraction recovered from thin-layer plates. The methyl esters were prepared by gently refluxing the monoglyceride fraction with 1 ml of boron trifluoride-methanol solution (14% w/v). The esters were isolated from the reaction mixture and analysed as described under 4.2.1.

4.4. Pectin-Monoglyceride Interaction.

4.4.1. Extraction of Potato Pectin.

Peeled and chopped potatoes (2 kg) were disintegrated in ethanol (1 ml/g) in a blender, filtered on Miracloth and washed with water. The filtrate, containing the bulk of the starch grains present in the original material, was discarded. The residue on the Miracloth was suspended in 200 ml water and then heated in a water bath (temperature inside the suspension being maintained at 70°C) for 10 min. After cooling, the pH was adjusted to 7.0 with 0.05 N KOH followed by the addition of 0.1 M acetate buffer (pH 4.8), bringing the total volume to 500 ml. Amyloglycosidase, 2 ml, and α amylase, 0.5 ml, were added to this solution, followed by incubation for 6 h at 48°C (the completion of the reaction being checked by the addition of KI_3). The mixture was then centrifuged at 5000 x g for 15 min. The residue (debris + CW) was

suspended in water (1 litre) and then refluxed for 12 h and filtered under suction. Four volumes of ethanol were added to the filtrate and the resultant precipitate of potato pectin was collected by centrifugation, washed twice with ethanol, then with ether and dried *in vacuo*.

4.4.2. Viscosity Measurements.

Potato pectin aqueous solution (1%, w/v) was prepared by slowly adding the pectin into continuously-stirred boiling water until all the powder was dissolved.

Solutions consisting of 0-0.5% (w/v) C_{16}-monoglyceride in aqueous pectin, solution were prepared by adding the monoglyceride into the stirred pectin solution and boiling for 5 min. The solution was cooled to 70°C and the viscosity measured at this temperature using the Haake Rotoviscometer. In this study the use of C_{18}-monoglyceride was omitted.

4.4.3. Differential Scanning Calorimetry.

Aqueous solutions of citrus pectin (1%, w/v) of varying degrees of esterification and potato pectin (1%, w/v) were prepared as described above. Mixtures consisting of 0.3% C_{16}-monoglyceride in aqueous pectin solution were prepared by adding the monoglyceride into the stirred pectin solutions and boiling for 5 min. On cooling to room temperature no precipitation was observed. However, a residue was seen when the solutions were evaporated to dryness in a water bath. A portion (15 mg) of this residue was then placed inside DSC pans and heated from -10°C to 165°C at a scanning rate of 5 C°/min.

IV. RESULTS AND DISCUSSION

1. CHARACTERIZATION OF POTATO STARCH AND ITS MONOGLYCERIDE COMPLEXES.

1.1. Particle Size Distribution.

The particle size distribution in native potato starch isolated from cv.Netted Gem is given in Table 1 (see also Figure 1a). When these grains were heated in water at 70°C with stirring as in a Brabender amylograph, a uniform melt was obtained (Figure 1b). Gelatinization in vitro was done without stirring to simulate starch gelatinization in a potato cell. As seen from Figure 1 (c,d) in such starch, even when heated at 80°C for 10 or 30 min, the grain entity was retained regardless of the extent of leached-out amylose.

Monoglyceride incorporation into grains by diffusion, as demonstrated in this study, has a profound effect on both leached-out amylose and grain integrity. Based solely on microscopic observations, it appeared that amylose was responsible for starch solubility and viscosity data, while the grain-lipid complex determined swelling power, transparency and strength upon heating.

1.2. Starch Swelling Power and Solubility.

As shown in this study, the swelling power (SP) of starch grains can readily be tailored by monoglycerides or fatty acid K-salts. Native potato starch SP was 171 and its solubility 32%. The high SP is due to low content of Ca^{+2} and Mg^{+2} present in phosphate ester groups of amylopectin. As proved in another study (Haydar et al., 1980), starch-P devoid of metal cations (H-starch) has a 2.3-times greater SP than native starch. The extent of starch-P ionization is enhanced in the absence of Ca^{+2} and

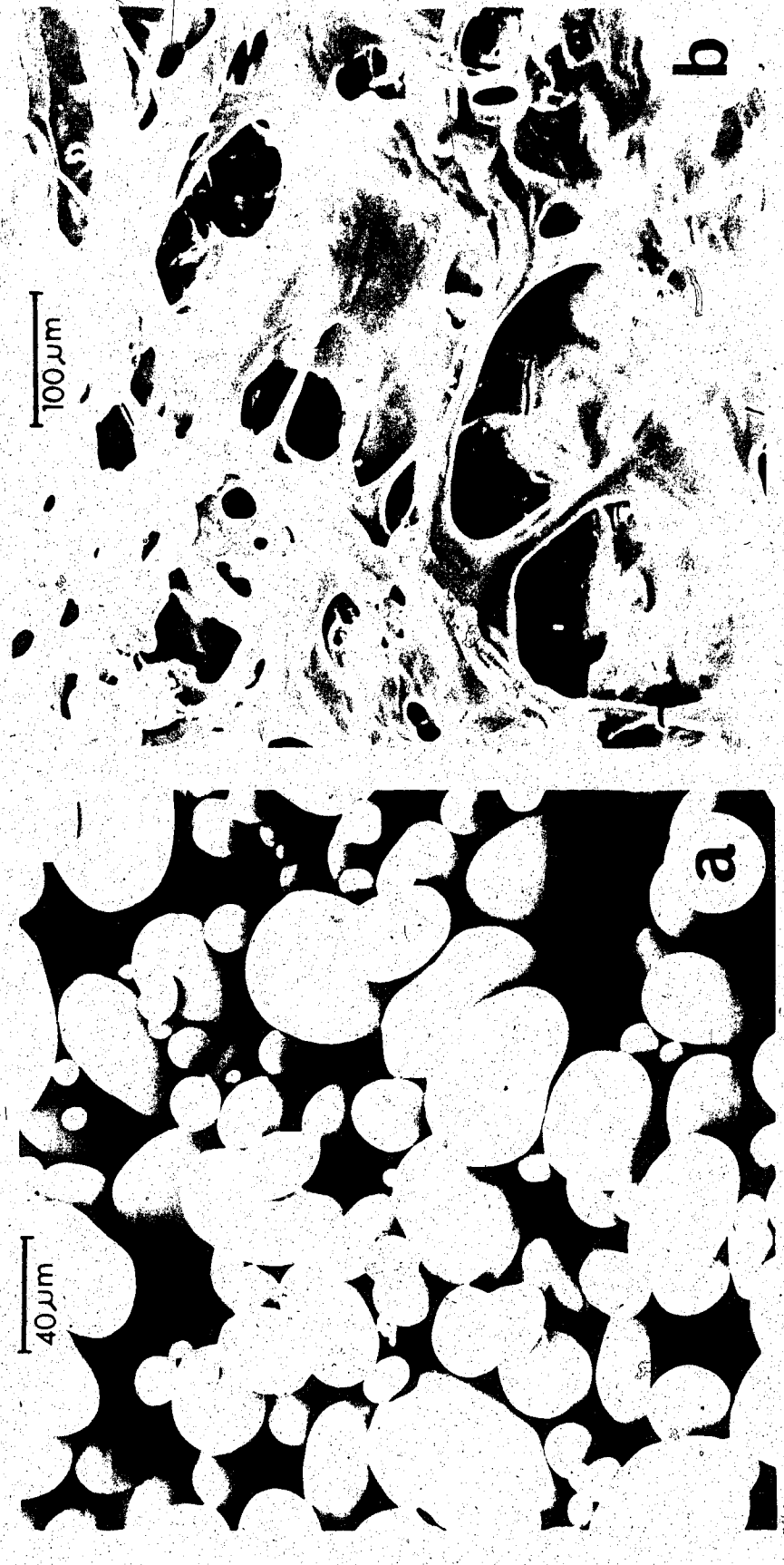
Table 1.

Particle Size Distribution in Native Starch Isolated From Potato Tuber cv. "Netted Gem" (Russet Burbank).

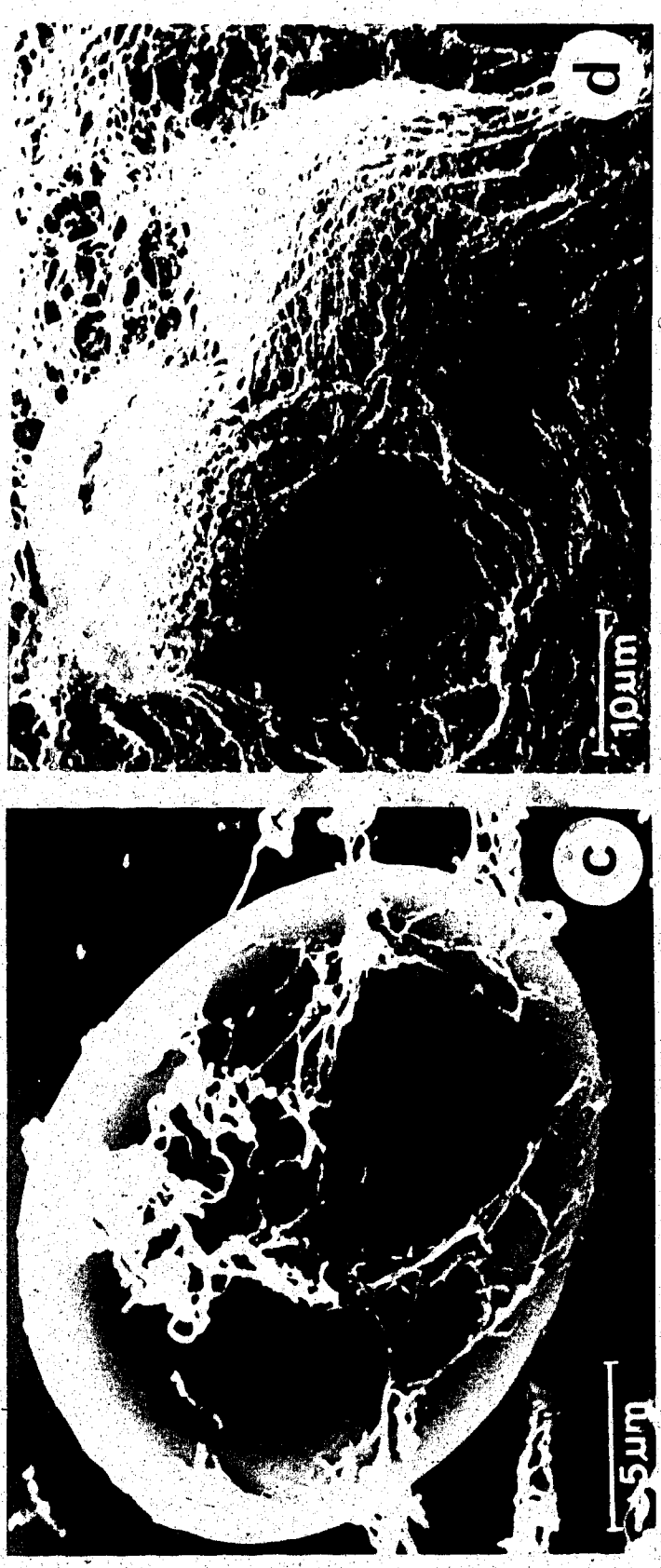
Particle Size (μm)	% Population* By Number of Grains
6.35	7.02
8.00	4.62
10.08	6.38
12.70	8.63
16.00	12.35
20.20	15.95
25.40	18.12
32.00	14.19
40.30	8.54
50.80	3.85
64.00	0.35

*Between successive size interval. The first population (7.02%) is for size < 6.35 μm.

Figure 1. SEM-Micrographs of Gelatinized Potato Starch Sampled With and Without Precautions Against Amylose Retrogradation (a) Starch Grains of cv."Netted Gem" Before Gelatinization; (b) Starch Suspension in Water (2.5%, w/w) Gelatinized by Stirring at 80°C for 30 min, and Freeze-Dried Without Prior Treatment in Liquid-N_2. Magnification x 3,800.


b
100 µm
a
40 µm

(c) Starch Suspension in Water (0.1%, w/w) Gelatinized at 80°C for 10 min Without Stirring and With Precautions Taken Against Realignment of Amylose Chains. Magnification x 3800; (d) As Under (c) but Gelatinized for 30 min. Two Starch Grains are Shown Enmeshed in the Interfaced Network of Leached-Out Amylose. Magnification x 2500.


d
10µm
c
5µm

Mg. In ionized form repulsive forces among starch molecules give higher solubility and SP values.

When starch was complexed with 0.7 mM of the α-crystallinity form of 1-monoglycerides through a prolonged diffusion process below the gelatinization temperature, there was a decrease in both solubility and SP values (Table 2). The SP dropped steadily from C_8 to C_{14} then increased slightly from C_{16} to C_{18}. The SP, relative to that of native starch, dropped by 15% with C_8 and 60% with [illegible]. The lowest SP, 16.1, obtained with C_{14}-monoglyceride, was about [illegible] less than that of native starch. A comple[illegible]$_{16}$ brought about rise of 5.5 in SP, which then equaled 12.6 [illegible] SP of untreated starch, while C_{18}-monoglyceride raised the SP [illegible] to that of an equimolar amount C_{12}.

Thus, SP was affected by addition of monoglyceride to starch before gelatinization. However, Lonkhuysen and Blankestijn (1976) found that it was not affected when monoglyceride was added after gelatinization. The stability ofswollen grains was, however, greatly enhanced.

During gelatinization in excess water, starch solubility is affected by the amount of amylose released from starch grains. Grains complexed with monoglycerides in equimolar amounts showed a dramatic drop in solubility. This decrease was 8% with C_8, 42.1% with C_{10} and 90% with C_{14}-monoglyceride. Although the trend reversed with C_{16} and C_{18}, the solubilities were still well below that of native starch.

Starch grains treated with 0.7 mM fatty acid K-salts, i.e. polar instead of nonpolar surfactants, showed slightly higher solubility and SP, but the trends were similar to monoglycerides. The greatest SP suppression was with C_{14} and the lowest with C_8. Of interest was the inability of arachidic acid (C_{20}) to effectively control SP or solubility.

Table 2.

Solubility (Sol) and Swelling Power (SP) at 85°C of Monoglyceride or Fatty Acid K-Salt Treated Starch as Affected by Fatty Acid Chain Length.*

Fatty Acid Chain Length	1-Monoglyceride		K-Salt	
	Sol %	SP	Sol %	SP
C_8-	29.7 ± 0.5**	145.6 ± 4.5	31.4 ± 0.1	157.6 ± 4.0
C_{10}-	18.6 ± 0.3	68.9 ± 4.5	22.9 ± 0.5	83.1 ± 7.5
C_{12}-	8.4 ± 1.2	34.2 ± 3.5	10.5 ± 1.2	36.2 ± 1.2
C_{14}-	3.3 ± 0.5	16.1 ± 0.9	5.[illegible] 0.5	22.6 ± 3.5
C_{16}-	4.9 ± 0.3	21.6 ± 2.0	7.0 ± 1.8	27.9 ± 3.2
C_{18}-	7.3 ± 0.5	30.2 ± 2.5	9.2 ± 1.2	35.6 ± 2.5
C_{20}-	-	-	29.4 ± 0.5	144.0 ± 3.5

*The Sol % and SP of untreated starch grains were 32.1 ± 1.2 and 171.2 ± 8.5, respectively.

**In this and following Tables, SD for n = 3.

Its efficiency matched that of C_8-acid. The above data agree with those of Gray and Schoch (1962) with respect to the effect of fatty acid K-salts on the SP of potato starch. They found that C_{14} was the best complexing acid at the 1% (w/w) level. However, results differed in respect to C_8 complexing ability. In this study it was proved to be low, as was also found in a related study by Krog (1971) who demonstrated on pure potato amylose that C_8-acid has a zero complexing index. He also calculated that 1 mole amylose reacts with 20 moles of monopalmitin to form a water-insoluble complex. As proved by Carlson et al. (1979), the fatty acid chain is within the amylose helix and the polar monoglyceride moiety is outside.

1.3. Starch Viscosity.

Starch solubility and SP values were closely related to viscosity data. When a starch grain is gelatinized without stirring, amylose chains enter the ambient aqueous phase and form a network which connects the individual grains, Figure 2 (a,b) shows such a network between two adjacent grains. In Figure 2 (c,d) the network is still visible even though no precautions were taken against amylose realignment (or retrogradation). Treatment of starch with monoglyceride decreases the amount of leached-out amylose (Figure 3). When microscopic observations were related to viscosity data of native and complexed starch (Table 3), it appeared that the viscosity in a temperature range of 50-80°C correlated closely with the extent of leached-out amylose rather than the swelling of starch grains. More leached-out amylose was visible microscopically as the starch viscosity increased, an observation which agreed with a similar finding on wheat starch (Miller et al., 1973).

Figure 2. SEM-Micrographs of Amylose Leached-Out from Potato Starch Grains After Gelatinization as in Figure 1, c-d, Sampled With and Without Precautions Against Amylose Retrogradation. (a) Dense Filaments of Amylose Obtained After 10 min Gelatinization. Magnification x 4200; (b) Amylose Network Between Adjacent Starch Grains Obtained After 30 min Gelatinization. Magnification x 5400; (c) Starch Grains Gelatinized for 30 min Without Precautions Against Amylose Realignment. Individual Grains are Covered By a Film of Realigned Amylose Chains. Magnification x 1500; (d) As Under (c), but With a Single Gelatinized Grain. Magnification x 1500.

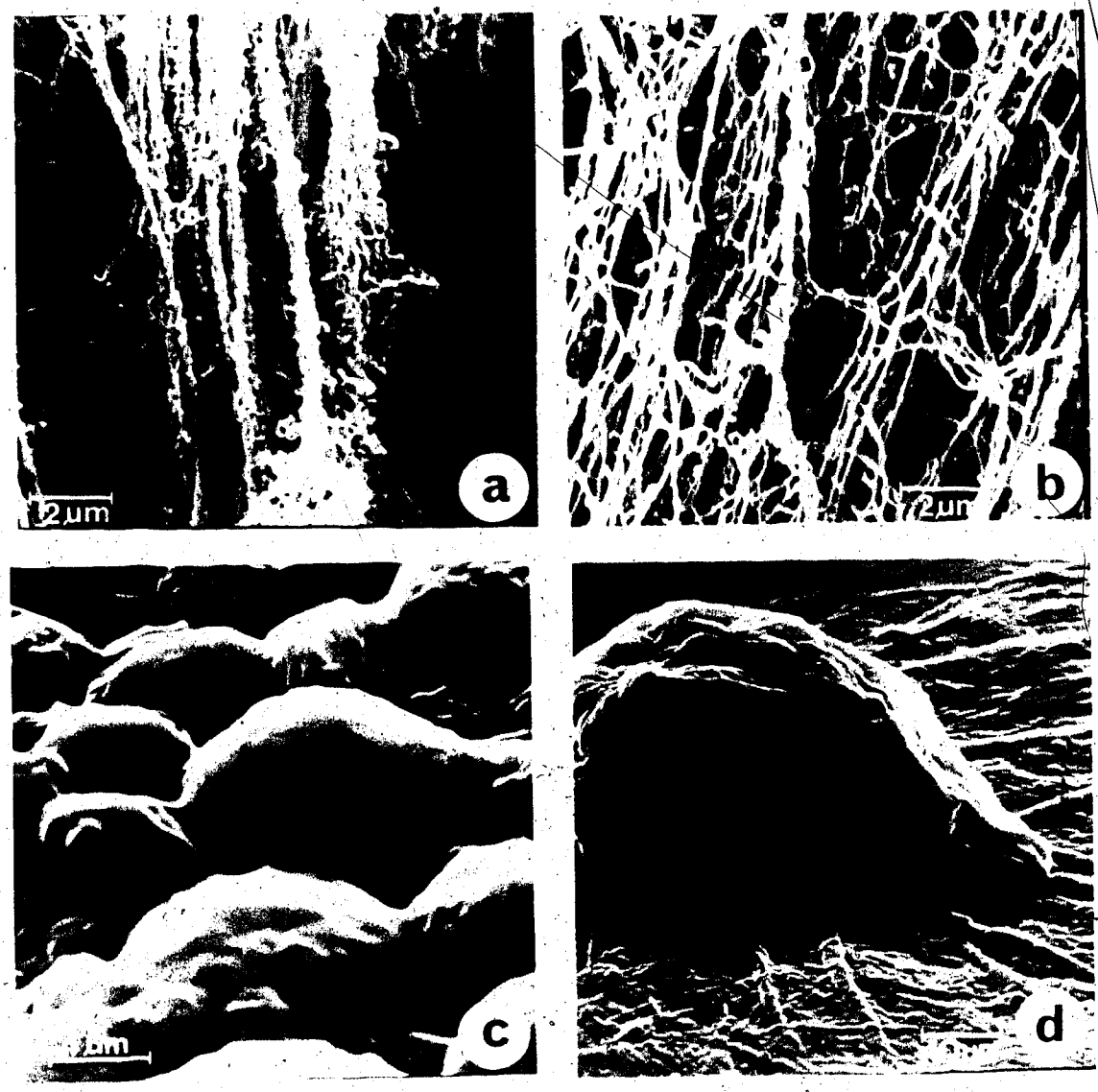
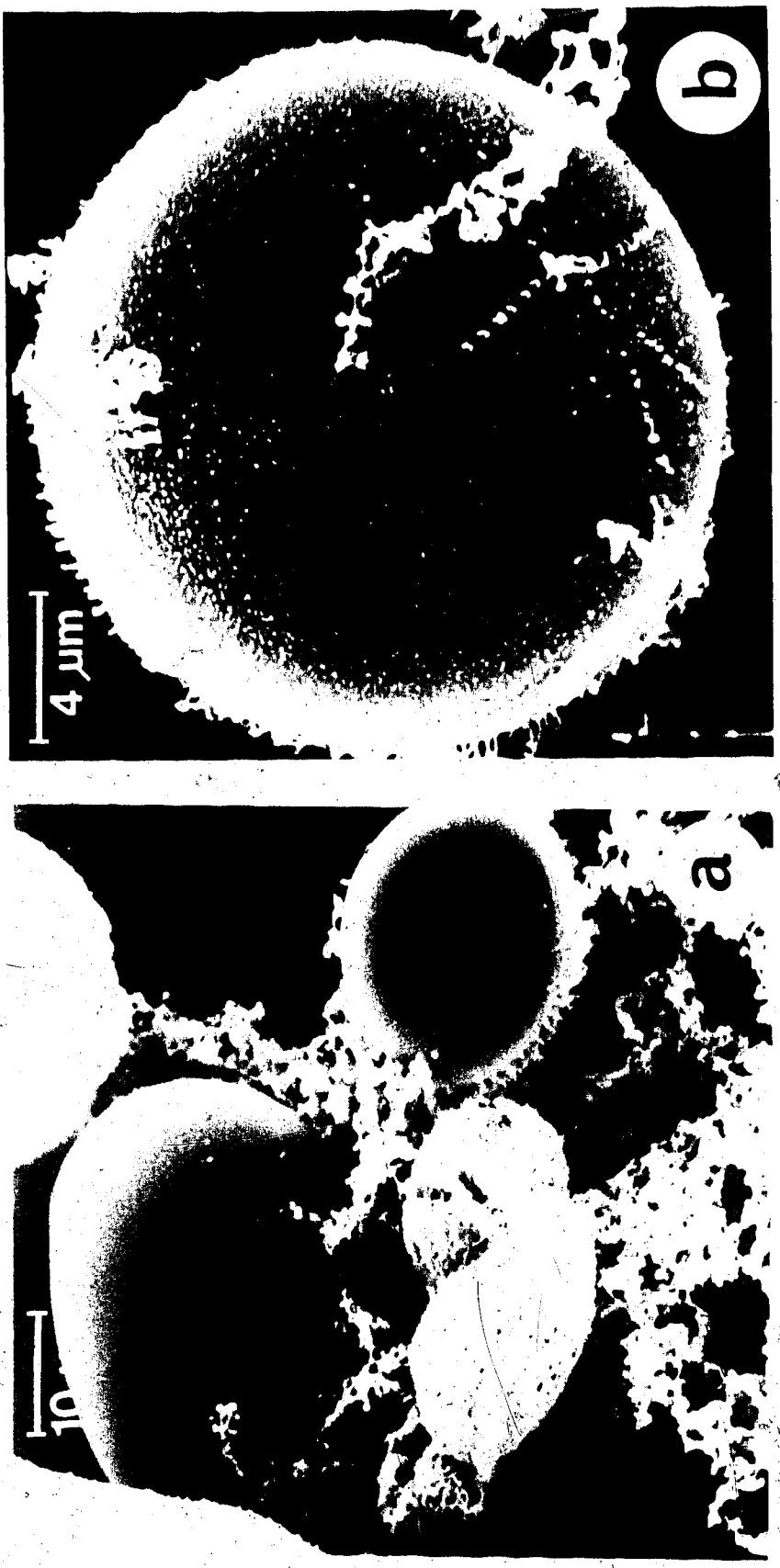

a
2 µm
b
2 µm
c
d

Figure 3. SEM-Micrograph of Potato Starch Grains Gelatinized at 80°C for 30 min in the Presence of 0.7 mM of [redacted]erides. (a) A Mixture of Untreated Starch Grains and Those Treated With C_{14}-Monoglyceride. The Grain Integrity Was Preserved Only in the Presence of Monoglyceride. Magnification x 800; (b) Starch Grains Gelatinized in the Presence of C_8-Monoglyceride. Magnification x 3800.


b
4 μm
a

(c) Starch Grains Gelatinized in the Presence of C_{14}-Monoglyceride. Note the Absence of an Amylose Network Between the Starch Grains. Magnification x 150; (d) As Under (c), but Gelatinized in the Presence of C_{16}-Monoglyceride. Magnification x 1000.

d
10 µm
c

Table 3.
Viscosity of Starch-Monoglyceride Complexes Heated at 50 - 80°C

Starch Complexed With Monoglyceride	Viscosity (cP) at °C			
	50°	60°	70°	80°
Untreated starch (control)	5.6 ± 0.2	6.7 ± 0.1	7.6 ± 0.2	10.8 ± 0.2
C_8-	5.4 ± 0.2	6.3 ± 0.3	7.2 ± 0.2	10.1 ± 0.3
C_{10}-	3.9 ± 0.1	4.6 ± 0.2	5.4 ± 0.2	7.6 ± 0.2
C_{12}-	2.8 ± 0.2	3.4 ± 0.2	4.3 ± 0.1	5.0 ± 0.3
C_{14}-	2.6 ± 0.2	3.2 ± 0.2	4.0 ± 0.2	4.5 ± 0.3
C_{16}-	2.6 ± 0.2	3.2 ± 0.2	4.0 ± 0.2	4.5 ± 0.3
C_{18}-	3.0 ± 0.2	3.6 ± 0.2	4.5 ± 0.1	5.2 ± 0.2

The amylose leaching extent was a function of temperature, and at a given temperature was controlled by monoglyceride fatty acid chain length. The lowest viscosity at any temperature was observed with starch complexed with C_{14} - C_{16}, while the highest (with C_8) matched that of untreated starch.

When viscosity was measured at 25°C (Table 4), the results were slightly higher but the trend found at elevated temperatures was retained. Native starch was highest in viscosity, while starch complexed with C_{14} or C_{16}-monoglyceride was lowest. These data suggested negligible realignment of complexed amylose chains during cooling. Potato amylopectin treated with monoglycerides did not change in viscosity (Table 5), strongly suggesting its inability to form a lipid complex.

Comparision of data from Tables 2,3 and 4 suggests that the extent of amylose leaching from complexed starch is more reliably determined gravimetrically as a solubility percent than by viscosity test. The less reliable viscosity data are supported by data of Kim and Robinson (1979) who used a Ubbelohde dilution-type capillary viscometer on the systems: amylose, 2% surfactants.

1.4. X-ray Diffraction.

Clathrate formation during starch grain treatment with 0.7-mM monoglyceride or fatty acid K-salts was verified by X-ray diffraction analysis.

Untreated potato starch had a "B" type diffraction pattern. Interplanar spacings in Å were at 3.70, 4.00, 6.14 and 15.80 (all medium intensity) and 5.16 (strong). In addition, there were five weak lines between 2.60 and 8.90. The overall pattern was weaker when starch moisture

Table 4.
Viscosity of Starch-Monoglyceride Complexes Heated at 50-80°C then Cooled to 25°C.

Starch Complexed With Monoglyceride	Viscosity (cP) at 25°C — The Complexes Were Previously Heated At 50°	60°	70°	80°
Untreated starch (control)	6.6 ± 0.2	7.7 ± 0.3	8.6 ± 0.3	11.8 ± 0.2
C_8-	6.2 ± 0.2	7.2 ± 0.2	8.0 ± 0.2	11.0 ± 0.2
C_{10}-	4.6 ± 0.2	5.2 ± 0.2	6.0 ± 0.2	8.4 ± 0.4
C_{12}-	3.2 ± 0.3	3.8 ± 0.3	4.6 ± 0.2	5.6 ± 0.2
C_{14}-	3.0 ± 0.4	3.6 ± 0.3	4.2 ± 0.2	5.0 ± 0.2
C_{16}-	3.0 ± 0.4	3.6 ± 0.3	4.2 ± 0.2	5.0 ± 0.2
C_{18}-	3.4 ± 0.2	4.0 ± 0.2	4.8 ± 0.2	5.8 ± 0.4

Table 5.
Viscosity of Potato Amylopectin and its Monoglyceride Mixtures.

Sample	Viscosity (cP) at 80°C
Potato amylopectin	11.3 ± 0.3
Amylopectin - C_{14}	10.9 ± 0.1
Amylopectin - C_{18}	11.0 ± 0.1

contents were less than 10% and stronger at higher levels.

When potato starch grains were dispersed in NaOH heated at 100°C and then, in the presence of fatty acids, gradually cooled to 25°C, a "V" diffraction pattern was obtained (Osman-Ismail, 1972). It was characterized by strong lines at 4.37, 7.20-7.90 and 12.10-12.90 Å. This pattern was close to that of pure amylose monoglyceride complexes reported by Osman et al. (1961), or the amylose n-butanol complex of Zobel (1964).

As seen from Figure 4 and Table 6, the potato starch complex prepared in this study had diffraction spacing and intensities different from those above since the starch complex was formed below the gelatinization temperature. Hence, there was a grain crystallinity pattern superimposed on that of the complex. Neverthless, the major lines of the complex were readily revealed. Exceptions were complexes of C_8 and C_{10} monoglycerides, when the strong spacing centered at 5.15 Å was shifted to 4.48-4.67.

1.5. Turbidimetric Measurements.

The extent of amylose complexing with monoglycerides was tested by turbidimetric assay. Since the complexing reaction occurred in the grains, insolubilization of amylose also took place within the grain. Hence, the transmittance (transparency) of the complex decreased when compared to native grains. The transmittance also decreased during starch-monoglyceride complex heating in excess water at 80°C for 30 min without stirring. There was a stepwise drop of transmittance for complexes of C_8 up to C_{12}, and a minimum was reached with C_{14}-complex (Table 7). The trend reversed with C_{16} and C_{18} complexes, showing a stepwise increase in transmittance. Similar results were obtained when

Figure 4. X-ray Diffraction Patterns of Potato Starch and Several of Its Monoglyceride Complexes. The Region Scanned Corresponds to 3-32^{o} 2θ.

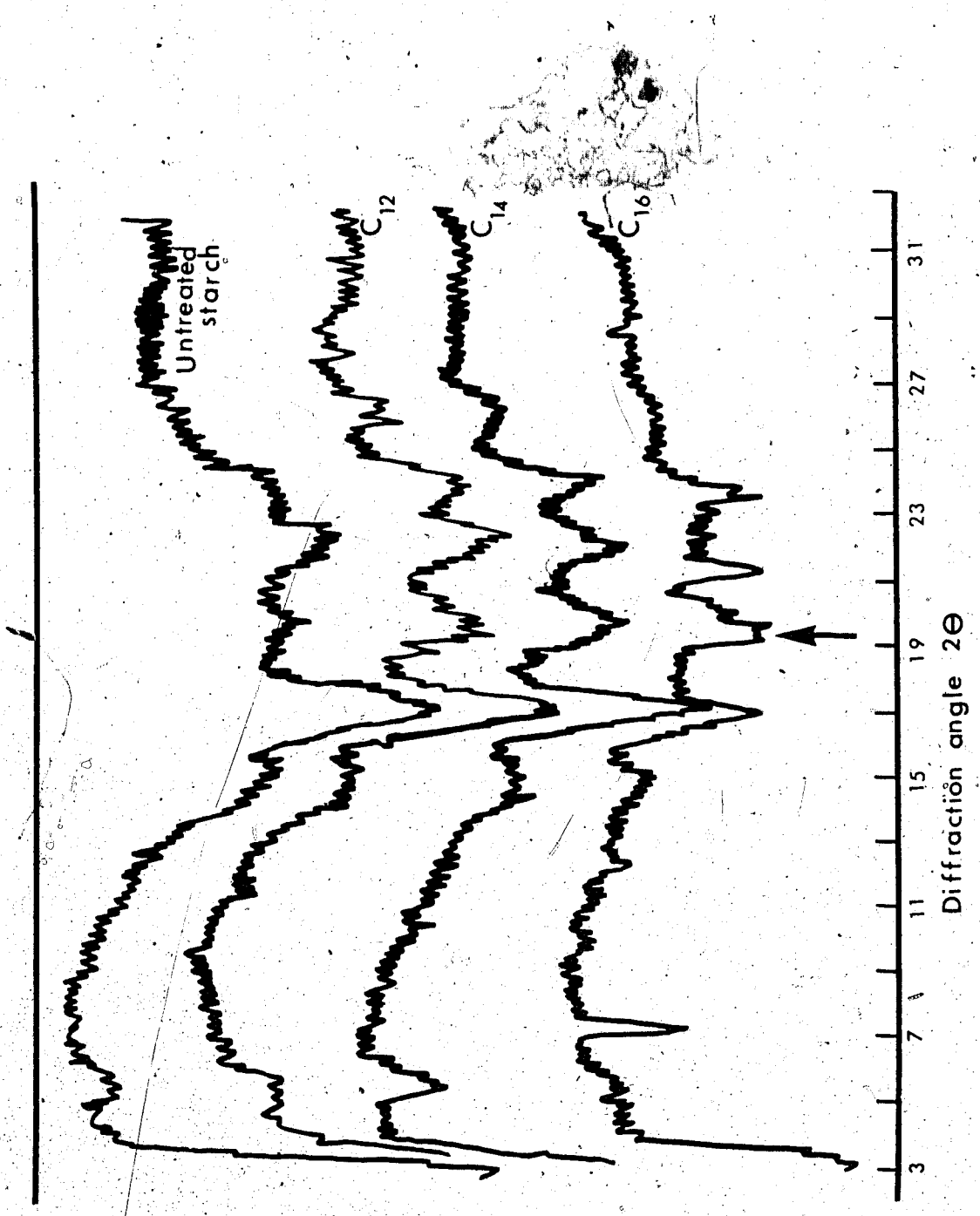

Untreated starch
C_{12}
C_{14}
C_{16}
3
7
11
15
19
23
27
31
Diffraction angle 2θ

Table 6.

X-ray Diffraction Spacings in Starch-Monoglyceride Complexes.

Starch Complexed With Monoglyceride	Complex Moisture Content,%	Interplanar Spacings, d, in Å With Medium (m) and Strong (s) Intensities						Number of Weak Spacings	Range Å
Untreated starch (control)	12.5	15.24(m)	6.07(m)	5.15(s)			3.97(m) 3.73(m)	13	3.73-17.67
C_8-	13.3			5.22(m)	4.48(s)			9	4.11-15.24
C_{10}-	13.4		6.51(m)	5.83(m)	4.67(s)			7	3.82-17.67
C_{12}-	13.9			5.09(s)	4.44(m)		3.90(m)	7	3.14-16.36
C_{14}-	13.3	15.78(m)		5.15(s)	4.43(m)		3.98(m) 3.67(m)	10	4.21-14.73
C_{16}-	13.3	12.11(m)		5.21(s)	4.53(s)	4.17(m)	3.73(m)	9	3.40-20.08
C_{18}-	13.9			5.18(s)	4.67(s)		3.70(m)	14	3.80-19.21
C_{18}-*	13.3			5.90(m)	5.18(s) 4.43(m)	4.13(m)		6	3.55-15.78

*1-monoglycerides from hydrogenated and distilled soybean oil.

Table 7.
Turbidimetric Measurements of Starch-Monoglyceride Complexes Heated at 80°C for 30 min.

Starch Complexed With Monoglyceride	Transmittance, % at 520 nm	
	At 80°C	After being cooled to 25°C
Untreated starch (control)	54.3 ± 1.6	68.4 ± 1.2
C_8-	49.3 ± 1.6	61.6 ± 1.4
C_{10}-	37.6 ± 1.3	44.2 ± 1.5
C_{12}-	27.5 ± 0.6	32.3 ± 0.7
C_{14}-	22.4 ± 0.2	24.8 ± 0.4
C_{16}-	24.8 ± 0.4	27.5 ± 0.6
C_{18}-	28.8 ± 0.4	33.9 ± 0.8

readings were taken at 24°C. These results support those of a study on soft wheat starch by Longley and Miller (1971). However, they found no transmittance change with fatty acid chains below C_{12}.

1.6. Differential Scanning Calorimetry.

1.6.1. Native Starch.

Thermograms (plots of heat flow as a function of temperature) of native starch are shown in Figure 5 (a). A narrow single endotherm was observed at 66°C at a high water level (ν_1 0.85). This is the gelatinization endotherm (G), which corresponded at this water level to an enthalpy change of 6.9 cal/g starch (Table 8). As the water level decreased, a shouldering endotherm (M_1) developed. It became a well-separated second endotherm at intermediate water levels (ν_1 0.50), while at lower water levels it was the only endotherm. The enthalpy of G + M_1 and of the single M_1 transitions decreased as the water level decreased. At ν_1 0.39 the enthalpy was only 4.29 cal/g. Linear regression analysis of the experimental data for a ν_1 range of 0.39-0.85 gave a least squares fit for enthalpy values of $Y = 2.0676 + 5.7025\ \nu_1$ ($r > 0.99$). When the enthalpy change per mole of D-glucose subunits (anhydroglucose M, 162; endotherm area/wt starch x 162) was plotted as a function of molar ratio of water to starch (wt water/18 ÷ wt starch/162), as suggested by Donovan (1979), the plot coincided closely with his findings. The G endotherm at 66°C appeared at a molar ratio of water to starch greater than 4 ($\nu_1 > 0.4$), with its maximum being at 14 and remaining constant at any water level above this ratio. The M_1 endotherm was observed at a molar ratio of water to starch less than 5, with its maximum at 4, while it disappeared above 14 ($\nu_1 > 0.7$). As has already

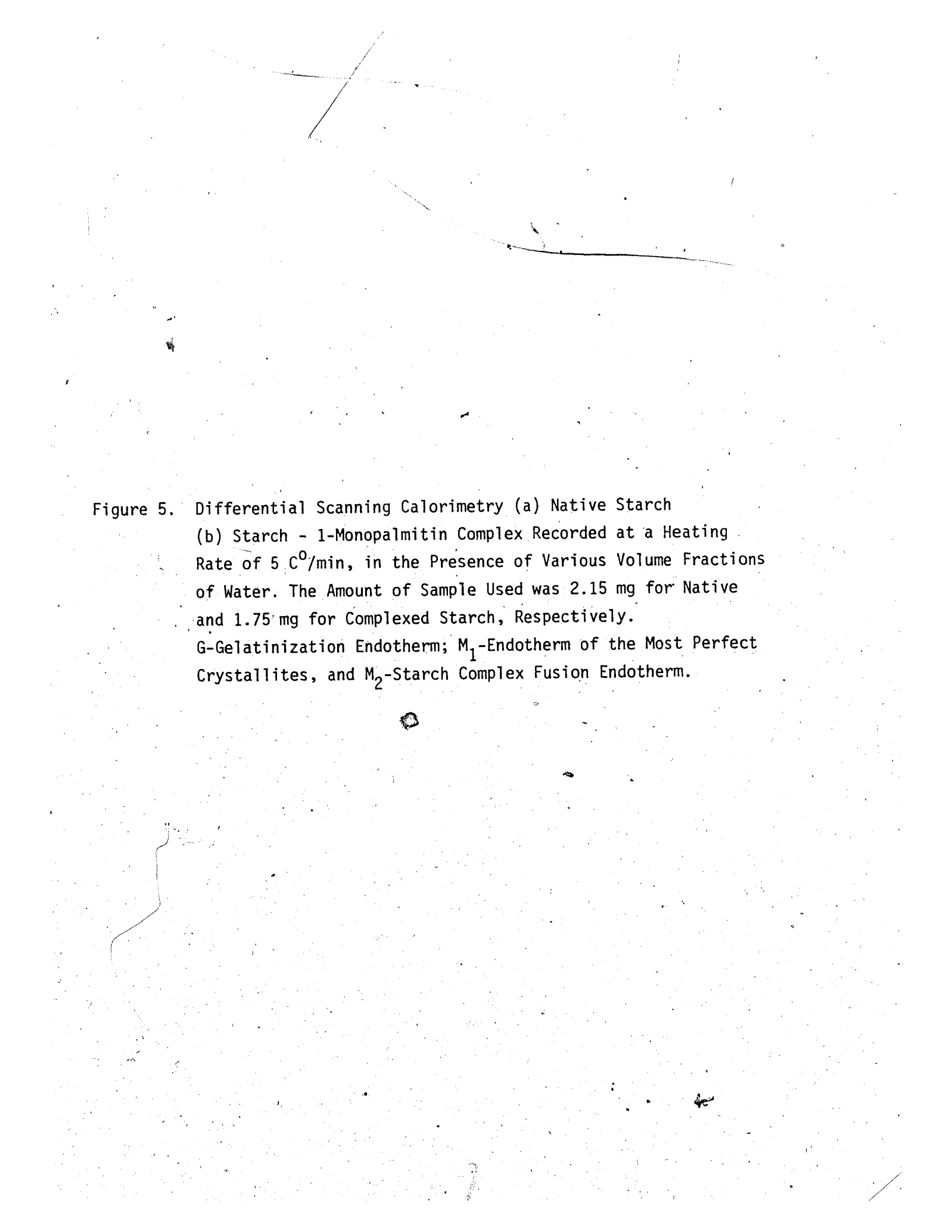


Figure 5. Differential Scanning Calorimetry (a) Native Starch (b) Starch - 1-Monopalmitin Complex Recorded at a Heating Rate of 5 C^{o}/min, in the Presence of Various Volume Fractions of Water. The Amount of Sample Used was 2.15 mg for Native and 1.75 mg for Complexed Starch, Respectively. G-Gelatinization Endotherm; M_1-Endotherm of the Most Perfect Crystallites, and M_2-Starch Complex Fusion Endotherm.

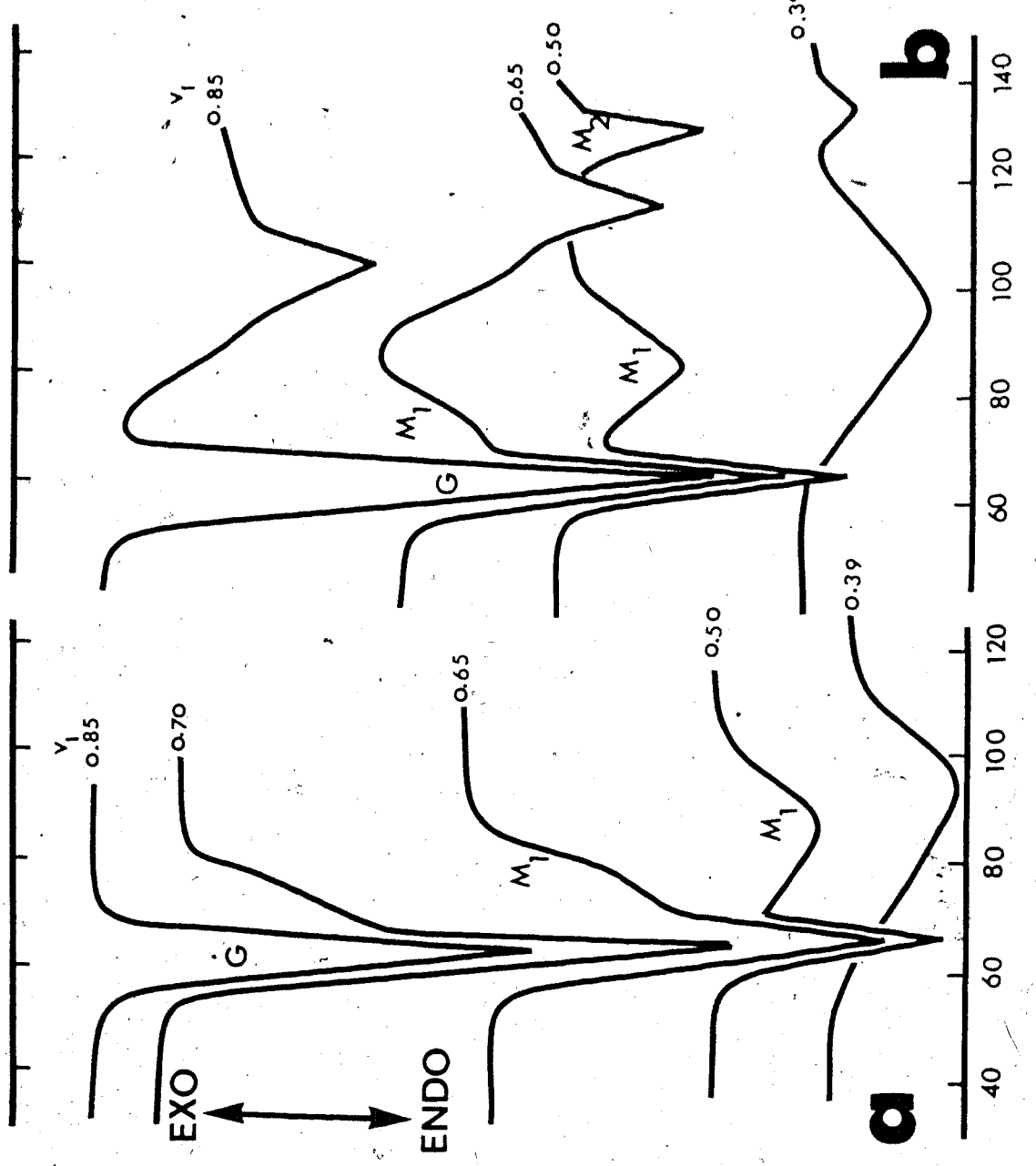

EXO
ENDO
V_1
0.85
0.70
G
M_1
0.65
0.50
0.39
M_2
a
b
40
60
80
100
120
140

Table 8.

Native Potato Starch Gelatinization Characteristics.

Volume Fraction of water, ν_1	Gelatinization (G), ^oC			Endotherm Area, cm^2	Enthalpy of Fusion, ΔH (cal/g starch)
	t_o	t_p	t_m		
0.39	53	94	117	6.0	4.29
0.50	57	66	105	7.0	5.50
0.65	56	66	88.5	8.1	5.77
0.70	56.5	66	84	8.5	6.07
0.85	56	66	70	9.7	6.91

been suggested (Donovan, 1979; Biliaderis et al., 1980), the two distinct endotherms appear to represent two distinct mechanisms for phase transition of starch grains. The M_1 transition at higher temperature results from the melting crystallites within the semicrystalline (spherulite) entity. The G transition involves swelling of the amorphous regions of the spherulite by water separating or stripping the starch molecules from the crystallite surface, and denaturing and hydrating the starch. This should then account for a consistently higher enthalpy for G transition than M_1.

The melting temperature of the crystallites in the starch grain became higher as the water level decreased. In order to obtain the melting point of the most perfect crystallites, Equation (1) was applied since it accounts for a thermodynamic relation of crystallite melting point and water concentration. Thus, t_m (^oC), expressed as $1/T$ (^oK), was plotted against v_1. Linear regression analysis (Figure 6) gave a least squares fit of $Y = 2.264 + 0.7669\ v_1$. When extrapolated to v_1 0 a T^o_m value of 441.7^oK (168.7^oC) was obtained. Similarly, a plot of v_1/T_m against $(1/T_m - 1/T^o_m)\ v_1$ (Figure 7) provided a least squares fit of $Y = 0.8309 - 0.0309\ v_1$ ($r = 0.95$) which at intercept $v_1/T_m = 0$ gave, for the fusion of the most perfect crystallites (M_1 transition), an enthalpy (ΔH_u) of 15.4 Kcal/mole D-glucose unit, i.e. slightly higher than the 14.3 reported by Donovan and Mapes (1980). As seen from Figure 5 (a), native potato starch, unlike wheat or maize starch (Donovan and Mapes, 1980), lacks the high melting endotherm M_2, i.e. shows no thermal transition for a starch-lipid complex. It is well established that starch amylose forms nonstoichiometric inclusion compounds (clathrate) with fatty acids. However, in wheat starch lysolecithin (not free fatty

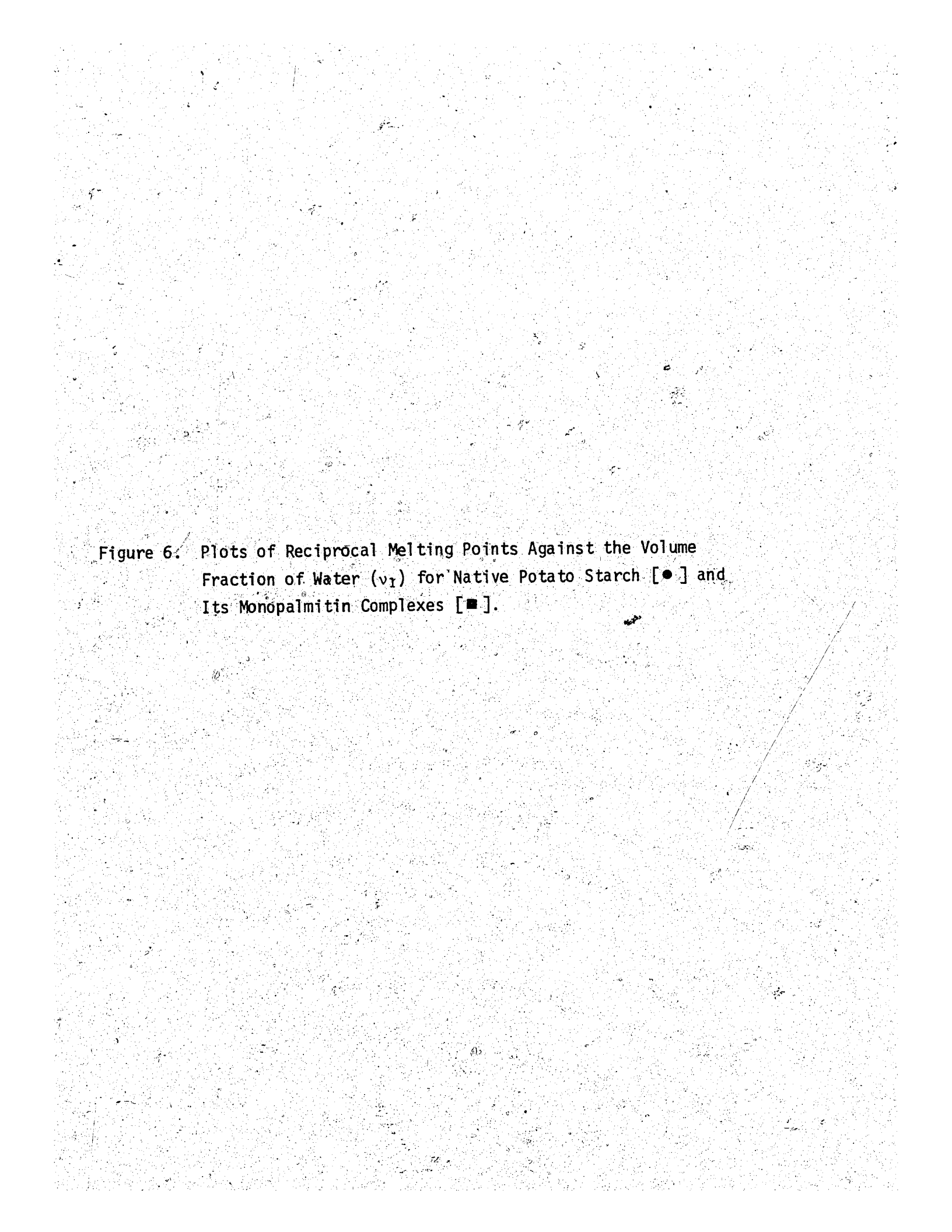


Figure 6. Plots of Reciprocal Melting Points Against the Volume Fraction of Water (ν_1) for Native Potato Starch [●] and Its Monopalmitin Complexes [■].

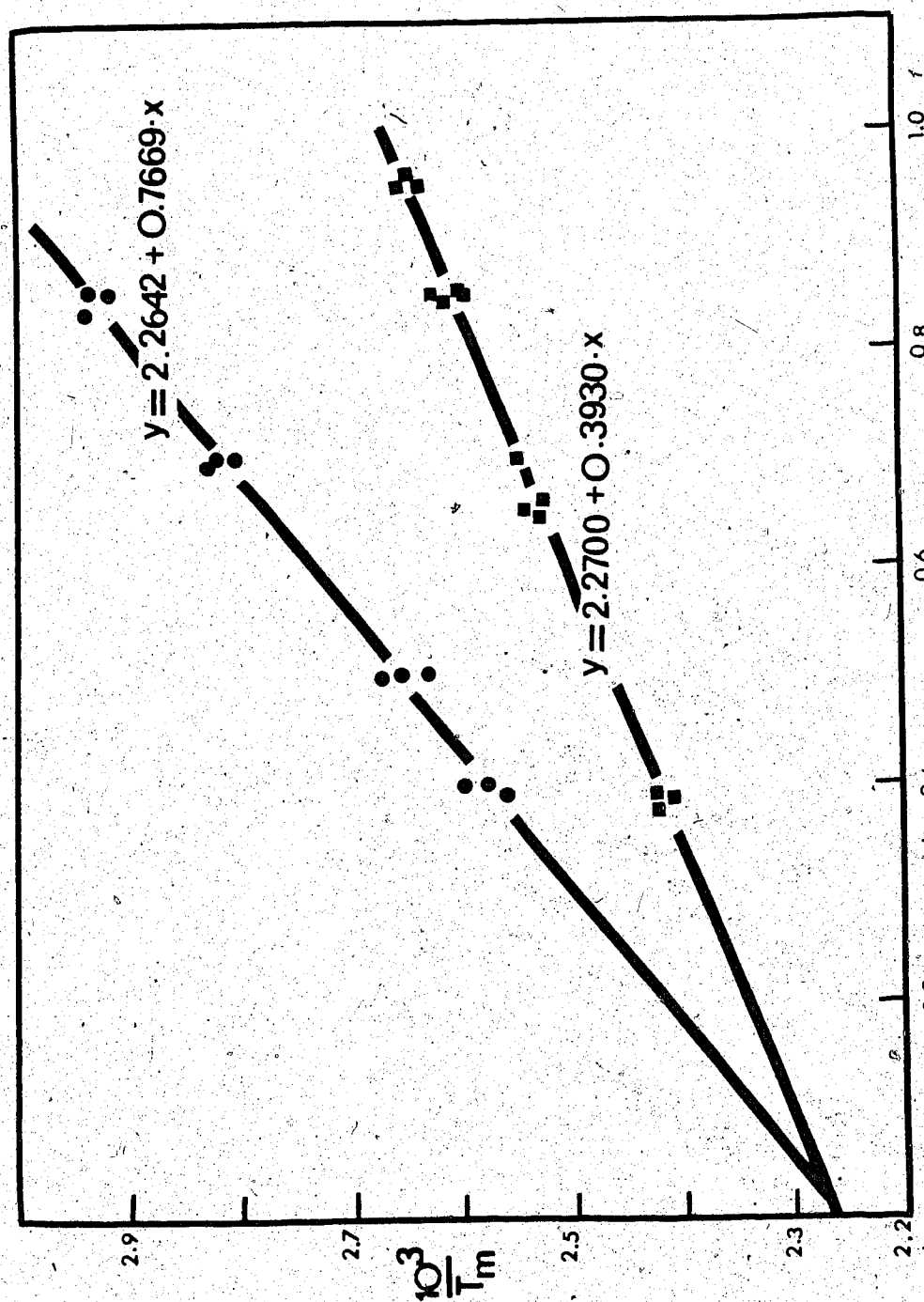
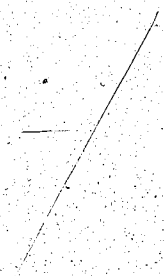
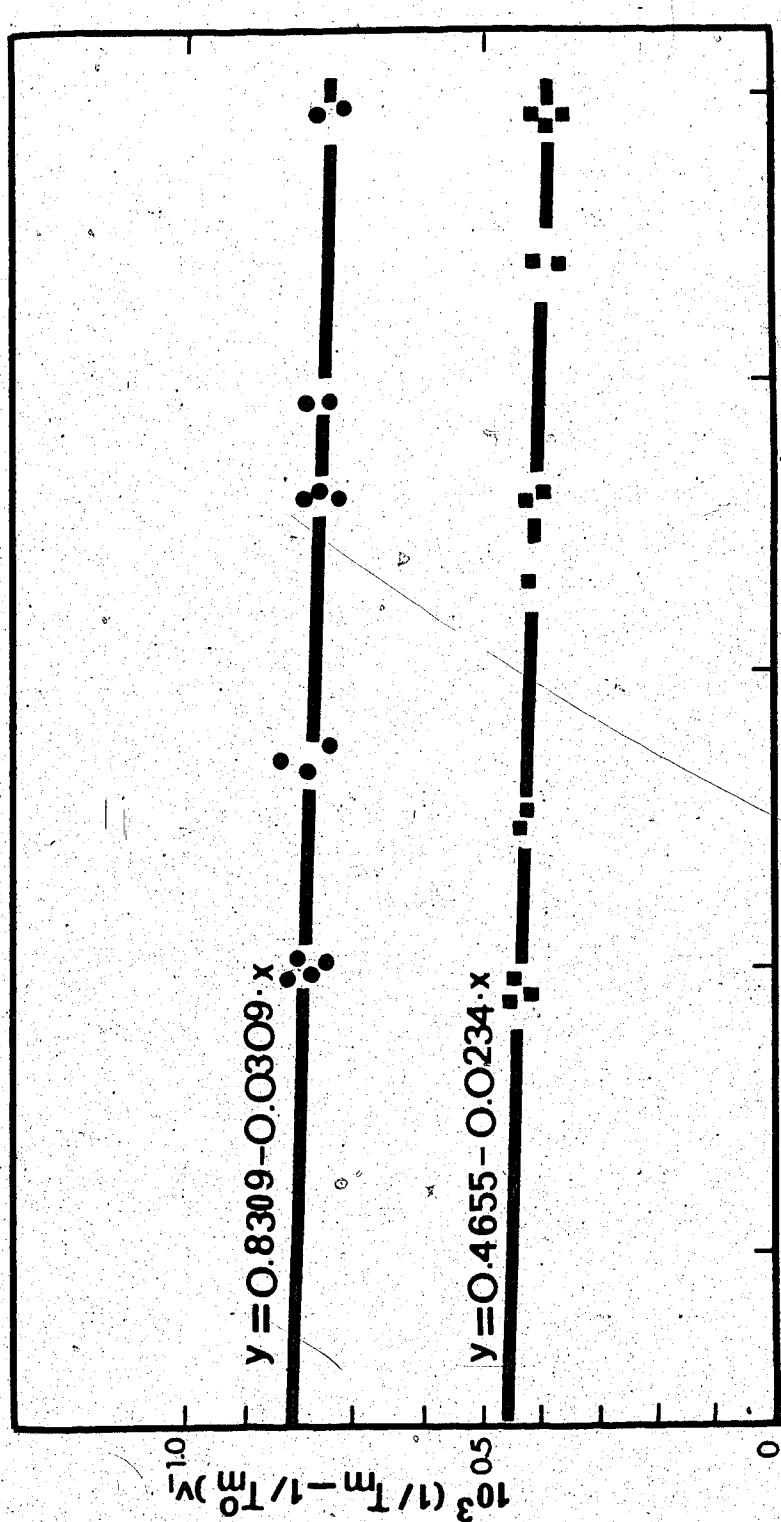

y = 2.2642 + O.7669·x
y = 2.2700 + O.3930·x
$\frac{10^3}{T_m}$
V_1
2.9
2.7
2.5
2.3
2.2
0.2
0.4
0.6
0.8
1.0

Figure 7. Plot of Experimental Data According to the Equation of Florry-Huggins.




$10^3 (1/T_m - 1/T_m^0)\nu_l$
$10^3 \nu_l / T_m$
y = 0.8309 - 0.0309 · x
y = 0.4655 - 0.0234 · x
0
0.5
1.0
1.5
2.0
2.5
0.5
1.0

acid) is the lipid constituent of this natural clathrate. The abundance of lysolecithin in wheat starch was demonstrated by Acker and Schmitz (1967), who found that 62% of the total starch lipid was lysolecithin. Potato starch isolated as in our study contained no phospho- or glycolipids nor their lyso-derivatives. Triglycerides, free fatty acids and/or free and esterified sterols were present only in traces. Hence, potato starch thermograms lacked the M_2 transition. However, when lysolecithin is added, the lipid-starch complex is formed, as shown by M_2 endotherm and by an exotherm immediately after the G transition (Kugimiya et al., 1980). Similar results were obtained in this study when lysolecithin was replaced with 1-monopalmitin, while amylopectin alone showed no evidence of formation of such a complex. Palmitic acid failed to form a complex with either starch grains or amylopectin.

Starch lintnerization brings about selective hydrolysis or chain scissions of the amorphous regions of the grains. Since water absorbed by the grain is associated only with its amorphous region (Kainuma and French, 1971), removal of the amorphous region would eliminate the gelatinization process assisted and driven by hydration and swelling. The crystalline region would be decoupled from the amorphous network, resulting in a shift of G transition to higher temperatures. Hence, extensive hydrolysis of the starch grain would remove the G transition and would retain the M_1 transition.

In accord with the above suggestion are the results of Biliaderis et al. (1980) for acid modified corn and smooth pea starches lintnerized to an extent of 5 to 10% in which the t_p and t_m melting points were raised by 9-10 and 3-8^{o}C, respectively. However, they found that specific enthalpies (ΔH cal/g starch) of both acid-treated starches

were lower than those of their native starch. A lower enthalpy for acid-treated wheat starch was reported by Wootton and Bamunuarachchi (1978). On the other hand, a limited acid hydrolysis of potato starch, as found by Donovan and Mapes (1980), merely increased the G transition temperature. The transition endotherm half-width as well as the specific enthalpy were unchanged. Longer acid treatment brought about significant endotherm broadening and the t_p was 9 C^o greater than for native starch. However, the specific enthalpy of the transition was unchanged.

The results of this study strongly support the above findings on potato starch. After treatment for 3 days with acid, potato starch, when compared to its native starch at a water level of ν_1 0.85, shifted its t_o from 56 to 60°C, t_p from 66 to 71°C, and t_m from 70 to 103°C. However, the specific enthalpy of 6.8 was retained, suggesting that little or no loss of crystalline structure occurred during lintnerization. Also, a plot of T_m as a function of ν_1 retained the close relationship of crystallite T_m and water levels found in native starch, with the melting point of the most perfect crystallite being 169.4°C.

1.6.2. Starch-Lipid Complex.

Thermograms of starch monopalmitin (0.7 mM) complex are shown in Figure 5 (b) and their endotherm characteristics are listed in Table 9. At a high water level (ν_1 0.85) there were G and M_2 endotherms, at an intermediate level (ν_1 0.50) G, M_1 and M_2 endotherms, and at a low water level (ν_1 0.39) M_1 and M_2. The G endotherm occurred over a narrow temperature range, as was also observed with native starch, and had a sharply centered t_p at 66°C. The enthalpy change depended on

Table 9.

Starch Monopalmitin Complex Endotherm Characteristics.

Volume Fraction of Water (ν_1)	Gelatinization(G)			Enthalpy of Fusion (cal/g starch)	Crystallite Fusion (M_1)	Complex Melting(M_2)			Endotherm Area (cm^2)	Enthalpy of Fusion, ΔH (cal/g starch)
	t_o	t_p	t_m		t_m	t_o	t_p	t_m		
0.39	-	-	-	5.26	116	127	134	140	0.5	0.439
0.50	59	66	71.5	5.70	103	124	130	133	1.0	0.878
0.65	57	66	71.5	6.14	88.5	109	115	122	1.3	1.141
0.70	55	66	71.0	7.46	84.5	108	115	119	1.6	1.404
0.85	54.5	66	70.5	8.77	-	94	105	112	2.0	1.755

water level and ranged from 5.26 at ν_1 0.39 to 8.77 at ν_1 0.85. These enthalpies were larger by an average of 3.5 to 21.2% than those of the uncomplexed native starch.

The starch-lipid complex melting temperature depended strongly on water content. The onset, midpoint and end of fusion were all shifted to higher temperatures as the water level decreased. In a range of 0.39-0.85 the onset was shifted by 33, the midpoint by 29 and the end of fusion by 28°C. Similarly, the M_2 transition enthalpy was a strong function of water level. It varied from 0.44 cal/g starch at ν_1 0.39 to 1.75 cal/g at ν_1 0.85.

The melting point of the most perfect crystallite of the complex was extrapolated to zero water content. It was calculated again by plotting $1/T_m$ (°K) against ν_1 (Figure 6). Linear regression analysis gave a significant correlation ($r = 0.99$) with an intercept of 440.5°K (167.5°C) at ν_1 0. Similarly, a plot (Figure 7) of ν_1/T_m against the left side of Eq (2) at the intercept $\nu_1/T_m = 0$ provided a value of 0.4655. This corresponded to a fusion enthalpy for the complex of 27.5 Kcal/mole D-glucose unit, a significantly larger enthalpy than that of the M_1 transition, surpassing even those of wheat and maize clathrate M_2 transitions (23.4 and 23.0 Kcal/mole), respectively (Donovan and Mapes, 1980), thereby suggesting the presence of a crystalline structure of higher stability.

The amount of amylose in the starch grain complexed with 0.7 mM 1-monopalmitin was calculated from the M_2 enthalpy observed in the presence of excess water (ν_1 0.85). It was assumed that the enthalpy of the amylose helix fusion in the complex was 7.4 cal/g amylose (Kugimiya et al., 1980). The starch amylose content of potato

cv.Netted Gem was 21.5%. Of this amylose available within the starch grain, 89.6% was found in the form of a starch-lipid complex.

Starch-monopalmitin complex data were typical for starch-lipid complexes (Table 10). Regardless of fatty acid chain length, the complexes had the same melting points in G and M_2 transitions, T^o_m, and complex fusion enthalpy per mole glucose unit. Exceptions were, however, the M_2 transition specific enthalpies, which differed and which were related to the extent of amylose complexing. Monomyristin (C_{14}) had the optimum complexing ability, hence, the highest enthalpy (1.78). The complexing ability decreased with chain length below C_{14}, but much less so with chain length above C_{14}. The slight superiority of monomyristin over monopalmitin amounted to an amylose complex increase of only 1.6%. Consequently, the specific enthalpies were practically the same.

Native starch and starch-C_{14} complex were used at ν_1 0.85 to examine the influence of 5 and 10 C^o/min heating rates on the G and M_2 transition endotherms (Table 11). When the scanning rate was increased, the melting points (t_o, t_p and t_m) shifted slightly to higher temperatures without an endotherm widening effect. Specific enthalpies for G and M_2 transitions also slightly decreased with increased scanning rates. The enthalpy ratio (5/10 C^o/min) for both transitions was 1:1 and was fairly constant.

A similar drop of specific enthalpy, but for wheat starch, was observed when the heating rate was doubled. The enthalpy ratio for an 8/16 C^o/min rise was 1.11, while for 16/32 it was 1.34 (Wootton and Bamunuarachchi, 1979). A lowered specific enthalpy at 10 C^o/min could be due to a different mechanism of starch gelatinization at higher heating rates. Discussion of such a possibility has been dealt with by several

Table 10.

Starch-Lipid Complex Endotherm Characteristics as Affected by Monoglyceride Chain Length*.

	Complex Melting Points (^oC) Regardless of Chain Length								
	G-transition			M_2-transition				M_2-transition**	
ν_1	t_o	t_p	t_m	t_o	t_p	t_m	Chain Length	Enthalpy (ΔH cal/g starch)	Amylose Complexed, %
0.39	-	-	-	126	134	140	C_8-	0.71	36.5
0.50	57	66	70.5	122	129.5	133	C_{10}-	0.86	43.8
0.65	56.5	66	71	109	115	122	C_{12}-	1.43	72.9
0.70	55.5	66	71	104	113	118.5	C_{14}-	1.78	91.2
0.85	54.5	66	70.5	92	104.5	110	C_{16}-	1.75	89.6

*Starch grains were treated with 0.7 mM monoglycerides (see Materials and Methods). The average moisture content of starch-lipid complexes held over P_2O_5 for 3 months was 10.2%.

**Values given were determined at ν_1 0.85. Linear regression analyses gave for all complexes an average T^o_m of 169.4 ± 2.1^{o}C and a 27.5 Kcal/mole D-glucose unit.

Table 11.
Potato Starch Endotherm Characteristics as Influenced by Heating Rate.

	Heating Rate, C^o/min		
	5^o		10^o
Native Starch			
Gelatinization (G)			
t_o	55.5 ± 0.0		56.2 ± 0.2
t_p	66.2 ± 0.2		67.0 ± 0.0
t_m	70.2 ± 0.2		71.2 ± 0.2
Enthalpy (ΔH cal/g starch)	6.76 ± 0.04		6.21 ± 0.05
$\Delta H_5 / \Delta H_{10}$ (average)		1.0878	
Complexed Starch			
Gelatinization (G)			
t_o	55.2 ± 0.2		55.2 ± 0.2
t_p	66.2 ± 0.2		66.5 ± 0.0
t_m	70.5 ± 0.5		70.5 ± 0.5
Enthalpy (ΔH cal/g starch)	7.52 ± 0.02		6.50 ± 0.07
$\Delta H_5 / \Delta H_{10}$ (average)		1.1570	
Complex (M_2)			
t_o	95.0 ± 0.0		96.5 ± 0.0
t_p	105.0 ± 0.0		105.5 ± 0.0
t_m	110.2 ± 0.2		112.2 ± 0.7
Enthalpy (ΔH cal/g starch)	1.75 ± 0.04		1.57 ± 0.01
$\Delta H_5 / \Delta H_{10}$ (average)		1.1044	

Amount of starch (complex) used, 2.15 mg, ν_1 = 0.85.

authors (Donovan, 1979; Wootton and Bamunuarachchi, 1979; Marchant and Blanshard, 1978). Lintnerized starch, when complexed with 0.7mM 1-monoglycerides derived from hydrogenated and distilled palm oil, gave thermograms similar to those of the uncomplexed lintnerized starch, with the exception of a shift in the endotherm of G transition to higher temperature. The melting point t_o rose from 60 to 63°C, t_p from 71 to 76°C, and t_m from 78 to 84°C. The lipid complex M_2 transition was centered at 105°C. The enthalpy of the complex rose from 6.8 to 7.4 cal/g starch. These findings suggested that part of the amorphous region left after acid treatment reacted with monoglycerides and, hence, was unable to further influence crystallite melting, while the enthalpy rise showed that the crystallinity within the starch grain was enhanced.

1.7. Water Binding Capacity.

Based on potato starch isotherm, pore structure test and thermodynamic properties, Van den Berg et al. (1975) concluded that the initial 10% moisture corresponded to close to one molecule of water per glucose residue on active absorption site, and the rest (up to 19%) to two. It was suggested that, due to steric hindrance, starch swells strongly during the uptake of the second water molecule, rupturing the hydrogen bonds between chains, resulting in large water agglomerates (the swelling imbibition or "free" water). The authors concluded from sorption isotherms that below a_w 0.95 (< 34% moisture) capillary condensation does not occur, suggesting that the starch grain is effectively a nonporous entity below this a_w value.

The standard quality control methods of water absorption by starches provide significantly different results. Water retention

against centrifugal force (Medcalf and Giles, 1965; Rasper and DeMan, 1980; Ooraikul and Moledina, 1980), a common method, reflects more the amount of water held intersticially than the water bound by starch chains. A novel DSC method (Wootton and Bamunuarachchi, 1978) was applied in this study on freshly isolated, non-defatted starch. Calculation of WBC is illustrated in Figure 8. A linear regression equation for native and lipid complexed starches ($W = A + B.\ W_f$, in which A is total water intercept at zero free water (WBC), B is unity and W_f, free water/g dry starch; $r = 1.0$) was used for calculation rather than the usual graphical assessment. Results are given in Table 12. Native starch had the highest WBC, 0.39 g water/g dry starch. This value suggested grain pore involvement in water accommodation. The value decreased as starch was complexed with monoglycerides. The decrease was a function of fatty acid chain length between C_8 - C_{14} and a minimum was reached with monomyristin. With a chain length of C_{16} the trend was reversed. The WBC rose slightly and the rise continued with C_{18}, but without attaining the original WBC of the native starch, a fact which might account for the low WBC of starches with natural clathrates.

The WBC of native starch, as found in this study, was close to that of 0.38 reported recently (Wootton and Bamunuarachchi, 1978). The slight difference might be due to amylose and ash content variability induced by environment (Chung and Hadziyev, 1980). The effect of amylose on WBC decrease has been verified by DSC on waxy, normal and high amylose maize starches (Wootton and Bamunuarachchi, 1978).

Figure 8. Free Water Content in Potato Starch Aqueous Suspensions as Affected by Monoglycerides. The Water Binding Capacity of Native and Complexed Starches was Obtained by Extrapolation to Zero Content of Free Water.

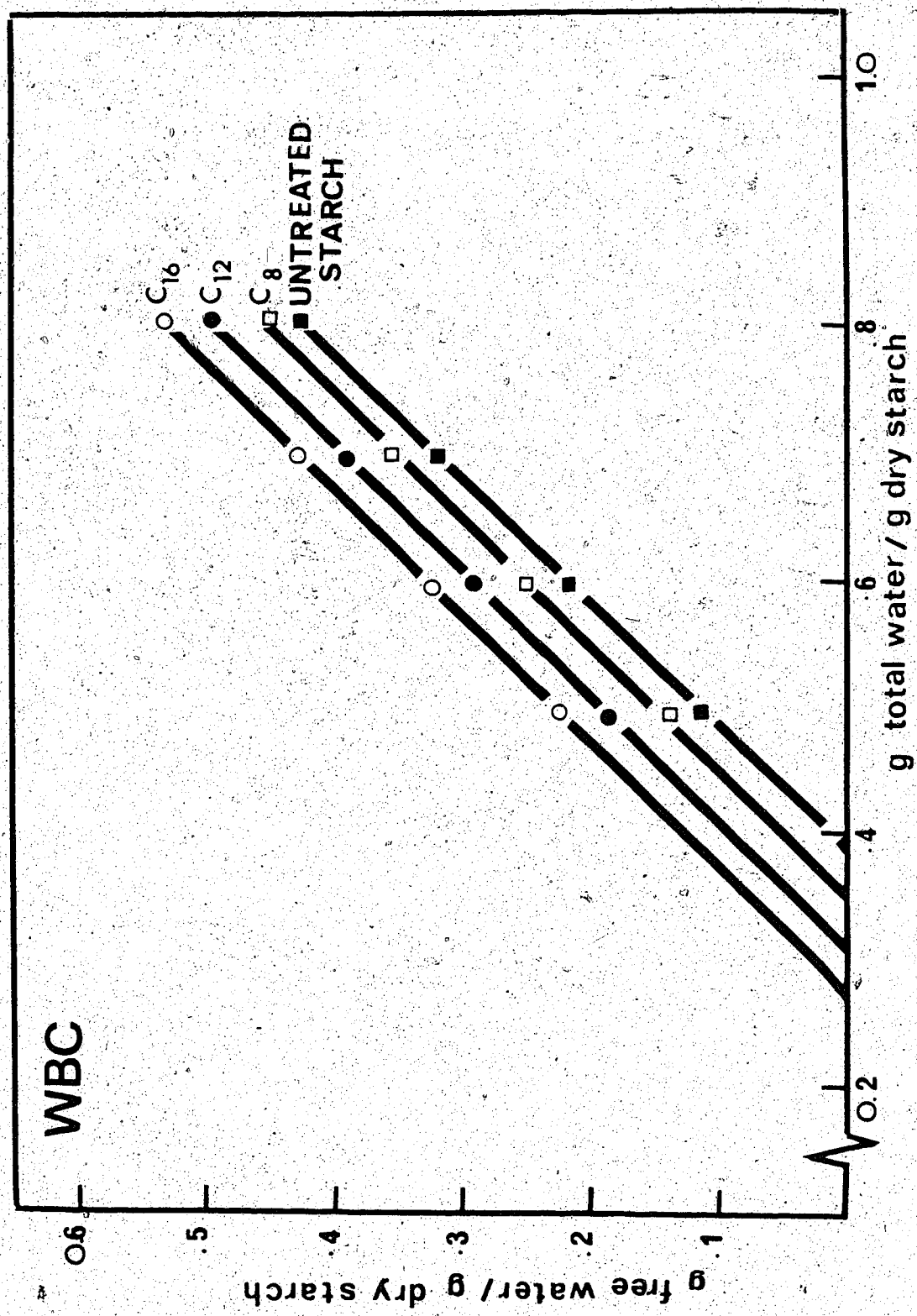

WBC
UNTREATED STARCH
C8
C12
C16
g free water / g dry starch
g total water / g dry starch
0.6
.5
.4
.3
.2
.1
0.2
.4
.6
.8
1.0

Table 12.

Water Binding Capacity of Starch-Monoglyceride Complexes.

Starch Complexed With Monoglyceride	Water Binding Capacity g water/g starch
Untreated starch (control)	0.39
C_8-	0.35
C_{10}-	0.32
C_{12}-	0.31
C_{14}-	0.25
C_{16}-	0.27
C_{18}-	0.29

2. THE EFFECT OF MONOGLYCERIDES ON AMYLOSE COMPLEXING DURING A POTATO GRANULE PROCESS.

2.1. Monoglycerides.

2.1.1. Application in a Granule Process.

In a medium size mashing unit (volume about 3 m^3) potato slices are separated into individual cells by auger and by mild shearing and pressing of the dry A-B granules against hot potato tissue. During the mash-mixing step, lasting about 20 min, the moisture content of the moist mix decreases from 75-80 to 30-40%, and the temperature drops from 90 to 60°C. Ingredients such as antioxidants, sulfites and Na-acid pyrophosphate are incorporated at this stage. Distilled monoglycerides in powdered form are metered in, mechanically blended with other dry ingredients and added directly through a dry feeder to the ricer or hot mash.

Alternatively, the monoglycerides are dispersed by vigorous stirring in water preheated to 65-69°C, until a homogenous translucent emulsion is obtained. Then the pH is adjusted as desired. Stirring is continued while the emulsion cools to 40°C or lower, then it is metered or pumped into the hot mash.

2.1.2. Physicochemical Characteristics.

Some physicochemical characteristics of two types of emulsifiers used in an A-B granule process are listed in Table 13. Both monoglycerides were free-flowing powders, as expected from their low iodine values. The 1-monoglyceride content was not less than 90%, the rest being 2-isomer. The sum of palmitic and palmitoleic acids was 73% of the total

Table 13. Some Analytical Data for Monoglycerides Used in an A-B Granule Process.

Analytical Data[a]	Type	
	C_{16}	C_{18}
1-Monoglyceride Content Minimum, %	90	90
Free Glycerol, Maximum	1	1.2
Acid Value	3	4
Saponification Value	160 - 170	150 - 165
Iodine Value, Maximum	3	5
Typical Slip Point, ^{o}C	65	77
Fatty Acid Composition		
$C_{10:0}$	0.3	0
$C_{12:0}$	0.4	trace
$C_{14:0}$	2.2	2.5
$C_{14:1}$	0.0	2.3
$C_{15:0}$	0.0	0.1
$C_{16:0}$	71.8	22.4
$C_{16:1}$	1.2	3.8
$C_{18:0}$	22.0	40.0
$C_{18:1}$	0	18.1
$C_{18:2}$	0	3.5
$C_{18:3}$	0	1.2
C_{20-24}	0.0	1.9
Unknown	2.1	4.1
C_{16}	73.0	26.2
C_{18}	22.0	62.8

[a]Data were obtained by applying AOCS Official and Tentative Methods of Analysis, 3rd. Ed. (1979): glycerol content, Ca 14-56; iodine value, Cd 1-25; acid value, Cd 3A-63; and saponification value, Cd 3-25.

acids in the first emulsifier, hence it was designated as a C_{16}-type, while in the second, a C_{18}-type, stearic acid content was 40.0%, with an additional 22.8% being oleic, linoleic and linolenic acids.

2.2. Crystallinity Forms of the Monoglyceride Preparations.

2.2.1. X-ray Diffraction.

X-ray diffraction data for the monoglycerides are given in Table 14. Gel preparations of pH 2.3 and pH 6.5, prepared from C_{16}- and C_{18}-types of monoglycerides, each provided a strong single diffraction line at 4.48 Å. In addition, the C_{16}-type gel had five weak and one medium intensity lines, and the C_{18}-type gel three weak and three medium intensity lines.

The microbead powder form of both emulsifiers exhibited three strong diffraction lines. The C_{16}-type of monoglyceride at 3.90, 4.39 and 4.62 Å, and the C_{18}-type at 3.93, 4.31 and 4.51 Å. In addition, the C_{16}-type revealed several lines with longer spacings, all weak in intensity, while the C_{18}-type also had lines with longer spacings but medium intensities (Figure 9).

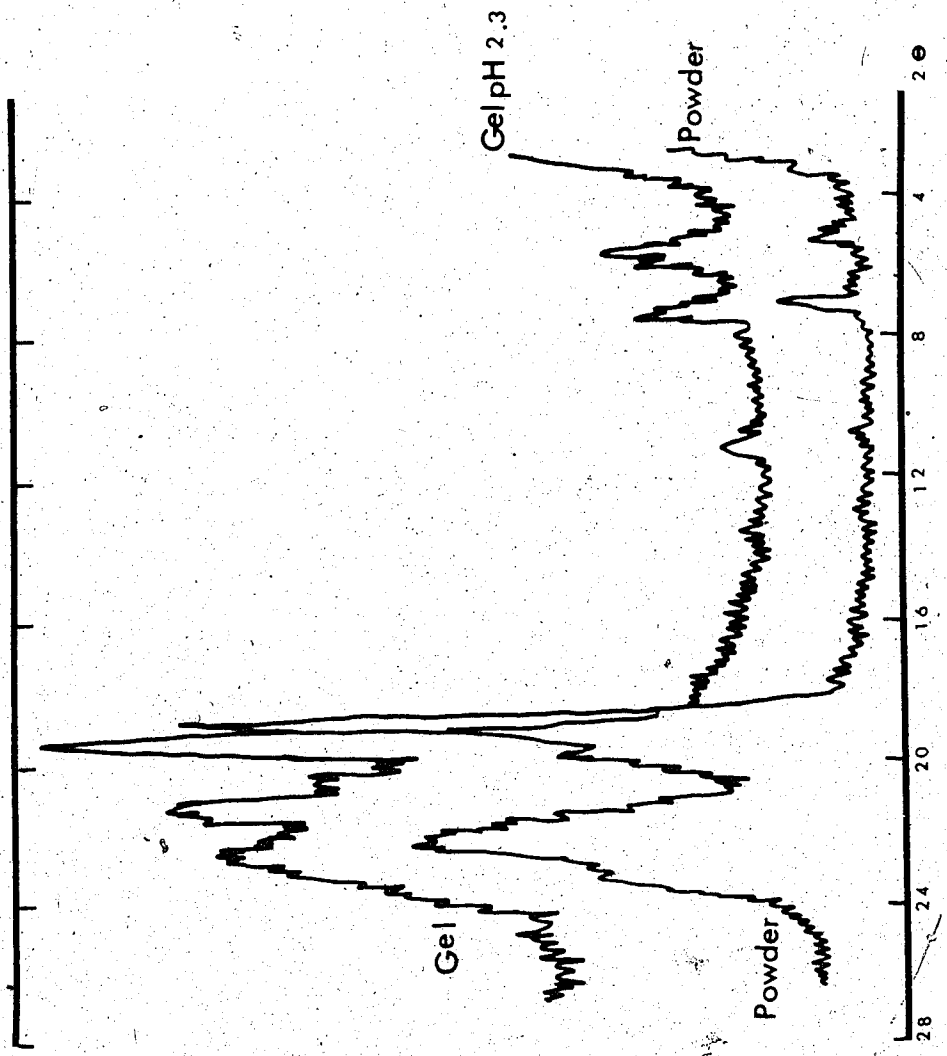
Lutton (1950) examined pure 1-monopalmitin and monostearin and found that the α-crystalline state is characterized by a single strong spacing at 4.18 Å, while the β-form has short spacings at 3.86, 4.37 and 4.55 Å. It was stated that the weak lines are unique for an α-crystalline state. These findings and the results of this study strongly suggest that the α-crystalline form should be ascribed to gel preparations of pH 2.3 or pH 6.5, and the β-form to microbead powders. The detection of additional diffraction lines in powders, an apparent

Table 14. X-ray Diffraction Patterns of Monoglycerides Used in an A-B Granule Process.

1-Monoglyceride	Interplanar Spacings d(Å) and Their Intensities[a]								
C_{16}									
Gel pH 2.3	3.80(w)	3.87(w)		4.07(m)		4,48(s)	7.76(w)	11.33(w)	15.24(w)
Powder (Microbeads)		3.90(s)		4.39(s)		4.62(s)	7.89(w)	11.95(w)	15.78(w)
C_{18}									
Gel pH 6.5		3.90(m)	4.07(w)	4.27(w)		4.48(s)	7.37(w)	11.63(m)	15.24(m)
Powder (Microbeads)		3.93(s)		4.31(m)		4.51(s)	7.89(w)	11.78(m)	15.24(m)
Gel pH 6.5, Kept for 5 days at 24°C	3.77(m)	3.90(m)	3.93(w)	4.07(w)	4.31(m)	4.55(s)	7.89(m)	11.94(m)	15.78(s)

[a]Intensities: (s) = strong; (m) = medium; (w) = weak.

Figure 9. X-ray Diffraction Patterns of Gel and Powder Forms of C_{16}-Type Monoglycerides Used in an A-B Granule Process. The Region Scanned Corresponds to 3-32^{o} 2θ.


Gel pH 2.3
Powder
Gel
Powder
4
8
12
16
20
24
28
2θ

discrepancy with Lutton's data, is due to greater sensitivity of diffraction analysis which avoids the camera photo technique.

2.2.2. Infrared Spectra.

The nature of the monoglycerides is shown by their IR spectra. The O-H stretching vibrations had maxima at 3245-3300 cm^{-1}. The strong bands from 2860-2950 cm^{-1} corresponded to sym- and anti-methylene group stretchings; those at 1730-1740 cm^{-1} as shown in Fig. 10 to carbonyl stretch of the ester group; bands at 1460 to 1480 cm^{-1} to C-H bending of methylene and methyl groups; 1380 cm^{-1} to sym C-H bend of methyl group; 1050, 1064 and 1180 cm^{-1} to C-O stretchings of primary and secondary -OH groups; 940-995 cm^{-1} to C-C single bond stretch; and the band at 720 cm^{-1} to methylene group rocking vibration. Evidence supporting the assignment of α-form to gels and β- to powders was also provided by IR spectra. Different polymorphic forms of 1-monoglycerides give rise to different IR spectra, but the 2-isomer exists only in one polymorphic form (Chapman, 1965). As seen from Table 15, the band at 1062 cm^{-1}, which corresponds to C-O stretch of primary -OH groups, is always present in the β-form of powders but absent in the α-form of gels. This might be due to formation of hydrogen bonds between the -OH groups and water in the gel. In addition, the two crystal forms are differentiated at the major frequency bands of C=O stretching at 1730-1739 cm^{-1}. While this band is consistent with the β-form, the α-form has an adjacent strong band at 1705 cm^{-1} which appears to arise from carbonyl-water association via hydrogen bonding. Of interest was the finding that a band appeared at 1062 cm^{-1} after the gel was kept for 6 days at 24°C. This suggests

Figure 10. Infrared Spectra of Gel and Powder Forms of C_{18}-Type Monoglycerides Used in an A-B Granule Process.

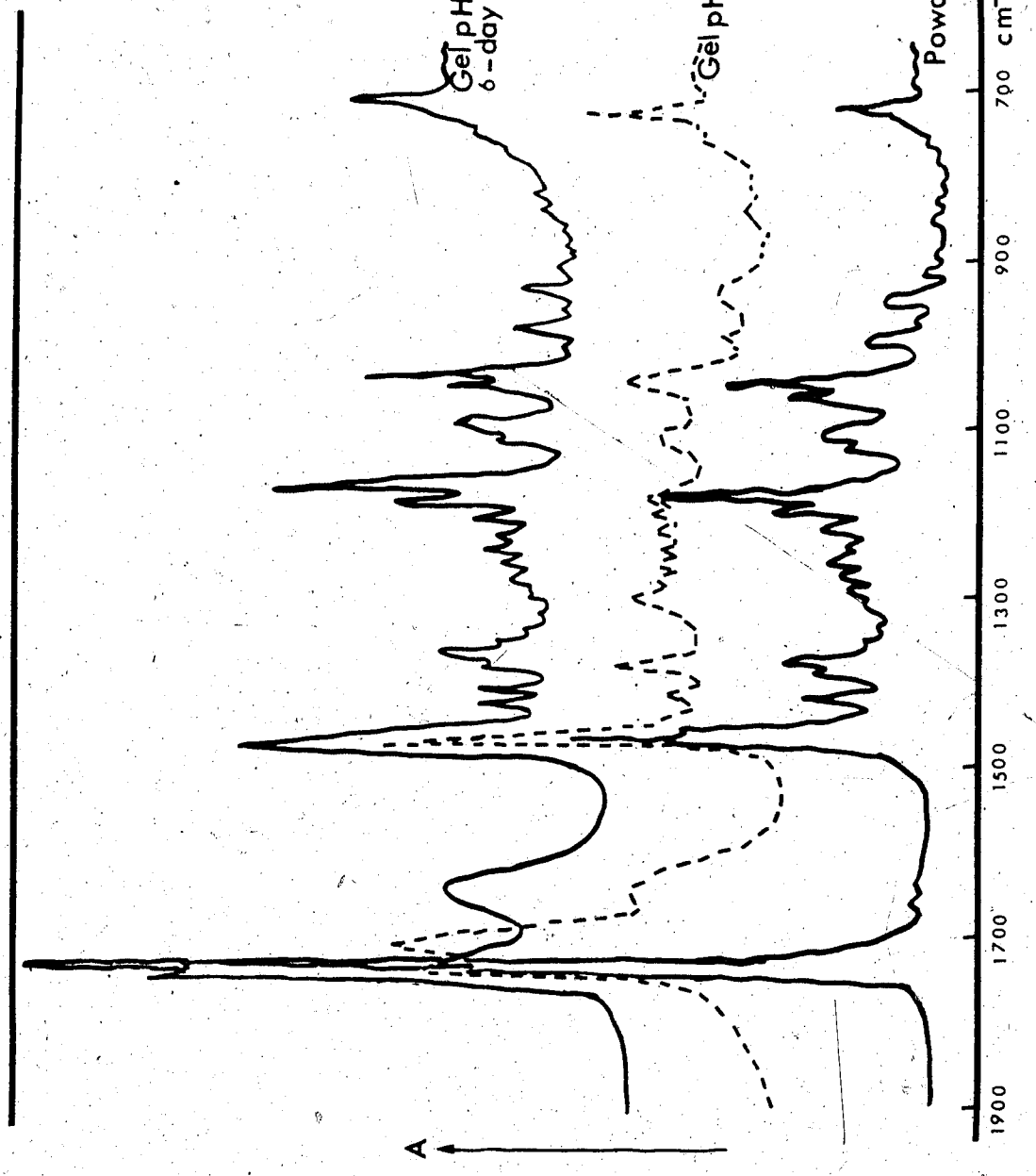

Gel pH 6.5
6-day old
Gel pH 6.5
Powder
A
1900
1700
1500
1300
1100
900
700 cm⁻¹

Table 15. Some Major Infrared Frequency Bands of the Two Crystallinity Structures of Monoglycerides Used in an A-B Process.

Crystallinity	Bands, cm^{-1}									
α										
C_{18}, Gel pH 6.5	1705		1737			1465	1377	1200	1185	
β										
C_{16}-Powder (Microbeads)		1730	1739			1469		1197	1181	1062
C_{18}-Powder (Microbeads)		1730	1739			1470		1195	1181	1062

	Frequency of Bands in the 1250 cm^{-1} Region							
C_{16} 1-Monopalmitin, A.G.[a]	1201	1227	1248	1271	1293			
C_{16} Powder, Commercial	1200	1220	1243	1255	1268	1288	1310(14)	1330(39)
C_{18} 1-Monostearin[b]	1219	1233	1258	1277	1297	1312	1332	
C_{18} Powder, Commercial	1219	1236	1258	1275	1289		1332	

[a]Analytical Grade with approximately 99% 1-Monoglyceride and only traces of 2-isomer.

[b]At least 90% 1-monoglyceride, the balance is 2-isomer.

that the β-form is the stable crystalline form of the monoglycerides. Further evidence for β-form stability was provided by the crystalline form of the C_{18}-emulsifier, which was stored in a warehouse for one year and then analyzed. It is a blend of 1-monoglycerides and propylene glycol monoesters. The latter is known to be an α-tending emulsifier used to stabilize the α-form of distilled monoglycerides during crystallization (Birnbaum, 1978). Nevertheless, only the β-form was evident. The IR findings partly support the earlier observations by Chapman (1955), that α- and β-forms of 1-monoglycerides show a frequency band shift of the carbonyl stretch from 1706 cm^{-1} in the liquid form to 1721 in α, 1730 in sub-α and to 1736 cm^{-1} in the β-form. Accordingly, the α-form of the gel could be considered as a liquid state. However, in the 1150-1300 cm^{-1} region, instead of having broad bands tending to merge into each other as in a liquid state, the gel had distinct bands typical of an α-form (Chapman, 1955).

The use of the frequency band progressions in the 1250 cm^{-1} region provide data about the glyceride chain length (Freeman, 1968). As seen from Table 15, the C_{16}- and C_{18}-type of monoglyceride bands resembled those of 1-monopalmitin and monostearin, respectively.

2.3. Amylose Release From Starch Grains.

Potato starch had a gelatinization temperature range of 56.8 to 68.5°C as indicated by the loss of birefringence. Starch gelatinization <u>in situ</u>, as visualized by SEM, was characterized by an extensive swelling of individual grains. This gave the fused starch the appearance of an irregular reticulum.

When starch is gelatinized as a 1-5% suspension in water under

mild stirring and then examined by SEM, some of the grains are identifiable at 65°C, while at 70°C they appear disintegrated and fused into a uniform mass in which no grain structure is detectable.

When starch is heated without stirring as a 0.1% suspension at 70, 80 or even 95°C, i.e. well above the gelatinization temperature, the grains do not disintegrate, but retain their visual integrity. However, they are surrounded by a continuous filamentous network which is more dense when the suspension is heated at higher temperature and for longer time (see Figures 11 and 12). The interlaced and connected network cannot be seen when network realignment is not prevented by the liquid-N_2 freezing technique (Figure 13). Individual fibres had a diameter ranging from less than 0.1 to 2.5 μm. They stained blue and precipitated with 0.02 N I_2 solution, while the enmeshed starch grains stained reddish brown. This finding proved that the released or "solubilized" starch is predominantly amylose, and strongly supported a similar conclusion of Miller et al. (1973). Since, in the same assay, pure potato amylopectin solutions could not be stained nor precipitated, the starch complexing index determined before or after monoglyceride addition would involve solely the starch amylose moiety.

As seen from Table 16, potato starch insolubilization by precooking, cooling and steam-cooking in an A-β granule process was not evident when precooking was not followed by a cooling step. The relative extent of amylose insolubilization by retrogradation was greater when steam-cooking was followed by a cooling step. Retrogradation was enhanced by 6.6% when the gelatinized starch temperature dropped from 70 to 50°C. However, in all cases the absolute, value of A_{680} was low, suggesting that extensive amylose leaching occurs at mash-mixing rather than precook

Figure 11. SEM-Micrograph of a Potato Starch Grain Heated at 80°C for 10 min. The Interlaced Network is the Leached-Out Amylose. Magnification x 3,800.

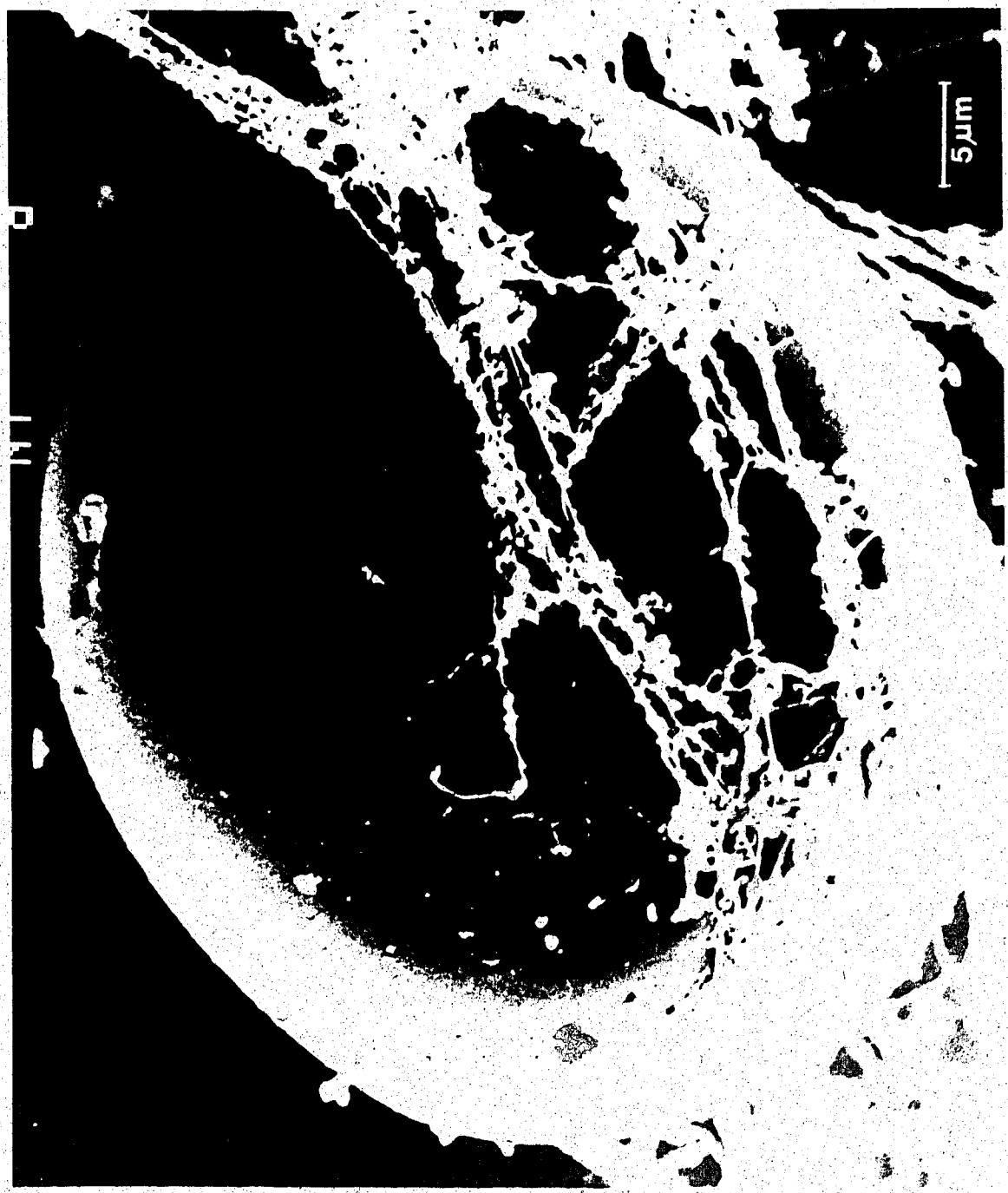

5µm

Figure 12. SEM-Micrograph of a Potato Starch Grain Heated at 80°C for 30 min. The Dense Network is Leached-Out Amylose. Magnification x 3,800.

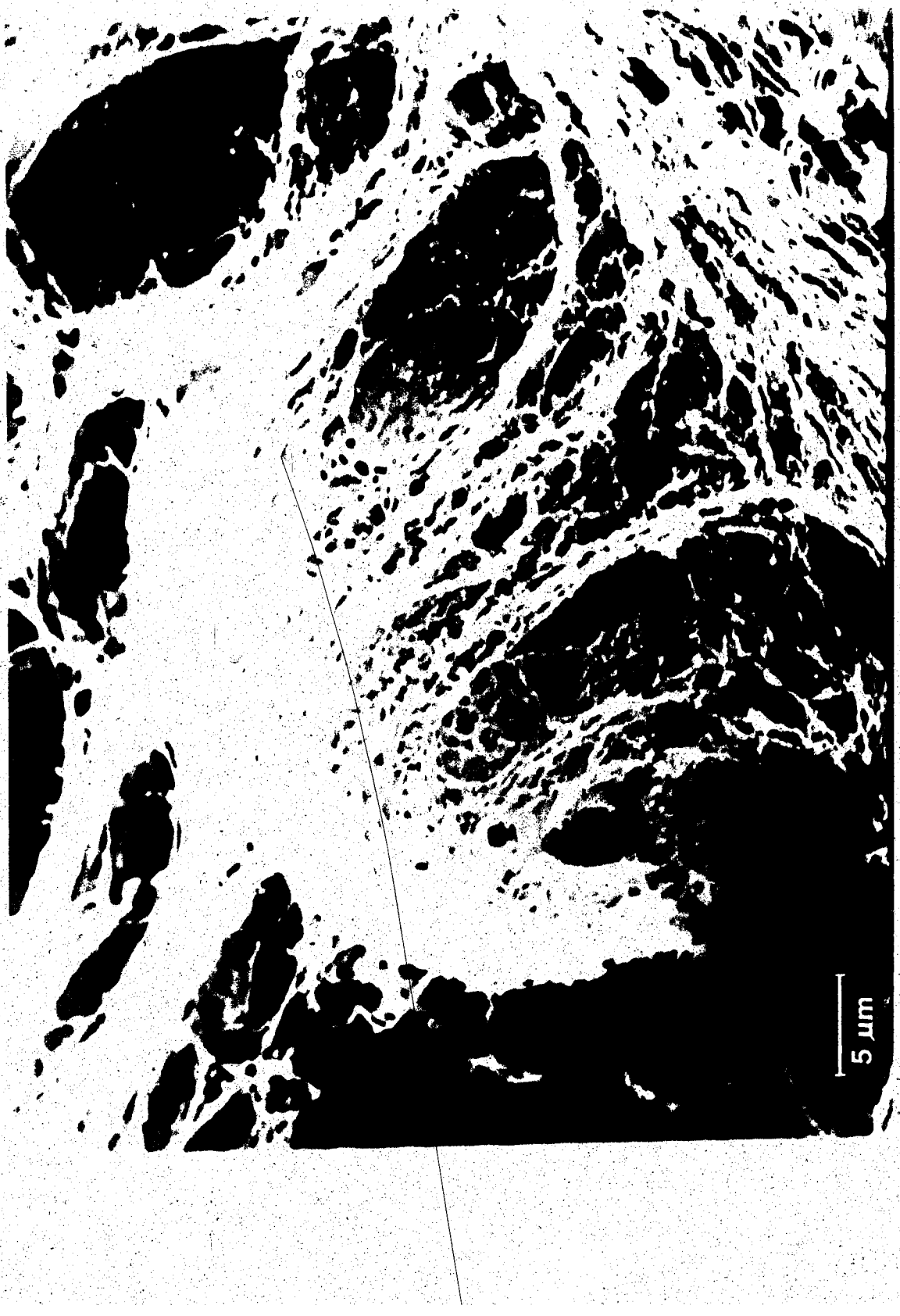
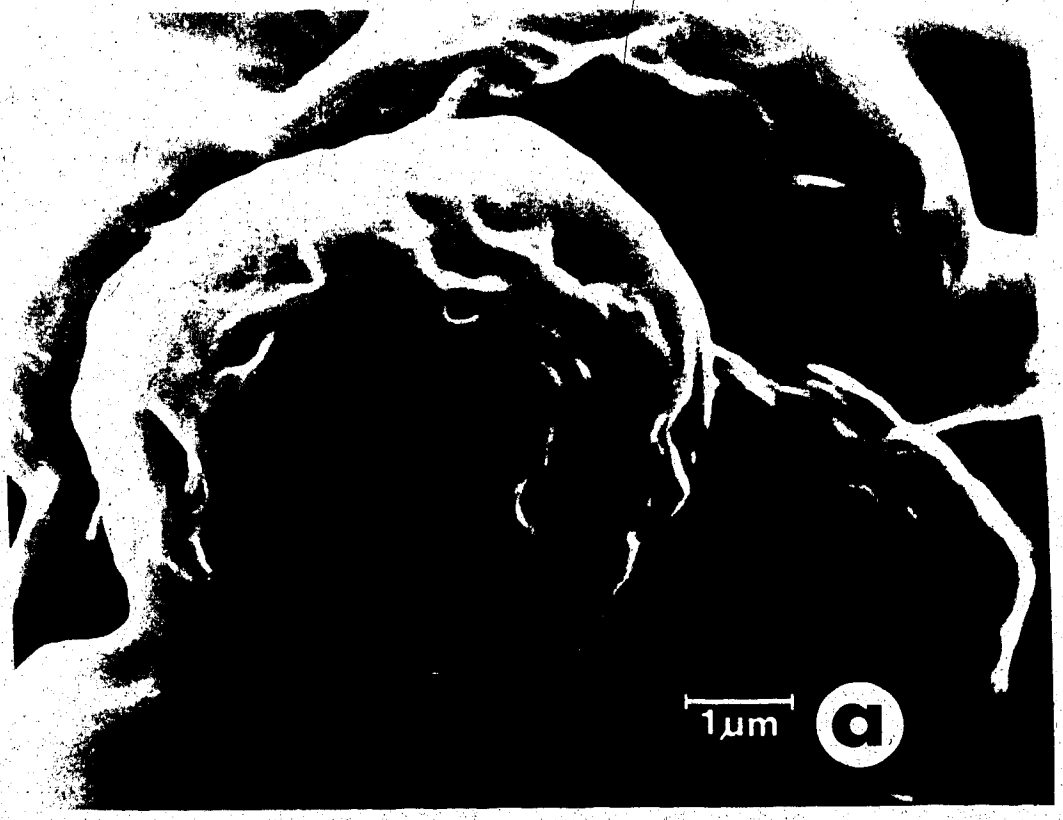

5 µm

Figure 13. SEM-Micrograph of Potato Starch Grains Heated at 80°C for 30 min Without Precautions Against Amylose Realignment. Magnifications: (a) x 1,500 and (b) x 500.


1µm
a

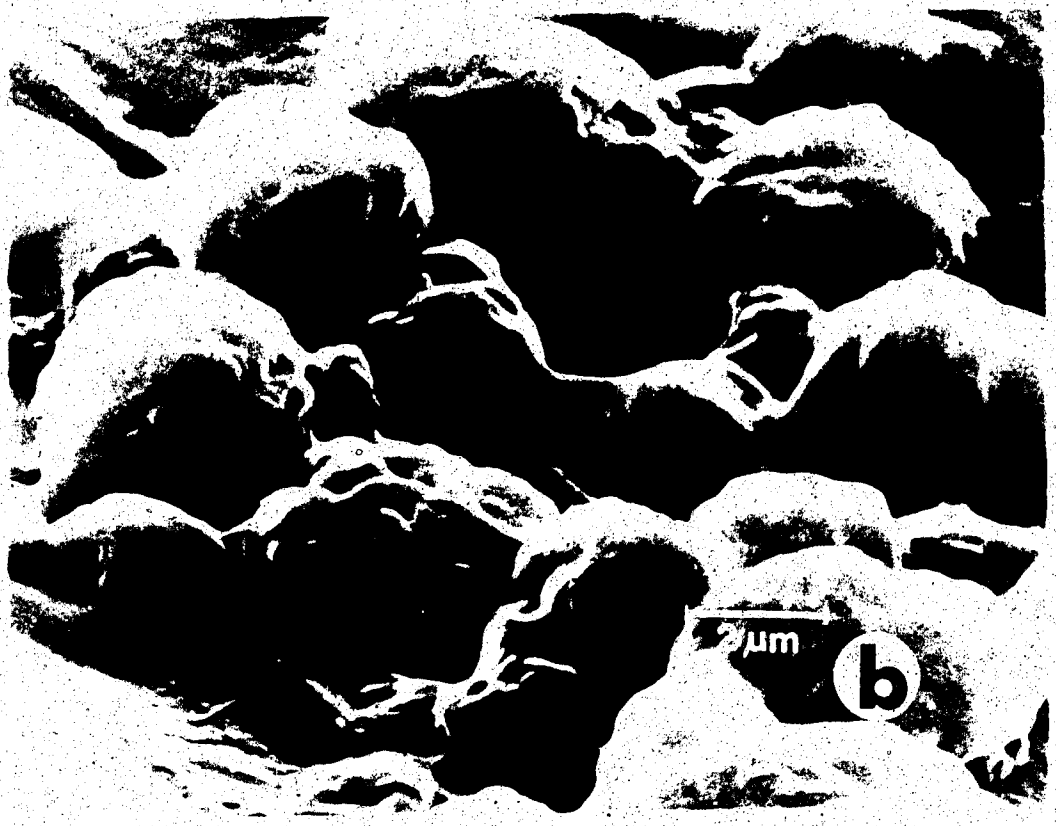

µm
b

Table 16. Potato Starch Retrogradation as Affected by Precooking, Cooling and Steam-Cooking Steps of an A-B Granule Process.

Starch Grains, Batch	Processing Steps						Retrogradation, Relative % at °C		
	Precooking 70°C	Cooling 25°C	Steam-Cooking	Cooled to °C					
				50	60	70	50	60	70
1			+[a]	8.6[b]	17	24	0	0	0
2	+		+	8.8	18	25	-2.3	-5.9	-4.2
3	+	+	+	6.6	14	20	23.2	17.6	16.6

[a] A sign of + indicates the processing step was carried out.

[b] A_{680} x 100 of treated starch suspension in water (1:4 w/w). Before color development the suspension was diluted 5-times with water, centrifuged, and 1 ml supernatant was used to develop the blue color.

and steam-cooking steps of the process.

2.4. Amylose Complexing with Monoglycerides.

2.4.1. Lintnerized (Soluble) Starch.

The effect of monoglyceride concentration and crystal form on the extent of soluble starch complexing at 60°C for 20 min is illustrated by results in Table 17. There was a beneficial amylose complexing up to 0.5% of added monoglyceride. Further addition initially improved the complexing index by only 1.5%, while higher concentrations gave an increase of 0.5-1%. At levels above 3% monoglyceride there was no additional beneficial effect. The complexing ability of the two crystal forms differed. Gel or α-form was more efficient at all levels than β-, the α- form complexing index being higher by an average of 11%. An exception was at 0.2% concentration, where the two forms appeared to be equally efficient. The reaction time effect on amylose complexing by C_{18}-monoglycerides is presented in Figure 14. The highest reaction rate was during the initial 15 min, then it levelled off and was practically completed within 20 min. The α-form had a higher rate complexing 63.7% of the available amylose in 20 min, while the β-form complexed 55.5%. A maximum of 66.7% (or 56.3% for β-form) was attained after 25 min.

2.4.2. Starch Grains.

A pictorial illustration of monoglyceride prevention of amylose leaching from heated starch grains, thus preserving the grain integrity above the gelatinization temperature, is shown in Figure 15 a,b.

Table 17. The Effect of C_{18}-Monoglyceride and its Two Crystallinity Structures on the Extent of Complexing Soluble Potato Starch at 60°C for 20 min.

C_{18}-Monoglyceride Concentration, %	Monoglyceride Crystallinity Form	
	α	β
	Gel pH 6.5	Powder (Microbeads)
	Complexing Index	
0.1	27.2 ± 4.5[a]	17.1 ± 1.9
0.2	39.3 ± 5.2	35.9 ± 0.8
0.5	64.2 ± 0.5	53.0 ± 2.6
1.0	65.7 ± 0.5	54.9 ± 3.4
2.0	67.8 ± 1.0	55.8 ± 3.3
3.0	68.8 ± 1.0	58.0 ± 3.3
3.5	68.8 ± 1.0	58.0 ± 3.4

[a]In this and following Tables, standard deviation is calculated with n = 3.

Figure 14. Complexing Index of Soluble Starch in Dependence on Reaction Time, and of C_{18}-Type Monoglycerides at 60°C.
□Gel pH 6.5; ■ Powder Form.

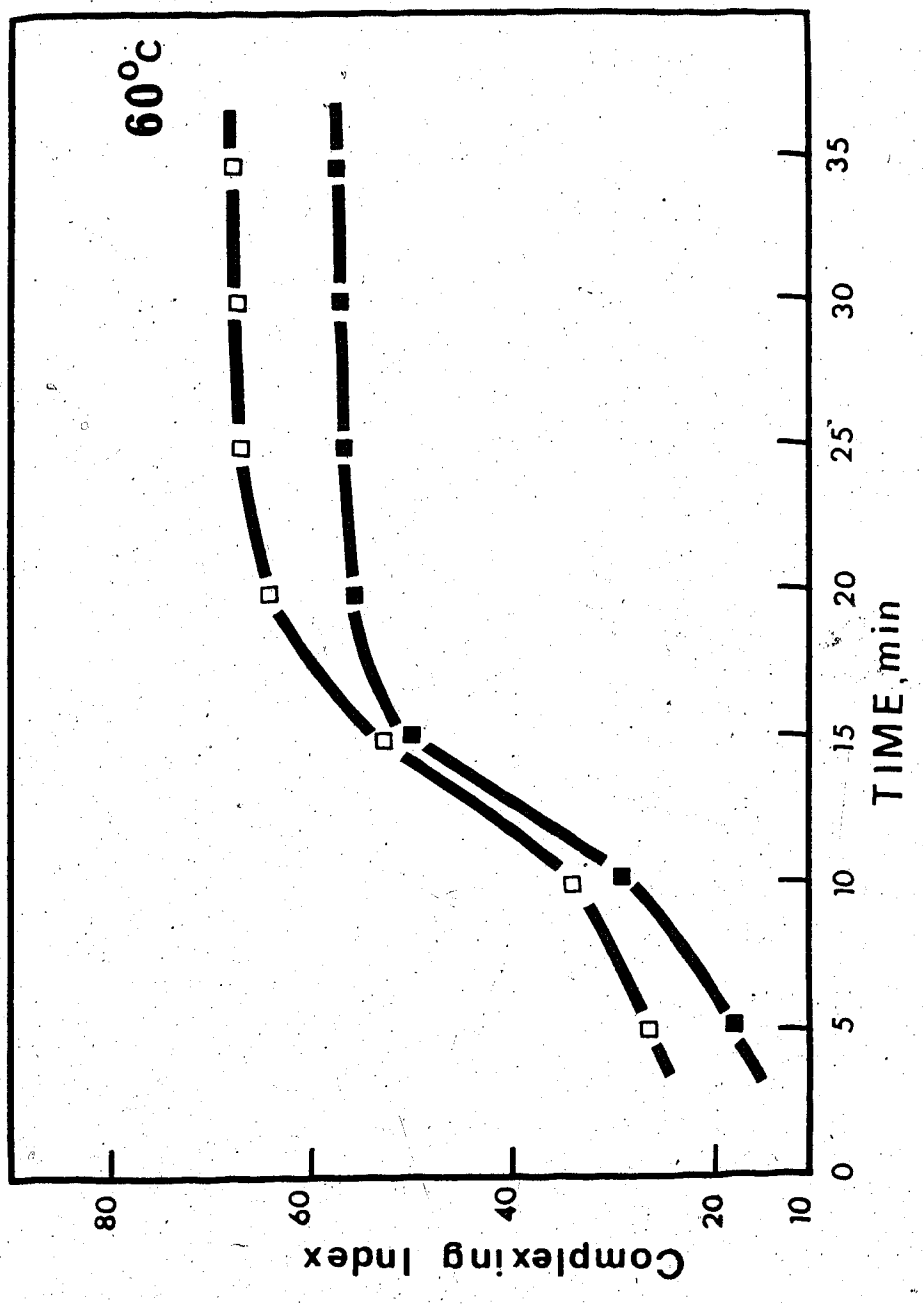
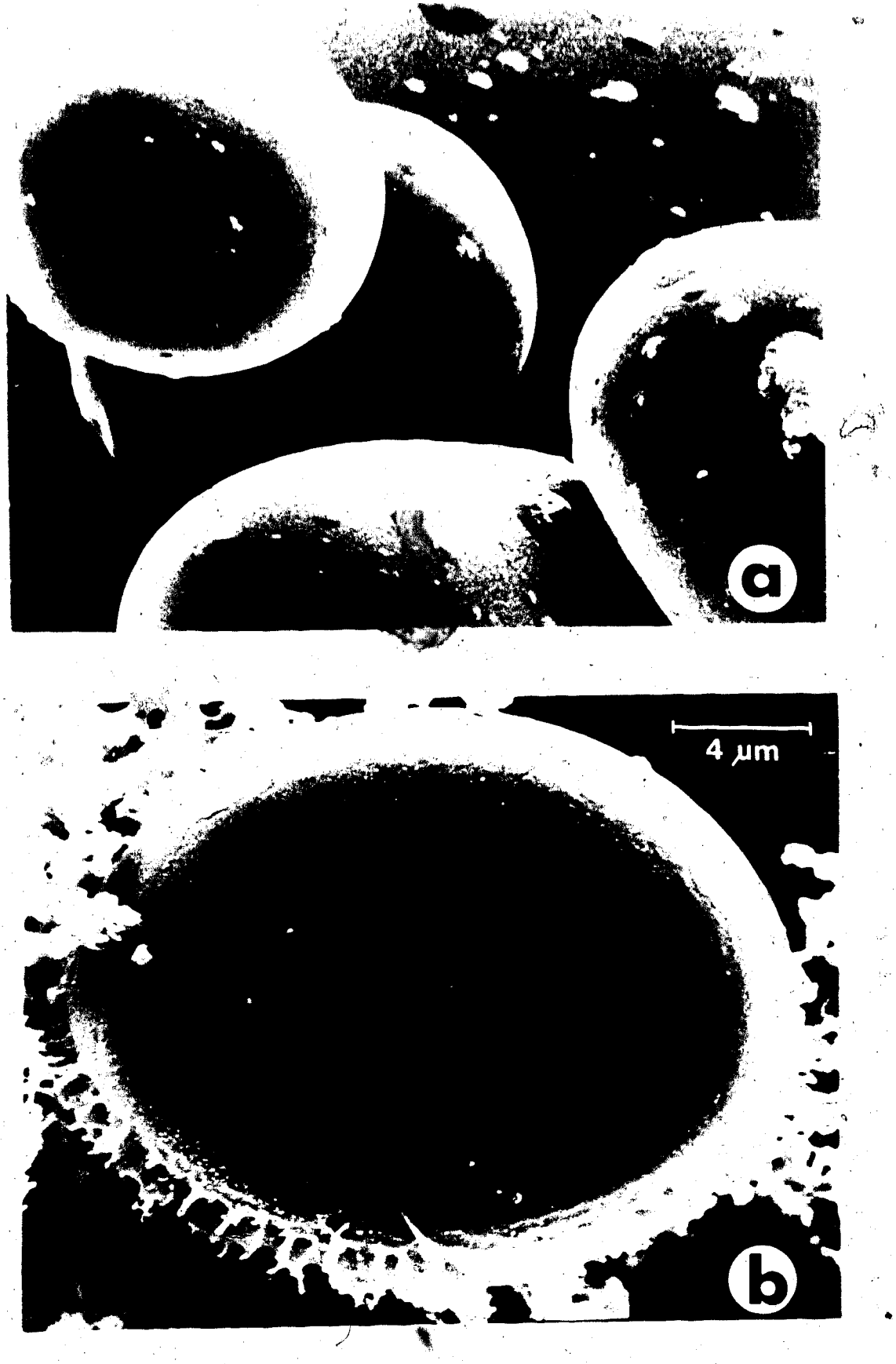

60°C
Complexing Index
10
20
40
60
80
TIME, min
0
5
10
15
20
25
30
35

Figure 15. SEM-Micrograph of Potato Starch Grains Treated As in Figure 12. (a) In the Presence of 0.25% C_{16}- and (b) 1.0% C_{18}-type Monoglycerides. Magnifications x 1,800 and 3,800, Respectively.

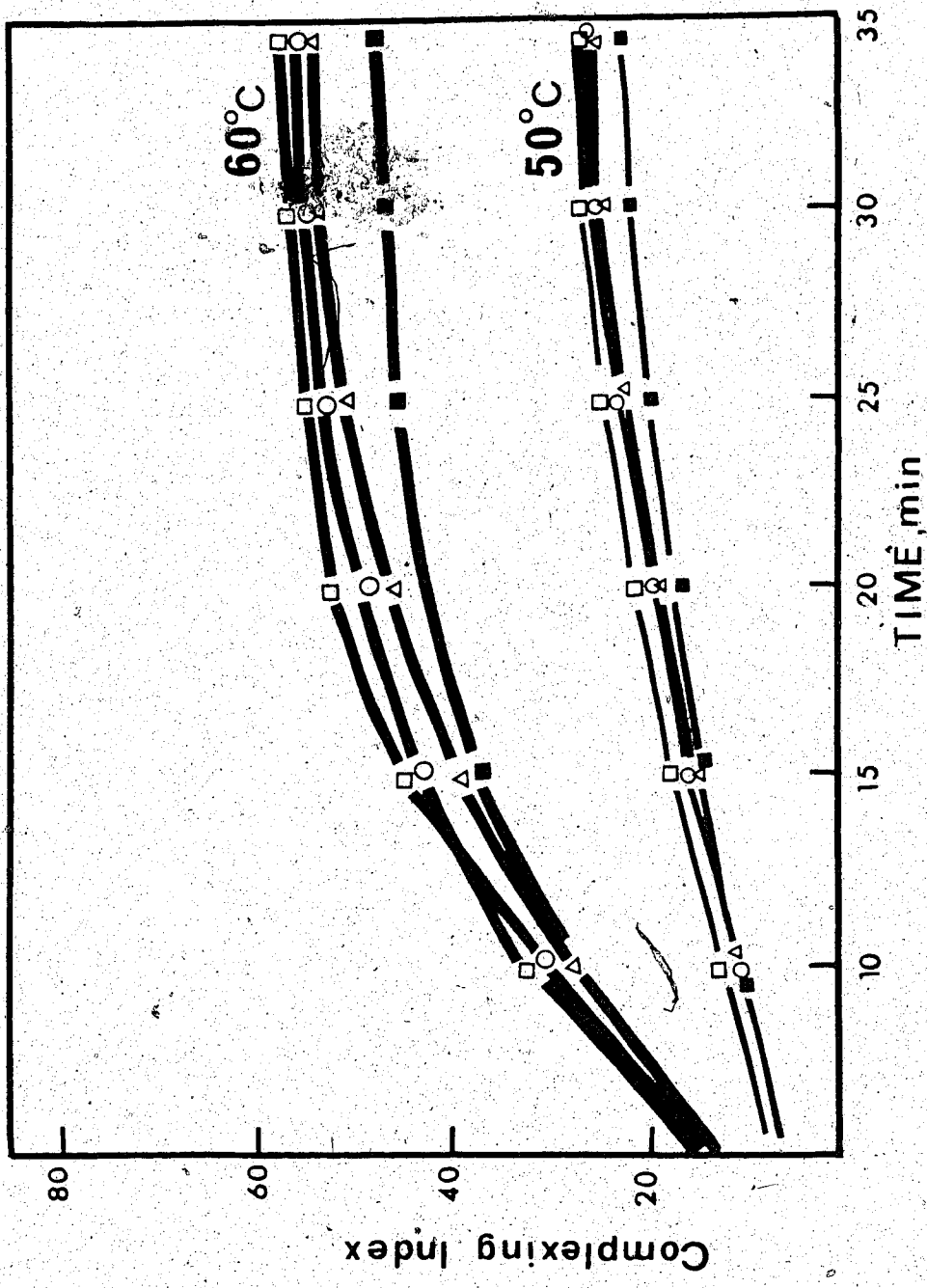

a
4 µm
b

At a level of 0.25% of added monoglycerides, all the monoglycerides apparently diffused into the grain and insolubilized the amylose within the grain, since amylose leaching was not evident (see also Figure 11 and 12). Consequently, grain integrity was well preserved. At a level of 1% the effect was the same, however, excess monoglycerides could not penetrate the grain but were left attached to its surface. Starch grains precooked, cooled, steam-cooked and then mash-mixed at 70°C with 0.5% C_{18}-monoglycerides had amylose complexing indices which were dependent on reaction time and crystal forms of glycerides (Table 18). Like lintnerized starch, gelatinized starch reacted with monoglycerides within 20 min regardless of the crystal form. During this time an average of 60% available amylose was forced to insolubilize. After 35 min there was slight additional complexing not exceeding 2% for gels and 5.1% for powder. The complexing ability of gels of pH 6.5 and pH 7.1 was the same while the pH 3.5 gel performed like the powder at the reaction onset. After 15 min its reaction rate simulated that of the α-form. In all cases the α-form was superior to β-, being higher by an average of 11%. This finding coincided with that of lintnerized starch at 60°C, implying that β- to α-crystal form transition did not occur at 70°C, or was too slow to be detectable even during mash-mixing for 35 min. Similar runs at 50 and 60°C gave results presented in Figure 16. At 60°C there was a consistent superiority of the α-form. Due to this lower temperature, the maximum complexing index of 53-57.5% for gels and 49% for powder was attained only after 35 min. In comparison to 70°C, mash-mixing at 60°C for 20 min decreased amylose complexing by 7.7-14.8% for gels and 8.7% for powder. At 50°C the reaction rate dropped further and amounted to only one third of that at 70°C.

Table 18. Interaction of C_{18}-Monoglycerides With Starch Grains Precooked, Cooled, Steam-Cooked and Mash-Mixed at 70°C.

	Monoglyceride (0.5%) Crystallinity Structure			
	α		β	
	Gel pH 6.5	Gel pH 7.1	Powder (Microbeads)	Gel pH 3.5
	Complexing Index			
Time, Min				
5	25.7 ± 1.3	24.2 ± 2.6	19.6 ± 2.2	20.0 ± 5.0
10	42.9 ± 2.2	42.4 ± 2.6	37.6 ± 3.1	40.0 ± 5.2
15	51.5 ± 2.6	51.3 ± 3.1	44.8 ± 3.4	50.0 ± 5.7
20	60.1 ± 1.4	60.0 ± 1.2	48.7 ± 2.2	60.0 ± 1.2
25	60.8 ± 1.2	60.0 ± 1.4	51.1 ± 1.4	60.0 ± 1.4
30	62.2 ± 0.4	61.5 ± 0.5	53.5 ± 1.2	62.0 ± 2.5
35	62.3 ± 0.4	61.5 ± 0.5	53.8 ± 2.6	62.0 ± 2.5

Figure 16. Complexing Rate of Amylose Leached from Starch Grains Which were Preheated, Cooled, Steam-Cooked and then Mash-Mixed with C_{18}-Type Monoglycerides at 50 and 60°C. ○Gel pH 3.5; □ Gel pH 6.5; △ Gel pH 7.1, and ■ Powder Form.


60°C
50°C
Complexing index
TIME, min
80
60
40
20
10
15
20
25
30
35

2.4.3. Potato Tissue.

The effect of C_{16}- and C_{18}-type monoglycerides in powder (β) form on the extent of amylose complexing in whole potato tissue during the mash-mixing step of an A-B process is illustrated by results in Table 19. Regardless of the monoglyceride used, amylose complexing was more efficient at higher temperatures and longer mash-mixing times. An increase of 10 C^o (in the range of 50-70^oC) brought about an increase in amylose complexing of 6-8% for C_{16} and 4-5% for C_{18}-monoglyceride. At any temperature and time chosen, the C_{16}-monoglyceride proved to be superior to C_{18}. After 20 min of mash-mixing, its complexing ability exceeded that of C_{18} by an average of 4.8% at 50^oC and by 8.6% at 60 or 70^oC.

The duration of mash-mixing had a profound effect on the extent of complexing. Thus, at 70^oC using the C_{16}-monoglyceride, amylose complexing increased by 9% for each 5 min increment up to 30 min, and 3.5% per increment thereafter. The highest complexing, 54.6%, was achieved after 35 min. For C_{18}-monoglyceride, the maximum complexing was 41%, with the reaction rate also being high during the first 20 min of mash-mixing and levelling off after 30 min. Over the same period of time the α-form, in comparison to the β-form, provided a higher extent of amylose insolubilization (Table 20). After 20 min mash-mixing, the C_{16}-monoglyceride exceeded its β-form by 15% at 70^oC and by 13% at 50 or 60^oC. The highest complexing value, 76%, was achieved after 35 min. The levelling off time was found to start after about 30 min mash-mixing. The complexing ability of the α-form of the C_{18}-monoglyceride exceeded that of its powder form by 16% after 20 min mash-mixing at 70^oC, and by 12% at 50 or 60^oC. The maximum complexing (59.6%), achieved after 35 min

Table 19. The Effect of Monoglyceride Chain Length and Its β-Crystallinity Structure on the Extent of Amylose Complexing in Whole Potato Tissue During the Mash-Mixing Step of an A-B Granule Process.

	Monoglycerides (0.25%)					
	C_{16}			C_{18}		
Temp, ^{o}C	50	60	70	50	60	70
	Complexing Index					
Time, Min						
5	6.5 ± 1.3	9.9 ± 1.2	12.5 ± 3.0	4.5 ± 1.2	8.7 ± 0.0	8.9 ± 2.0
10	18.5 ± 2.5	20.5 ± 1.4	22.7 ± 2.4	13.5 ± 4.0	16.7 ± 1.4	20.0 ± 2.4
15	23.1 ± 2.1	28.8 ± 1.2	30.7 ± 0.6	18.0 ± 2.2	23.9 ± 0.0	25.5 ± 2.2
20	27.7 ± 0.0	37.1 ± 1.2	39.4 ± 1.2	22.9 ± 2.2	28.2 ± 0.0	31.1 ± 2.1
25	32.4 ± 1.2	39.1 ± 1.4	44.3 ± 0.4	27.0 ± 0.0	31.1 ± 1.5	35.5 ± 2.2
30	36.8 ± 1.2	44.7 ± 1.2	51.1 ± 1.7	31.5 ± 2.1	37.6 ± 1.5	41.1 ± 1.2
35	39.7 ± 2.1	45.4 ± 0.0	54.6 ± 1.2	32.4 ± 1.2	37.6 ± 1.5	41.6 ± 1.2

Table 20. The Effect of Monoglyceride Chain Length and Its α-Crystallinity Structure on the Extent of Amylose Complexing in Whole Potato Tissue During the Mash-Mixing Step of an A-B Granule Process.

	Monoglycerides (0.25%)[a]					
	C_{16}			C_{18}		
Temp, °C	50	60	70	50	60	70
	Complexing Index					
Time, Min						
5	20.3 ± 2.1	21.7 ± 0.0	24.0 ± 0.0	15.3 ± 2.1	17.4 ± 0.0	19.2 ± 0.0
10	28.7 ± 2.2	31.9 ± 1.2	36.0 ± 0.0	23.4 ± 2.2	26.1 ± 2.5	32.0 ± 2.5
15	37.0 ± 1.2	39.1 ± 0.0	45.3 ± 2.1	31.5 ± 2.4	35.4 ± 1.2	38.5 ± 0.0
20	40.7 ± 2.4	50.7 ± 1.5	54.6 ± 2.2	35.1 ± 0.0	39.8 ± 1.4	47.4 ± 2.2
25	50.9 ± 1.2	56.5 ± 1.5	64.0 ± 2.4	45.0 ± 1.6	46.3 ± 2.1	53.8 ± 2.4
30	56.1 ± 1.5	62.3 ± 3.1	73.3 ± 2.2	47.7 ± 1.5	53.5 ± 2.2	58.2 ± 1.5
35	56.1 ± 1.5	62.3 ± 3.1	76.0 ± 0.0	47.7 ± 1.5	53.5 ± 2.2	59.6 ± 1.5

[a] 1-Monoglycerides added in form of gels of pH 2.3 (C_{16}) and pH 6.5 (C_{18}), respectively.

mash-mixing, surpassed the β-form by 18%, and its levelling-off time coincided with that of C_{16}. However, though the reactivity of the C_{18}-monoglyceride was improved with the α-form, it could not surpass at any temperature or time the complexing ability of the α-form of C_{16}-monoglyceride. The difference was 7.2% after 20 min mash-mixing, and 10.2-16.4% during an additional 15 min. As seen from Figure 17, the C_{16}-monoglyceride exists as hollow microbeads (a), while C_{18} consists of solid microbeads (b).

The superiority of the C_{16}-monoglyceride powder in the granule process over that of C_{18} could be attributed partly to their physical forms. However, our preliminary results do not support such a suggestion. The improved reactivity of the α-form (gel) with amylose could be explained by the presence of hydrophilic OH- groups on the crystal surface of the monoglyceride gel rather than nonpolar fatty acid methyl end groups, as in β-form. As stated by Krog (1977), in such gels the specific surface of the monoglyceride is 700-times greater than that of the powder. Freeze-dried leaflets of C_{16} and C_{18}-monoglyceride gels (Figure 18) had thicknesses of 0.1-0.5 μm, which, according to Krog, would correspond to a specific surface of not less than 20 m^2/g. This should result in better distribution of the gel in the hot potato mash and enhanced complex formation with free amylose.

3. EFFECT OF MONOGLYCERIDE ON SOME REHYDRATING PROPERTIES OF POTATO GRANULES.

3.1. Extent of Amylose Leaching.

As seen from Table 21, the extent of amylose leaching (BVI) from potato granules was dependent on the level of monoglyceride added in the

Figure 17. SEM-Micrograph of Commercial Monoglycerides. (a) C_{16}-Type; (b) C_{18}-Type. Magnifications: (a) x 500 and (b) x 50.


a
50 µm

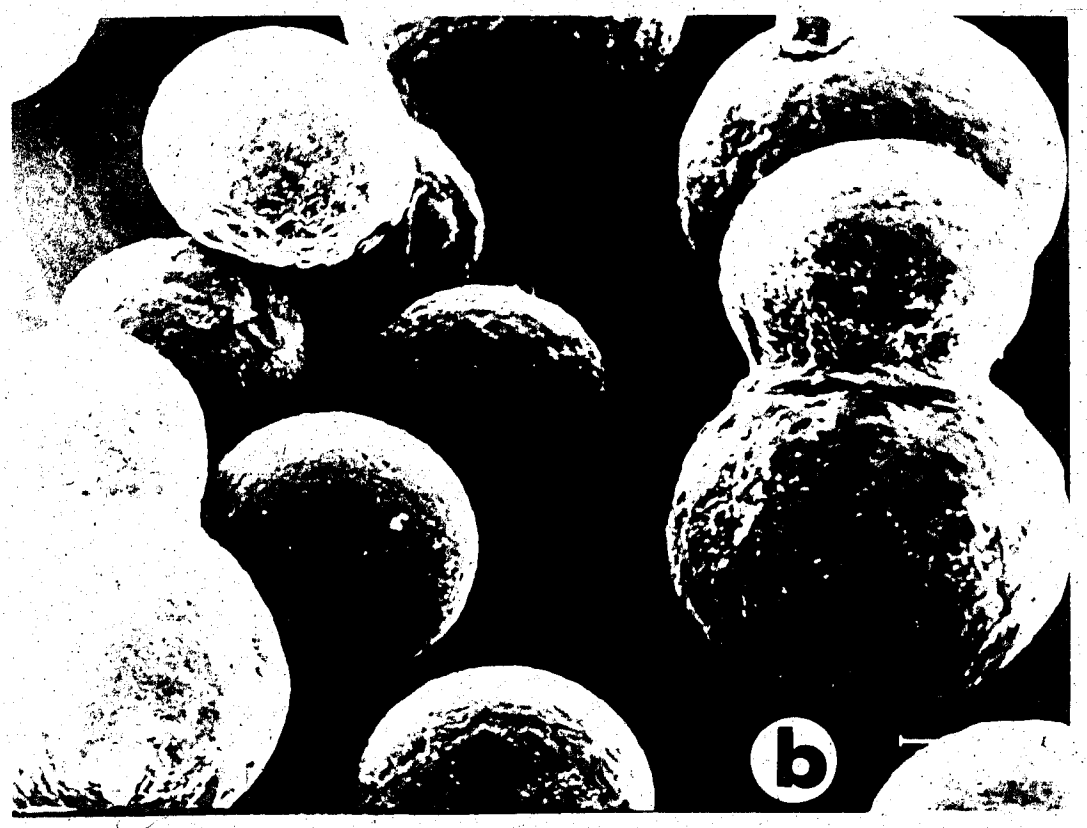

b

Figure 18. Leaflet Structure of Freeze-Dried C_{18}-Type Monoglyceride Gel of pH 6.5. Magnification x 5,100.


2 µm

Table 21. - Effect of Monoglyceride Concentration on the Extent of Amylose Leaching in F-T and A-B Granules.

Monoglyceride, %	Granules Moisture Content, %		Granules Blue Value Index (Dry Basis) $A_{640} \times 10^3$	
	F-T	A-B	F-T	A-B
0	7.25 ± 0.01[a]	7.98 ± 0.03	121 ± 0.23	157 ± 0.58
0.1	7.15 ± 0.06	7.82 ± 0.04	62 ± 1.99	82 ± 0.60
0.2	7.25 ± 0.06	7.95 ± 0.03	43 ± 1.73	58 ± 1.55
0.3	7.09 ± 0.01	7.80 ± 0.03	39 ± 0.58	53 ± 1.20
0.4	7.16 ± 0.02	7.85 ± 0.04	38 ± 1.55	51 ± 0.58
0.5	7.20 ± 0.04	7.75 ± 0.03	37 ± 1.55	50 ± 0.60

[a]SD for n = 3.

process. At a level of 0.1% the monoglyceride was able to reduce the BVI of F-T granules by 48.8% when compared to a control. Monoglyceride increase to 0.2% and then to 0.3% decreased the BVI by an additional 30.6 and 9.3%, respectively. An increase above 0.3% brought about only a negligible change. This same trend of BVI dependence on monoglyceride added was also found with A-B granules, where an increase from 0 to 0.1% reduced the BVI by 47.8%. When the level was increased to 0.2% and from 0.2 to 0.3%, the BVI decreased by 29.3 and 8.6%, respectively. On the average, A-B granules had 25.3% more leached-out amylose than F-T granules.

It has been stated that the success of precooking in a granule process is due to starch (amylose) retrogradation (Potter et al., 1959). Precooking followed by cooling produces an even greater degree of retrogradation (Harrington et al., 1959; Potter, 1954; Reeve, 1954a,b). Our results indicated that, in spite of precooking and cooling steps, A-B granules had a higher BVI than F-T granules. Thus, the freezing step in the F-T process causes a greater degree of retrogradation of amylose than the precooking and cooling steps of the A-B process.

Ooraikul et al. (1974) and Ooraikul and Hadziyev (1974) found that, as the monoglyceride concentration was increased to 0.1% or to 0.2%, the BVI of F-T granules decreased by 45.4 and 60.2%, respectively. These authors used a monoglyceride mixture containing 62.8% stearic and 26.2% palmitic acids. The corresponding decreases in BVI values obtained in this study for F-T granules were 48.8 and 64.5%, respectively.

3.2. Swelling Power.

The addition of monoglyceride at a concentration of 0.1% caused the SP of untreated F-T and A-B granules to decrease by 6.7 and 7.2%, respectively (Table 22). Further increase in monoglyceride level to 0.2% and then to 0.3% decreased the SP of F-T granules by 3.1 and 3.4%, respectively, and of A-B granules by 3.3 and 3.4%. An increase above 0.3% did not cause further decreases in SP. The SP of F-T granules treated or untreated with monoglyceride was consistently higher than that of A-B granules.

Moledina et al. (1981) found that the primary aim of precooking is to gelatinize starch (a major source of Ca^{+2}) rather than to activate pectin methylesterase in potato cell wall (CW). The calcium released from the gelatinized starch would, given sufficient time, diffuse to the CW where it would form bridges with free COO^- groups of pectin. Cooling reduces the solubility of calcium pectate, thereby stabilizing calcium bridges and causing tissue firming. This would result in a lower water intake into the cell. In addition, the cross-linking of pectin chains would decrease the WBC of CW per se. Thus, two factors would contribute to the lower SP values of A-B as compared to F-T granules. In addition, part of the tuber Ca^{+2} in an A-B process could form cross-linkages between two phosphoric ester groups, either in the same amylopectin chain or, preferentially, between two adjacent chains (Haydar et al., 1980). Such cross-linking during the precooking and cooling steps would tighten up the starch network and restrict water entry. This could also contribute to a reduced SP value of A-B granules.

The added monoglyceride is unable to reduce the SP and WBC of

Table 22. Effect of Monoglyceride Concentration on the Swelling Power of F-T and A-B Granules.

Monoglyceride, %	Swelling Power (ml/10g Dry Matter)	
	F-T	A-B
0	42.0 ± 1.2	38.8 ± 0.5
0.1	39.2 ± 0.6	36.0 ± 0.2
0.2	38.0 ± 0.5	34.8 ± 0.2
0.3	36.7 ± 0.5	33.6 ± 0.2
0.4	36.7 ± 0.7	33.2 ± 0.1
0.5	36.7 ± 0.7	33.2 ± 0.1

the potato granule to the same extent as it does with isolated native potato starch (Hoover and Hadziyev, 1981). This suggests that the CW (pectic substances 55%, hemicelluloses 6.8%, protein 9.8% and cellulose plus lignin 27.5%) is not fully permeable to the diffusion of the monoglyceride into the cell interior, and/or once the starch is gelatinized it is not readily complexed with the monoglyceride at the mashing temperature. These results on SP, taken together with those of BVI, suggest that monoglyceride complexes mainly with leached-out amylose and, to a lesser extent, with amylose retained within the potato cell.

3.3. Water Binding Capacity.

As seen in Table 23, in untreated form the WBC of F-T granules was 5.3% higher than that of A-B granules. At monoglyceride levels of 0.2 and 0.4% this difference was 7.2 and 8.3%, respectively. Monoglyceride at 0.2% reduced the WBC of untreated F-T and A-B granules by 6.3 and 8.0%, respectively. A further increase in level from 0.2 to 0.4% decreased the WBC of F-T and A-B granules by an additional 2.7 and 3.6, respectively.

Jadhav et al. (1976) reported that the WBC was higher for F-T than for A-B granules. They attributed the difference to the presence of a thin coating on the A-B granule which protects it from immediate contact with water. The presence of this thin coating , which is readily stained blue with iodine, was confirmed in our light microscopy assay. The authors also stated that the shape of dehydrated or rehydrated granules is an additional factor that influences WBC, since it is related to the total surface area. Relevant to this observation is the finding

Table 23.

Effect of Monoglyceride Concentration on the Water Binding Capacity of F-T and A-B Granules.

Monoglyceride, %	Water Binding Capacity, g H_2O/g Dry Granules	
	F-T	A-B
0	1.58	1.50
0.2	1.48	1.38
0.4	1.44	1.33

of Morrow and Lorenz (1974) that potato starch WBC in a dilute suspension is dependent on the final size of the starch grain. Our light microscopy studies showed that F-T granules had a larger surface area than A-B granules. The centrifugal technique employed by Ooraikul and Moledina (1980) gave a value of 3.5 g water/g dry matter as the WBC for F-T granules treated with 0.2% C_{18}-based monoglyceride. Our results with DSC gave a value of 1.48 g water/g dry matter for the bound water in F-T granules treated with 0.2% C_{16}-based monoglyceride. Since the WBC's of potato starch complexed with C_{16} and C_{18}-monoglycerides are approximately the same (Hoover and Hadziyev, 1981), it could be stated that the intersticially held water amounts to about 2 g water/g dry matter.

3.4. X-ray Diffraction.

Clathrate formation between starch and monoglyceride in a potato granule process was verified by X-ray diffraction analysis. Uncomplexed F-T granules consistently had a "B"-type diffraction pattern similar to that found for native potato starch (Hoover and Hadziyev, 1981). These granules showed one strong spacing at 5.16 Å and eight weak ones between 4.04 Å and 4.77 Å. No medium intensity spacings were observed. Granules treated with 0.2 and 0.4% monoglyceride each showed one strong spacing (at 5.21 Å and 5.15 Å, respectively). In addition, they exhibited medium intensity spacings, numbering four and three, respectively (Figure 19). Also, complexing brought about a reduction in the number of weak spacings (Table 24). Untreated granules had 8 weak spacings, which were reduced to three after treatment. The spacing typical of complex formation, which is around 4.48 Å, was of a

Figure 19. X-ray Diffraction Patterns of Untreated and Monoglyceride-Treated F-T Granules. The Region Scanned Corresponds to $3\text{-}33^{o}$ 2θ.

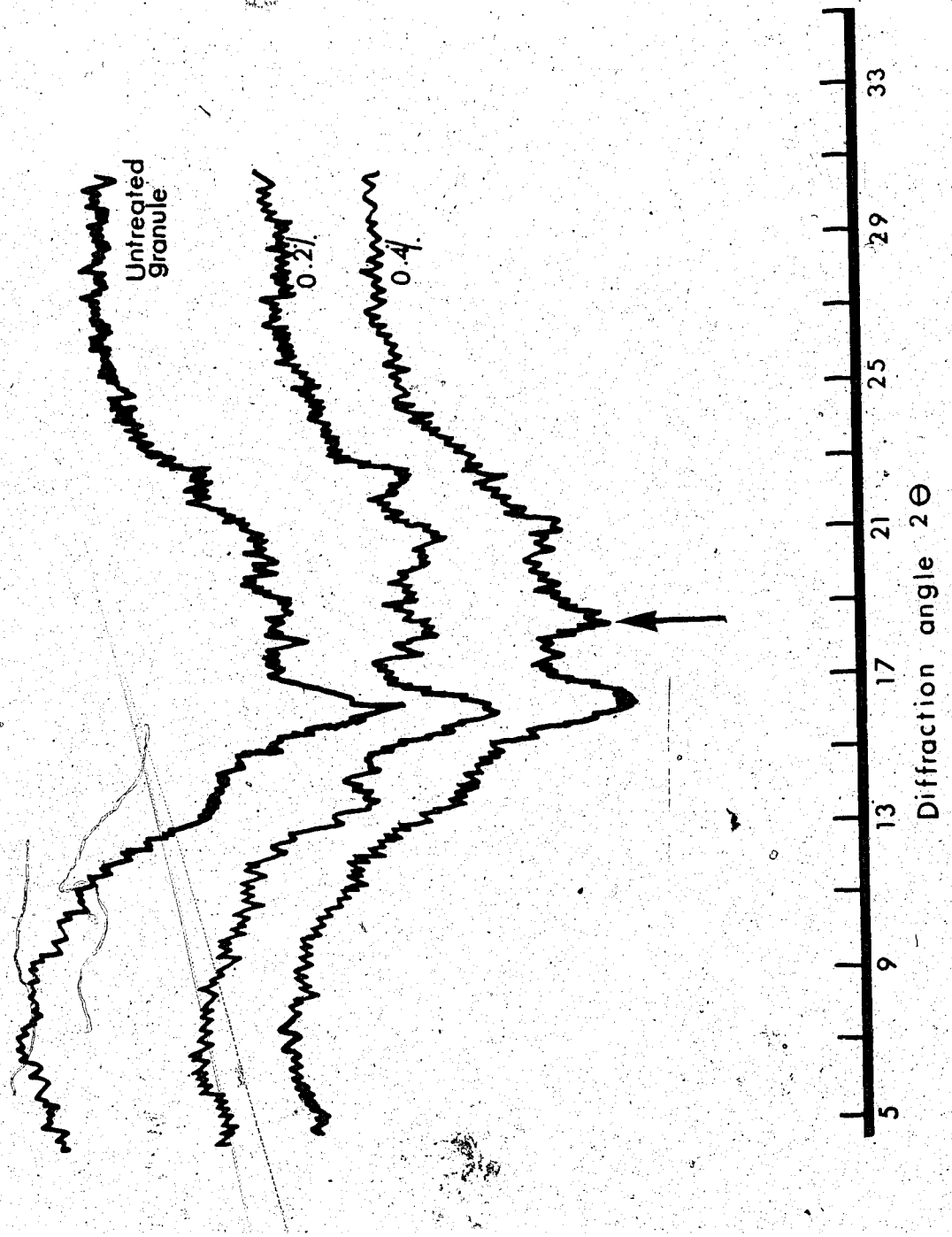

Untreated granule
0.2%
0.4%
5
9
13
17
21
25
29
33
Diffraction angle 2Θ

Table 24. X-ray Diffraction Spacings in F-T Granules Complexed with Increasing Amounts of C_{16}-type Monoglyceride.

Monoglyceride, %	Moisture Content %	Interplanar Spacings d in Å With Medium (m) and Strong Intensities (s)				Number of Weak Spacings	Range, Å
0	7.98	5.97(s)				8	4.04 - 4.77
0.2	7.95	5.21(s)	4.35(m)	3.93(m)	3.75(m)	3	4.15 - 4.90
0.4	7.86	5.15(s)	4.48(m)	3.93(m)	3.73(m)	3	4.09 - 4.90

higher intensity in the granules treated with 0.4 than with 0.2% monoglyceride. However, this spacing was much weaker in intensity than the corresponding spacing observed with complexed potato starch. This again reflects the inability of the monoglyceride to effectively diffuse through granule CW and/or to complex the amylose of the gelatinized starch within the granule at 75°C.

3.5. Light Microscopy.

In an uncomplexed A-B granule there was a distinct separation between the CW and the swollen gelatinized starch matrix (Figure 20a). Such separation was 26.7% of the total cell count. In the uncomplexed F-T granules, on the other hand, the starch matrix was seen to occupy the entire cell volume (Figure 21a). Treatment with monoglycerides at 0.2 or 0.4% levels resulted in the starch matrix contracting even more and thus separating from the CW (Figures 20b and 21b). The percentages of cells showing this contraction were 38.3 and 43.3 in the A-B and 11.7 and 16.6 in the F-T granules, respectively (Table 25). Monoglyceride added above 0.4% did not bring about further contraction. Hence, these values are much lower than some market specifications which require a starch matrix - CW separation of 60%. However, as shown by Haydar et al. (1980), the required separation can be obtained merely by an increase of Ca^{+2} levels in the precooking water.

3.6. Scanning Electron Microscopy.

Due to partial water removal from potato cells during freezing and thawing, followed by rapid dehydration during predrying, considerable shrinkage of the cells occurs. This results in F-T granules having

Figure 20. Light Photomicrographs of A-B Potato Granules Reconstituted in Water. (a) Untreated; (b) Treated With 0.4% Monoglyceride. Magnification x 50.

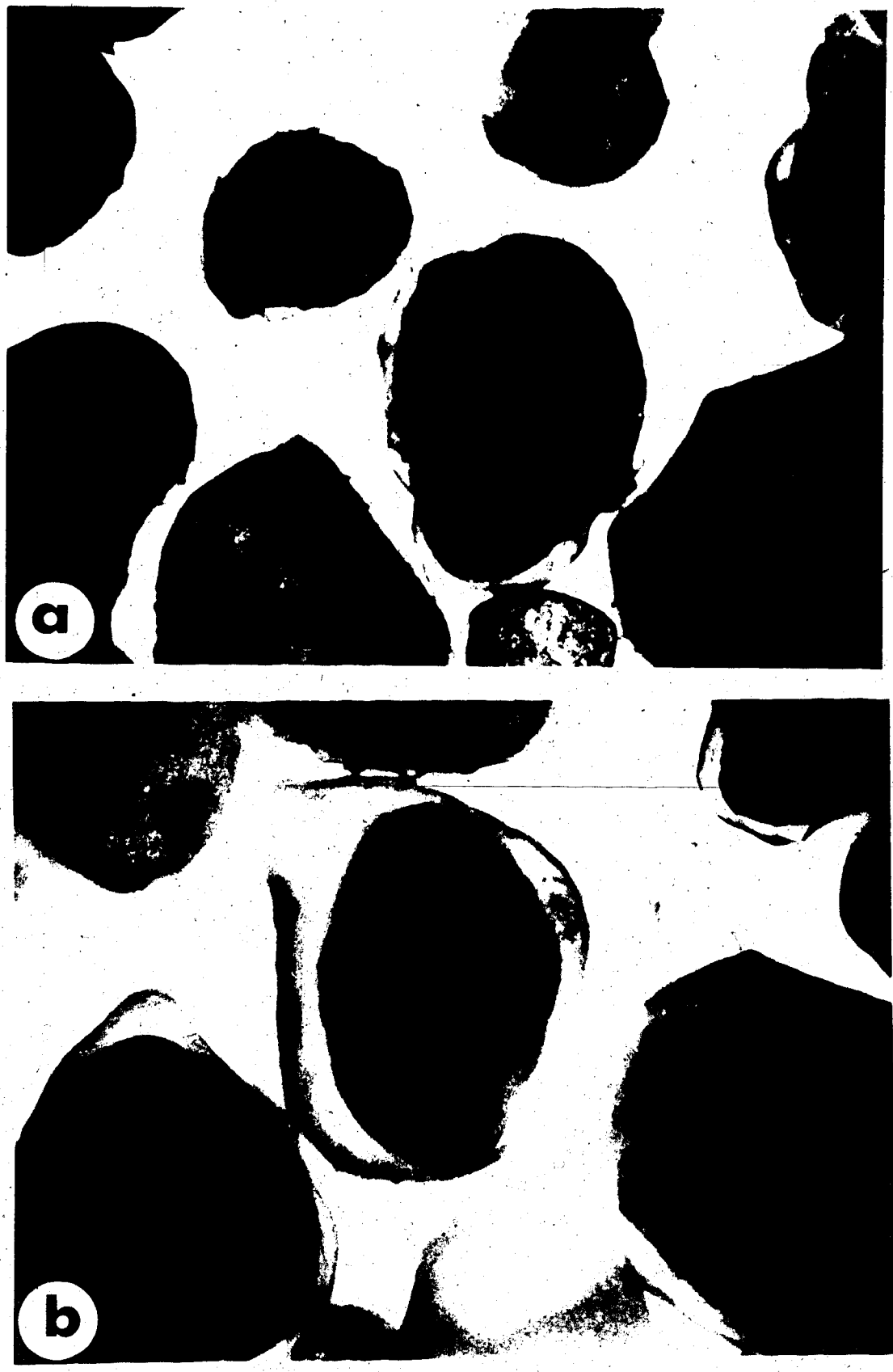

a
b

Figure 21. Light Photomicrographs of F-T Granules Reconstituted in Water. (a) Untreated; (b) Treated With 0.4% Monoglyceride. Magnification x 50.


a
b

Table 25. Effect of Monoglyceride Concentration on the Extent of Starch Matrix Separation from the Cell Wall in F-T and A-B Granules.

Monoglyceride, %	Cells Showing Starch Matrix-Cell Wall Separation %	
	F-T	A-B
0	2.0 ± 1.0	26.7 ± 3.0
0.2	11.7 ± 2.0	38.3 ± 2.6
0.4	16.6 ± 2.0	43.3 ± 3.0
0.5	16.6 ± 2.5	43.7 ± 2.5

an angular shape and shrunken appearance, and gives rise to a lower bulk density (0.80-0.85 g/cm^3) when compared to that of A-B granules, which are mostly round (Figure 22) and have a bulk density close to 0.9 g/cm^3.

Surface structures of A-B and F-T granules are presented in Figure 23. The first is more compact and dense, while the latter surface is spongy and porous with a preponderance of small pores.

The porous nature of the F-T surface could account for the fast rehydration rate of these granules. Figure 24 also shows that fissures on the surface of F-T granules may penetrate very deeply, thus contributing towards an increase in internal surface area which could also account for fast rehydration. Figure 25 shows the untreated A-B and F-T mash before further processing. As in light microscopy, the number of cells showing separation of the starch matrix from the CW was found to be higher in the mash of the A-B process. The mash, after treatment with 0.2 and 0.4% monoglyceride, is shown in Figure 26. At both levels the contraction of the starch matrix was greater in A-B than F-T mash. Also, an increase of monoglyceride level from 0.2 to 0.4% brought about only a negligible change in the extent of starch matrix - CW separation. This separation was retained by reconstituted granules (treated with 0.4% monoglyceride) hydrated at 24°C (Figure 27). Even here, A-B granules showed greater separation than F-T granules. Hence, the count of cells showing this separation was greater with A-B than F-T granules, confirming the findings of light microscopy.

Figure 22. SEM-Micrographs of (a) A-B and (b) F-T Potato Granules Showing Single Cells and Cell Aggregates Smaller than 80 Mesh. Magnification x 150.

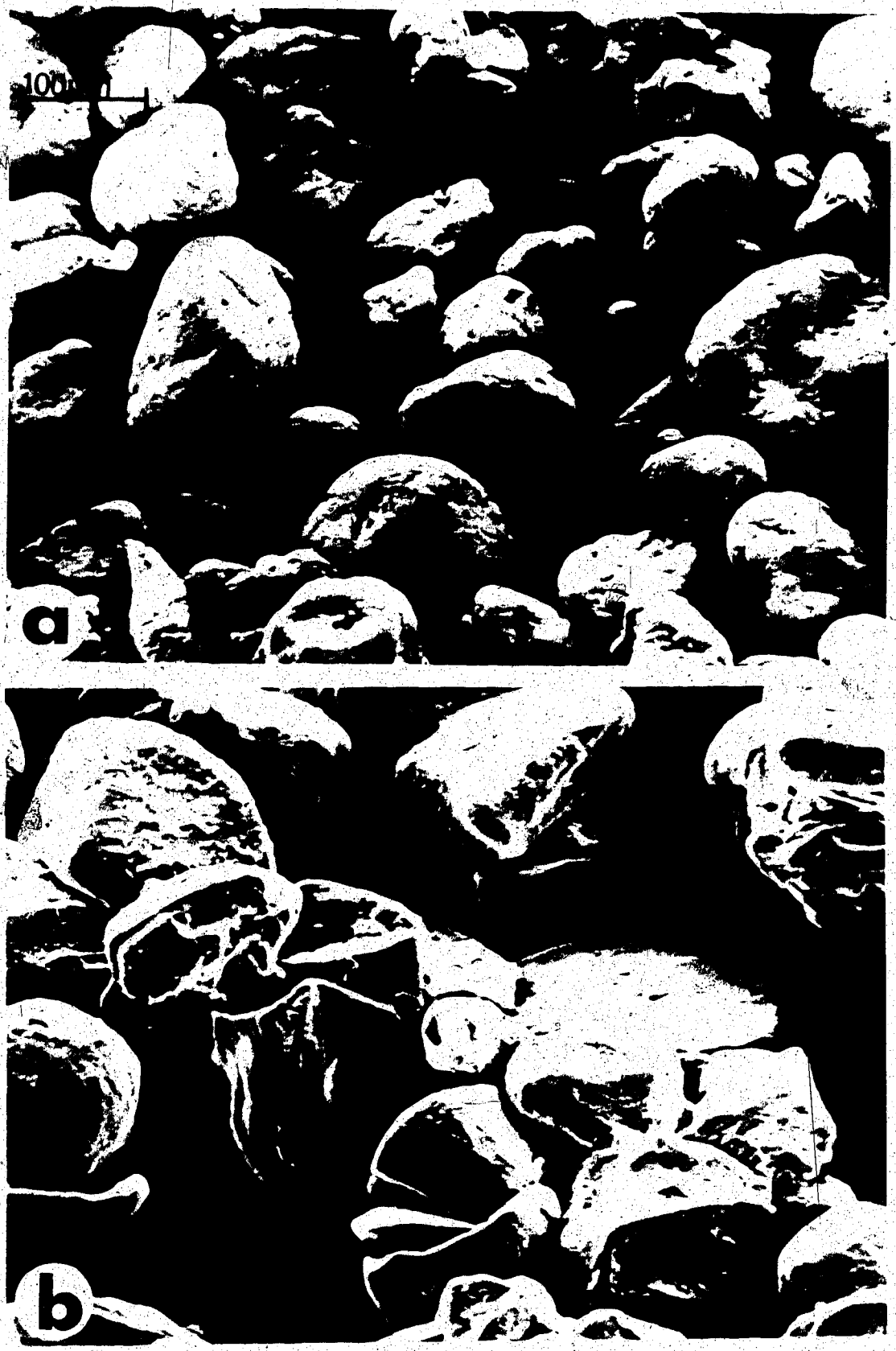
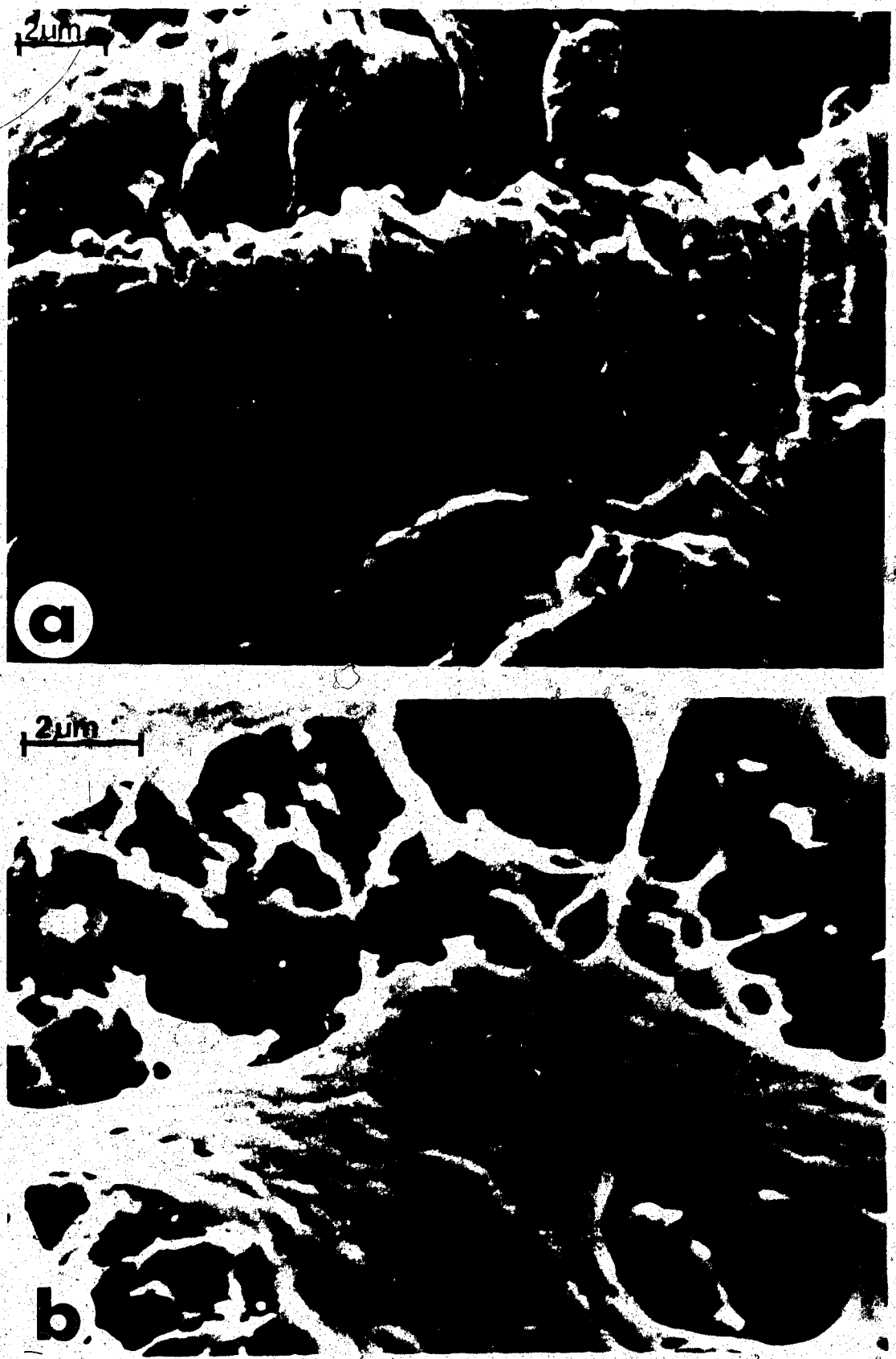

a
b

Figure 23. SEM-Micrographs of Potato Granule Surfaces (a) A-B Granules; (b) F-T Granules. Magnification x 7000.


2um
a
2um
b

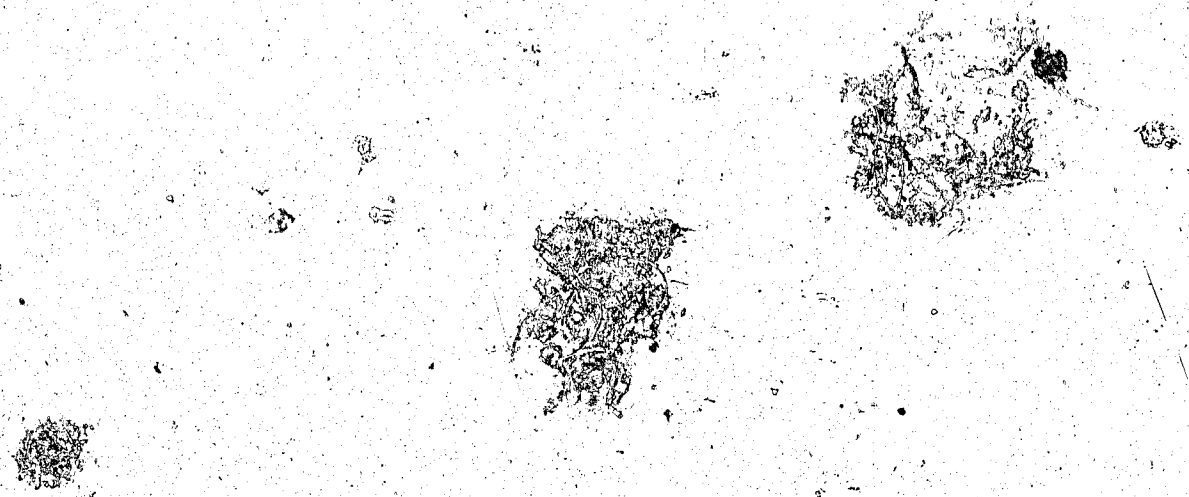


Figure 24. SEM-Micrograph of an F-T Granule With Fissures on its Surface. Magnification x 100.

Figure 25. SEM-Micrographs of Potato Mash not Treated With Monoglycerides. (a) A-B Process; (b) F-T Process. Magnification x 2800.

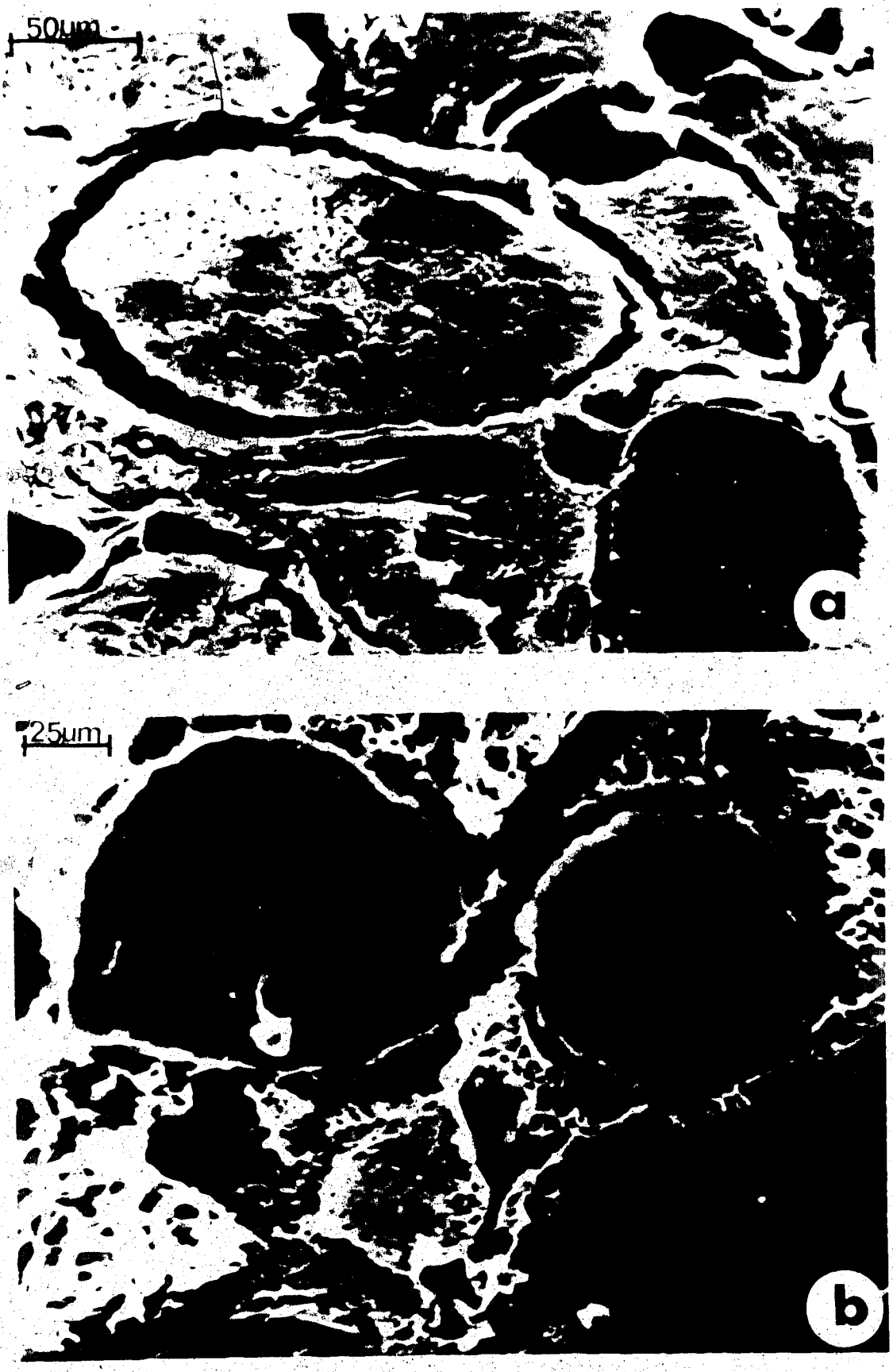

50µm
a
25µm
b

Figure 26. SEM-Micrographs of Potato Mash Treated With 0.2 and 0.4% Monoglyceride. (a) A-B Process; (b) F-T Process. Magnifications: (a) x 280 and (b) x 2200.

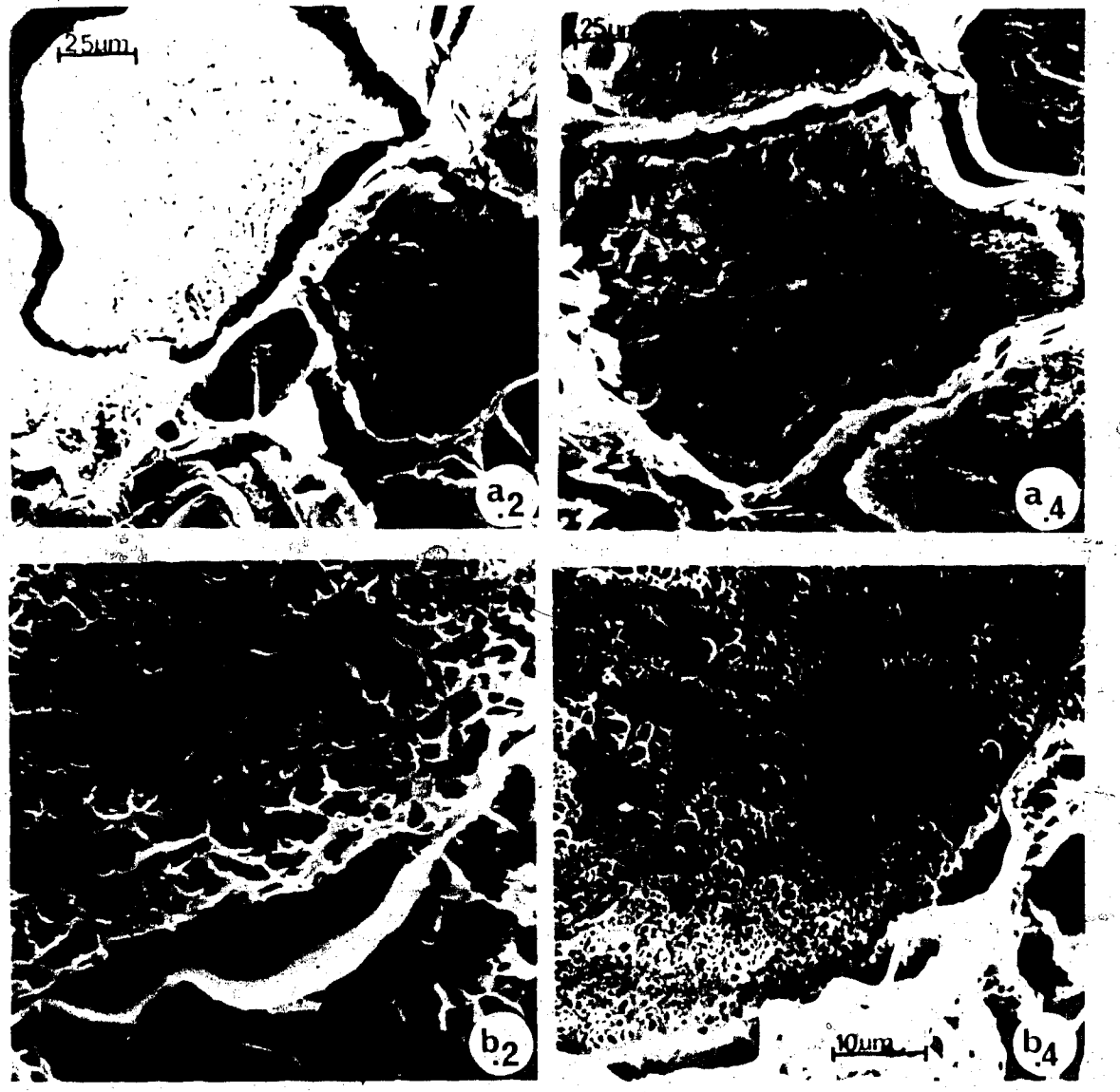
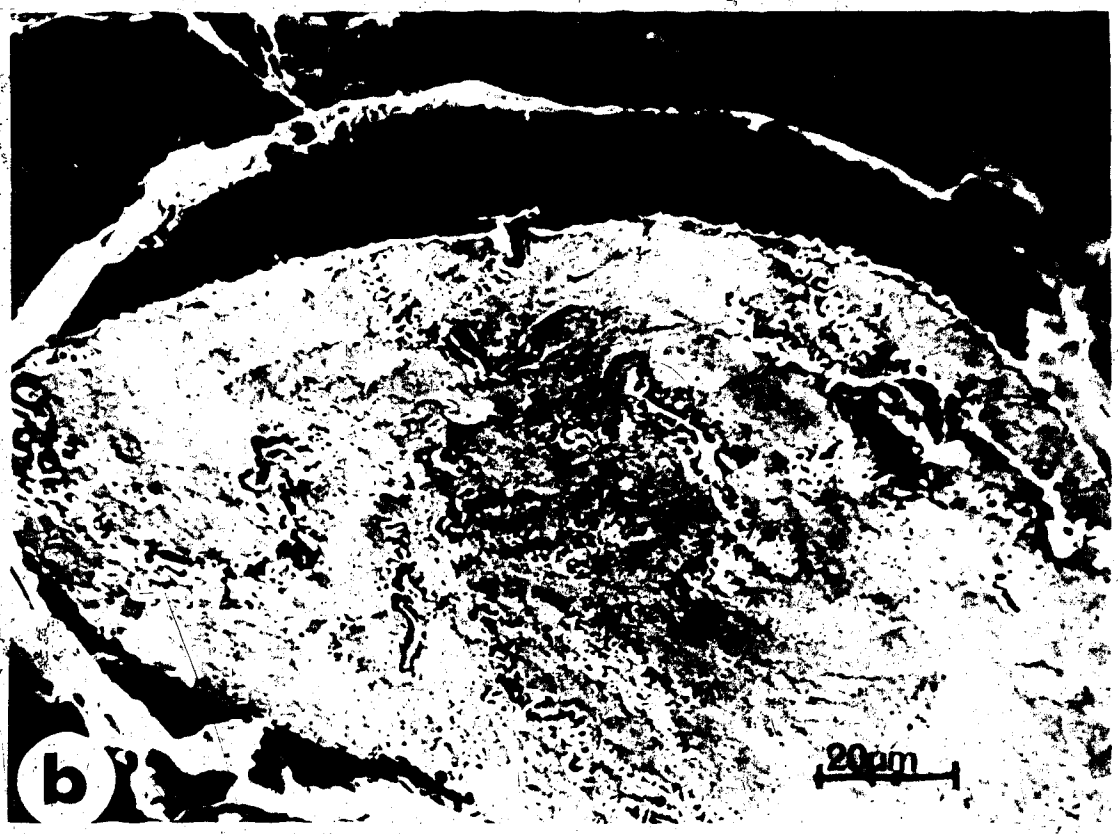

25um
a2
a4
b2
10um
b4

Figure 27. SEM-Micrographs of Rehydrated Granules Processed With 0.4% Monoglyceride. (a) A-B Granules; (b) F-T Granules. Magnification x 1500.


a
10μm


b
20μm

3.7. Relative Rehydration Rate.

The rehydration rates of F-T and A-B granules are presented in Table 26. The rates decreased after monoglyceride treatment. The rate of F-T exceeded that of A-B granules by 7.0% in the untreated state and by 6.8% when treated with 0.4% monoglyceride. No further change in rehydration rate was observed above 0.4%. The findings suggested that an economical tailoring of the granules' rehydration rate is within the 0.2% level of added monoglyceride. The results, with respect to the increased rehydration rate of F-T over A-B granules, agree with those of Jadhav et al. (1976) and Jericevic and Le Maguer (1975).

A controlled rate of rehydration of potato granules in cold water is important in manufacturing high quality extruded French-fries. The rate of water reabsorption by dry granules must be sufficiently low to allow uniform rehydration and mixing of the granules. Ooraikul and Moledina (1980) stated that a dough with satisfactory handling and extrusion properties for French-fry manufacture could be produced only with granules with a rehydration rate of about 5.7×10^{-2} sec. As shown in our study, such a low rate cannot be achieved solely by addition of monoglycerides.

Table 26. Effect of Monoglyceride Concentration on the Rehydration Rate of F-T and A-B Granules.

Monoglyceride, %	Rehydration Rate, X 10^{-2} $sec.^{-1}$	
	F-T	A-B
0	8.90 ± 0.40	8.32 ± 0.45
0.1	8.18 ± 0.49	7.66 ± 0.45
0.2	7.78 ± 0.25	7.28 ± 0.25
0.3	7.73 ± 0.11	7.23 ± 0.15
0.4	7.68 ± 0.10	7.19 ± 0.10
0.5	7.68 ± 0.10	7.19 ± 0.10

4. EFFECT OF STORAGE TEMPERATURE ON SOME REHYDRATING PROPERTIES OF POTATO GRANULES.

4.1. Moisture Content.

During the initial 14 weeks of storage at 4°C the moisture content of untreated granules increased by 7.6 (F-T) and 9.0% (A-B) and then decreased (Table 27). During the same period at 25°C, the moisture content of these granules increased by only 3.7 (F-T) and 4.8% (A-B). The corresponding values for treated granules were 5.9 (F-T) and 7.5% (A-B) at 4°C and 2.8 (F-T) and 3.6% (A-B) at 25°C (Table 28).

The moisture content of untreated granules at 4°C increased during the first 2 weeks by 1.2 (F-T) and 1.6% (A-B) and thereafter increased by 2.0, 2.4 and 1.7% (F-T) and by 2.3, 2.8 and 2.0% (A-B) at intervals of 4 weeks until attaining the 14 week storage period. However, at 25°C the moisture content of these granules remained unchanged during the first 2 weeks and then increased by 1.1, 1.6, 0.9, 0.7 and 0.5% (F-T) and by 1.4, 2.0, 1.3, 1.0 and 0.7% (A-B) at intervals of 4 weeks until attaining the 22 week storage period.

The corresponding values at 4°C for treated granules were 1.0, 1.5, 2.0 and 1.3% (F-T) and 1.3, 2.0, 2.3 and 1.8% (A-B) and at 25°C these were 0.8, 1.2, 0.7, 0.5 and 0.3% (F-T) and 1.1, 1.6, 0.9, 0.7 and 0.5% for A-B granules.

4.2. Swelling Power.

The swelling power of untreated granules at 4°C decreased during the initial 14 weeks by 29.0 (F-T) and 30.4% (A-B) and then increased. During the same period but at 25°C the SP decreased by only 12.4 (F-T)

Table 27.

Changes in Moisture Content of Untreated F-T and A-B Granules During Storage.

Storage Period (Weeks)	Granules Moisture Content, % Storage Temperature, °C 4° F-T	4° A-B	25° F-T	25° A-B
0	7.25 ± 0.02[a]	7.98 ± 0.02	7.25 ± 0.02	7.98 ± 0.02
2	7.34 ± 0.01	8.11 ± 0.01	7.25 ± 0.02	7.98 ± 0.02
6	7.49 ± 0.02	8.30 ± 0.02	7.33 ± 0.01	8.09 ± 0.03
10	7.67 ± 0.03	8.53 ± 0.04	7.45 ± 0.02	8.25 ± 0.01
14	7.80 ± 0.02	8.70 ± 0.02	7.52 ± 0.01	8.36 ± 0.03
18	7.74 ± 0.01	8.62 ± 0.03	7.57 ± 0.01	8.44 ± 0.02
22	7.70 ± 0.01	8.57 ± 0.02	7.61 ± 0.01	8.50 ± 0.01

[a]In this and following Tables, SD for n = 3.

Table 28.

Changes in Moisture Content of F-T and A-B Granules Treated with 0.2% Monoglyceride.

Storage Period (Weeks)	Granules Moisture Content, % Storage Temperature, ^{o}C 4^{o} F-T	4^{o} A-B	25^{o} F-T	25^{o} A-B
0	7.25 ± 0.02	7.95 ± 0.02	7.25 ± 0.02	7.95 ± 0.02
2	7.32 ± 0.01	8.05 ± 0.01	7.25 ± 0.02	7.95 ± 0.02
6	7.43 ± 0.03	8.21 ± 0.03	7.31 ± 0.02	8.04 ± 0.01
10	7.58 ± 0.01	8.40 ± 0.03	7.40 ± 0.03	8.17 ± 0.02
14	7.68 ± 0.03	8.55 ± 0.04	7.45 ± 0.01	8.24 ± 0.01
18	7.63 ± 0.01	8.50 ± 0.01	7.49 ± 0.02	8.30 ± 0.02
22	7.60 ± 0.01	8.46 ± 0.01	7.51 ± 0.01	8.34 ± 0.01

and 13.4% (A-B). However, at this temperature no SP increase was observed even at the end of the storage test (Table 29). The corresponding decreases at 4°C (Table 30) for treated granules were 25.8 (F-T) and 27.0% (A-B) and at 25°C 11.0 (F-T) and 12.1% (A-B). These values indicate that the percentage decrease in SP (during the 14 weeks storage period) shown by untreated granules are lowered in granules treated with monoglyceride. This reduction averaged for both granules 11.1 at 4°C and 10.5% at 25°C, respectively.

The SP of untreated granules at 4°C decreased during the first 2 weeks by 4.8 (F-T) and 5.2% (A-B) and thereafter decreased by 9.0, 12.1 and 6.8% (F-T) and by 9.2, 12.6 and 7.2% (A-B) at intervals of 4 weeks until attaining a storage period of 14 weeks. However, at 25°C the SP of these granules remained unchanged during the first two weeks and then decreased by 4.8, 5.0, 3.2, 2.2 and 1.7% (F-T) and by 5.2, 5.4, 3.5, 2.6 and 2.4% (A-B) at intervals of 4 weeks until attaining a storage period of 22 weeks. The corresponding values at 4°C for treated granules were slightly lower for both F-T and A-B granules, and also lower for both granules at 25°C.

4.3. Water Binding Capacity.

The water binding capacity (WBC) of treated granules at 4°C decreased during the initial 14 weeks by 25.0 (F-T) and 26.8% (A-B) and then only slightly increased. However, during the same period at 25°C, the WBC of these granules decreased by only 10.8 (F-T) and 11.6% (A-B). As in SP, no increases in WBC were observed at this storage temperature (Table 31).

Table 29.

Changes in Swelling Power of Untreated F-T and A-B Granules During Storage.

Storage Period (Weeks)	Swelling Power (ml/10 g dry matter) Storage Temperature, °C 4° F-T	4° A-B	25° F-T	25° A-B
0	42.0 ± 0.1	38.8 ± 0.1	42.0 ± 0.1	38.8 ± 0.1
2	40.0 ± 0.1	36.8 ± 0.1	42.0 ± 0.1	38.8 ± 0.1
6	36.4 ± 0.1	33.4 ± 0.2	40.0 ± 0.1	36.8 ± 0.1
10	32.0 ± 0.1	29.2 ± 0.1	38.0 ± 0.1	34.8 ± 0.1
14	29.8 ± 0.1	27.0 ± 0.1	36.8 ± 0.1	33.6 ± 0.0
18	30.4 ± 0.1	28.0 ± 0.1	36.0 ± 0.0	32.8 ± 0.0
22	31.6 ± 0.1	30.0 ± 0.1	35.4 ± 0.0	32.0 ± 0.0

Table 30.

Changes in Swelling Power of F-T and A-B Granules Treated with 0.2% Monoglyceride.

Storage Period (Weeks)	Swelling Power (ml/10 g dry matter) Storage Temperature, ^{o}C			
	4^{o}		25^{o}	
	F-T	A-B	F-T	A-B
0	38.0 ± 0.1	34.8 ± 0.0	38.0 ± 0.1	34.8 ± 0.0
2	36.4 ± 0.1	33.2 ± 0.1	38.0 ± 0.1	34.8 ± 0.0
6	33.4 ± 0.1	30.4 ± 0.0	36.4 ± 0.0	33.2 ± 0.0
10	30.1 ± 0.0	27.2 ± 0.1	34.8 ± 0.1	31.6 ± 0.1
14	28.2 ± 0.1	25.4 ± 0.1	33.8 ± 0.0	30.6 ± 0.0
18	28.2 ± 0.1	25.4 ± 0.1	33.2 ± 0.0	30.0 ± 0.0
22	28.6 ± 0.0	25.8 ± 0.0	32.8 ± 0.0	29.6 ± 0.0

Table 31.
Changes in Water Binding Capacity of Granules Treated with 0.2% Monoglyceride.

Storage Period (Weeks)	Water Binding Capacity, g H_2O/g Dry Granule			
	Storage Temperature ^oC			
	4^o		25^o	
	F-T	A-B	F-T	A-B
0	1.48	1.38	1.48	1.38
2	1.42	1.32	1.48	1.38
6	1.32	1.22	1.42	1.32
10	1.20	1.10	1.36	1.26
14	1.11	1.01	1.32	1.22
18	1.11	1.01	1.29	1.19
22	1.15	1.08	1.26	1.16

4.4. Rehydration Rate.

The rehydration rate of treated granules at 4°C (Table 32) decreased during the initial 14 weeks by 25.7 (F-T) and 28.0% (A-B) and then increased. However, during the same period at 25°C, the rehydration rate of these granules decreased by only 11.4 (F-T) and 12.4% (A-B). As in SP and WBC, no increases in rehydration rates were observed at this temperature.

The rehydration rate of the above granules during the initial two weeks at 4°C decreased by 4.1 (F-T) and 4.5% (A-B) and thereafter by 7.2, 9.4 and 7.8% (F-T) and by 8.0, 10.7 and 8.6% for A-B granules. However, at 25°C the rehydration rate remained unchanged during the first two weeks and thereafter decreased by 4.2, 4.4, 3.2, 1.8 and 1.6% (F-T) and by 4.5, 4.9, 3.6, 2.8 and 2.4% (A-B).

All these results show that during the initial 14 weeks the average decreases in rehydration parameters SP, WBC, and rate of rehydration amounted to 25.5 (F-T) and 27.3% (A-B) at 4°C and 11.1 (F-T) and 12.0% (A-B) at 25°C, respectively.

The observed decreases in SP, WBC and rate of rehydration, and the increases in moisture content could be partially attributed to starch retrogradation within the potato granules (Potter et al., 1954; Ooraikul and Moledina, 1980), which makes unavailable free hydroxyl groups for water absorption. Retrogradation was observed even at moisture contents of 7.3%, as was also found in a related study by Ooraikul and Moledina (1980). Retrogradation rates were seen to be highly temperature dependent with increased rates exhibited at lower storage temperatures (4°C). These results agree with similar observations by Katz (1928); Whistler (1965) and Brenan and Sodah-Ayernor (1973).

Table 32.
Changes in Rehydration Rate of Granules Treated with 0.2% Monoglyceride.

Storage Period (Weeks)	Rehydration Rate ($\times 10^{-2}$ sec^{-1}) Storage Temperature ^{o}C 4^{o} F-T	4^{o} A-B	25^{o} F-T	25^{o} A-B
0	7.78 ± 0.20	7.33 ± 0.10	7.78 ± 0.20	7.33 ± 0.30
2	7.46 ± 0.15	7.00 ± 0.20	7.78 ± 0.20	7.33 ± 0.30
6	6.92 ± 0.10	6.44 ± 0.10	7.45 ± 0.15	7.00 ± 0.20
10	6.27 ± 0.10	5.78 ± 0.20	7.12 ± 0.10	6.66 ± 0.10
14	5.78 ± 0.15	5.28 ± 0.10	6.89 ± 0.10	6.42 ± 0.10
18	5.78 ± 0.15	5.28 ± 0.10	6.77 ± 0.10	6.24 ± 0.10
22	6.01 ± 0.10	5.65 ± 0.10	6.66 ± 0.10	6.09 ± 0.10

The slower rates at elevated temperatures (25°C) could be either due to kinetic motion of molecules and more random association (Sterling, 1978) or to the formation of a more symmetrically perfect crystal structure (Colwell et al., 1969). The latter authors indicate that formation of such a structure could impose limitations in the availability of molecules for crystal formation resulting to a less total crystallization. When compared to a control, a decreased rate of SP reduction and a decreased rate of moisture content increase was observed with granules complexed with monoglyceride. These observations support the statement by Krog (1971) that complex formation between monoglyceride and amylose helix hinders further realignment (retrogradation) of amylose chains. Therefore the main cause for the decreases found for complexed granules would be the increased binding of monoglyceride to the available amylose helix during storage.

After the initial acceleration phase the rate of decrease in the rehydration parameters (in both complexed and uncomplexed granules) was found to decrease with time, with greater decreases at 4°C. This could be explained in the case of complexed granules, as being due to binding of the major portion of the earlier uncomplexed monoglyceride to the helix to occur during the initial 10 weeks storage. However, in untreated granules the initial acceleration phase could be attributed to rapid amylose retrogradation (Whistler, 1965), whereas the subsequent slow deceleration phase could be attributed to retrogradation of the linear portions of the amylopectin chains.

4.5. Thin-Layer and Gas Liquid Chromatography.

The extent of amylose complexing by the added monoglyceride in

fresh and stored granules was revealed by thin-layer and gas liquid chromatography.

Table 33 shows the total lipid content in fresh and stored granules. On storage at 25°C, monoglycerides which were initially free became gradually bound to the amylose helices. From Tables 34 and 35 it is seen that in the fresh granules 15.5% of the total monoglyceride was bound to amylose, whereas in 6 months stored granules this amounted to 30.5%.

4.6. X-ray Diffraction.

Prolonged storage at 4 and 25°C brought about an increase in intensity of the diffraction patterns, especially that of "V"-lines. However, these patterns were of higher intensity in granules stored at 4°C (Figure 28 and Table 36).

It has been shown by an X-ray camera technique that freshly prepared starch pastes show an "V"-pattern when precipitated with alcohol, while during retrogradation the alcohol-precipitated paste gradually develops an increasing intensity of the "B"-pattern and a decreasing intensity of the "V"-pattern (Katz, 1930; Sterling, 1960).

Our results on granules differ. On the basis of X-ray diffraction studies of oriented "B"-amylose fibres prepared from potato amylose, Sarko and Wu (1978) suggested that the amylose chain in "B" starch is characterized by a right-handed, parallel stranded double helix packed in an antiparallel manner. In the presence of complexing agents, the double helix converts to a single helix ("V" amylose). These authors were not in favor of a "V" to "B" transformation. Furthermore, Dragsdorf and Varriano-Marston (1980) showed from X-ray studies on starch, washed

Table 33.

Total Lipid Contents in Fresh and Stored A-B Granules.*

Sample	Weight in mg per 100 g Dry Weight**
Fresh	548.7*
Stored (6 months at 25°C)	542.8

*In this and following Tables, granules were complexed with 0.2% monoglyceride.

**An average of three determinations, which do not differ more than ± 2.0%.

Table 34.

Monoglyceride Contents In Ether and WSB-Extracted A-B Granules.

Extracting Solvent for Monoglycerides	Weight of Monoglyceride in mg per 100 g dry weight*	
	Fresh Granules	Stored Granules
	Free Monoglycerides	
Petroleum ether (b.p. 40-60°C)	197.5	161.0
	Bound Monoglycerides	
Water-saturated n-butanol	36.3	70.6
	Total Monoglycerides	
	233.8	231.2
	Ratio Free/Bound	
	34.1	14.2

*A method of Thin-Layer Chromatography separation was applied.

Table 35.

Monoglyceride Contents in Ether and WSB-Extracted A-B Granules as Determined by Gas Liquid Chromatography.

Extracting Solvent for Monoglycerides	Peak height of C_{16} fatty acid* (μV-sec)	
	Fresh Granules	Stored Granules
	Free Monoglycerides	
Petroleum ether (b.p. 40-60°C)	20809	17214
	Bound Monoglycerides	
Water saturated n-butanol	3942	7531
	Ratio Free/Bound	
	5.28	2.29

*Palmitic acid was chosen as a marker since it represents 72% of the total fatty acids in applied monoglyceride.

Figure 28. X-ray Diffraction Patterns of F-T Granules Stored at 4 and 25°C. The Region Scanned Corresponds to 3-32° 2θ.

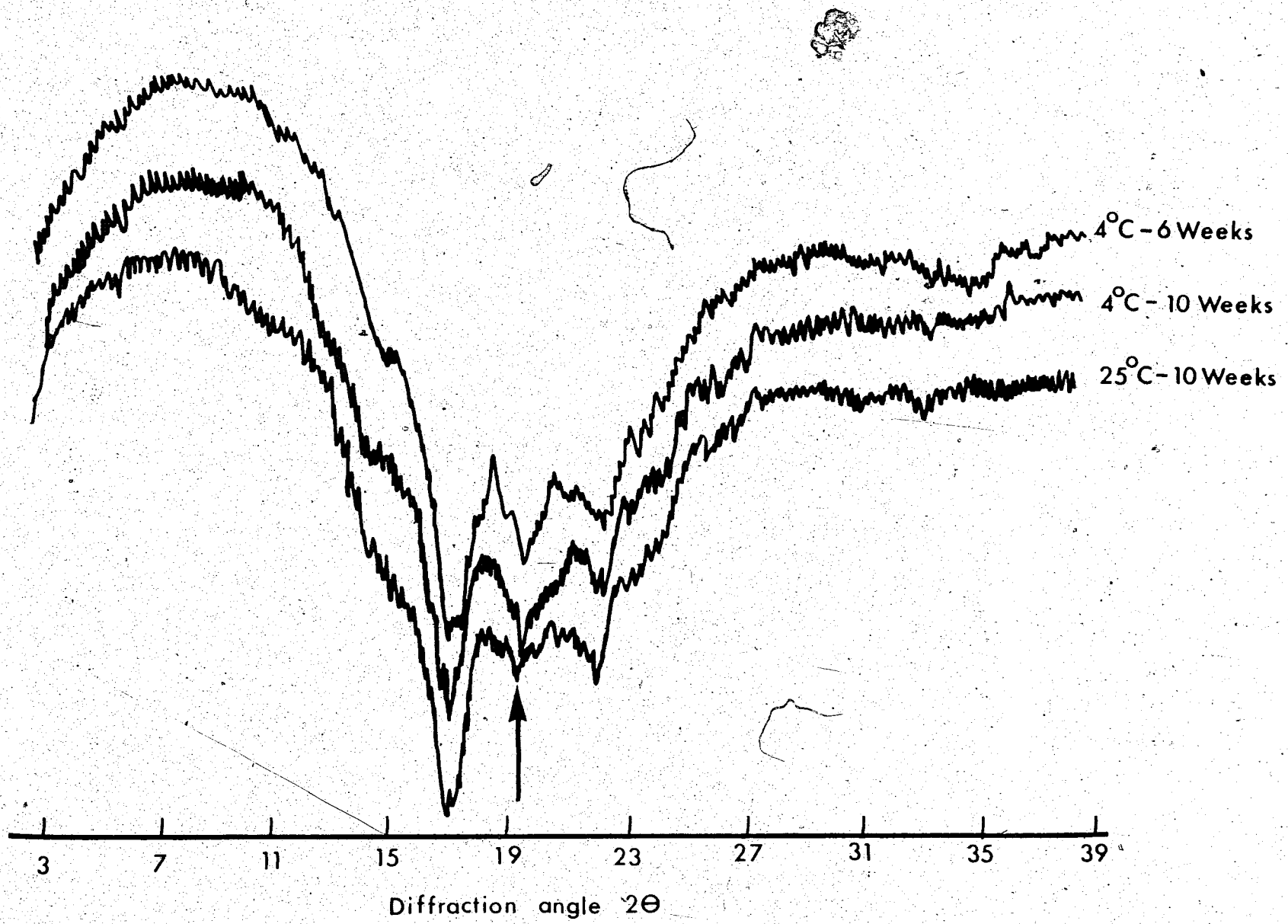

4°C – 6 Weeks
4°C – 10 Weeks
25°C – 10 Weeks
3
7
11
15
19
23
27
31
35
39
Diffraction angle 2θ

Table 36.
X-ray Diffraction Spacings in F-T Granules Subjected to Storage at 4 and 25°C.

Storage Period (Weeks)	Complex* Moisture Content %	Interplanar Spacings d in Å, Medium (m) and Strong Intensities (s)	Number of Weak Spacings	Range
		Storage at 4°C		
0	7.95	5.15(s) 4.48(m) 4.35(m) 3.93(m) 3.75(m)	3	4.15 - 4.90
6	8.21	5.15(s) 4.48(s) 4.21(m) 4.02(s) 3.77(m) 3.44(m) 3.35(m)	2	3.52 - 3.77
10	8.40	5.15(s) 4.48(s) 4.21(m) 4.02(s) 3.83(m) 3.45(m) 3.37(m)	2	3.62 - 3.83
		Storage at 25°C		
0	7.95	5.15(s) 4.48(m) 3.93(m) 3.75(m)	3	4.15 - 4.90
6	8.04	5.15(s) 4.48(m) 4.02(s) 3.42(m) 3.30(m)	3	3.68 - 3.77
10	8.17	5.15(s) 4.48(m) 4.02(s) 3.53(m) 3.44(m)	3	3.30 - 3.71

*Granules treated with 0.2% of C_{16}-type monoglyceride.

from fresh and stored bread, that the "V" hydrate form was maintained initially with its intensity increasing on storage. Furthermore, Zobel (1973) has shown that freshly baked bread, without added surfactants, has only "V" crystallinity due to amylose complexing with the naturally present fatty acids in the starch. The remaining pattern was an amorphous halo caused by gelatinized starch. During storage, the amorphous starch crystallized ("B" type) while the intensity of "V" lines remained unchanged. However, the intensity of "V" lines consistenly increased when surfactants were used. Our results are in agreement with the above observations. A molecule like ethanol would not complex amylose as effectively as would a C_{16}-monoglyceride used in this study. This assumption is based on our finding that a chain length of C_{16} is superior to that of the more hydrophilic C_8 in complexing amylose. Therefore, with ethanol the possibility of a "V" to "B" transformation on storage is not ruled out. However, this is not so with C_{16} monoglyceride, which would prevent the proper alignment needed for double helix reoccurence. Thus, increase in "V" lines intensity during storage, could be attributed to increased binding of the monoglyceride as proven by us by thin-layer and gas liquid chromatographic analyses. The greater intensities of this pattern at 4 rather than at 25°C could be due to low kinetic motions of the molecules at a lower temperature, favoring better interaction between the incoming monoglyceride and amylose helix.

4.7. Scanning Electron Microscopy.

Corroborating the above findings are the micrographs provided in Figures 29 and 30. The starch matrix separation from CW was seen to increase during storage at 4°C, reaching maximum separation at the end

Figure 29. SEM-Micrographs of Rehydrated F-T Granules Processed With 0.2% Monoglyceride and Stored at 4°C. (a) Fresh Granules; (b) After Six Weeks Storage; (c) After Ten Weeks Storage; (d) After Fourteen Weeks Storage. Magnification x 700.

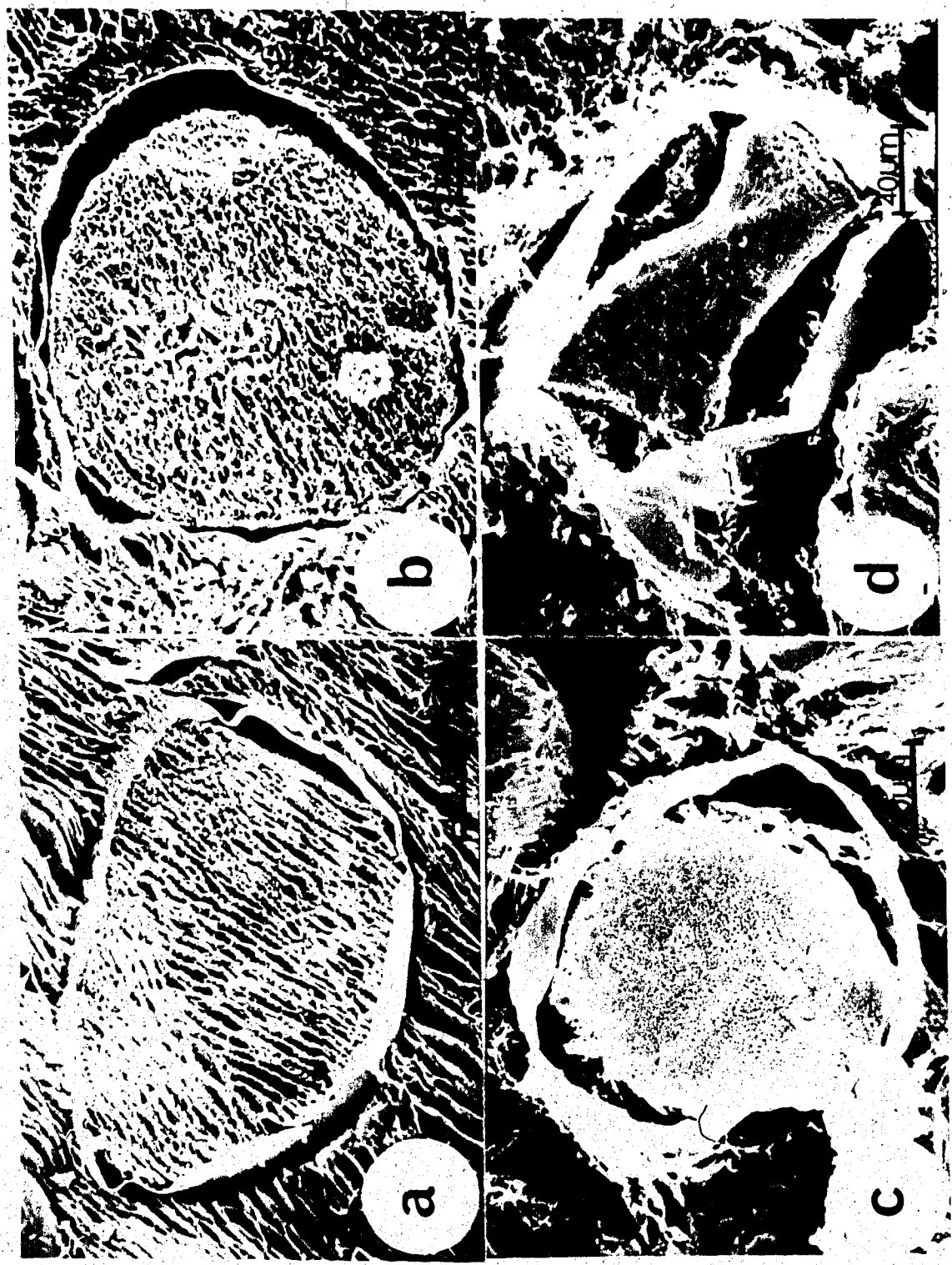
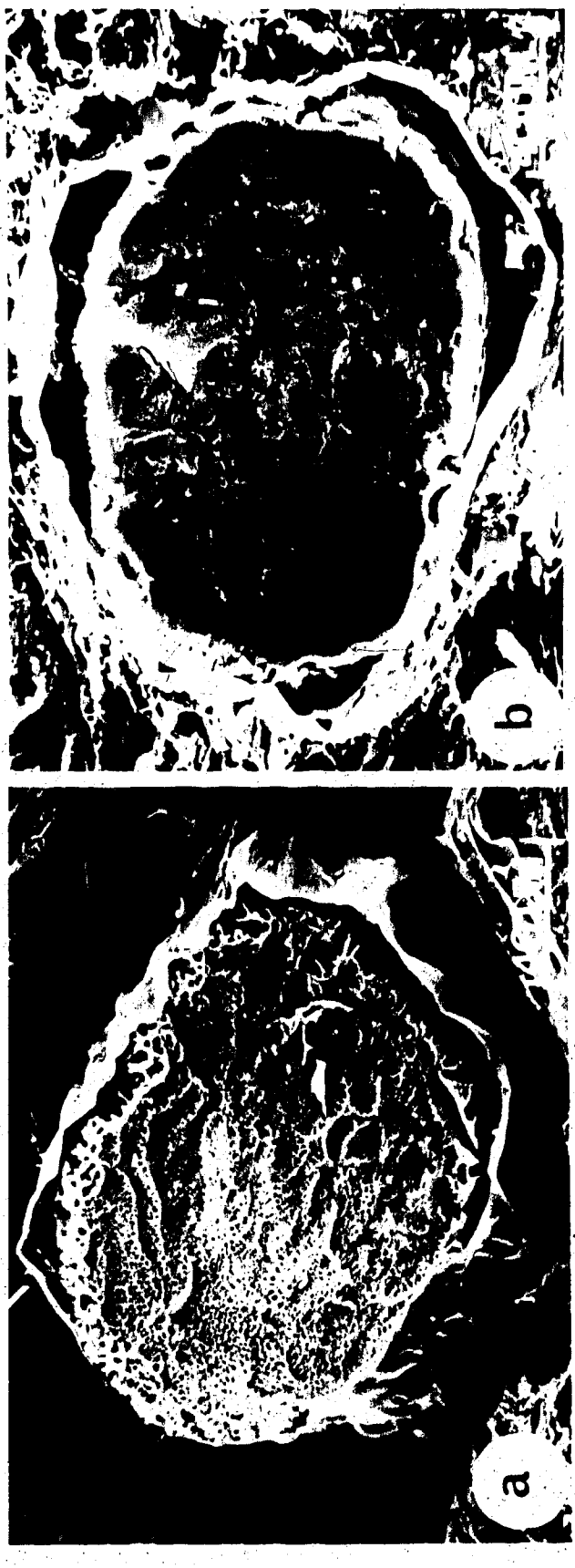

a
b
c
d
40µm

Figure 30. SEM-Micrographs of Rehydrated F-T Granules Processed With 0.2% Monoglyceride and Stored at 25°C. (a) After Ten Weeks Storage; (b) After Fourteen Weeks Storage. Magnification x 1000.


b
a

of 14 weeks (Figure 29d). However, granules stored at 25°C for the same length of time showed only negligible separation (Figure 30b). Crystals, were observed on the surface of freshly prepared granules by Fedec et al. (1979) and Ooraikul and Moledina (1980). These crystals were assumed by Fedec et al. (1979) to be those of KCl, based on an earlier observation by Steele and Hadziyev (1976) that granules prepared in a similar manner readily formed propylene chlorohydrins upon exposure to gaseous propylene oxide.

However, such KCl crystals were not observed in this study. Ooraikul and Moledina (1980) observed that these crystals disappeared on storage, and attributed the increase in rehydration parameters (after the initial decrease) to K^+ which diffuses into granules after being dissolved in the water released by retrogradation and which binds with the orthophosphate groups of amylopectin. This would seem rather unlikely, since the existing Ca^{+2} bridges between two phosphoric acid ester groups either in the same amylopectin chain or between two adjacent chains would prevent such a binding, and a change in rehydration characteristics.

Morsi and Sterling (1963) and Ciacco and Fernandes (1979) have shown that retrogradation rates in starch gels containing halogen ions increased in the following order: I^-, Br^-, Cl^-, F^- and those containing cations in the order: K^+, Li^+ and Na^+. Morsi and Sterling (1963) have suggested that electron clouds of large anions such as Br^- and I^- are easily polarized in an electric field, resulting in charges concentrated at the poles. These negative poles, partially can separate the proton of the hydroxyl groups of starch, causing the starch core to be charged negatively. Thus, on storage, similarly charged molecules lose their tendency to retrograde. However, small anions such as F^- and Cl^- have a

symmetrical charge distribution and therefore would have a relatively small tendency to attract protons from the hydroxyl groups of starch.

On the basis of the above evidence, diffusion of KCl into the granules on storage would in fact decrease, rather than increase the rehydration parameters as envisaged by Ooraikul and Moledina (1980). Thus, some other mechanism rather than KCl diffusion must be responsible for these changes.

5. PECTIN-MONOGLYCERIDE INTERACTION.

5.1. Viscosity.

Monoglyceride at a concentration of 0.2% caused a 5.0% reduction (minimum value) in viscosity of a 1% (w/v) potato pectin solution at 70°C. Any further increase in monoglyceride levels resulted only in viscosity increases (Table 37). The viscosity of a monoglyceride/water solution differed from those of monoglyceride potato pectin solution at 70°C by only 5.0, 5.2 and 4.6% at monoglyceride concentrations of 0, 0.2 and 0.5%, respectively (Table 37).

The viscosity of a solution of 1% (w/v) citrus pectin with degrees of esterification ranging from 43-54, 54-65, and 65-72 were also reduced to minimum values by a 0.2% monoglyceride concentration. This reduction amounted to 5.2, 5.0 and 4.5%, respectively, and hence appears not to be affected by esterification degree (Table 38).

A decrease of approximately 5.0% was also observed in a 1% (w/v) slow-set genu pectin solution (70°C) containing 0.1% surfactant consisting of a blend of glyceryl monostearate and propylene glycol monostearate (Ooraikul and Hadziyev, 1974). A surfactant increase beyond 0.1% level

Table 37.
The Effect of Increasing Concentration of Monoglyceride on Viscosity of Potato Pectin at 70°C.

Monoglyceride Concentration, %	Viscosity (cP) at 70°C	Viscosity (cP) at 70°C of Monoglyceride/Water Solutions
0	4.0 ± 0.0	3.8 ± 0.2
0.05	4.1 ± 0.1	-
0.1	3.8 ± 0.1	-
0.2	3.8 ± 0.0	4.0 ± 0.2
0.3	4.0 ± 0.0	-
0.4	4.0 ± 0.1	-
0.5	4.2 ± 0.1	4.4 ± 0.1

Table 38.

The Effect of Increasing Concentration of Monoglyceride on Viscosity of Citrus Pectin of Different Degrees of Esterification at 70°C.

Monoglyceride Concentration, %	Viscosity (cP) at 70°C Degree of Esterification %		
	43-54	54-65	65-72
0	3.8 ± 0.0	4.0 ± 0.1	4.4 ± 0.2
0.05	3.8 ± 0.0	4.0 ± 0.1	4.4 ± 0.2
0.1	3.6 ± 0.1	3.8 ± 0.0	4.2 ± 0.1
0.2	3.6 ± 0.1	3.8 ± 0.0	4.0 ± 0.1
0.3	3.8 ± 0.1	4.0 ± 0.1	4.0 ± 0.1
0.4	3.8 ± 0.1	4.0 ± 0.1	4.2 ± 0.0
0.5	4.0 ± 0.1	4.2 ± 0.1	4.4 ± 0.2

resulted only in viscosity increases. In the assay a Brookfield Synchro-Lectric Viscometer was used. The increase in viscosity after reaching a minimum value, the authors attributed to micelle formation by the excess monoglyceride.

The initial decrease in viscosity as verified in this study should not be attributed to clathrate formation between pectin and monoglyceride. The absence of precipitate formation on cooling the pectin/monoglyceride solution, the close similarities in viscosities between monoglyceride/water solutions, and monoglyceride-potato pectin solutions at 70°C corroborates such a suggestion. In addition, a true clathrate formation would be reflected by at least 45% decrease in viscosity (Hoover and Hadziyev, 1981).

It is highly unlikely that pectin with its negatively charged carboxyl groups could form stable helical segments, similar to amylose, a prerequisite for clathrate formation. In addition, the methoxyl groups might sterically hinder the interaction between pectin and monoglyceride.

Hence, the observed viscosity drop in a monoglyceride-pectin system could be attributed to a surface adsorption phenomenon.

5.2. Differential Scanning Calorimetry.

Corroborating the viscosity findings are the results of differential scanning calorimetry. As seen in Table 39, the endotherm temperatures of a monoglyceride pectin system resembled closely those of its components native pectin and pure monoglyceride. This finding can be considered as a strongest proof that no clathrate formation occurs between pectin and monoglycerides. Therefore, monoglycerides added during granule processing complexes solely with the amylose moiety of the starch.

Table 39.
Endotherm Characteristics of C_{16}-Monoglyceride, Pectin and Pectin-C_{16} Monoglyceride Systems.

Sample	Endotherms, °C											
C_{16}-monoglyceride	63	70	77									
Potato pectin						110	115	123	132		153	160
Citrus pectin, DE* 43-54				87	101	110			132	147		160
54-65				87	100	112			132	147		163
65-72				88	102	115			135	149		164
Potato pectin + C_{16}-monoglyceride	63	70	77			110	115	124	132		154	160
Citrus pectin + C_{16}-monoglyceride, DE 43-54	63	70	77	87	102	110			132	147		160
54-65	63	70	77	87	102	112			132	148		163
65-72	63	70.5	77.5	87	102	116			135		150	165

*Degree of Esterification.

V. SUMMARY AND CONCLUSIONS

Microscopic observation and analytical data obtained by X-ray diffraction, viscosity, turbidimetry and differential scanning calorimetry proved that starch grains and 1-(C_8-C_{18} fatty acid) monoglycerides (or fatty acid K-salts) interact to form clathrate compounds which contribute to improved grain stability. The highest stability was achieved with monomyristin, hence, such grains had the lowest solubility, SP, WBC and viscosity based on leached-out amylose. Relative to native starch, the starch grain complex had double the enthalpy of fusion per glucose unit irrespective of monoglyceride chain length. However, the specific enthalpies revealed that equimolar amounts of monoglycerides bind the available amylose to an extent of 36.5 to 91.2%, with the highest binding achieved by monomyristin.

Since amylose complexing with monoglycerides was related to other data, it appears that the starch grain stability data merely reflect the extent of amylose complexing within the grain.

The interaction of monoglycerides with amylose in model systems consisting of solubilized and intact starch grains and whole potato tissue revealed that monoglycerides possessing α-crystallinity (gels) were found to have a higher complexing ability with amylose than those with β-crystallinity (microbeads). Furthermore, palmitic acid type monoglycerides were found to be more effective than stearic acid types in causing amylose insolubilization. Regardless of monoglycerides used, amylose complexing was more efficient at higher temperatures and longer mash-mixing times. Thus, the commercial A-B potato granule process is best performed by the addition of C_{16}-type monoglycerides (as a gel of pH 6.5) into hot mash at 70°C and mash-mixing time for at least 20 min.

Monoglyceride addition in a potato granule process was found to decrease the SP, WBC, BVI and rehydration rate and increase the count of intact sound cells. However, increasing the level of monoglycerides above 0.2% changes these quality parameters by only a negligible extent. Therefore, the application of monoglycerides in a granule process at a level above 0.2% is not beneficial.

Microscopy, X-ray diffraction and data obtained for SP, WBC and rehydration rate proved that storage of potato granules at $4^{o}C$ rather than at $25^{o}C$ brings about a faster and greater reduction in rehydration parameters, thus leading to rehydration rates more suitable for extruded French-fry manufacture. The reduction of SP, WBC and rehydration rates during storage is due to the additional binding of monoglycerides, which were free in the fresh granules, with the amylose helix. However, storage up to 3 months at $4^{o}C$ may not be economically advisable and may also result in the development of off flavors. Therefore, the most practical method of obtaining low rehydration rates would still be the addition of Ca^{+2} to precooking water, as suggested earlier in a parallel study in this Department.

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