THE EFFECT OF VARIOUS SUGARS AND SIRUPS ON THE VISCOSITY AND GEL STRENGTH OF A FIVE PER CENT CORNSTARCH PASTE

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Elizabeth M. Osman
Major professor

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by

Maura Lyons Bean

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ABSTRACT

MAURA LYONS BEAN

The purpose of this investigation was to study the effects of various sugars and sirups on the viscosity and gel strength of a 5% cornstarch paste. The 5% paste represents the approximate concentration of cornstarch present in cream pie fillings. Fructose, glucose, sorbitol, lactose, maltose, sucrose, invert sirup and three corn sirups of different D.E. values were added to the aqueous cornstarch slurry before cooking. The dry substance of the sweetening agent was present in concentrations equal to 5, 10, 20, 30, and 50% of the total water present.

The Corn Industries Viscometer was used for pasting and also for measuring and recording the viscosity of the hot paste during cooking. The paste was heated by a glycerol-water bath maintained at 100.0 ± 0.2°. Pasting was terminated 5 minutes after maximum viscosity had been reached.

Gel samples were prepared immediately after cooking and were aged for 18 hours at approximately 3°C. Gel strength was determined by an embedded disk method that utilized the recording device of the Corn Industries Viscometer.

In amounts greater than 20%, there were significant differences between the effects of the different sugars and sirups. The monosaccharides were markedly different from the other sweetening agents.

ABSTRACT MAURA LYONS BEAN

With all the sweetening agents, the maximum hot-paste viscosity increased as the sugar and sirup solids were increased up to 10 or 20%. At the 30 and 50% levels, the viscosity decreased. The pastes containing monosaccharides had higher viscosities than those containing di- or polysaccharides at corresponding concentrations with the exception of the 5% level.

Gel strength was increased above that of the control when 5% concentrations of monosaccharides or some monosaccharide-containing sirups were present. Above 10% all of the sugars and sirups progressively lowered the strength of the gels. The decreases were greater with the disaccharides and sirups than with fructose, glucose and sorbitol.

The differences in the gelatinization behavior of the starch granules seemed to be related to the size of the sugar and sirup molecules. These differences showed their effects in the resulting gels. Sufficient swelling of the starch granules, as evidenced by the viscosity of the paste, was necessary for gel formation when the paste was cooled. The stereochemistry of the sugars may also influence starch behavior. There seemed to be no direct relationship between the thickening and gel-forming behavior of the pastes and the number of sugar hydroxyl groups present.

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INTRODUCTION

Cornstarch is used in food preparation for its thickening and gel-forming properties. In many dessert-type products, such as puddings and cream pie fillings, it is cooked in the presence of sucrose, milk, and other ingredients. Methods of combining and cooking these ingredients are relatively simple but the behavior of starch sometimes becomes complex in the presence of other ingredients and failures often occur when these products are prepared.

A comparison of recipes for cream pie fillings showed that the amount of starch used varied over a wide range (1.6 to 6.1% in those examined), the amount of sugar also varied (13.6 to 31.1%), and the other ingredients varied to a lesser degree.

In recent years, several studies have been reported on the effect of sucrose on the behavior of cornstarch during cooking (12, 26, 41), the effect of various aqueous media on the gelatinization of cornstarch (23), and the effects of combinations of ingredients as found in cream pie fillings (11, 21, 25). Some studies have been reported on the effect of sucrose on pastes and gels of various starches (20, 31, 60). Buchanan and Lloyd (15) studied the effect of corn sirups on some properties of cooked starch.

With the increased use of various sugars and sirups other than sucrose in food preparation, a better understanding of their effects on other food ingredients, such as starch, seems desirable. Generalizations can be made to explain the behavior of starch when gelatinized in milk but unless the effect of each of the food constituents present in the milk, including lactose, is known, the basic reasons for the behavior of the starch cannot be known. With increasing use of dry milk solids and stress put on doubling or tripling the amount present in fluid milk, it seems even more important to study the effect of the various basic constituents.

This investigation was undertaken to study the effects of various sugars and sirups on the viscosity and gel strength of a 5% cornstarch paste. Distilled water was the liquid medium for pasting, and various levels of glucose, fructose, sucrose, lactose, maltose, sorbitol, corn sirup, or invert sirup were added to the cornstarch slurry before cooking. The concentrations of the sweetening agents ranged from 5% to 50% of the weight of the water present and covered the amounts used in preparing cream pie fillings.

It is hoped that the work described here will provide some of the basic information needed for further work on the effects of food constituents on the physical properties of starch thickening agents.

REVIEW OF LITERATURE

Progress in explaining the behavior of starch during cooking was hindered until recently by a lack of knowledge concerning the composition of the starch. Early investigators reported inconsistent results on pasting different starches and on pasting the same starch under different conditions. It is now known that starches vary due to the structure and the amounts of the constituent molecules within the granules (38) and that the properties of a single starch can vary depending on the manufacturing process it has undergone (47) as well as on the variety and on the conditions during the growing season (59). Differences in gelatinization procedure are also known to affect the resulting pastes (3, 29).

Starch Fractions

Many early studies assumed starch to be a single entity. Some workers mentioned the possibility of more than one component but due to inadequate methods of separation their results varied and in some cases contradicted each other.

In a review of the starch fractions, Schoch (53) pointed out that as early as 1716 Leeuwenhoek, in his microscopic studies, recognized the presence of more than one substance in the starch granule. He described a hull that remained undissolved when starch was heated in water. He termed this component an "undigestible hull" and called its contents the "nutritive substance". A century later other European authors described two fractions on the basis of their relative solubility in water. Further work produced a theory which described three components by their degree of solubility in hot and cold water. Schoch pointed out that this latter theory is frequently mentioned but has never been widely accepted.

In the latter part of the nineteenth century, C. W. Naegeli, interested in the botanical nature of starch, contributed much to the basic knowledge of our present-day concepts of starch structure. Schoch named him the father of starch chemistry. Naegeli considered the insoluble component as being similar to wood cellulose and thought of the soluble component as a different modification of the same substance. Only recently has this concept been proved to be in error. However, he was among the first to consider the theory of micellar organization within the starch granule.

Early in the twentieth century Maquenne and Roux (35) by leaching starch with hot water, were able to dissolve part of it. This dissolved material precipitated on standing. These workers used the term "retrogradation" to describe the phenomenon of insolubilization. The deposited material could be redissolved when heated to 150°C. and the solution gave a blue color with iodine.

As Schoch (53) pointed out they did not actually isolate the other fraction but mentioned it as a minor component, amylopectin. Actually this fraction is now known to make up about 70-85% of the cornstarch granule. Such an error was due to the inadequacy of their method of separation; however, these studies initiated further study of starch from a chemical point of view.

Later investigators used enzymes to study the components. Incorrect assumptions were made about the fractions due to a lack of knowledge of the behavior of the enzymes and of the interference by the non-carbohydrate impurities in the starch.

More recent studies have utilized certain polar organic substances for the fractionation of starch. In 1941 and 1942, Schoch (48, 49) reported the precipitation of the amylose component by butyl or amyl alcohol. This selectively precipitated component is soluble only in hot water, and on cooling retrogrades or forms an irreversible gel. The supernatant liquor can be treated with methanol to give a precipitate that is easily dissolved and which does not retrograde.

Confusion in naming the fractions of starch has added to inaccuracies in interpreting various authors' works. Some investigators have used the terms, amylose and amylopectin, in a manner opposite to others. K. H. Meyer (37) proposed naming the linear fraction "amylose" and the branched component "amylopectin". Schoch (50) preferred to use the terms

"A-fraction" and "B-fraction" to describe the linear and branched chains respectively. More recently Schoch (52) suggested the terms "linear starch fraction" and "branched starch fraction" to simplify the nomenclature.

Although differing in their naming of the fractions, these and other starch chemists generally are in agreement as to the properties of the two carbohydrate components of starch. The A-fraction or amylose is usually accepted to be the linear fraction or one containing very few branched chains. It is a polymer of glucose units joined by an α-1→4-glucosidic linkage. Such long linear chains of a polysaccharide contain quantities of hydroxyl groups which allow for hydrogen bonding forces. Schoch (51) pointed out that the A-fraction is soluble in hot water but shows a tendency to retrograde or revert to an insoluble state on cooling due to the strong associative forces generated by the hydrogen bonds. In low concentrations (1%) this insolubilization produces a precipitate of amylose. In greater amounts (5%), an irreversible gel is produced from the A-fraction.

The B-fraction or amylopectin is considered to be a relatively branched molecule. Molecular weights from one to six million have been reported for amylopectin (45). The branches have been shown to be 22 to 27 glucose units in length (44), joined by the same α-1→4-glucosidic linkage as in the linear chains. At the points of branching the units are connected by an α-1→6-glucosidic linkage. Many branches are combined in one tree-like molecule containing several thousand glucose units. This highly branched structure does not allow for the orderly association between molecules possible with the linear chains; hence this component does not have a tendency to retrograde or gel, thereby showing greater colloidal stability. It is useful as a thickening agent because of its capacity to hold water within its branches. Its presence in a granule diminishes the precipitating and gel-forming tendencies of the linear fraction.

In reactions with iodine, the A-fraction shows a strong affinity for the halogen giving a deep blue color, while the B-fraction shows weak affinity with the production of a red color (6).

Granular Structure

To interpret the mechanism of starch behavior in water, a knowledge of granular structure is necessary. Early studies considered the starch granule to be composed of an outside membrane or "sac" that was insoluble and the contents of such a "sac" to be the soluble portion. Caesar and Cushing (18), in discussing some of T. C. Taylor's unpublished work, pointed out that he challenged the membrane theory by showing through electrophoresis that the so-called "shell" was composed of the same proportions of the A- and B-fractions as the entire granule.

K. H. Meyer (39) supported and modified some of the earlier work to explain the structure of the starch granule.

He proposed that starch molecules are laid down in concentric layers about a nucleus to form a granule. Both fractions are oriented within these layers in a radial direction. At many points, segments of the linear fraction and the linear outer branches of the B-fraction associate side by side to form crystalline bundles to which the term "micelles" was given by Naegeli and retained by Meyer. These bundles or crystalline regions are connected by parts of the chains or branches which are not included in the micelles and which form the looser, amorphous areas that allow some hydration and swelling without rupture of the granule.

Meyer thought the micelles differed in size and that some could be destroyed in warm water thus allowing further swelling of the granules. Meyer felt that possibly larger micellar regions occurred in the outer layer thus functioning as a shell to hold the granules intact during swelling.

This latter theory, coupled with the concept that the branched chain contributes most of the structure to the crystalline regions, has given rise to a new hypothesis that a membrane does exist which is composed mainly of the branched fraction. Badenhuizen (5), in discussing this, reported that in studies on various starches, he has found no decrease in the amount of linear fraction from the center of the granule to its periphery. He found that the linear fraction was either localized in the center or distributed regularly throughout the granule. This latter finding is in agreement with Taylor's work which was mentioned earlier.

Swelling

Starch is insoluble in water at room temperature. The granules will become somewhat hydrated with water entering into the intermicellar spaces but they will not swell appreciably. This hydration is slow and is reversible (24). Meyer (39) has stated that the granules can take on 25-30% of their weight in cold water.

As the temperature of the water is increased the hydrogen bonds which have held the molecules together in a compact granular form are weakened and tend to dissociate. This loosens many areas in the structural network and more water is able to permeate the granules, thus causing noticeable swelling. Some of the small crystallites dissolve and aid in further loosening of the granule network. The larger micelles function to keep the swollen granules intact. Some amylose molecules, which are not held as firmly in the network as the branched amylopectin, diffuse out of the granules (39). This leaching out of the amylose or A-fraction is the phenomenon which served as a basis in some of the early fractionation studies on starch.

Gelatinization

The term gelatinization is used to refer to the changes which starch undergoes as it swells in water under the influence of heat, salts, or other agents (59). The temperature at which the granules swell to produce a noticeable increase in the viscosity of the paste has been designated by many as the gelatinization temperature. Many studies have been undertaken to determine this temperature for various starches.

Kerr (35), in a review of the various methods used, felt that the choice of a method for determining the temperature of gelatinization would depend on the investigator's concept of which phenomenon in starch behavior defines the point of gelatinization.

Alsberg and Rask (1), in 1924, observed in viscosity studies on corn and wheat starches, that gelatinization does not occur as a sharp transition point but instead is a continuous process which extends over a temperature range. They felt that the gelatinization temperature was affected by many factors both inherent in the starch and due to techniques of manufacture and of preparation of the pastes.

Other workers have used microscopic techniques in gelatinization studies. Uncooked starch exhibits a "maltese cross" effect when viewed under a polarizing microscope. On swelling the granules lose this polarization cross. This phenomenon has been associated with gelatinization and there is a temperature range over which it occurs that is characteristic for each starch (41, 54).

Photomicrographs have also been used to study gelatinization of starch. Starches differ in their appearance and size depending on the plant source of the granules. Behavior during gelatinization is also typical for each variety of starch. These identifying characteristics have been shown by Sjostrom (54) in a series of photomicrographs on various plant starches, both before gelatinization and at different stages of hydration and swelling. Woodruff and MacMasters (59) have studied the gelatinization of corn and wheat starches through the use of photomicrographs.

Morgan (40) used a photoelectric method for following the swelling of starch pastes. When heated in water, starch suspensions increase in translucency. By measuring the light transmitted during heating of a starch slurry and plotting it against the temperature of the paste, Morgan developed characteristic curves for each type of starch. The curves showed the progress and completion of gelatinization and from these curves the gelatinization temperature could be determined.

Anker and Geddes (4) reported gelatinization studies using a Brabender Amylograph. They preferred to term the temperature at which the initial rise in viscosity occurred as the transition temperature and felt that this point designated the commencement of the gelatinization process.

Viscosity

One of the most important uses of starch in food preparation is its ability to thicken an aqueous liquid. The degree of thickening or viscosity referred to in such a paste is usually an apparent or anomalous viscosity rather than true viscosity. Brimhall and Hixon (14) have shown that starches exhibit true viscosity only in very dilute pastes, below 2% for cornstarch. Such low concentrations are usually impractical in food preparation. Higher concentrations produce a structural viscosity which is a function of the rate of shear. Starch investigators usually refer to this apparent or anomalous viscosity simply as "viscosity" or in some cases as "consistency" (16).

Katz and coworkers (34) pointed out that starch pastes are not colloidal solutions but are suspensions of highly swollen granules. They concluded that the viscosity of starch pastes is due to the flow of water which is made more difficult by the swollen granules and is also due to the rubbing of the granules against each other.

Anker and Geddes (4) stated that the viscosity exhibited by starch pastes depends on the extent of aggregation of the granules, the extent of swelling, and the extent of granule disintegration or rupture. These factors are influenced by the variety of the starch, the method of manufacture, and the techniques used in preparing the starch paste (36).

Many investigators have reported the influence of such factors as rate and duration of heating, method and rate of agitation, concentration of starch, pH, and presence of other substances.

Bechtel (8) studied pasting of starches with the Corn Industries Viscometer and found that rapid heating lowered the gelatinization temperature and increased the maximum viscosity of 5% pastes of unmodified cornstarch. These results were in agreement with those observed by Caesar and Moore (17), using a Caesar Consistometer.

Harris and Jesperson (29) studied the swelling power of some cereal starches and found that beyond the first marked rise in viscosity there was no increase in the volume of swollen granules with a long heating period. After a peak viscosity was reached, there seemed to be a decrease in viscosity with continued cooking. Anker and Geddes mentioned granule disorganization as the commonly accepted reason for this decrease in viscosity and also suggested that an increase in the permeability of the swollen granules might play a part.

Bechtel and Fischer (9) concluded that the rate of pasting is the variable most affected by the rate of agitation. They pasted one sample in a double boiler, having a capacity of one liter and fitted with a high speed mechanical stirrer. Another sample was pasted in the Corn Industries Viscometer, which also had a capacity of one liter. The stirring device of the viscometer was operated on slow speed.

Both pastes were heated in a 92°C. water bath. The 10% cornstarch slurry, pasted in the double boiler with more rapid agitation, was gelatinized in less than one-half of the time required for the paste cooked in the viscometer.

Caesar (16) pointed out that viscosity decreased with severe agitation and that this was a disturbing factor in early gelatinization studies where the agitation in the instruments used, the Stormer and MacMichael viscosimeters, influenced the viscosity.

Anker and Geddes (4) found that the concentration of starch influenced markedly the characteristics of the paste. They reported that as the starch concentration increased, there was an appreciable decrease in the temperature at the initial rise in viscosity, a marked increase in maximum viscosity, and a more rapid decrease in viscosity after maximum. Bechtel (8), in studying the same variable on the Corn Industries Viscometer, reported similar results. He also found that successive equal increases in starch concentration caused increasingly large differences in viscosity. Both studies showed that there was a linear relationship between the logarithm of the starch concentration and the logarithm of the maximum paste viscosity.

Anker and Geddes in their studies on the effect of pH on the gelatinization of starch used buffered solutions to regulate pH values. They found that the maximum viscosity was decreased as the pH was increased from 4 to 7. They used bimaleate and citrate buffers and found that the different buffers affected the viscosity of the pastes to different degrees. They suggested that the results could be due to the ions present rather than to the pH.

Bechtel (8) used sodium hydroxide and hydrochloric acid in his pH studies in order to avoid the possible effects of the ions contained in the buffers. His results showed no marked differences in the maximum or final viscosity on unmodified cornstarch between a pH of 4 and 7. Higher or lower pH values did show some effect. At a pH of 9, the highest reported, the unmodified starch had a higher maximum viscosity and a greater degree of breakdown than at lower pH values.

Gel Properties

In addition to the thickening ability of a starch, its gel-forming properties are also important in characterizing a particular type of starch. As mentioned previously, the A-fraction or amylose is responsible for gel formation in starch paste. The highly ramified structure of the B-fraction does not allow for association of its branches and so it cannot form a gel.

Some early workers thought that on heating in water, the swollen granules disintegrated to form colloidal solutions that set on cooling in a manner analagous to gelatin. Alsberg (2) did not agree with this analogy. He felt that at lower temperatures some of the rigidity of the granules was recovered and that possibly the granule surfaces were sticky, favoring their agglutination, therefore making the pastes more resistant to flow.

Meyer and coworkers (38) were able to explain gel formation on the basis of granule structure. They stated that during gelatinization one end of a chain diffused out of a granule while the other end was retained in the crystalline regions or micelles. The so-called "dissolved" end became entangled with chains from other granules and on cooling formed a turbid, coherent, elastic gel. This reassociation of chains of molecules has been attributed to the presence of hydrogen bonds (19, 56). The number of such connecting links that formed in a given paste would directly affect its gel strength.

The gel properties of starch have been measured by numerous types of instruments which have actually measured different characteristics of a gel, such as breaking point, elasticity, rigidity, and resistence to cutting.

Some very early work, cited by Saare and Martens (46), attempted to measure the stiffness of a starch by soaking threads with the starch paste, allowing them to dry in a vertical position, then observing the position of a bend when the threads were suspended horizontally. The farther out on the thread that the bend occurred, the stiffer was the starch. These workers cited another test whereby metal spindles were dropped into a starch paste and the depth of penetration was a measure of the solidity of the paste. Their own method consisted of implanting a disk in a warm paste, allowing it to cool, and then measuring the force necessary to pull it out. This method has undergone many modifications and the latest mechanized refinement of it (32) is the one used in this study.

Woodruff and Nicoli (60) studied starch gels by observation of the molded gel when turned out of its container. Photographs were used as a permanent record of the gel's characteristics.

Woodruff and MacMasters (59) used a Tarr-Baker jelly tester which measured the hydrostatic pressure necessary for a plunger to break through the surface of a gel. Their studies on viscosity as measured by a Stormer viscosimeter and on gel strength as described above gave good evidence that these two properties measured two unrelated characteristics of starch pastes.

Brimhall and Hixon (13) felt that actual disruption of the gel structure involved variability in the degree it stretched and so was not accurate. They devised a rigidometer which measured the resistance offered by a paste to being stretched or its elasticity.

Bechtel (10), in a study on the gel properties of native and modified cornstarch, compared several gel testing instruments, the rigidometer mentioned above, several plunger-type instruments, and a modification of the embedded disk instrument. The latter instrument gave the best results on replicate tests and the values obtained correlated well with those obtained by the other instruments. However, as pointed out by the author, all the instruments were in the range acceptable for industrial evaluation.

Various authors point out the need for precision in preparing and testing starch gels. The variety of starch, as well as its concentration has a great effect on the strength of the gel. The temperature to which a paste is cooked directly affects the gel strength. Woodruff and Nicoli (60) determined the gelatinization temperature in 5% pastes of various starches by noting a sharp change in translucency. They pasted these starches to their respective gelatinization points, all of which were below 88°C. and found that although the pastes thickened they did not form gels. By heating similar pastes to 90°C. and above, gels were formed on cooling when cereal starches were used. Effects of cooking temperature were also noted by Brimhall and Hixon (13) in their rigidity studies. Bechtel (10) found that unmodified cornstarch gels increased in breaking strength when the cooking temperature was increased to 94°C. A further temperature increase seemed to decrease the gel strength.

Osman and Mootse (43) studied gels of many starches pasted in distilled water in the Corn Industries Viscometer. They found that the length of the cooking period after the maximum viscosity was reached markedly influenced gel characteristics. The gel strength, as measured by an embedded disk method, was greater for all the starches pasted to five minutes after maximum viscosity as compared to the strength of those pasted only to maximum viscosity. The gels prepared from pastes cooked for 20 minutes after maximum showed increased strength for some starches and decreased strength for others.

The time and temperature of aging also affects the gel strength and so must be controlled in order to get reproducible results. Bechtel (10) stated that starch gels increase rapidly in strength during the first 10 hours and then the rate drops off. Gel strength decreases with increasing temperatures. The latter phenomenon has been observed in the writer's laboratory and steps were taken to standardize the testing conditions for this study.

Effects of Sugars

Most of the work reporting the influence of sugars on starch behavior has been connected with studies on cornstarch as affected by sucrose. Some authors have studied other starches but very few have used other sugars.

Woodruff and Nicoli (60) studied gels of various starches as affected by sucrose. Using 100 grams of a 5% starch paste, they added 10, 30, 50, and 60 grams of sucrose and gelatinized the pastes in test tubes heated in a water bath to 90°C. The gels were poured into small crucibles, aged 24 hours, and then turned out of the molds for comparison by observation. The cereal starches, including cornstarch, gave well-formed but increasingly more tender gels with 10, 30, or 50 grams of sucrose. With the addition of 60 grams of sucrose a thick sirup rather than a gel was obtained. The authors wondered if the 60 grams of sucrose might not have acted as a diluent since the volume of the paste had been increased to 132 cc. However, when the control slurry was diluted with water to 132 cc. a firm gel was obtained. These authors suggested that large amounts of sucrose prevented the starch granules from imbibing the water necessary for swelling.

Nevenzal (41) also varied the concentration of sucrose in a 5% starch paste. Fifteen grams of sucrose in 100 grams of starch paste resulted in a gel that was tender yet firm; 30 grams of sucrose produced a gel that was too tender; and no gel was formed when 50 to 66 grams of sucrose was present in 100 grams of starch slurry. Comparison of photomicrographs of starch granules with and without sucrose showed that at 69°C. control pastes without sucrose exhibited very little anisotropy when viewed under a polarizing microscope, while pastes gelatinized with 50% sucrose had much anisotropy even at 80°C. Since the granules lose this "maltese cross" effect on swelling, it appeared that the sucrose inhibited swelling of the granules. The photomicrographs in this study also showed decreased swelling of the starch granules pasted with sucrose.

Using laboratory prepared starch, Chidester (21) noted similar effects on gels of a 6% cornstarch paste prepared with increasing amounts of sucrose. She pasted 5 grams of starch, 78.3 grams of water and amounts of sucrose ranging from 16.6 grams to 37.5 grams. The latter amount yielded a gel that did not hold the shape of the mold but did have some body.

In the same laboratory, Bowersox (12) pasted various concentrations of cornstarch in water in the presence of sucrose. A 10% sucrose addition decreased the viscosity and the gel strength slightly, 20 and 30% additions caused a more marked decrease in these properties. The addition of 30% sucrose resulted in a thick sirup in a 4% cornstarch paste, an extremely tender gel in a 5% paste, and a tender but well-formed gel in a 6% paste.

In a bakers' trade journal, Trempel (57) stated that sugar interfered with the swelling of the starch granules during cooking and advised the addition of not more than three and one-half times as much sugar as starch by weight in preparing pie fillings. If more sugar is needed, he suggested it should be added after the starch is gelatinized. He suggested that corn sirup could be present up to four and one-half times the weight of the starch without producing too great an effect.

Whittenberger and Nutting (58) found somewhat different behavior with potato starch. On pasting the starch in water, a temperature of 85°C. was sufficient for complete gelatinization and well-formed gels. Above this temperature the granules ruptured and the gel strength decreased. When 8% potato starch slurries were pasted with sucrose, the gelatinization temperature was raised and the gel strength increased with increasing sucrose concentrations up to 50%. Sixty-five per cent sucrose caused insufficient granular swelling, as observed microscopically, even when the pastes were heated to 95°C. and held for 20 minutes. It had been erroneously suspected from the results of the increase in gel properties with sucrose that a mechanism similar to that in pectin gels might be present. It was thought that the lack of gel formation in the concentrated sugar pastes might be caused by persistent granules interfering with possible hydrogen bonding effects of the sucrose. Subsequently, these workers prepared starch-sugar pastes in which the granules had been destroyed by mechanical shearing. No gels resulted, thereby showing the need for intact granular structure for gelation and the fact that sucrose does not play a role in starch gels similar to that in pectin jellies. They reported similar results using dextrose and glycerol.

By studying x-ray diffraction patterns of potato starch as affected by sucrose, Nikuni and coworkers (42) concluded that sucrose prevented the retrogradation (linear association) of starch by binding the water.

Hester (30, 31) studied the changes induced by sucrose on various starches. A control cornstarch paste contained

6.5 grams of the dry starch per 100 grams of water. Four increments of sucrose from 15.9 grams to 39.5 grams per 100 grams of water were used and the mixtures were pasted in the Brabender Amylograph. Cooking was terminated as soon as the pastes reached 95°C. Gels were prepared and measured by the Exchange Ridgelometer after aging overnight at room temperature. The viscosity attained during gelatinization to 95°C. was greater when 15.9 grams of sucrose was added but with higher concentrations of sucrose the viscosity at this temperature became progressively lower. The lowest level of sucrose decreased the strength of the cornstarch gel. The next increment yielded a very tender gel which collapsed within a minute after removal from its container. With greater concentrations of sucrose, thin pastes were obtained in place of gels. Chemical determinations of the amount of amylose in solution showed a decrease with increasing amounts of sucrose. Hester then hypothesized that less amylose was available for gel formation. Other effects of sucrose noted by this worker included a higher temperature at the initial rise in viscosity, decreased granular swelling, and less disintegration of swollen granules with increasing concentrations of the sweetening agent. Hester reasoned that the dissolved sugar molecules hydrated, thus leaving less free water for starch hydration.

Hains (26) prepared 11% cornstarch pastes to which were added amounts of sucrose equal to 20, 40, and 60% of the weight of the water. She found that 20% sucrose raised the maximum hot-paste viscosity as measured by the Corn Industries Viscometer, while the 40 and 60% additions decreased the maximum viscosity. Increasing amounts of sucrose increased the temperature and the time of initial rise in viscosity and of the maximum viscosity. Gel strength as measured by a Fuchs penetrometer showed a decrease as sugar was increased.

Halliburton (27) studied the effect of sucrose on the thickening and gel properties of wheat flour and the flour fractions. With the starch fraction, 7.22 grams of starch was pasted to 95°C. in 100 grams of water. Using a Brookfield viscosimeter, she found that the viscosity was increased by 13.2 and 26.4 grams of sucrose and then decreased when 39.6 grams was present. She stated that less disintegration of the granules might have occurred when the lower amounts of sucrose were present. This would increase the number of intact swollen granules and thus increase the viscosity. Larger amounts of sucrose tended to inhibit swelling of the granules. Gel strength, measured by an Exchange Ridgelometer, decreased with successive increases of sucrose until no gel was formed with the greatest addition of sucrose. She stated that sucrose reduced the hydration capacity and swelling of the starch, thus decreasing the amount of amylose available for gel formation.

Ferree (23), using a Corn Industries Viscometer, found that 15% and 21% sucrose present in an 11% cornstarch paste increased the maximum hot-paste viscosity significantly as compared to the control. Twenty-seven per cent sucrose gave a maximum viscosity value similar to that of the control. The temperature at the initial viscosity rise and at the maximum viscosity increased with successive increments of sucrose.

PROCEDURE

Equipment

Viscometer

The instrument used to cook the starch pastes and to measure the viscosity was the Corn Industries Viscometer, developed for the cornstarch industry, and described by Kesler and Bechtel (36). It measures and records continuously the viscosity of a paste during the heating period and also during a cooling period if so desired.

A steel beaker is immersed in a liquid bath for cooking the paste. The bath may be water if a heating temperature of less than 100°C. is required. The temperature of the liquid is maintained by a submerged electric heating element, thermostatically controlled to ± 0.2°C.

In this study it was necessary to use a mixture of glycerol and water in order to keep the bath at 100°C. and have a minimum amount of evaporation. Both the concentration and the height of the bath were checked and adjusted daily before a day's run was begun. The specific gravity of the liquid medium was kept at 1.13 and the height was such that during cooking it was about one to two cm. below the top of the hot paste.

Evaporation losses in the pastes during cooking are kept at a minimum with an efficient condenser-type cover. This cover, which comes in two sections, is designed for use as an air condenser or as a water condenser. In this study it was used very effectively as an air condenser. There is an opening in one side of the cover for a thermometer for recording paste temperature during cooking.

The starch paste is kept suspended during cooking by an intricate stirring device containing scraper blades which effectively remove the layer of cooked paste from the sides and bottom of the cooking beaker. This design aids to minimize any insulating effect caused by an adhering layer of paste.

The scraper blades are mounted on a hollow shaft through which is suspended a propeller which serves to stir the center of the paste and also to measure its viscosity. As the propeller moves in a counterclockwise direction, it is subjected to a force, the intensity of which depends on the viscosity of the paste being cooked. This force or torque is transmitted through a set of differential gears to a drum connected by a cable to a dynamometer built into a recorder. The dynamometer contains a weight arm and has an attached pen which records the torque on a strip-type chart. The dynamometer arm has interchangeable weights so that the full scale reading of the chart can be varied from zero to 225, 450, 900, or 1800 g.-cm. depending on the viscosity of the starch paste being studied. In this study no weights were used since all the pastes were in the lower range of zero to 225 g.-cm.

The stirring mechanism has four speeds. For optimum agitation of the paste and minimum shearing of the swollen granules, Bechtel (7) recommends that speed 2 be used for laboratory testing of starch pastes. This speed, which turns the scraper at 24 r.p.m. and the propeller at 60 r.p.m., was used in this study.

The chart recording device moves the chart downward at the rate of one-half inch per minute. The charts have a scale of 0 to 100. Bechtel's tables (7) are used for changing the chart readings to g.-cm. of torque.

Gel Tester

The gel strength was measured by a gel tester, designed by Hjermstad (32) and built on this campus for our laboratory. It utilizes the embedded disk method of measuring gel properties. The principle of implanting a disk in a hot paste, allowing it to set, and then measuring the force required to remove the disk was first reported by Saare and Martens (46). The force required to pull the disk out of the set paste is a measure of the resistance or strength of the gel. This method was later modified by Hamer (28), Kerr (35), and Bechtel (10). The latter worker claims that this means of measuring gel strength has a precision of approximately 3%. His study showed that the embedded disk method was somewhat more sensitive than other instruments for measuring properties of starch gels. It also correlated very highly with other instruments in performance.

The apparatus, as designed by Hjermstad, is a device which lowers a stage at a slow even rate of 4.25 mm. per minute. A jar containing the gel to be tested can be clamped onto the stage. The gel contains an embedded disk which is attached to a rod with a hooked top. A cord is attached to the rod and also to the dynamometer of the Corn Industries Viscometer.

Since the dynamometer of the viscometer is adjusted to zero for the viscosity of water, it is necessary to attach a counter weight to the cord to supplement the weight of the rod. The combined weight should be such that a zero reading is obtained on the chart recorder. The cord rides on a low-friction pulley which is set directly above the center of the gel.

As the stage is lowered, the embedded disk is pulled down with the gel. Therefore a continuously increasing force is exerted on the gel by the dynamometer arm. This force is recorded on the chart of the viscometer which is started at the beginning of the test. A curve results which gives a measure of the deformation of the gel with time and also the yield point of the gel. Tender gels show a leveling off of the curve at the yield point; stronger gels produce a curve that drops suddenly at this point.

The disks made for our instrument were the same as those proposed by Bechtel (10) and recommended by Hjermstad (32). In place of the jars described by these investigators, 250-ml. beakers were used. These were etched with a line to designate the pouring level of the hot paste. When the paste was poured to this level, the disk was immersed 3 cm. below the surface of the gel when supported by a slotted cover designed to fit the beaker and to center the disk in the gel. It was felt that the use of the 250-ml. beakers in place of the jars which had a 150-ml. capacity would lessen effects due to the side of the container.

Ingredients

The cornstarch for this study was part of a lot obtained from the Corn Products Refining Company of Argo, Illinois. It was the ordinary cornstarch of commerce. The entire amount was placed in a polyethylene bag and was stored at room temperature.

The sugars and sirups were obtained from various sources. These are listed in Table I along with the water content of the sirups. The solids in the invert sugar sirup were 54.92% inverted according to the analysis supplied by the manufacturer (33). The three samples of corn sirup were of different degrees of hydrolysis as denoted by the term

TABLE I

SOURCES OF SUGARS AND SIRUPS

Sugars	Water Content %	Source
D-Fructose, C. P. Special		Pfanstiehl Chemical Company, Waukegan, Illinois
Glucose (Cerelose)		Corn Products Refining Company, Argo, Illinois
D-Sorbitol, Crystalline		Atlas Powder Company, Wilmington, Delaware
D-Lactose, C. P. Special*		Pfanstiehl Chemical Company, Waukegan, Illinois
D-Maltose, C. P.*		Pfanstiehl Chemical Company, Waukegan, Illinois
Sucrose		Campus Food Stores
Sirups		
Invert Sugar Sirup	22.36	Refined Syrups and Sugars, Inc., Yonkers, N. Y.
Corn Sirup Unmixed, 63.7 D.E.	18.4	Corn Products Refining Company, Argo, Illinois
Corn Sirup Unmixed, 56.3 D.E.	18.9	Corn Products Refining Company, Argo, Illinois
Corn Sirup Unmixed, 43 D.E.	19.7	Corn Products Refining Company, Argo, Illinois

* Contains one molecule of water of crystallization

"dextrose equivalent" or D.E. This is the copper reducing power of the solids expressed as dextrose. The higher the D.E. value the greater the hydrolysis of the sirup. The 63.7 D.E. sirup was an acid-enzyme converted sirup, and those with lower D.E. values were straight acid converted sirups. The term "unmixed" means that the flavorings which are present in corn sirups for retail sales have not been added.

The sucrose was stored in a covered glass container. The sorbitol was stored in a polyethylene bag. The other samples were kept tightly covered in the containers in which they were received. All samples were stored at room temperature.

Formulas

A 5% cornstarch slurry was used as the basic mixture. This consisted of 5 grams of cornstarch per 95 grams of distilled water. This ratio of starch to water remained constant throughout the study. The weight of the starch was calculated on the dry weight basis; the moisture content was found to be 10.93% as determined by drying in a vacuum oven at 120°C. to constant weight.

The amounts of sugars and sirups were also calculated on the dry weight basis. The concentrations of dry sugar and sirup solids were calculated as 5, 10, 20, 30 and 50% of the weight of the liquid. A control paste containing no sweetening agent was also included in the study.

The weights of starch, sugar, and water were calculated to yield approximately one liter of slurry. This gave a paste level in the cooking beaker which was just below the height of the scraper blade of the viscometer, thus allowing for the most efficient stirring of the paste during cooking.

In order to minimize the effect of pH on viscosity and gel strength, sodium hydroxide was added to the slurry to adjust the pH of the cooked paste to approximately 6.60. It would then be close to the pH of milk.

It was found in preliminary work that 3.5 ml. of 0.1 N sodium hydroxide was needed in the control paste to obtain a final pH of 6.60 after cooking. A proportional amount was also added to the sweetened pastes.

The pH of the sugar solutions was adjusted to 6.60 just before using. The sodium hydroxide solution was included in the weight of the water.

Table II lists the quantities of ingredients at each concentration of sugar or sirup solids.

TABLE II

FORMULAS FOR STARCH MIXTURES

Sugar Concentration % of Water Wt.	Starch* g.	Sugar* g.	Water g.	0.1 N NaOH Included in Water Weight ml.
0	50.0	--	950.0	3.50
5	50.0	47.5	950.0	3.50
10	50.0	95.0	950.0	3.50
20	47.5	180.5	902.5	3.30
30	45.0	256.5	855.0	3.15
50	40.0	380.0	760.0	2.80

* Dry weight basis

Preparation

Ingredients

The sugars and sirups were weighed into 1000 ml. beakers on a single beam platform balance. Five hundred grams of distilled water was added to each dry sugar sample to dissolve it. The mixture was then heated slightly to aid solution. The sirups used were diluted with water to the same concentration. The sirup and water was heated in order to mix thoroughly. The total weight of the sugar, water, and beaker was noted before heating so that an adjustment could be made for any evaporation loss when the solution cooled.

All solutions were prepared the day they were used. They were made sufficiently in advance to allow them to cool to room temperature before use. By dissolving the dry sugars, the effects of the rate of solution on viscosity of the starch paste during cooking were eliminated. The dry sugars were then on a comparable basis with the sirups.

Just before use, the pH of the cooled solutions was determined with a Beckman pH meter, model H2. If needed, adjustment of the pH to 6.60 was made by adding 0.1N sodium hydroxide. The amount of alkali added was noted. After the pH adjustment the solution was weighed and a correction made for water which was lost during heating and cooling.

The cornstarch for each sample was weighed into a tared aluminum dish using a triple beam balance.

The distilled water to be used for mixing was weighed just before it was needed. This water included the sodium hydroxide necessary to adjust the pH of the cornstarch paste to 6.60.

Slurries

The weighed starch was put through a powder funnel into a one-liter Florence flask. Approximately 150 ml. of water was used to rinse out the aluminum dish and the powder funnel. This water and starch was then swirled in the flask about 50 times to insure complete mixing free from lumps.

For the control sample, all but 100 ml. of water was added to the flask and the slurry mixed well before pouring into the cooking beaker. The remaining 100 ml. of water was used to rinse the flask.

For the sweetened pastes, the sugar solution was added to the flask after the starch and 150 ml. of water were thoroughly mixed. Part of the remaining water was used to rinse out the flask after the starch and sugar slurry was poured into the cooking beaker.

All the ingredients were at room temperature, 28 ± 2°C. Once the cornstarch was moistened the mixing of the slurry proceeded quickly. The total mixing time never exceeded two minutes and the method was the same for all samples.

Viscosity Tests

The Corn Industries Viscometer, described in the section on equipment, was used for cooking and for obtaining a pasting history of the slurries.

The cooking beaker, stirring device, and one-half the condenser cover were placed in the viscometer during the heating of the glycerol-water bath to 100°C. When the bath was at 100°C. for a few minutes, the stirring device was started. The slurry was then mixed and poured into the cooking beaker. Immediately the recording device was turned on, then the other half of the condenser cover and the thermometer were put in place.

The paste was cooked for five minutes after the maximum viscosity was reached. In some instances with large amounts of certain sugars, a decided peak or maximum viscosity was never reached. In these cases the endpoint of cooking was arbitrarily chosen after a considerable leveling off of the viscosity rise.

The temperature of the paste was recorded at one minute intervals during cooking.

Preparation of Gels

Gel strength was determined by an embedded disk method using the Hjermstad apparatus, described in the section on equipment.

The cooked sample of paste was removed from the viscometer and poured immediately into four 250-ml. beakers. The first sample poured contained any skin or lumps that might have formed during cooking and was used to measure the pH of the cooked paste.

The remaining three beakers, used for gel strength determinations, were filled to a predetermined mark. Immediately the covers were put in place, the disks immersed in the hot paste to a level 3 cm. below the surface of the paste and supported by the slotted cover. Ten ml. of mineral oil was poured on the surface of the gel to minimize skin formation. The samples were then placed on a level refrigerator shelf and aged for 18 hours at 3°C.

The low aging temperature was decided upon in order to have conditions that would be comparable to the normal handling of puddings containing cornstarch.

Measurement of Gel Strength

After 18 hours the samples were removed from the refrigerator and held at room temperature for 15 minutes before being subjected to the gel strength test. The samples were removed singly so that each one stood just 15 minutes before the test was started.

This holding period was decided upon when preliminary tests showed that gel strength measurements varied appreciably when started during the first 10 minutes after removal from the refrigerator. As the temperature of the gel increased, the strength decreased markedly and then leveled off after about 10 minutes.

Most workers studying gel properties have aged their samples at room temperature or in 25°C. water baths and so did not observe this phenomenon.

After the 15 minute period of holding, the slotted cover was removed and the sample was clamped onto the stage of the gel-lowering device. The cord from the dynamometer was looped around the hook on the embedded disk. The stage was adjusted until the cord was almost taut and the pen of the recording device rested on zero. The gel-lowering device and the pen were started simultaneously and the test was made automatically.

At the breaking point of the gel, the test was stopped and the point noted on the chart. This point was used as the measure of gel strength of the sample. In some samples this point was at the end of a plateau where the deformation curve had leveled off. In others there were higher points on the curve and then a drop in the measured strength of the gel before it broke. Hjermstad (32) states that this higher strength just prior to breaking is believed to be due to surface-skin effects at the oil-starch gel interface.

Since this phenomenon could not be explained as being due to treatment, order of sample, or temperature of sample or of room, it was decided to use the actual yield point of the gel as a measure of its strength.

The average of three replications was reported as the gel strength of a sample.

RESULTS AND DISCUSSION

Viscosity

The qualitative effects of the different sugars and sirups were similar in their influence on the hot-paste viscosity of the cornstarch pastes. Duplicate samples gave very similar gelatinization curves. In order to show the history of gelatinization as affected by each of the sugars and sirups at the various concentrations, curves were constructed for the average torque values of the duplicate runs and are reproduced in Figure 1.

Lower concentrations of the sweetening agents tended to increase the viscosity of the paste while increments above 20% of the weight of the water used gave decreasing viscosities. Time of gelatinization increased slowly with additions of small amounts of most sweetening agents; some sugars and sirups noticeably increased the time of gelatinization at the 30% level, and all of them markedly increased the gelatinization time at the 50% level.

Some differences in gelatinization behavior of cornstarch due to the type of sweetening agent present can be noted at the lower concentrations but the most obvious differences are brought out by comparison of the gelatinization

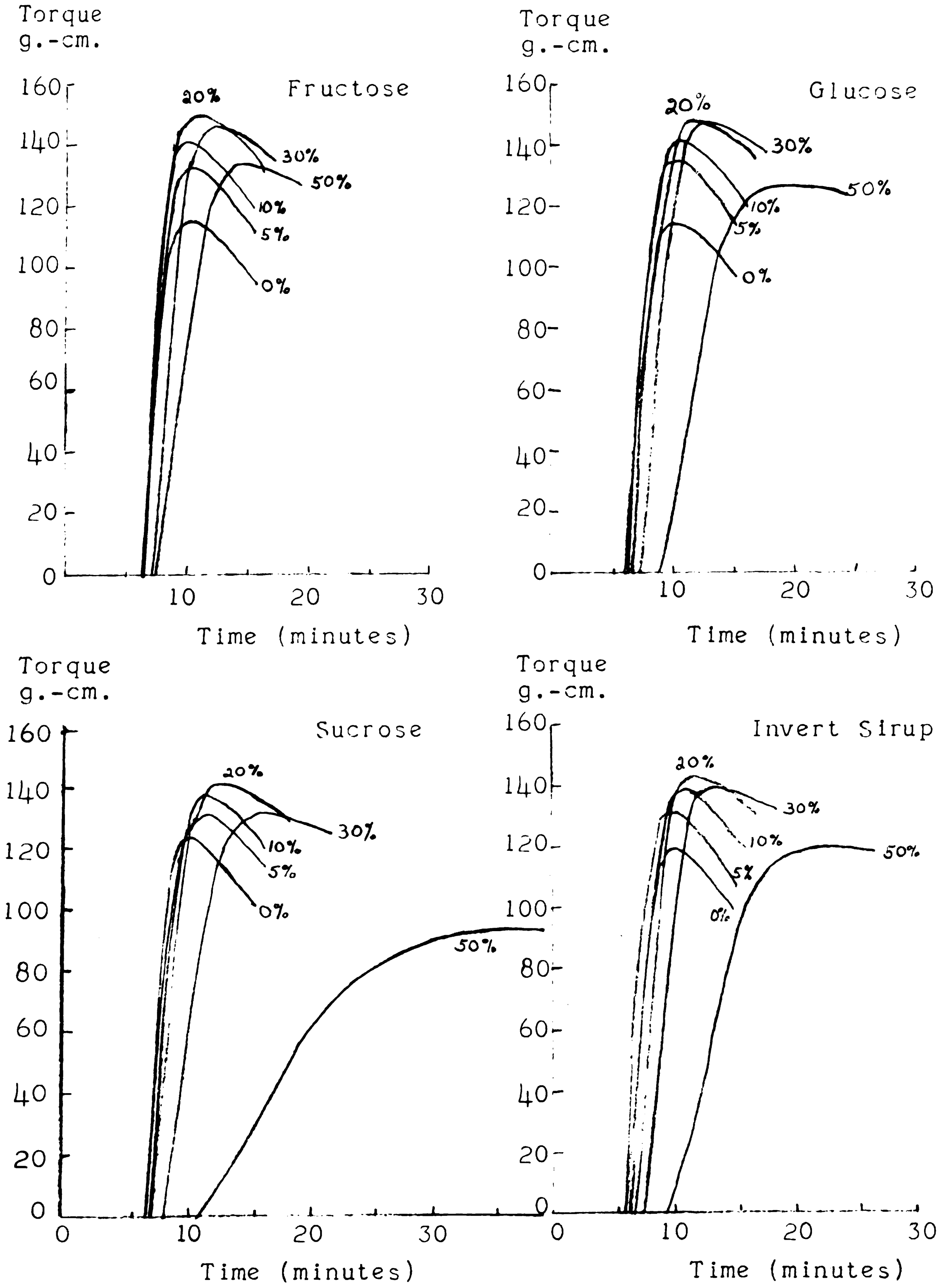

Figure 1. Effect of sugars and sirups on the gelatinization of cornstarch.

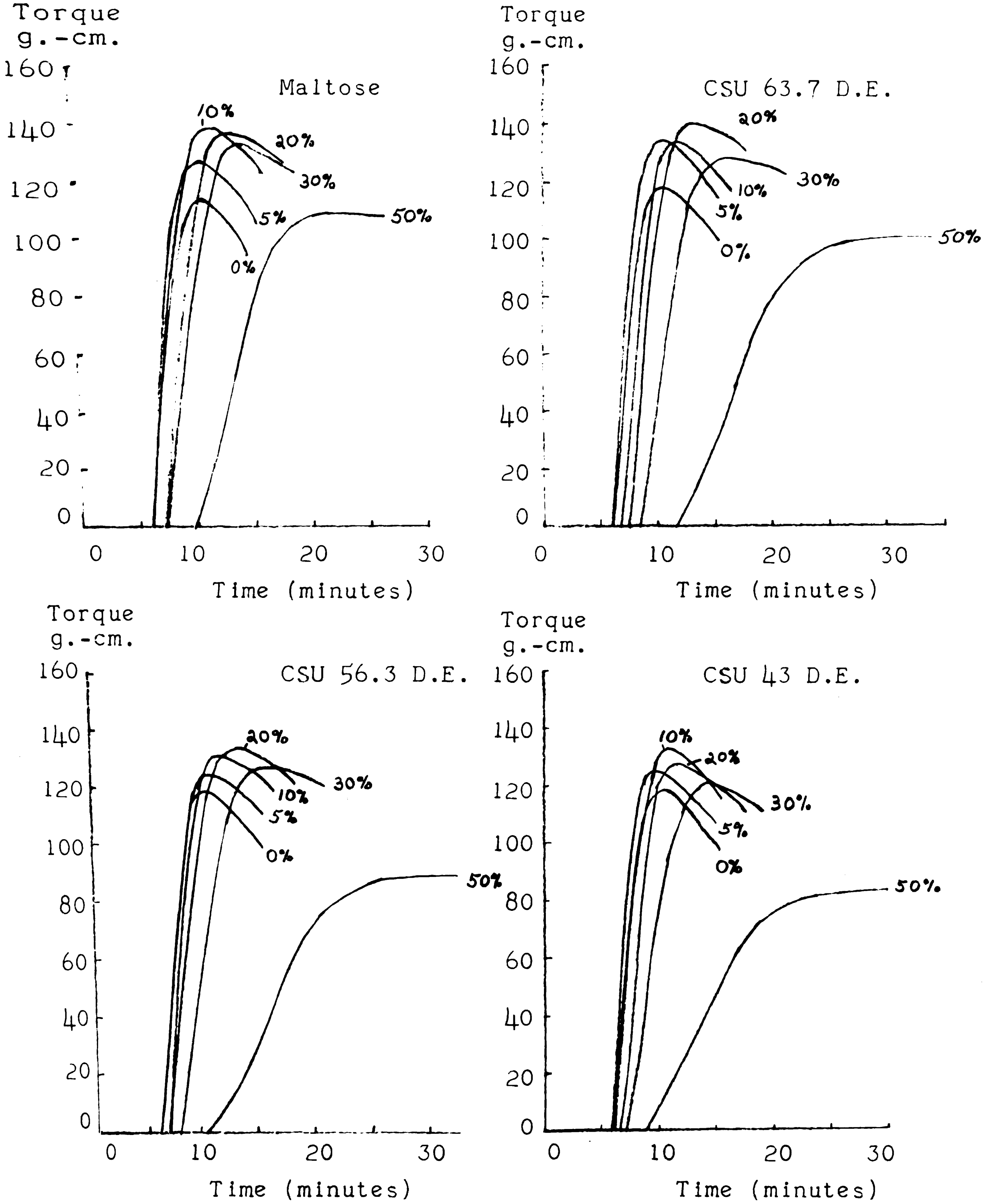

Figure 1. Continued.

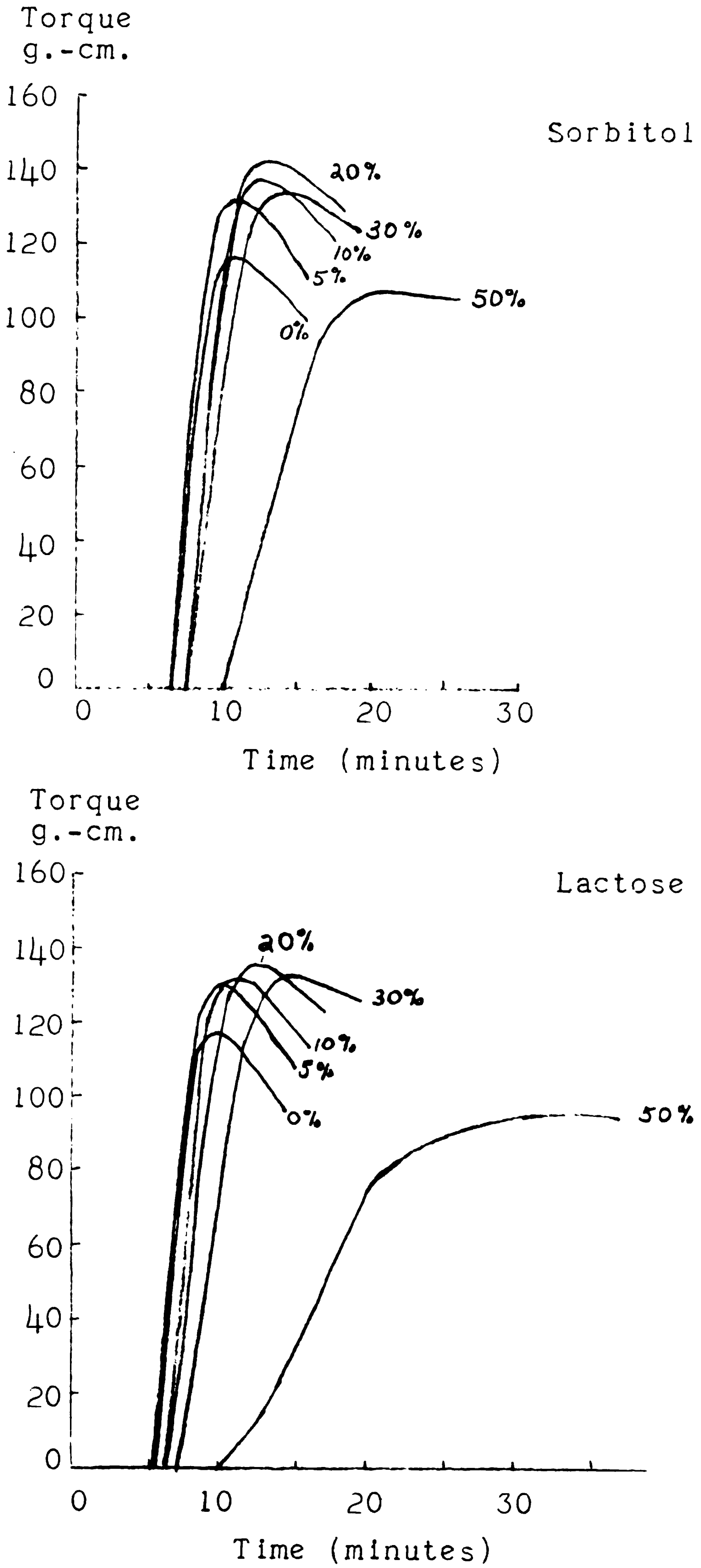

Figure 1. Continued

curves of the pastes containing 50% levels of the various sugars or sirups.

Figure 2 compares the effect of 50% glucose, fructose, sucrose and the inverted sirup with a control paste. The paste containing sucrose at the 50% level showed behavior markedly different from the pastes containing the monosaccharides. The monosaccharides increased the time of gelatinization but allowed enough swelling of the cornstarch granules so that the maximum viscosities were above the control paste. Fructose and glucose possibly allow swelling of more granules without subsequent rupturing, thereby adding to the overall viscosity. Fifty per cent sucrose retarded the initial rise in viscosity appreciably longer than the monosaccharides at this level and inhibited swelling of the starch to a marked degree. This was shown by the much more gradual increase and the lower final paste viscosity which was less than the control.

The invert sirup, which was 54.92% inverted, gave results which were probably due to the ratio of glucose, fructose, and sucrose present.

The pastes containing the monosaccharides showed some decrease in viscosity after maximum suggesting the probability of some granular rupture, while the sucrose-containing paste did not show a decrease in viscosity. Preliminary tests showed that, even with cooking 30 minutes past maximum

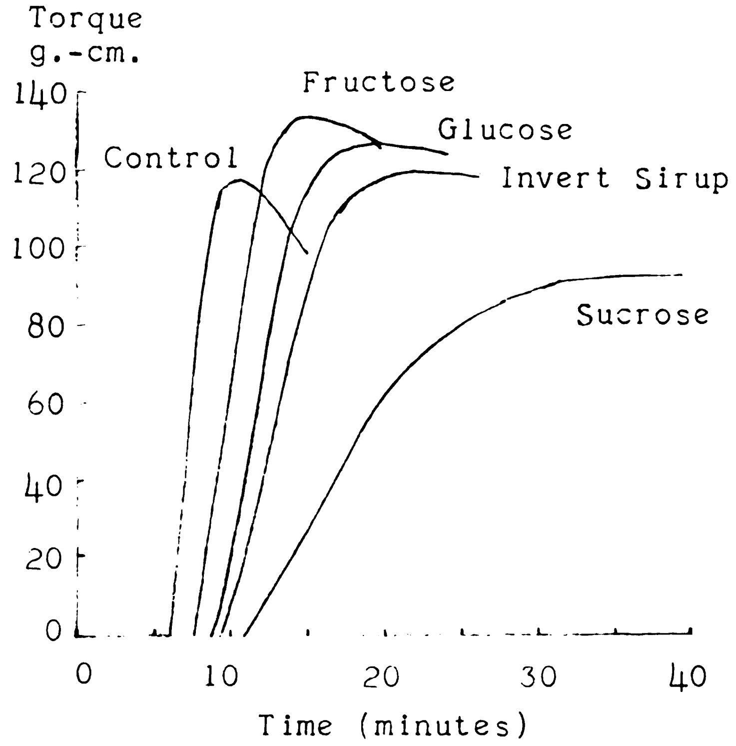

Figure 2. Gelatinization curves for cornstarch pastes containing 50% fructose, glucose, sucrose, and invert sirup.

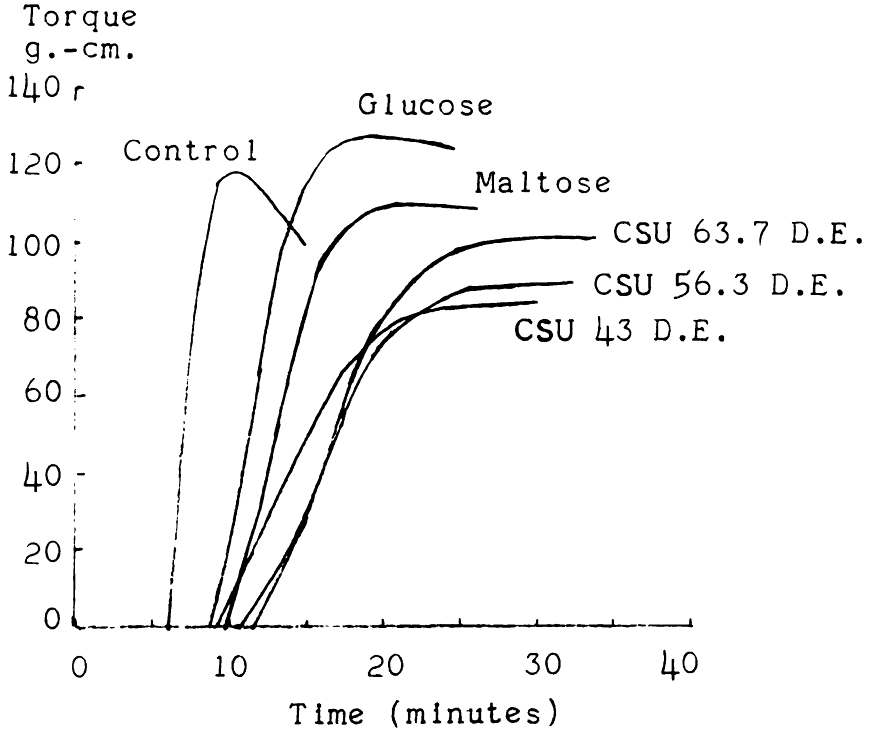

Figure 3. Gelatinization curves for cornstarch pastes containing 50% glucose, maltose, and corn sirup hydrolyzed to 63.7, 56.3, and 43 D.E.

viscosity, the pastes containing sucrose did not decrease in viscosity. The starch granules probably had not swollen enough to start to rupture.

Figure 3 shows the influence of 50% levels of glucose, maltose, and the three corn sirups on the gelatinization behavior of the starch. A control paste was added for comparison. At the 50% level, the glucose permitted enough swelling of the starch to give a maximum viscosity above that of the control paste. There was some granular rupture as evidenced by a decrease in viscosity after maximum. The viscosities of the pastes containing 50% levels of maltose or any of the corn sirups were lower than the control paste and showed no decrease in viscosity after maximum. These results appear to be evidence for decreased hydration of the starch granules resulting in lower hot-paste viscosities and negligible granular rupture.

A knowledge of the composition of the corn sirups, as shown in Table III, is helpful in understanding their behavior (55).

TABLE III

APPROXIMATE COMPOSITION OF THE CORN SIRUPS

Corn Sirup	Glucose %	Maltose %	Trioses and Above %
63.7 D.E.	37	30	33
56.3 D.E.	32	18	50
43 D.E.	20	15	65

The corn sirup with the highest D.E. value showed a markedly higher viscosity than the lower converted sirups. The higher proportion of glucose and maltose in this sirup probably explains this higher viscosity.

For comparison of the effects of the various single sugars, the gelatinization curves of the pastes containing 50% sugar are reproduced in Figure 4. The monosaccharides show an appreciably different effect on gelatinization behavior of the cornstarch than the disaccharides, lactose and sucrose. Maltose and the sugar alcohol, sorbitol, show intermediate effects.

The earlier time of gelatinization, the increase in viscosity above the control, and the decrease in viscosity after maximum are all phenomena that give evidence that the monosaccharides allow enough free water in the mixture to be available for maximum swelling of the starch granules. At the other extreme, the lactose and sucrose appear to bind sufficient water to inhibit complete swelling of the starch.

Maltose apparently did not tie up as much of the water as the other disaccharides as evidenced by the higher maximum viscosity of the pastes in which it was used. However, it did prevent complete gelatinization of the starch granules, resulting in a maximum viscosity lower than the pastes containing monosaccharides and also lower than the control pastes. The lack of a decreased viscosity after maximum

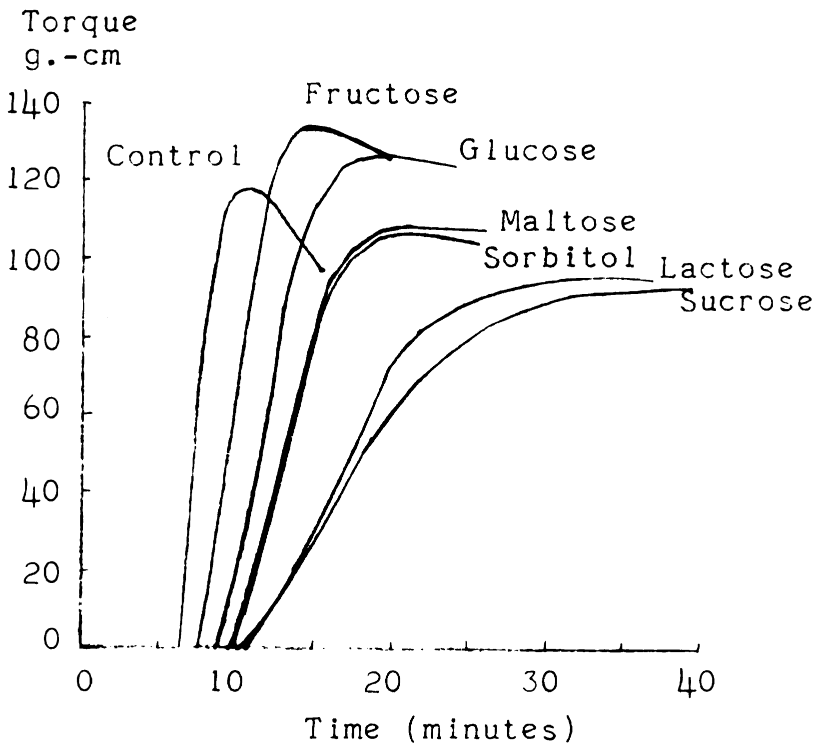

Figure 4. Gelatinization curves for cornstarch pastes containing 50% fructose, glucose, sorbitol, lactose, maltose, and sucrose.

is indicative of insufficient swelling to cause rupture of the starch granules.

Sorbitol showed a different effect on the gelatinization of the starch than did the monosaccharides. Possibly the six hydroxyl groups present in the open chain molecule of sorbitol bind more water than the monosaccharides containing five hydroxyl groups in a cyclic structure; thus sorbitol makes less water available for swelling of the granules. The decrease in viscosity after maximum was inconsistent. In one run there was no decrease while the duplicate run showed a slight decrease with five minutes additional cooking.

The influence of sucrose on the behavior of cornstarch during gelatinization is in agreement with results reported by other workers (23, 26, 27, 30). It is commonly accepted that sucrose in large amounts decreases the viscosity of a starch paste by interfering with the hydration and subsequent swelling of the starch granules. The above comparisons show that the other sugars affect gelatinization in a similar manner but to a different degree.

Table IV gives the maximum hot-paste viscosity of the duplicate pastes for all the sugars at all concentrations.

The average maximum viscosity for the duplicate pastes as affected by the concentration of sweetening agent is shown in Figure 5. The sugars are separated from the sirups for ease in reading.

TABLE IV

EFFECT OF SUGARS AND SIRUPS ON MAXIMUM HOT-PASTE VISCOSITY*

Sugars	Sugar Concentration (% of Water Weight)					
	0%	5%	10%	20%	30%	50%
Fructose	117	131	138	148	146	132
	119	135	145	152	147	135
Glucose	111	136	141	148	146	123
	119	135	142	148	148	131
Sorbitol	113	132	135	141	131	102
	116	130	139	141	135	111
Lactose	118	132	134	137	136	99
	117	130	130	132	129	91
Maltose	112	122	130	132	130	105
	115	133	148	140	136	113
Sucrose	129	135	139	142	133	95
	119	128	134	139	131	88**
Sirups						
Invert Sirup	120	133	139	146	143	121
	119	130	137	139	136	116
CSU 63.7 D.E.	118	138	137	139	135	99
	114	130	130	141	122	100**
CSU 56.3 D.E.	115	123	129	131	125	89
	117	125	132	135	128	86**
CSU 43 D.E.	121	129	135	130	121	89
	117	123	130	123	118	75**

* g.-cm. of torque

** No maximum reached

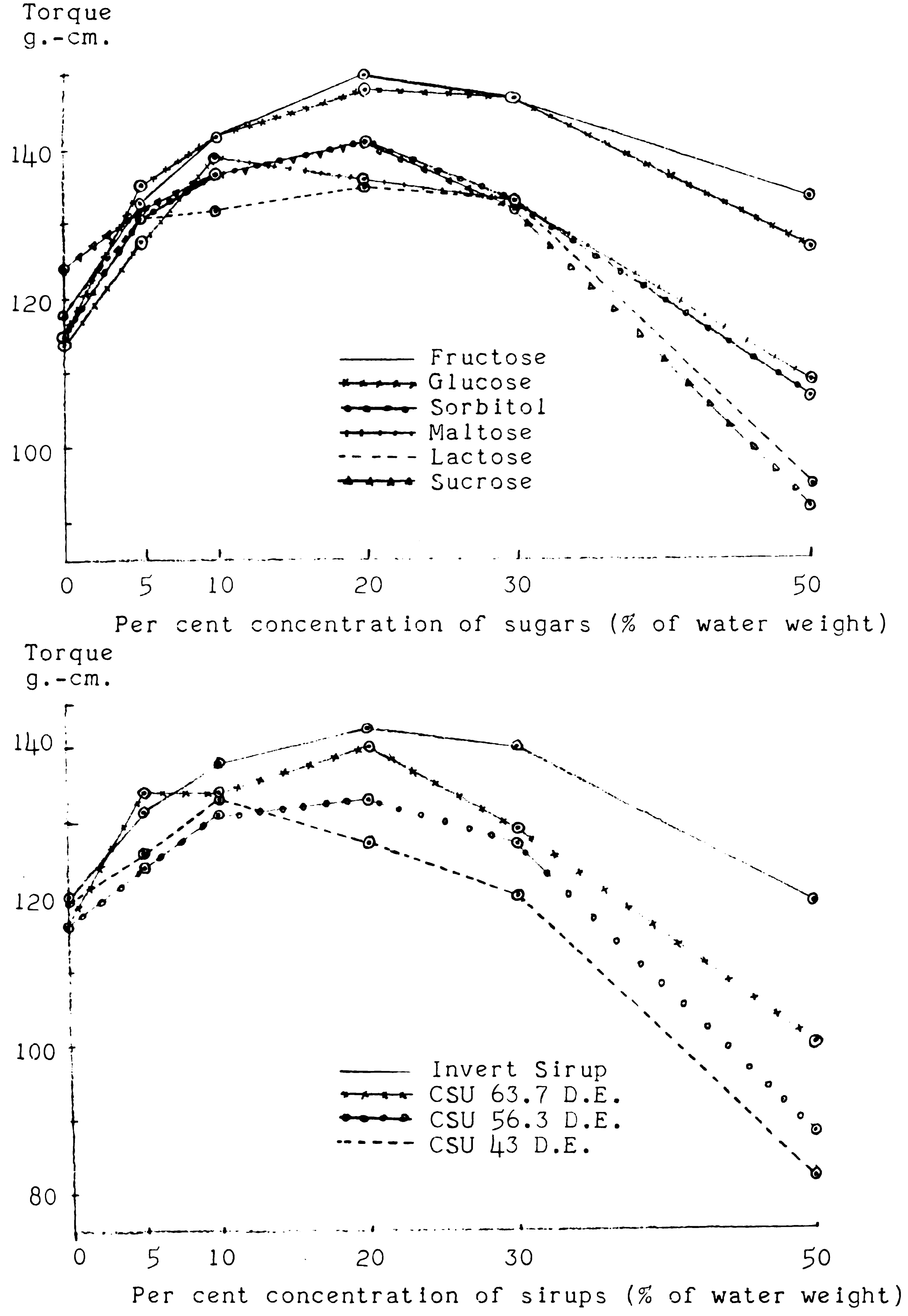

Figure 5. Effect of per cent concentration of sugars and sirups on maximum hot-paste viscosity.

Because of the differences in the viscosity effects between the mono- and disaccharides, the molal concentrations of these ingredients were calculated and plotted against the maximum viscosity values of the pastes. This graph, Figure 6, shows the sharp differences in behavior due to the sugars when they are compared on the basis of molal concentrations. Not only does the effect appear to be independent of the molality of the sugar present, but there seems to be no direct relationship between the number of sugar hydroxyl groups present and the viscosity of the pastes. At approximately corresponding molal concentrations (about 1.5 molal) the disaccharides contributed more hydroxyl groups to their respective pastes and the hot-paste viscosities were lower. However, the 50% concentration of a monosaccharide contained a larger total number of sugar hydroxyl groups than this concentration of a disaccharide. The resulting paste had a higher maximum viscosity. The monosaccharides were not as effective in preventing swelling of the granules as were the disaccharides.

The stereochemistry of the sugars may play a part in the gelatinization behavior of the starch.

The analysis of variance for the maximum viscosities, Table V, showed that there were highly significant differences between the averages of the maximum viscosities due to the sweetening agents and to the concentrations used.

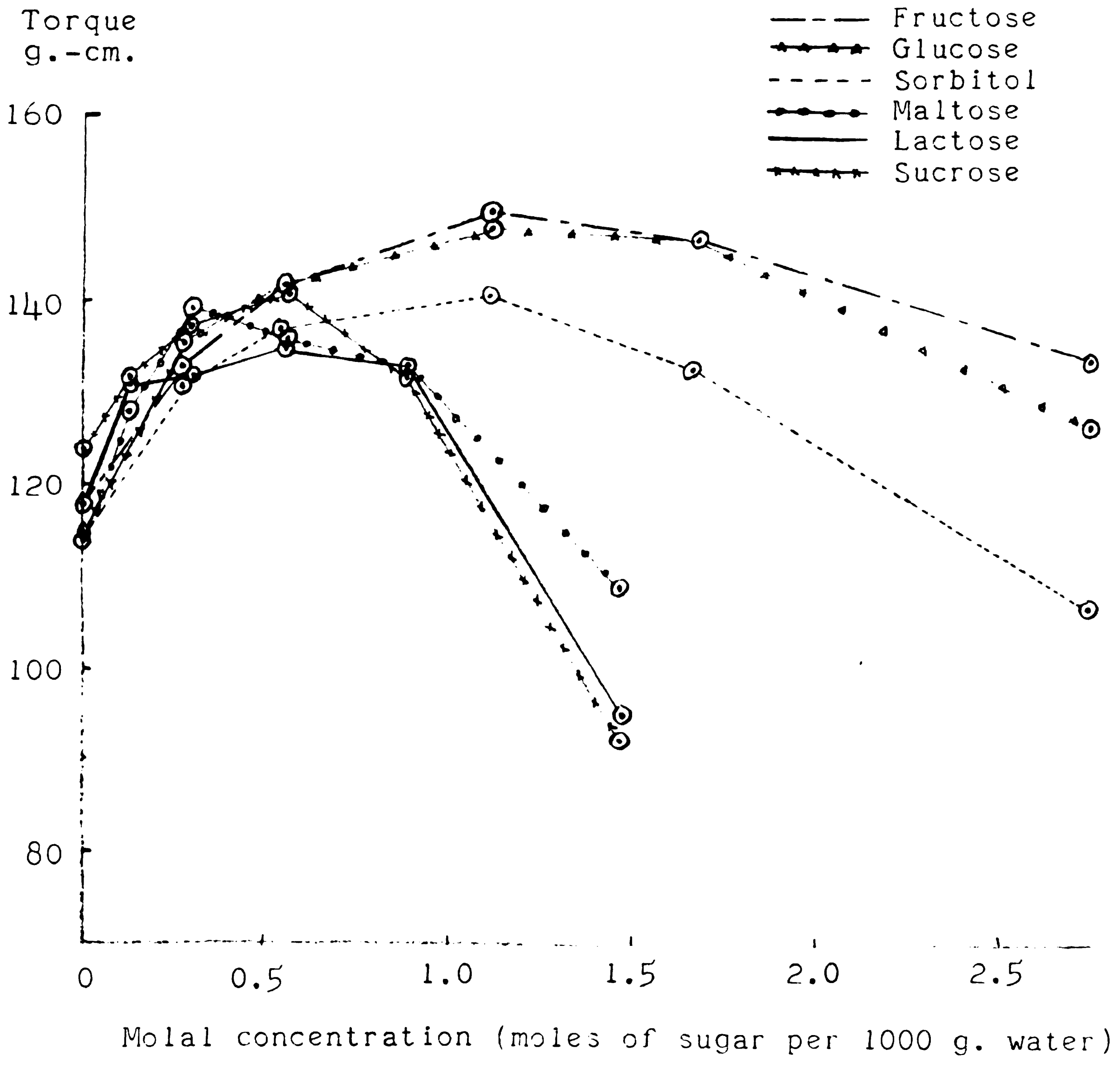

Figure 6. Effect of moles of sugar on maximum hot-paste viscosity.

TABLE V

ANALYSIS OF VARIANCE FOR MAXIMUM HOT-PASTE VISCOSITY

Source of Variance	D.F.	M.S.	F
Total	119		
Between sweeteners	9	475.42	10.00**
Between concentrations	5	3480.24	73.20**
Error	105	47.54	

** Significant at the 1% level of probability

The differences between these averages were tested by the Multiple Range Test (22). The averages pertaining to fructose, glucose, and invert sirup were significantly different from the averages for all the other sweetening agents in their influence on the maximum viscosity. The averages for sorbitol, maltose,and sucrose were significantly different from those for the 43 D.E. and the 56.3 D.E. corn sirups. The averages for the corn sirup hydrolyzed to 63.7 D.E. and for lactose were significantly different from that for corn sirup hydrolyzed to 43 D.E. The averages for the two lower D.E. corn sirups did not vary significantly from each other.

The concentration of sweetening agent affected the viscosity significantly, with the average maximum viscosity at the 50% level differing from the averages of all the other concentrations. The 20% level gave pastes having the highest maximum viscosities in nearly all cases and the average at this level was significantly different from all except the 10% level. The average for the 10% level was significantly different from the 5%, the control, and the 50% levels.

The analysis of variance for each concentration of sweetening agent showed that no significant differences existed in the average maximum viscosities due to the variety of sugar at the 5% and at the 10% levels. Highly significant differences were observed at the 20, 30, and 50% levels. These analyses are presented in the Appendix in Tables IX to XIII.

Temperature

Increasing concentrations of the various sugars and sirups caused progressively higher paste temperatures at the initial rise in viscosity, at maximum viscosity, and at the terminal viscosity. With the Corn Industries Viscometer, temperature is a function of the time required to paste the starch mixture. Pastes which were retarded in swelling by the sugar present tended to reach higher temperatures before reaching maximum viscosity. The temperatures at maximum viscosity are listed in Table VI for all the sweetening agents.

Gel Strength

The effects of the different sweetening agents on the gel strength of the cornstarch pastes, aged 18 hours in a refrigerator, were qualitatively the same. A few of the sweeteners increased the gel strength slightly when added as 5% of the water weight, but in general all the sugars

TABLE VI

PASTE TEMPERATURE AT MAXIMUM VISCOSITY*

Sugars	Sugar Concentration (% of Water Weight)					
	0%	5%	10%	20%	30%	50%
Fructose	90.2	90.2	90.3	91.0	91.3	93.5
	90.5	90.2	90.5	91.0	91.8	94.0
Glucose	90.2	90.3	91.0	91.5	92.4	95.2
	90.5	90.8	91.0	91.8	92.8	95.7
Sorbitol	90.2	90.4	90.6	92.0	93.2	96.2
	90.4	90.7	91.0	91.7	93.0	96.0
Lactose	90.0	91.0	92.0	92.4	94.5	97.7
	90.3	91.0	91.5	93.0	94.3	97.8
Maltose	90.3	90.3	91.0	92.0	93.4	96.2
	90.5	91.0	91.0	92.0	93.5	96.0
Sucrose	90.3	90.8	91.5	92.8	94.9	97.7
	90.5	91.0	91.8	93.0	95.0	97.5**
Sirups						
Invert Sirup	90.3	91.0	91.0	92.2	93.3	96.0
	90.3	90.8	91.0	92.0	93.1	96.0
CSU 63.7 D.E.	90.2	90.8	91.4	92.3	94.0	97.0
	90.3	91.0	91.8	92.7	94.3	97.0**
CSU 56.3 D.E.	90.5	90.8	91.7	93.2	94.5	97.0
	90.5	91.0	91.0	93.2	94.3	97.0**
CSU 43 D.E.	90.3	90.4	91.0	92.5	93.7	94.0
	90.3	91.2	92.0	92.5	93.7	96.5**

* °C.

** No maximum reached

and sirups progressively decreased the gel strength. At the 50% level, the gels containing glucose and fructose had very tender gel structure which broke easily, while the other pastes exhibited no gel structure. Instead thick sirupy liquids resulted. Table VII gives the gel strength of each of the samples. Each value is an average of triplicate tests. At the 50% concentrations, in all samples except those containing monosaccharides, the torque values are actually a measure of the consistency of the resulting sirupy liquids rather than of gel strength.

Figure 7 shows the effect of concentration of fructose, glucose, sucrose, and invert sirup on the gel strength. Fructose-containing gels were stronger than the others at all levels. Glucose gave more tender gels than fructose but observations on samples during testing showed that gel structure was actually present in all samples. Pastes containing sucrose and invert sirup gave weaker gels than the others at corresponding sugar levels, and at the 50% level all signs of gel structure disappeared.

Results appear to indicate a relationship between the gelatinization history and strength of the resulting gels. Meyer and coworkers (38) hypothesized that the formation of starch gels involved the association of the free ends of amylose chains partially diffused from the swollen starch granules with one end remaining fixed in the crystallite . regions of the granule or granular segment. Thus bonds

TABLE VII

EFFECT OF SUGARS AND SIRUPS ON GEL STRENGTH*

Sugars	Sugar Concentration (% of Water Weight)					
	0%	5%	10%	20%	30%	50%
Fructose	149	166	163	147	96	44
	149	152	152	132	95	39
Glucose	149	149	147	101	68	24
	142	150	142	106	82	27
Sorbitol	150	162	138	117	76	26
	143	159	144	101	71	25
Lactose	164	164	137	92	63	17
	151	150	129	94	57	16
Maltose	154	144	130	95	64	18
	141	142	137	92	68	21
Sucrose	157	149	130	98	60	18
	145	128	123	82	46	12
Sirups						
Invert Sirup	152	159	146	109	73	24
	138	144	139	101	67	26
CSU 63.7 D.E.	139	148	129	85	50	16
	140	141	123	91	53	15
CSU 56.3 D.E.	151	135	111	77	53	14
	150	134	109	80	43	11
CSU 43 D.E.	147	138	124	91	55	11
	144	132	114	80	52	15

* g.-cm. of torque

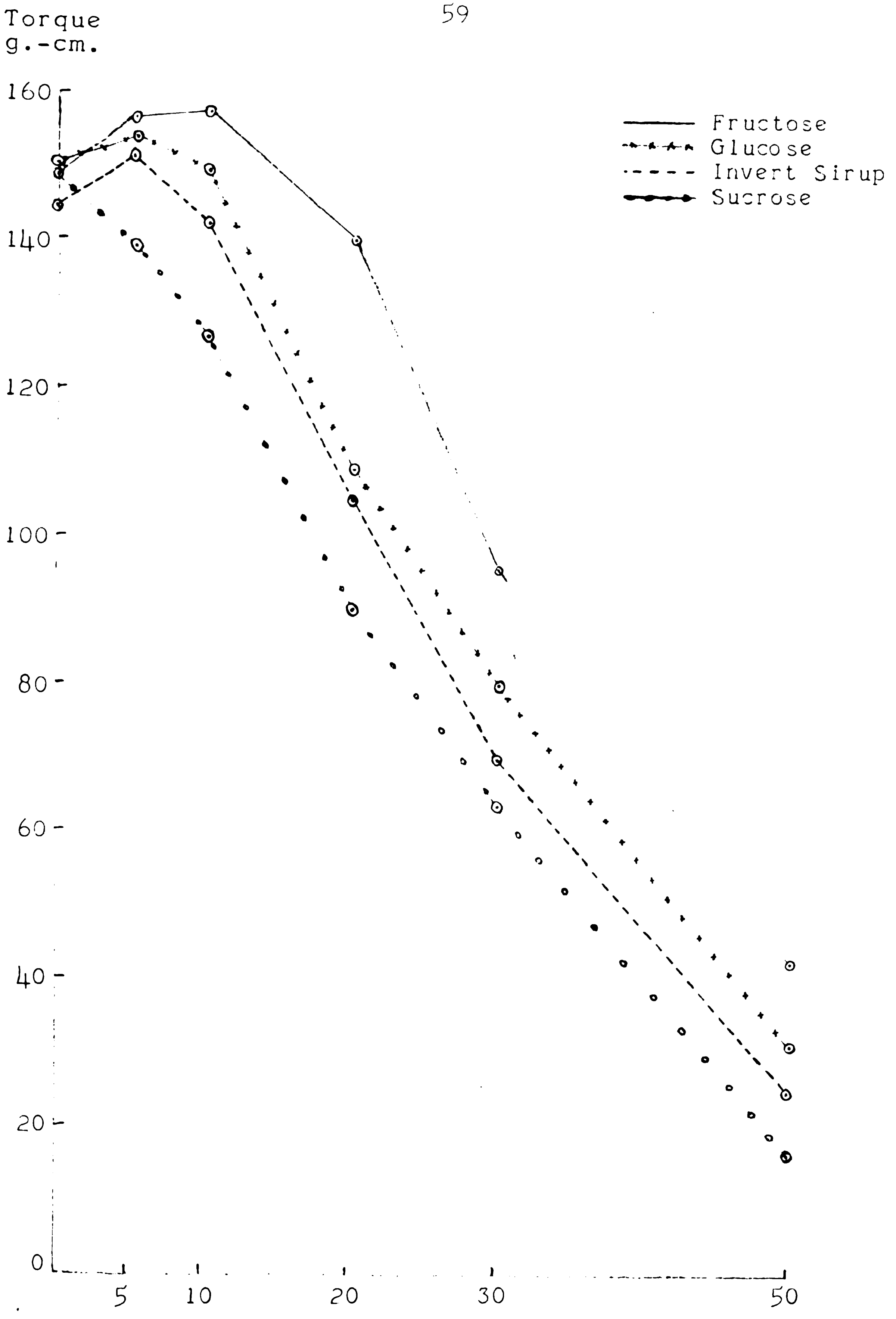

Figure 7. Effect of per cent concentration of fructose, glucose, sucrose, and invert sirup on gel strength.

would be formed between the swollen granules, giving rise to a gel structure. A considerable degree of swelling of the granules would be necessary before the amylose would be sufficiently loosened from the micellar structure in the granule for such gel formation to be possible. If the gelatinization history indicates such swelling with rupturing of some of the granules, as evidenced by a decrease in viscosity, then the pastes would be expected to set a gel.

Figure 1 showed that the pastes containing fructose and glucose, the sugars giving the gels of highest strength, also gave higher maximum viscosities than the other sugars and sirups at all levels, except the 5% level. They also exhibited more breakdown in viscosity than the other pastes. These results then indicate that those pastes in which the granules are more highly swollen, or even partially ruptured, give gels of higher strength.

Figure 8 shows the effect of concentration of glucose, maltose, and the three corn sirups on the gel strength. Differences in the influence of these sweetening agents are significant in only a few cases as noted later in the analysis of variance. However, again the strength of the resulting gels can be compared with the gelatinization characteristics of the pastes, Figure 1. The pastes containing glucose attained a higher maximum viscosity than the others, and somewhat more breakdown in viscosity following the maximum. The highly swollen granules with some ruptured ones acted to

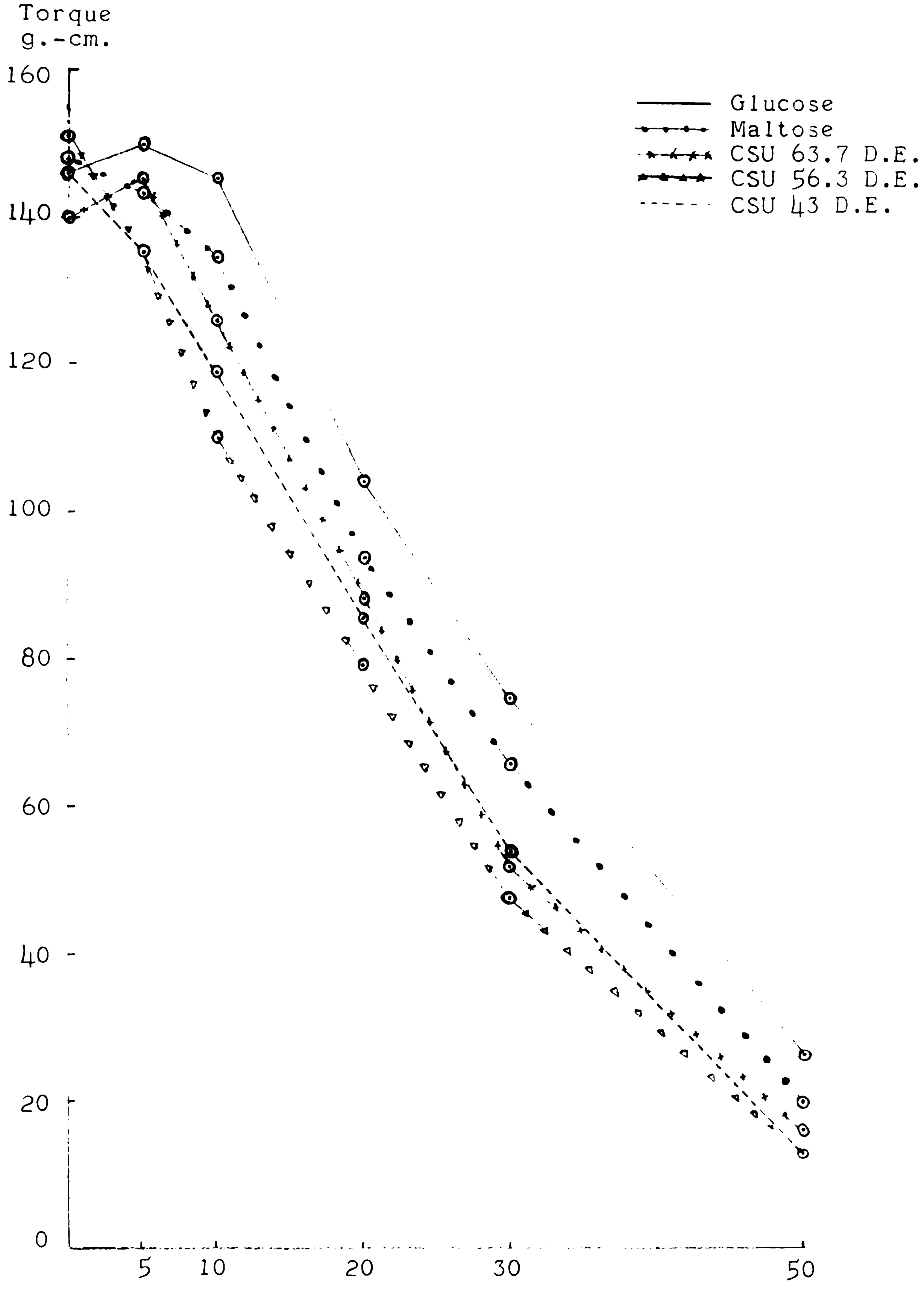

Figure 8. Effect of per cent concentration of glucose, maltose, and three corn sirups on gel strength.

give some structure to the gel, even at the 50% level. The other sweeteners in this set produced no gels at the 50% level and weaker gels by comparison at the other levels.

A comparison of the effect of the moles of sugar on the gel strength is made in Figure 9. This graph shows sharp differences in the gel strength as influenced by mono- and disaccharides. In general all of the disaccharides studied gave the same effects. Glucose and sorbitol were very similar, while fructose interfered the least with gel formation. Except for the position of the glucose curve, these results are analagous to those obtained in Figure 6 where the maximum hot-paste viscosity is shown as affected by the molal concentration of the sugars.

The degree to which the various sugars interfere with gel formation is significantly different. The mechanism of gel formation is not well enough understood to explain why the sugars showed different effects on the gel characteristics. Pasting history appears to offer some basis for an explanation but the reasons for the different effects of the various sugars on paste history is not understood. The degree to which the various sugars interfere with hydrogen bonding of the amylose chains must also be considered as a possible factor affecting gel formation.

The analysis of variance for the gel strength data, Table VIII, showed that the differences due to sweetening agents and to concentrations used were highly significant.

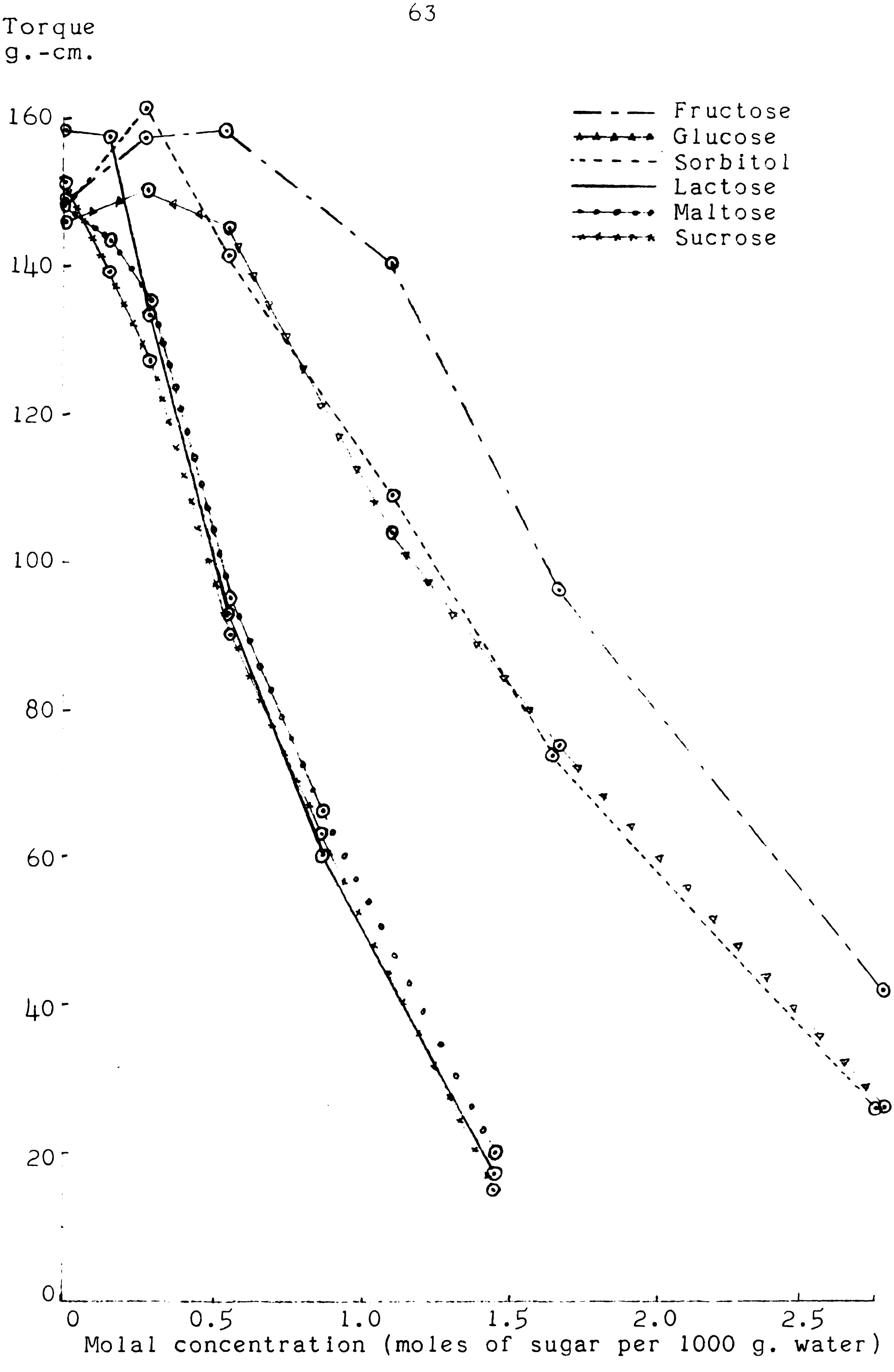

Figure 9. Effect of moles of sugar on gel strength.

TABLE VIII

ANALYSIS OF VARIANCE FOR GEL STRENGTH

Source of Variance	D.F.	M.S.	F
Total	119		
Between sweeteners	9	1261.40	19.50**
Between concentrations	5	52430.79	810.73**
Error	105	64.67	

** Significant at the 1% level of probability

When tested by the Multiple Range Test (22), the average gel strength of the fructose gels was found to be significantly different from all the other averages. The average pertaining to the sorbitol gels was significantly different from those of maltose, sucrose, and the corn sirups. Those averages for glucose, invert sirup, and lactose were significantly different from those for sucrose and the corn sirups, while the maltose average differed significantly from those for the two lower D.E. corn sirups. The averages for sucrose and the corn sirups did not differ significantly from each other.

The concentration of sugars and sirups caused highly significant differences in gel strength. The average gel strength for each concentration above 5% was significantly different from the average for every other concentration. No significant differences existed between the average strength of the control gels and that of the gels containing 5% sweetening agent.

The analysis of variance for each concentration of sweetening agent showed highly significant differences in the averages of the gel strengths due to the variety of sugar or sirup at the 10, 20, 30, and 50% concentrations. The 5% level showed significant differences due to the sweetening agent present. These analyses are presented in the Appendix in Tables XIV to XVIII.

SUMMARY

The influence of ten different sugars and sirups on the viscosity and gel strength of 5% cornstarch pastes was studied. Fructose, glucose, sorbitol, lactose, maltose, sucrose, invert sirup, and three corn sirups (63.7, 56.3, and 43 D.E.) were added in such amounts that the dry substance of the sweetening agent was present as 5, 10, 20, 30, and 50% of the total weight of the water.

With all the sweetening agents, the maximum hot-paste viscosity increased as the sugar or sirup solids was increased up to 10% or 20%. Above these concentrations, the viscosity decreased. At the higher concentrations, differences in viscosity due to the type of sweetening agent present were obvious. The monosaccharide-containing pastes had higher maximum viscosities than the pastes containing disaccharides or sirups. At the 30% and 50% levels, the sugars and sirups caused obvious increases in the temperature and time of gelatinization.

At the 5% level, the monosaccharides and some monosaccharide-containing sirups caused an increase in gel strength. Further increases of all of the sugars and sirups caused a decrease in gel strength. These decreases were more marked with the disaccharides and sirups than with the

monosaccharides. At the 50% concentration of sweetening agent, gel structure was present only in the fructose and glucose samples. Thick, sirupy liquids were formed from the other pastes at this sugar level.

CONCLUSIONS

Small but significant differences exist in cornstarch pastes and gels when various sugars and sirups are present in amounts greater than 20% of the weight of the water. The common carbohydrate sweetening agents used in food preparation produce, in general, the same qualitative effect on the gelatinization and gel-forming properties of the starch. Although the direction of influence is generally the same, the results of this study indicate that the direct substitution of one carbohydrate-type sweetening agent for another in starch-containing food products should be undertaken with caution. Aside from affecting flavor, these sweetening agents produce pastes of different viscosities and gels of different strengths when present in the same concentration in a starch and water mixture. These effects might be obscured by the presence of other ingredients in a food mixture, but such influences remain to be investigated.

With all of the sugars and sirups studied, there was a slight increase in maximum hot-paste viscosity up to the 10% or 20% level of concentration. Further increases in concentration of sweetening agent produced a decrease in viscosity. The pastes containing monosaccharides had higher viscosities than those containing disaccharides or sirups at comparable concentrations except the 5% level. Such results indicate that the number of sugar units present in the molecule apparently affects the gelatinization behavior of the starch granules.

There seemed to be no direct relationship between the viscosity of the pastes and the number of sugar hydroxyl groups present. The slight differences between the monosaccharides and among the disaccharides leads to the conclusion that the stereochemistry of the various molecules may play a part in their influence on starch behavior.

The differences in gelatinization behavior seem to show their effects in the resulting gels of the various pastes. The ability of the starch granules to swell sufficiently during pasting so that some amylose diffuses out appears to be necessary for the development of a gel when the paste is cooled. The smaller the interference of a sugar with granular swelling, the smaller is the effect of that sugar on the strength of the resulting gel.

While monosaccharides and some monosaccharide-containing sirups appeared to cause a slight increase in gel strength at the 5% level, subsequent increases of the sweetening agents caused progressive decreases in gel strength. The other sugars and sirups lowered the gel strength at concentrations of 10% and above.

The composition of the various sirups used seemed to explain their effects. The presence of large amounts of fructose and glucose in the invert sirup caused its influence to be closer to that of the monosaccharides than to that of sucrose. With the corn sirups, more comparable behavior to glucose and maltose was noted as the degree of hydrolysis of the sirup and, hence, the concentration of these sugars increased.

Further investigation is needed on the relationship between gelatinization behavior and gel formation and also on the reasons why the various sugars affect these properties of starch to different degrees. The interrelation of these effects with those of noncarbohydrate food ingredients also requires examination.

APPENDIX

APPENDIX

TABLE IX

ANALYSIS OF VARIANCE FOR MAXIMUM HOT-PASTE VISCOSITY AT THE 5% CONCENTRATION OF SWEETENING AGENT

Source of Variance	D.F.	M.S.	F
Total	19		
Between sweeteners	9	.26	1.69
Error	10	.15	

TABLE X

ANALYSIS OF VARIANCE FOR MAXIMUM HOT-PASTE VISCOSITY AT THE 10% CONCENTRATION OF SWEETENING AGENT

Source of Variance	D.F.	M.S.	F
Total	19		
Between sweeteners	9	30.91	1.19
Error	10	25.90	

TABLE XI

ANALYSIS OF VARIANCE FOR MAXIMUM HOT-PASTE VISCOSITY AT THE 20% CONCENTRATION OF SWEETENING AGENT

Source of Variance	D.F.	M.S.	F
Total	19		
Between sweeteners	9	98.35	8.47**
Error	10	11.60	

** Significant at the 1% level of probability

TABLE XII

ANALYSIS OF VARIANCE FOR MAXIMUM HOT-PASTE VISCOSITY AT THE 30% CONCENTRATION OF SWEETENING AGENT

Source of Variance	D.F.	M.S.	F
Total	19		
Between sweeteners	9	146.68	8.47**
Error	10	17.30	

** Significant at the 1% level of probability

TABLE XIII

ANALYSIS OF VARIANCE FOR MAXIMUM HOT-PASTE VISCOSITY AT THE 50% CONCENTRATION OF SWEETENING AGENT

Source of Variance	D.F.	M.S.	F
Total	19		
Between sweeteners	9	587.66	20.91**
Error	10	28.10	

** Significant at the 1% level of probability

TABLE XIV

ANALYSIS OF VARIANCE FOR GEL STRENGTH AT THE 5% CONCENTRATION OF SWEETENING AGENT

Source of Variance	D.F.	M.S.	F
Total	19		
Between sweeteners	9	188.13	3.25*
Error	10	57.90	

* Significant at the 5% level of probability

TABLE XV

ANALYSIS OF VARIANCE FOR GEL STRENGTH AT THE 10% CONCENTRATION OF SWEETENING AGENT

Source of Variance	D.F.	M.S.	F
Total	19		
Between sweeteners	9	378.22	14.19**
Error	10	26.65	

** Significant at the 1% level of probability

TABLE XVI

ANALYSIS OF VARIANCE FOR GEL STRENGTH AT THE 20% CONCENTRATION OF SWEETENING AGENT

Source of Variance	D.F.	M.S.	F
Total	19		
Between sweeteners	9	592.21	11.77**
Error	10	50.30	

** Significant at the 1% level of probability

TABLE XVII

ANALYSIS OF VARIANCE FOR GEL STRENGTH AT THE 30% CONCENTRATION OF SWEETENING AGENT

Source of Variance	D.F.	M.S.	F
Total	19		
Between sweeteners	9	422.08	13.52**
Error	10	31.20	

** Significant at the 1% level of probability

TABLE XVIII

ANALYSIS OF VARIANCE FOR GEL STRENGTH AT THE 50% CONCENTRATION OF SWEETENING AGENT

Source of Variance	D.F.	M.S.	F
Total	19		
Between sweeteners	9	155.93	28.09**
Error	10	5.55	

** Significant at the 1% level of probability

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