EFFECT OF REPLACEMENT SUGARS
ON VISCOSITY OF FRUIT PRESERVES

by

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EFFECT OF REPLACEMENT SUGARS
ON VISCOSITY OF FRUIT PRESERVES

INTRODUCTION

According to the sixteenth census of the United States, the fruit preservers' industry produced in 1939 a pack of jams, jellies, preserves, and fruit butters valued at $37,979,678.\(^1\) In the manufacture of these products 122,183,909 pounds of sugar, valued at $5,506,094 were used. Of the sugar thus utilized, 42,480,643 pounds were beet; 74,078,757 pounds were cane; and 5,224,529 pounds were corn. If, on the average, 60 percent of the fruit preserve products consisted of sugar added in processing, then the reported values correspond to a pack requiring 81,000,000 pounds of fruit resulting in 203,000,000 pounds of jams, jellies, and fruit preserves.

THE FRUIT PRESERVE

Fruit preserves, or jams, are essentially fruit jellies in which the finished product retains the fruit pulp. The product, to be acceptable to the consuming public, must have, in addition to the characteristic fruit color, flavor and aroma, a pleasing consistency. It must be neither thin and watery nor stiff and gummy. Consequently, the property of viscosity as applied to this product is of primary importance to the manufacturer.
With the demonstrable advantages to color and flavor of the finished preserve, where a part of the traditionally used sucrose is supplanted by dextrose, or even more advantageously by high conversion corn syrups, it has become a matter of industrial as well as scientific interest to learn the effect of such replacement, where it has been practiced, upon some of the physical properties of fruit preserves. Ohm,\(^{(2)}\) working on relative viscosities of pectin colo, studied the effects of various acids and sugars and in connection with this work made observations on the nature of jellies using dextrose, fructose, and lactose, as well as sucrose, as the sugar component. His conclusions were that pectin-acid-sugar jellies containing dextrose were less firm in appearance and less stable than those containing sucrose. Kluehl and Dehn,\(^{(12)}\) reviewing the work of Cole, Cox, and Joseph, state that dextrose may be substituted for sucrose in the pectin-sugar-acid gel as long as the concentration is correct. They point, however, to the work of Fiedler who stated that inversion of sucrose by boiling may prevent gel formation although the jelling power of the pectin remains undestroyed. These workers, however, did not consider the partial replacement of sucrose by dextrose or by commercial syrups containing dextrose and other corn starch conversion products. It is with this information used in
mind that the present study of the effect on viscosity of replacement of sucrose by corn conversion products was undertaken.

In this study experimental packs of preserves made from strawberries, peaches, Loganberries, Boysenberries, and raspberries were prepared embodying the replacement of varying amounts of sucrose by dextrose and two corn conversion syrups for comparison with each other and with preserves made with the addition of sucrose only. The results of these studies may be of value to both the sugar manufacturer in guiding his manufacturing process and technical sales recommendations and to the preserve trade in its use of replacement sugars.

THE PECTIN GEL AND VISCOSITY

Pectin, present in fruit and vegetable materials, is a reversible hydrophilic colloid which forms opalescent solutions which exhibit the Tyndall effect and other manifestations of typical colloidal behavior. Pectin is weakly electro-negative and may be precipitated by oppositely charged metal ions under proper conditions overcoming its strong hydroxide proportion. On the other hand, when the pH of the solutions is properly regulated, the familiar rigid gel is readily formed by dehydrating agents which reduce its association with water. It is pointed
out by Cortner(3) that pectin sols differ from most hydrophilic sols in that the pectin micelle is larger, in reality a "gel fragment," and for this reason is so readily precipitated by dehydrating agents such as alcohol, acetone, ammonium sulfate, and sugar solutions.

In the theoretical concept of a fruit jelly, the original three-phase system consisting of pectin-water-sugar is transformed into a two-phase system of an emulsion character consisting of hydrated pectin and hydrated sugar. The pectin micelles form the framework of the jelly and the sugar solution is contained in the interstices. The viscosity measurement, as here expressed, will then be an index of the cumulative effect of the strength of the pectin fibrils and the viscosity of the contained sugar syrup. The problem of determination of viscosity of a fruit preserve, then, resolves itself into the measurement of that physical property in a typical colloidal gel— with all of its attendant difficulties—complicated by the presence of minute to very large pieces of the fruit itself. It may be assumed, however, after the preserving process has been completed, that the individual fruit pieces have established an equilibrium, after an adequate time interval as evidenced by constant refractometer readings, of the soluble materials with the continuous phase. If this is true, then colloidal composition inside the fruit piece
will be the same as that outside and there remains only the necessity of removing the effect of the fibrous surfaces by mechanical reduction of their size to particles that are small enough to afford no practical interference with the measurement of viscosity by the method employed. Reconstitution of the gel structure, after rendering thus the whole mass sufficiently homogeneous, is accomplished by heating to a temperature slightly above the liquefying point and cooling to permit reformation of the gel.
Figure 1

Diagrammatic representation of the pectic acid molecule according to Nanji, Patton and Ling\textsuperscript{(12)}:

\[ \begin{align*}
\text{HOOC} & \quad \text{A} \\
& \quad \text{B} \\
\text{A} & \quad \text{COOH} \\
\text{HOOC} & \quad \text{A} \\
& \quad \text{C} \\
& \quad \text{COOH}
\end{align*} \]

A = Galacturonic acid  
B = Arabinose  
C = Galactose

Combination by 1:5 glucosidic linkage

---

Relationships of \( \alpha \)-galactose, \( \delta \)-galacturonic acid, and \( \lambda \)-arabinose:

\[
\begin{align*}
\text{CHO} & \quad \text{CHO} \\
\text{HO-CH} & \quad \text{HO-CH} \\
\text{H} & \quad \text{H} \\
\text{HO-C} & \quad \text{HO-C} \\
\text{H} & \quad \text{H} \\
\text{CH}_2\text{OH} & \quad \text{COOH}
\end{align*}
\]

\( \alpha \)-galactose  \quad \delta \)-galacturonic acid  \quad \lambda \)-arabinose
DESCRIPTION OF REPLACEMENT SUGARS

The corn conversion products used in these experiments were:

3. Corn syrup (CSU). Corn syrup of lower purity (sugar content) but higher solids than argose.

Both Argose and CSU contain non-sugar solids resulting from incomplete conversion of corn starch.

THE TORSIONAL VISCOMETER

A torsional viscometer (9) is an instrument for determining the viscosity of a liquid by a torsional balance and usually consists of two concentric cylinders, one of which has angular motion about their common axis. The torsional viscometer usually encountered is of the commercial type, such as the Stormer or MacMichael, which cannot be used in determination of absolute viscosity without previously calibrating the instrument by use of a reference liquid.

The Stormer type of apparatus consists of concentric cylinders, the outer one of which contains the sample and the inner one of which is connected by means of cord and pulleys to a weight. When the weight is released it falls vertically, causing the inner cylinder to revolve.
at a speed governed by the viscous resistance of the sample material. A revolution counter enables the operator to determine the number of revolutions completed by the inner cylinder in a given time interval. The number of revolutions will then be proportional to the viscosity of the sample material.

In the Haake-Michael instrument the outer cylinder, containing the sample, is revolved at a constant speed. The inner cylinder is suspended by a fine wire forming a torsional pendulum. As the outer cylinder is revolved, the inner cylinder rotates until the torsional force of the suspending wire balances the viscous resistance and then remains in a fixed position. A reading may then be made. The inner cylinder, or pendulum, consists of a tube which encloses the wire and has a dial near the point of support. The dial is graduated from 0 to 300 for reading the angular deflection of the pendulum. A selection of wires is supplied with the machine to allow the determination of a wide range of viscosities from highly mobile liquids to heavy oils and syrups.

MEASUREMENT OF VISCOSITY

Viscosity is a physical property of fluids, somewhat difficult of definition—although it is usually regarded as a manifestation of internal friction—and much
more difficult of precise measurement.

I. Theoretical considerations; \( (S, G) \)

When a fluid flows, or when its form is altered, internal force occasioned by the relative motion of contiguous portions of the fluid offer resistance to the force causing flow or change of form. In considering the mechanism of viscosity, two parallel planes A and B are separated by a layer of fluid of \( S \) thickness. If a shearing force \( F \) per unit area is applied to A there will result a velocity \( V \) in reference to B. The velocity of each stratum, between A and B, will be proportional to its distance from B and the rate of shear \( \frac{dV}{dS} \) is constant throughout a homogeneous fluid, under these conditions. The layer of molecules is contact with the plane surface (A or B) is attracted by the molecules of the surface and it is generally assumed that this layer remains stationary and viscous flow is considered as a sliding motion of adjacent liquid layers over one another. Since the force \( F \) is required to maintain uniform velocity, it must be opposed by another which is equal in amount, due to the internal friction of liquid layers sliding in contact with each other. The ratio of this force to the rate of shear is called the coefficient of viscosity and is denoted by the symbol \( \eta \), where \( \eta = \frac{FS}{V} \).
Figure 2

MacMichael and Stormer Viscometers
II. Selection of the Viscometer

In the case of fruit preserves, here under consideration, the property to which we refer as viscosity is obviously quite different from the example of a simple solution of a colloid whose viscosity varies directly with concentration. In the product are to be found solid particles of large and small size, colloids in solution, and colloidal particles distributed throughout the heterogeneous mass. Will the application of shearing stress result in truly viscous flow; will there merely be elastic deformation which will disappear when the stress is removed; or, will the application of shearing force above a definite value result in deformation indicating the property of plasticity? Obviously these are considerations which must be taken into account when the selection of the method for measurement of the property is undertaken.

It was originally thought, when the project was planned, that the Stormer viscosimeter would be a suitable instrument for use. Preliminary trials, however, showed that the particular apparatus at hand was incapable of coping with the high viscosity values encountered in preserves. Even when the original cylindrically-shaped spindle supplied by the manufacturers had been replaced by a specially made disc and shaft of much smaller surface
area, the operation was erratic and therefore further consideration of this particular apparatus was discontinued.

Attention was turned to the MacMichael viscometer which has been used industrially for viscosity measurements covering a wide range. Preliminary tests with this instrument showed that it was readily adaptable to work with preserves, with but one apparent fault.

It will be remembered that most of the preserves contained relatively large pieces of fruit and the difficulty experienced with the operation of the MacMichael instrument arose when, with the sample cup rotating, one or more of these pieces came in contact with the inner cylinder. The effect, then, of one layer of medium sliding over another layer held fast in contact with the cylinder, was lost and momentary slippage occurred. Pratical removal of the fruit pieces was, of course, impossible, but it was found that reduction of their size by treatment described below made their effect negligible in so far as obtaining a constant reading, without apparent slippage, was concerned.

The MacMichael viscometer has the further advantage that, if plasticity is a significant factor in producing the property designated as "consistency," then the degree to which it is responsible will be indicated by the behavior of the instrument. It is accepted that a
criterion of plasticity is the requirement that an initial shearing force be imposed before flow, corresponding to viscous flow, can begin. The magnitude of this force required to overcome the elasticity of the material is called the "yield value" and in measurement on the MacMichael instrument is shown when the dial does not return immediately to the zero position upon cessation of the rotation of the outer cylinder. The value, to which the dial does return, when compared with the total reading, indicates what fraction of the total force applied was used in overcoming what might be termed the elastic resistance of the product.

Until measurements were made, it was impossible to predict to what extent, if any, plasticity played a role in influencing the "consistency" of the preserves, but experimental results showed an insignificant lag in returning to the zero position in all of the samples tested.

III. Calibration of the MacMichael Viscometer

To express the viscosity of a material, either absolute or relative units may be used. The absolute unit is named the poise and its submultiple, one hundredth as large, is called the centipoise. It just so happens that the viscosity of water at 20°C is almost exactly one centipoise (1.005 cp) so that correlation of absolute and relative units is very simple. It was realized early in
this study that the results would be of little value if a comparison of viscosities was made between samples prepared from the same fruit but with the use of different sugars unless an attempt was made to express the results in viscosity units rather than in arbitrary units employed by the particular type of viscometer used.

When the MacMichael viscometer was found to be satisfactory for operations in the required range, it was then necessary to calibrate the instrument using a reference liquid of known, high viscosity. Unfortunately no appropriate liquid was at hand and it then became necessary to determine the viscosity of a liquid sufficiently viscous to be of value. Such a liquid was found in argose which has been found to be truly viscous, relatively non-hygroscopic and quite easily handled.

In order to determine the absolute viscosity of argose, the falling sphere method was selected because of its relative simplicity of apparatus and manipulation. The general method of Bishop and Young\(^7\), who demonstrated the truly viscous nature of corn syrup, was followed with acceptable results (see Table I). The reference liquid was then used in the calibration of the MacMichael machine using the torsion wire whose degree of stiffness allowed operation within the desired range.

A sufficient quantity of argose was placed in the
<table>
<thead>
<tr>
<th>Sphere</th>
<th>Av. Diam.</th>
<th>Radius</th>
<th>Vol.</th>
<th>Wt.</th>
<th>Density</th>
<th>( \frac{F}{R} )</th>
<th>( \frac{F}{h} )</th>
<th>Time</th>
<th>Temp.</th>
<th>Viscosity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>cm.</td>
<td>cm.</td>
<td>cm³</td>
<td>g.</td>
<td>g/cc</td>
<td>sec.</td>
<td>sec.</td>
<td>cm.</td>
<td>°C</td>
<td>Poise</td>
</tr>
<tr>
<td>Group 1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>0.6351</td>
<td>0.3176</td>
<td>0.1341</td>
<td>1.0455</td>
<td>7.796</td>
<td>0.1792</td>
<td>0.0121</td>
<td>46.7</td>
<td>12.2</td>
<td>25</td>
</tr>
<tr>
<td>B</td>
<td>0.6323</td>
<td>0.3164</td>
<td>0.1327</td>
<td>1.0550</td>
<td>7.800</td>
<td>0.1709</td>
<td>0.0121</td>
<td>46.9</td>
<td>12.2</td>
<td>25</td>
</tr>
<tr>
<td>C</td>
<td>0.6330</td>
<td>0.3165</td>
<td>0.1325</td>
<td>1.0365</td>
<td>7.604</td>
<td>0.1785</td>
<td>0.0121</td>
<td>46.6</td>
<td>12.2</td>
<td>25</td>
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<tr>
<td>D</td>
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<td>0.3168</td>
<td>0.1332</td>
<td>1.0426</td>
<td>7.827</td>
<td>0.1796</td>
<td>0.0121</td>
<td>46.2</td>
<td>12.2</td>
<td>25</td>
</tr>
<tr>
<td>E</td>
<td>0.6327</td>
<td>0.3164</td>
<td>0.1326</td>
<td>1.3060</td>
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<td>0.1793</td>
<td>0.0121</td>
<td>46.5</td>
<td>12.2</td>
<td>25</td>
</tr>
<tr>
<td>Group 2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A₂</td>
<td>0.4698</td>
<td>0.2549</td>
<td>0.0545</td>
<td>0.4255</td>
<td>7.836</td>
<td>0.1331</td>
<td>0.009</td>
<td>74.5</td>
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<td>25</td>
</tr>
<tr>
<td>B₂</td>
<td>0.4757</td>
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<td>C₂</td>
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<td>0.2589</td>
<td>0.0556</td>
<td>0.4350</td>
<td>7.824</td>
<td>0.1324</td>
<td>0.009</td>
<td>59.8</td>
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<td>D₂</td>
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<td>0.4582</td>
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<td>0.009</td>
<td>73.6</td>
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<td>25</td>
</tr>
<tr>
<td>E₂</td>
<td>0.4730</td>
<td>0.2585</td>
<td>0.0554</td>
<td>0.4360</td>
<td>7.670</td>
<td>0.1340</td>
<td>0.009</td>
<td>72.2</td>
<td>12.2</td>
<td>25</td>
</tr>
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</table>

Average (omitting °C) 344

Equation: 
\[ n = \frac{2 \pi \pi^2 (S - o) t}{9 \pi \left(1 + 2.4 \frac{F}{R}\right) \left(1 - 3.3 \frac{F}{R}\right)} \]

- \( n \) = Viscosity in poise
- \( S \) = Acceleration of gravity (980 cm/sec²)
- \( r \) = Radius of sphere in cm.
- \( s \) = Density of sphere in g/cc
- \( c \) = Density of liquid in g/cc
- \( t \) = Time of fall in seconds
- \( L \) = Distance of fall in cm.
- \( R \) = Radius tube in cm.
- \( h \) = Total height liquid in cm.
sample cup to fill it to a predetermined depth, as indicated by a standard depth gauge. The cup and sample were brought to 25° C. and the MacMichael reading, at 54 revolutions per minute using wire number 26, observed. The average of six readings was 162 MacMichael units. Since the viscosity of argose at 25° as determined by the falling sphere method was found to be 350 poises, then each MacMichael unit was equivalent to 350 poises, or 2.16.

EXPERIMENTAL PROCEDURE

I. Preparation of Samples

In order that a basis be established for comparison of preserves containing no corn sugar products with those containing either dextrose or corn syrup, it was necessary to devise a technique which produced a definite content of soluble solids in each number of series of preserves made from a particular fruit. It was decided that the soluble solids content should be 69 percent (as determined by refractometer). One-half of one percent was established as the maximum allowable deviation. The use of cooking methods employing a steam-jacketed kettle, as in commercial preserve manufacture, and attempting to determine the exact end point by boiling temperature or refractive index met with little success in obtaining the
desired uniformity.

The soluble solids content of a preserve as measured by the refractometer is almost always less after a period of standing following cooking. It is always necessary to allow for this "dropback" of solids content of the syrup upon which the measurement is made and the dropback will vary with the rate of cooking and other factors, not excluding the type of sugar used, which control penetration of sugar into the fruit and establishment of equilibrium. The phenomenon of mutarotation\(^4\) may also be a factor in this connection when an observation of refractive index is made soon after the preserves have cooled. Further, since the fruit used was frozen with added sugar, the rate of freezing and the thawing time and temperature materially affect initial sugar inversion and penetration which are finally reflected in the magnitude of the dropback from the observed endpoint at the completion of cooking.

The amount of natural sugar present in the frozen mixture was known from original analyses of the fruit before freezing. Also known was the amount of sugar added in each case, at the time of preparation for freezing. With this information at hand, the amounts of each kind of sugar to be added to make a 50-50 cooking mixture could be calculated. The final weight of the mixture, after
cooking, which would contain soluble solids at 69 percent (using a definite initial weight of fruit-sugar mixture) could be calculated. In this manner it was possible to obtain positive assurance that any member of a series of preserves prepared, using different sugar mixtures, would have the same soluble solids content as that of any other member of the series and a valid comparison between the two could be made.

The sugar calculations were made on the dry basis and correction for water content applied where replacement of sucrose by dextrose, argose, or corn syrup were used. The following calculations for peach preserves are typical.

A. Data:

1. Peaches .............. 8.5% soluble solids
2. Freezing mixture .... 4 parts fruit and 1 part sucrose
3. Preserves cooked with equal parts fruit and dry sugar.
4. Moisture contents used for purposes of calculation:

   Sucrose .............. 5%
   Dextrose .............. 8.5%
   Argose .............. 18.3%
   Corn syrup ........... 13.3%
5. The samples prepared for each fruit to contain sucrose or sucrose and corn sugar products as follows:
   a. 100% sucrose
   b. 90% sucrose, 10% dextrose
   c. 80% sucrose, 20% dextrose
   d. 60% sucrose, 40% argose
   e. 30% sucrose, 70% argose
   f. 50% sucrose, 10% corn syrup (CSU)
   g. 80% sucrose, 20% corn syrup (CSU)

B. Calculations:

For each 100 grams of the frozen mixture, the following applies:

1. 100 grams contain 50 grams original fruit and 50 grams added sucrose.

2. To make a 50-50 mixture it is necessary to add 60 grams sugar (dry basis).

3. Soluble solids content of original fruit (peaches) equals 8.6%.

Then:

\[ (0.085) \times (80) = 6.8 \text{ grams soluble solids from fruit} \]

\[ 6.8 + 60 = 66.8 \text{ grams total soluble solids present} \]

\[ 66.8 = 69\% \text{ final product} \]
Final product = 125.94 grams after cooking.

4. Keeping in mind that part of the sucrose is already present from the freezing mixture, the following amounts of sugar will be added for the cooking mixtures for each 100 grams of frozen mixture:

Table II

<table>
<thead>
<tr>
<th>Sugar</th>
<th>Weight of sugar in grams</th>
<th>Sucrose</th>
<th>Dextrose</th>
<th>Argose</th>
<th>CSU</th>
</tr>
</thead>
<tbody>
<tr>
<td>100% sucrose</td>
<td></td>
<td>60.00</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>90% sucrose</td>
<td></td>
<td>52.00</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10% dextrose</td>
<td></td>
<td></td>
<td>8.74</td>
<td></td>
<td></td>
</tr>
<tr>
<td>80% sucrose</td>
<td></td>
<td>44.00</td>
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<tr>
<td>20% dextrose</td>
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<td></td>
<td>17.43</td>
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<tr>
<td>90% sucrose</td>
<td></td>
<td>52.00</td>
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<td>9.78</td>
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<td>10% argose</td>
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<td>20% CSU</td>
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</tbody>
</table>

C. Cooking Operations:

The fruit was removed from freezing storage about twenty-four hours previous to cooking and allowed to thaw at room temperature for approximately twenty-four hours. The mixture was placed on
draining screens and the fruit and syrup collected and weighed separately. The fruit and syrup were then each divided into 16 equal portions (14 cooks plus 2 extra) and one portion of syrup poured back on one portion of fruit. This procedure assured equal amounts of fruit and sugar in each batch for cooking.

Based on the calculation above (B) the required amount of additional sugar was placed with the fruit-syrup mixture and the whole cooked in a stainless steel pan to the required weight. Since the amount of water to be removed was nearly the same in all cases for each fruit, the length of time of the cooking was quite uniform for each series.

After cooking, the preserves were cooled quickly and sealed in glass jars. After allowing sufficient time for dropback, the soluble solid content was checked for each jar by refractometer.

It should be noted that, regardless of deficiencies in some cases, no pectin or acid was added since it was felt that such addition would introduce complicating factors that would make evaluation of final viscosity
results much more difficult.

II. Preparation of Sample for Viscosity Measurement:

After removing from the jar, the sample was mixed thoroughly and passed through a Russell No. 3 food chopper using the nut butter plate. The ground preserves were placed in 6-ounce, screw-capped, wide-mouth jars and, with the cover in place, heated in a water bath at 80° C. After cooling, the samples stood overnight and the viscosity was measured.

III. Control of Temperature

Since the speed of operation of the MacMichael machine obviated the necessity of holding the sample for long periods of time at a constant temperature, control of temperature of the sample was quite easily accomplished. In this work the sample, in its prepared form in the outer cylinder, was placed in a shallow constant temperature bath for an adequate period of time to bring the outer cylinder and the sample to the required temperature. The cylinder was then removed to the machine and the determination of viscosity made within a matter of minutes. Since the temperature differential between the sample and the air of the room was seldom more than one or two degrees, the temperature deviation was too slight
to be of consequence.

IV. Measurement of Viscosity

The actual measurement of viscosity of the preserves followed the same procedure that was described above for calibration of the viscometer. The outer cylinder of the instrument was filled to a standard depth with prepared sample. It was then brought to 25° C. in the constant temperature bath and the MacMichael reading at 34 revolutions per minute, using wire number 26, was observed. The factor 2.16, obtained from the calibration, was used in converting the MacMichael units to absolute units and the results are shown in Tables II to VI.

V. Determination of pH

The determination of pH was made following the viscosity determinations on the preserves, by means of the glass electrode using a Beckman Laboratory Model pH Meter after standardization with carefully prepared buffer solutions.
Figure 3

Constant Temperature Bath
### Experimental Results

#### Table III

**Peach Preserves**

<table>
<thead>
<tr>
<th>Sugar</th>
<th>Sol. Solids by Refractometer as Percent Sucrose</th>
<th>pH</th>
<th>Viscometer Reading</th>
<th>Viscosity Poises</th>
</tr>
</thead>
<tbody>
<tr>
<td>100% Sucrose</td>
<td>69.8</td>
<td>4.16</td>
<td>52</td>
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<tr>
<td>90% Sucrose + 10% dextrose</td>
<td>68.9</td>
<td>4.15</td>
<td>41</td>
<td>88.6</td>
</tr>
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<td>80% Sucrose + 20% dextrose</td>
<td>69.1</td>
<td>4.09</td>
<td>46</td>
<td>99.4</td>
</tr>
<tr>
<td>90% Sucrose + 10% argose</td>
<td>69.5</td>
<td>4.12</td>
<td>52</td>
<td>112.3</td>
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<td>69.5</td>
<td>4.11</td>
<td>47</td>
<td>101.5</td>
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<tr>
<td>90% Sucrose + 10% CSU</td>
<td>68.9</td>
<td>4.08</td>
<td>42</td>
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<tr>
<td>80% Sucrose + 20% CSU</td>
<td>68.1</td>
<td>4.07</td>
<td>40</td>
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</table>

The factor 2.16 (poises per MacMichael unit, cf. calibration of the MacMichael viscometer) was used to convert viscometer readings to absolute viscosities, Tables III through VIII.
<table>
<thead>
<tr>
<th>Sugar</th>
<th>Sol. Solids by Refractometer as Percent Sucrose</th>
<th>pH</th>
<th>Viscometer Reading</th>
<th>Viscosity Poises</th>
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</thead>
<tbody>
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<td>99.4</td>
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<tr>
<td>80% Sucrose + 20% dextrose</td>
<td>70.1</td>
<td>3.47</td>
<td>41</td>
<td>88.6</td>
</tr>
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<td>90% Sucrose + 10% argose</td>
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<td>95.0</td>
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<td>80% Sucrose + 20% argose</td>
<td>69.9</td>
<td>3.44</td>
<td>43</td>
<td>92.9</td>
</tr>
<tr>
<td>90% Sucrose + 10% CSU</td>
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<td>3.46</td>
<td>43</td>
<td>103.7</td>
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<tr>
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<td>3.47</td>
<td>43</td>
<td>103.7</td>
</tr>
<tr>
<td>Sugar</td>
<td>Sol. Solids by Refractometer as Percent Sucrose</td>
<td>pH</td>
<td>Viscometer Reading</td>
<td>Viscosity Poises</td>
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<tr>
<td>10% CSU</td>
<td>69.1</td>
<td>3.33</td>
<td>54</td>
<td>116.6</td>
</tr>
<tr>
<td>80% Sucrose +</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20% ACU</td>
<td>68.6</td>
<td>3.32</td>
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</table>
### Table VI

**Loganberry Preserves**

<table>
<thead>
<tr>
<th>Sugar</th>
<th>Sol. Solids by Refractometer as Percent Sucrose</th>
<th>pH</th>
<th>Viscometer Reading</th>
<th>Viscosity Poises</th>
</tr>
</thead>
<tbody>
<tr>
<td>100% Sucrose</td>
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<td>3.08</td>
<td>47</td>
<td>101.5</td>
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<tr>
<td>80% Sucrose + 10% dextrose</td>
<td>70.2</td>
<td>3.02</td>
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<td>86.4</td>
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<tr>
<td>80% Sucrose + 20% dextrose</td>
<td>70.1</td>
<td>3.03</td>
<td>44</td>
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</tr>
<tr>
<td>80% Sucrose + 10% argose</td>
<td>70.0</td>
<td>3.02</td>
<td>45</td>
<td>92.9</td>
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<tr>
<td>80% Sucrose + 20% argose</td>
<td>69.1</td>
<td>3.05</td>
<td>46</td>
<td>99.4</td>
</tr>
<tr>
<td>90% Sucrose + 10% CSU</td>
<td>70.5</td>
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<td>80% Sucrose + 20% CSU</td>
<td>70.4</td>
<td>3.04</td>
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</table>
### Table VII

Boysenberry Preserves

<table>
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<th>Sugar</th>
<th>Sol. Solids by Refractometer as Percent Sucrose</th>
<th>pH</th>
<th>Viscometer Reading</th>
<th>Viscosity Poises</th>
</tr>
</thead>
<tbody>
<tr>
<td>100% Sucrose</td>
<td>71.3</td>
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<td>112.3</td>
</tr>
<tr>
<td>90% Sucrose + 10% dextrose</td>
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<td>80% Sucrose + 20% dextrose</td>
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<tr>
<td>90% Sucrose + 10% argose</td>
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<td>3.01</td>
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<td>103.0</td>
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<tr>
<td>90% Sucrose + 10% CSU</td>
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<td>3.01</td>
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<tr>
<td>80% Sucrose + 20% CSU</td>
<td>71.1</td>
<td>3.06</td>
<td>45</td>
<td>97.2</td>
</tr>
</tbody>
</table>
DISCUSSION OF RESULTS

1. Soluble Solids

In the section entitled "Experimental Procedure," the ideal sought in preparation of the experimental preserves was indicated. Because of circumstances beyond the laboratory's control, due to war conditions, it was impossible to make the viscosity measurements as promptly as was desired. Consequently, longer storage of the preserves was necessary than had been anticipated and inevitably some dehydration took place. Further, the effects of sugar inversion on total soluble solids, further discussed later, were apparent after the storage period. The resultant soluble solids content of the individual preserves was more variable than was desired. It must be borne in mind, in anticipation of possible criticism, that the soluble solids were determined by means of the refractometer and reported as percent of soluble solids as sucrose. According to Browne and Zerban(10), in a review of the work on solutions containing the same percentages of various sugars, the refractive indices do not differ greatly. It has been established, however, that these differences become progressively greater as the concentration increases. According to these data the refractive indices of 10 percent solutions of sucrose and levulose
differ by an amount corresponding to 0.1 percent sugar, but at 80 percent concentration the difference is equivalent to about 2 percent of sugar. Reliable data have not been established for dextrose solutions and two different authorities, Stolle and Fulvermacher(11), respectively report lower and higher refractive indices for dextrose solutions than for sucrose solutions of the same concentrations.

2. Acidity

The measurement of pH, by means of the glass electrode, following the determination of viscosity shows good agreement, as should be expected between individual members of each fruit series. Since no acid was added in the making of the preserves, it is clearly shown that, for commercial purposes, more effective use of sugar is to be obtained by correcting acid deficiencies in order that optimum conditions be supplied for gel formation. All series except peach and strawberry, however, were below the upper pH limits set by Tarr(9) of 3.46. Strawberry preserves were at the borderline with a range of 3.46 to 3.48.
3. Viscosity

Qualitative differences in sugars used in preparing preserves have not been demonstrated to have a consistent and predictable effect upon the viscosities of the preserves. A very definite trend, however, is observable that in most instances the use of replacement sugars serves to decrease the viscosity of the preserve, although not necessarily in proportion to the quantity of replacement sugar employed. This trend is more clearly apparent in the strawberry and peach series than in the others examined. It might be expected that the high viscosity (cf. falling sphere measurements) of corn syrups, argose and C&U, which contain relatively high percentages of non-sugar starch conversion solids (dextrins, etc.) would increase the final viscosities of preserves in which they were used. The smaller quantities of actual sugars present and available for gel formation, however, when these syrups were used in partial replacement of sucrose, more than compensated for the added viscosity supplied by the syrups and the net result was a lowered viscosity in each of 85 percent of the syrup-containing preserves.

An attempt to find an orderly pattern of viscosities by correlation with soluble solids content was unsuccessful, which again is evidence to support a contention that qualitative differences of component sugars may be
important.

The apparently anomalous character of the viscosity results demands that an explanation be attempted. As previously stated (page 2), Fiedler's work indicated that inversion of sucrose accounted for many instances of jelly failure. Further, Cole, Cox, and Joseph(20) determined the degree of inversion in the acid medium of a fruit jelly. Although the pH of the medium in that case was lower than any encountered in these preserves, the time factor is more than adequately compensatory.

It is inevitable, then, that a consideration must be given to the cumulative effect of the hydrolysis of sucrose which has taken place (a) during the sugaring of fresh fruit for freezing, (b) during freezing, (c) during thawing and tempering, (d) during boiling of the preserves, and (e) during storage of the finished preserves. The effect of this hydrolysis, unfortunately, is not simple as the following discussion will indicate.

It has been accepted that sucrose forms a hexahydrate in water solution(13). The hydrolysis of one molecule of sucrose will then release six molecules of water that were previously unavailable for solvent purposes. One molecule of this water will be used in the hydrolysis and the net gain to the system will be five molecules of free water. On a weight basis, there will also be an
increase in sugar concentration due first to the formation of two molecules of six-carbon sugars with a combined molecular weight of 360 as compared with the molecular weight of sucrose of 342, and secondly to the removal of 18 grams of water from solution for each gram-mole of sucrose hydrolyzed. This increase in sugar concentration, however, will not offset the gain in free water as the following specific example will demonstrate:

If a 68.4 percent sucrose solution is considered there will be present, in 1000 grams of solution, 684 grams of sucrose, and 316 grams of water of which 216 grams are the water of hydration of sucrose hexahydrate and 100 grams exist in the free state. If, then, 50 percent of the sucrose is hydrolyzed, the solution will contain 342 grams of sucrose, 360 grams of monosaccharides, 198 grams of water of hydration, 100 grams of original free-water, and 90 grams of water from the net gain of five molecules of water for each molecule of sucrose hydrolyzed. Instead of containing 68.4 percent of sugar, as it originally did, the solution now contains 70.2 percent but, where previous to hydrolysis there had been present only 100 grams of free water there are now 190 grams.

If, as stated by Gortner, the formation of the pectin gel is the result of dehydration of the pectin
micelle, then the ability of the sugar to act as the de-
hydrating agent must be dependent both upon its ability
to attract the water already loosely held by the pectin
and upon the available quantity of free water in the
system.

The whole line of reasoning, stated above, is con-
troverted by the contention of Clayton(15) who states
that Fiedler's work can be interpreted on the basis of
hydrolysis of pectin by acid and cites the work of
Joseph(16) in preparation of good pectin jellies from
honey containing 69 percent invert sugar. Clayton also
cites Jordan(17) who describes the regular use of invert
syrup in jam manufacture. He further points to the
preparation of jellies by use of glucose syrup or sucrose
inverted by means of invertase to 96 percent inversion
in which no difficulty was experienced with respect to
gel strength, clarity, or syneresis. It must be realized
in this connection that regardless of whether the hy-
drolysis of sugar or the hydrolysis of pectin is the more
important change, the whole subject of "aging" of pectin
gels has been greatly neglected and a valuable field of
inquiry is largely unexplored.

Manji and Norman(18) conducted experiments in which
pectin was hydrolyzed under controlled conditions to yield
the mono-, di-, and trimethyl pectates from pure pectin.
which was considered to be the tetramethyl pectate
(Fig. 1), and attempted to correlate jelling power with
degree of de-methoxylation. According to their findings,
with the removal of more than one methoxyl group from the
pectin molecule, jelling power was entirely destroyed.
They state, "This remarkable result explains why jams
which have been boiled too long will not set. It would
seem that the jelling power of a sample of pectinogen
(pectin) is a function of its methoxyl content, and that
the greater the amount of the tri- and tetra-methyl pectates
present, the greater the jelling power, provided
the other factors concerned are kept constant." The flaw
in their work, which is widely quoted, lies in the fact
that they did not keep "the other factors concerned" con-
stant, for by their method of preparation of the jellies
hydrolysis of sucrose would almost certainly occur with
the possible further de-esterification of the pectin
crude.

On the other hand, Myers and Baker\(^{19}\) state that
jelling power increases with the degree of polymerization
of the pectin molecule and is independent of the number
of radicals or groups such as methoxyl, acetyl, etc.,
that may be combined with the pectic chain. Viscosity,
on the other hand, of pectic solutions is a function of
the molecular weight of the entire pectin molecule and
consequently must vary with both the number of constituents on the chain and with degree of polymerization. Therefore, changes involving the loss of methoxyl groups (hydrolysis), but not involving degree of polymerization, would result in lowered viscosity but not lowered jelling power.

In view of such conflicting findings by authorities in the field of pectin chemistry, it is admittedly difficult to offer a definite and final explanation of the cause of the somewhat irregular results produced by this study. It is clear that the problem should be given further consideration from a different approach by which the troublesome interfering factors of sugar inversion and possible pectin hydrolysis might be more closely controlled. Such an attack, using pure standardized pectin, fruit acid, water, and sugars—in which the preparation of the jellies would be conducted in such a way that pectin hydrolysis could be avoided—might go far in answering some of the questions raised here. It would be necessary, in addition to the determination of the effect of replacement sugars in such freshly prepared artificial jellies, to make observations of the "aging" characteristics of the jellies. Correlation of viscosity data, under these controlled conditions, with subjective evaluations of "pleasing consistency" of fruit preserves
would then tie together the laboratory conclusions with their commercial application.

SUMMARY

1. The Machinichol viscometer was found to be a satisfactory instrument for the measurement of the property of viscosity in fruit preserves when the samples were treated properly for practical elimination of the effect of large fruit pieces.

2. Replacement sugars (crystalline dextrose-hydrate and corn conversion syrups) affect the viscosity of fruit preserves. In most instances (90%), the effect was a lowering of the viscosity of the preserves as compared with a sample containing only sucrose as added sugar. The amount of the lowering, however, was not found to be regular and predictable.

3. The variable nature of the results may be explained, on a theoretical basis, by the relationships of water with pectin and the sugars used.

4. It is suggested that a study of the "aging" characteristics of the pectin-acid-sugar gel be undertaken as a continuation of this work. Conditions should be provided for the control or measurement of such changes as hydrolysis of pectin and sugar. In such a way, the direct effect of the use of replacement sugars might
be observed and evaluated more successfully.
LITERATURE CITED

1. Sixteenth Census of the U. S., 1940 Manufactures 1939, Vol. 2, part 1, Reports by Industries. Values reported by 168 establishments reporting data on materials consumed amounting to 99.8% of total products for the industry.


11. ___________ ___________, loc. cit.


