THE EXTRACTION OF PECTIN FROM PECTIC MATERIALS*

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INTRODUCTION

A project, involving a systematic study of the factors influencing the jellation of fruit juices and pectin solutions, was instigated by the Chemical Department of this Station some years ago. So far five bulletins have been published relating to fruit jellies.1, 2, 3, 4, 5

Pectin, the jellying substance of fruit juices, has proven to be by far the most complicated of the factors studied, due to its highly complex chemical and colloidal nature. Indeed the study of pectin has presented so many problems that it has been almost impossible to investigate and report on each one in a single undertaking. Therefore it was decided to divide the work into several distinct problems, to study each problem separately and to publish the results as soon as the data became available.

This publication is the second one dealing with pectin put out by this Station. It presents data relative to the extraction of pectin from pectic material with the idea of establishing the conditions whereby a pectin may be recovered in the most economical way and yield the greatest possible amount of jelly.

HISTORICAL

The insoluble pectic substance of plants is called protopectin, a term first applied by Tschirch,6 Chodnew,7 Payen,8 Fremy9 and other early investigators considered protopectin to be an insoluble calcium compound. Norris and Schryver10 also considered protopectin to be an insoluble calcium salt since, as they say, "it invariably appears that pectinogen is extracted by agents which

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throw down an insoluble calcium salt by double decom-
position, leaving the pectinogen in solution. Ammonium
oxalate and oxalic acid are familiar examples and even
carbon dioxide is capable of liberating appreciable quan-
tities of pectinogen. On the other hand, salts such as
sodium chloride are unable to effect the change.” How-
ever, pectin may be extracted by boiling with water or
with hydrochloric, sulphuric, phosphoric, tartaric, citric,
sulphurous or other acids which is not concordant with
this generalization.

Fellenberg\textsuperscript{11} says that protopectin is not a calcium
salt and his view has been confirmed by Devaux\textsuperscript{12} and
D. Haynes.\textsuperscript{13}

Nanjji, Paton and Ling\textsuperscript{14} consider protopectin as
pectin in loose combination with metallic ions, such as
iron, which are capable of dissociating in the presence of
water and especially at a high temperature.

Smolenski\textsuperscript{15} believes that protopectin may be a com-
pound between pectin and a pentosan.

Weisner\textsuperscript{16} and Mangin\textsuperscript{17} were the first to suggest
that protopectin is a compound of pectin and cellulose and
Sucharipa\textsuperscript{18} has quite definitely established their claims.

The problem of the extraction of pectin from in-
soluble pectic materials resolves itself into the hydrolysis
of protopectin to cellulose and soluble pectin as far as the
yield of pectin is concerned. This may be done by the
action of enzymes;\textsuperscript{19, 20} by boiling with water;\textsuperscript{21} by
heating with dilute acids such as lactic, citric, tartaric,
acetic, malic, hydrochloric, phosphoric, sulphurous and
sulphuric.\textsuperscript{22}

Conrad\textsuperscript{23} has studied the effects of variation of
acidity, temperature and time of heating upon the hy-
drolysis of protopectin. He finds that N/30 to N/50
hydrochloric acid results in the highest yield of pectin;
that temperatures higher than 110°C. are destructive to
the liberated pectin (this has also been pointed out by
Hardy,\textsuperscript{24} and Farnell\textsuperscript{25} and others) and that a period of
heating at boiling temperature with N/30 acid longer
than one hour destroys some of the liberated pectin.
Hardy\textsuperscript{24} states that the quantity of pectin extracted appears to vary directly with hydrogen ion concentration when extraction is carried out at temperatures below the boiling point, and directly with temperature when the final reaction of the extract is less acidic than pH 2.0. He also states that alkaline extracts contain no pectin and that autoclave treatment (126 degrees) at concentrations of hydrogen ion greater than that represented by pH 2.0 brings about destruction of pectin by hydrolysis.

Mehlitz\textsuperscript{26} states that N/50 tartaric acid as extraction solution is the best for the extraction of pectin and that only those organic acids, whose dissociation constants lie in the neighborhood of that of tartaric acid, such as malic, citric, formic and salicylic acid may be used for the extraction of pectin. He also suggests that there is some connection between the hydrogen ion concentration of the extracted juice and the yield of pectin.

The percentage recovery of pectin from the pectic material is of importance and of course this will vary with the method employed. Bigelow and Gore,\textsuperscript{27} find that by boiling six hours with water under a reflux condenser with a change of water at the end of each hour does not completely remove the pectin from apple pomace. Goldthwaite,\textsuperscript{28} Caldwell,\textsuperscript{29} Poore\textsuperscript{19} and others have confirmed this observation.

Carre\textsuperscript{30} finds that all pectin may be extracted from apple by autoclaving the pulp with N/20 hydrochloric acid for about one hour at 110° C.

The value of an extraction method from a commercial point of view depends not only upon the yield of pectin but also on its jellying power. The literature contains many references to the methods of extracting pectin but contains very little information relative to the value of the resulting pectins. More attention has been given to the yield of pectin, expressed as percentage calcium pectate, pectin acid or alcohol precipitate than to its jelly value. In this connection Poore\textsuperscript{19} states: "Many of the methods given produce pectic acid and related compounds instead of pectin.\textsuperscript{31} In a series of preliminary experi-
ments, the methods of Hunt, Magoon and Caldwell, Schryver and Haynes, and Clayson, Norris and Schryver did not yield pectins suitable for making fruit jellies.”

The majority of investigators in the field of pectin research make no attempt whatever to evaluate the jellying power of the pectins. The exceptions are Sucharipa, Poore, Mehlitz, Fellers, Lüers and Lochmüller, Rooker, Myers and Baker, Wilson and a few others. Most of the methods used are comparative in nature; Poore and Sucharipa determine the minimum amount of pectin necessary to obtain a good jelly; Mehlitz determines the jellying power by determining the percentage calcium pectate, a method which is questionable; Lüers and Lochmüller state that the jellying power of a pectin is dependent upon its methoxyl content as does Sucharipa and a few others; Rooker uses a finger test and compares the test jellies with a standard jelly; Myers and Baker and Wilson have shown that the viscosity of a pectin solution is a measure of its jellying power. Wilson is the only one who has made an attempt to assign a definite value to the jellying power of a pectin. He measures the jellying power in terms of jelly grade expressed as parts of sugar one part of pectin will support which is a measure of the quantity of jelly obtainable from a pectin. This is a distinct step forward and should become generally accepted as a means of standardizing pectins so that results of pectin researches would be more comparable.

In the literature we find means of expressing results on extraction of pectin from pectic material that are entirely adequate and may be expressed in absolute units, jelly units, which take into consideration the yield of pectin and its jellying power. The product of the yield times jelly grade of pectin is really a measure of the quantity of jelly obtainable from a pectic material by a certain method of extraction and is an excellent means of comparing the value of the various methods of extracting pectin.
PLAN OF PROCEDURE

Before undertaking the outline of the problem involved in this investigation, considerable preliminary work was undertaken in order to determine some of the factors involved in the extraction and recovery of a high quality pectin. From this preliminary investigation suitable methods were derived for the extraction of pectin which were used throughout these researches. The methods are reported later.

It is not necessary to report the results of the preliminary investigation here as they may be found elsewhere. Suffice it to say that indications were obtained that; first, the hydrolysis of protopectin to free pectin depends directly upon the hydrogen ion concentration of the extracting medium and directly upon the length of the boiling period, and second, that the quality, or jellying power of the pectin, depends directly upon the hydrogen ion concentration at which it is extracted and indirectly upon the length of the boiling period.

In view of these results the study was outlined as follows:

1. The Effect on the Yield and Jellying Power of Pectin of Varying the Time of Boiling during Extraction while Maintaining the Hydrogen Ion Concentration Constant at a pH of 2.62.

2. The Effect on the Yield and Jellying Power of Pectin of Varying the Hydrogen Ion Concentration of the Extracting Medium, by the Addition of Tartaric Acid, while Maintaining the Boiling Period Constant at 20 Minutes.

3. The Effect on the Yield and Jellying Power of Pectin of Varying the Hydrogen Ion Concentration of the Extracting Medium, by the Addition of Hydrochloric Acid, while Maintaining the Boiling Period Constant at 20 Minutes.

To secure pectins as pure as possible, albedo, or the white part of lemons was used as raw material throughout these investigations. This material was very kindly furnished by the California Fruit Growers Exchange. Before proceeding with the extraction the albedo was ground in a Wiley mill to pass a 40 mesh screen.

The method of extraction used in this series of experiments was as follows:

25 g. portions of albedo were extracted with 1500 cc. of distilled water containing an equivalent of 100 cc. 1.0 N tartaric acid. The portions of albedo were introduced into the boiling acid solution and boiled for exactly 5, 10, 15, 20, 30, 45, 60, 120 and 180 minutes respectively. As soon as the boiling period was over the contents of the beaker were rapidly poured into three liters of previously cooled 90% alcohol in order to immediately arrest the hydrolysis of protopectin and of the liberated pectin. The alcoholic suspension was then rapidly cooled to 25° C. or below and filtered through silk, pressing as dry as possible. The entire residue was then transferred to a beaker and leached with 2500 cc. of distilled water about 20 hrs. at room temperature. (It was necessary to increase the dilution to 2500 cc. in order to speed up the clarification of the extract and check the yields). At the end of the leaching period the solution was vigorously agitated with a mechanical stirrer for 30 minutes. 60 g. of acid treated filter cell was then dumped into the mix and again agitated, this time for 15 minutes. The mixture was then divided into three equal parts and clarified as follows: A filter paper was placed in a Büchner funnel and covered with a layer of asbestos previously treated with aqua regia. 40 g. of acid treated filter cell was made into a suspension with distilled water and poured onto the mat in the funnel and washed with distilled water until the filtrate became clear. Three funnels were so prepared for
each extraction, each one being used to clarify one third of the extract. The extract was poured into the funnels, sucked dry and each washed with 150 cc. distilled water and again sucked dry. The combined filtrate, approximately 2700 cc. was poured into double its volume of 90% alcohol containing 5 cc. of 1.0 N tartaric acid per liter. The precipitated pectin was allowed to rise to the surface; the alcohol was siphoned off and the pectin filtered through silk, pressing as dry as possible. It was then rinsed in two changes of 95% alcohol and once in ether, pressed as dry as possible after each rinsing, and dried in the oven at 60° C. for 18 hours. It was then weighed and from this weight the yield was calculated. The pectin was then ground in a Wiley mill, thoroughly mixed by rotating in an Abbé mill (using no balls) and dried at 60°C. for 6 hours. The yield of pectin so prepared could easily be checked within 0.5%.

The jellying power of each pectin (measured in parts of sugar one part of pectin will support) designated in these researches by the term "jelly grade" was determined in the following manner:

A series of jellies was made from each pectin in which the pH of the pectin solution was varied. The jellies were made according to the standard method of this laboratory. Briefly this method is as follows: 100 g. of cane sugar is added to 100 cc. of the 0.5% pectin solution. Tartaric acid is added when necessary and the solution is boiled until the weight is 144 g. In this manner all jellies contain approximately 69.4% sugar. After boiling the jelly is poured into a standard jelly glass, maintained at 26° C. for 24 hours after which its strength is measured by the Tarr Jelly Strength Tester. By this procedure the hydrogen ion concentration at the optimum point of jelly formation is determined for each pectin.

A second series of jellies is made in which the hydrogen ion concentration of the 0.5% pectin solution is maintained constant at the pH corresponding to the optimum
point of jelly formation while the amount of sugar added to the solution is varied. The strengths of the jellies are then measured and plotted against added sugar. The jelly grade of the pectin is then determined by interpolating the curve, thus ascertaining the amount of sugar necessary to add to the pectin solution in order to yield a jelly of strength 50.

The jelly units are obtained by multiplying the yield of pectin by the jelly grade. Jelly units, therefore, really are a measure of the quantity of jelly that may be obtained from the pectin extracted from a given weight of albedo by a certain method of extraction. An attempt is made in these researches to determine the conditions of extraction that will yield the greatest number of jelly units.

The results of the first series of experiments are reported in Table I and Figures I, II, III.

TABLE I
Data Showing the Variation in Jelly Grade, Yield and Jelly Units of Pectin with Time of Boiling During Extraction. Hydrogen Ion Concentration Maintained Constant at a pH of 2.62 by the Addition of Tartaric Acid.

<table>
<thead>
<tr>
<th>Time of Boil. Min.</th>
<th>Jelly Grade</th>
<th>Yield %</th>
<th>Jelly Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>410</td>
<td>20.48</td>
<td>84.0</td>
</tr>
<tr>
<td>10</td>
<td>368</td>
<td>22.98</td>
<td>84.6</td>
</tr>
<tr>
<td>15</td>
<td>355</td>
<td>24.90</td>
<td>88.4</td>
</tr>
<tr>
<td>20</td>
<td>355</td>
<td>26.20</td>
<td>93.0</td>
</tr>
<tr>
<td>30</td>
<td>353</td>
<td>27.27</td>
<td>96.3</td>
</tr>
<tr>
<td>45</td>
<td>315</td>
<td>29.64</td>
<td>93.4</td>
</tr>
<tr>
<td>60</td>
<td>254</td>
<td>31.40</td>
<td>79.8</td>
</tr>
<tr>
<td>120</td>
<td>177</td>
<td>33.32</td>
<td>59.0</td>
</tr>
<tr>
<td>180</td>
<td>102</td>
<td>33.38</td>
<td>34.0</td>
</tr>
</tbody>
</table>

In Figure I jelly grade is plotted against time of boiling during extraction. There are three distinct breaks in the curve occurring at 15, 30 and 60 minutes boiling. From 60 to 180 minutes boiling the jelly grade is a straight line function of the time of boiling. It should be noted that the boiling period may be varied from 15 to 30 minutes without any reduction in jelly grade.
The jelly grade of the pectins extracted by boiling 5 and 180 minutes was 410 and 102 respectively. The former, therefore, will support four times as much sugar as the latter and thus make four times as much jelly.

In Figure II the yield of pectin is plotted against time of boiling during extraction and results in a regular curve reaching an optimum when the albedo is boiled for two hours. Boiling longer than two hours increases the yield but slightly. The hydrogen ion concentration of the extracting medium was regulated to a pH of 2.62 during the extractions so that the time of boiling was the only variable. The hydrolysis of protopectin to pectin therefore varies directly with the time of boiling.

FIGURE I
FIGURE II

FIGURE III
In Figure III jelly units, yield times jelly grade, are plotted against time of boiling during extraction. The jelly units increase rapidly up to a boiling period of 30 minutes and then decrease abruptly to 60 minutes. From 60 to 180 minutes boiling, the jelly units are a straight line function of the time of boiling. Approximately three times as much jelly may be obtained from the albedo, by extracting the pectin at a pH of 2.62 and boiling for 30 minutes, than by boiling for three hours at the same hydrogen ion concentration.

96.3 jelly units were obtained by extracting the albedo at a pH of 2.62 while boiling for 30 minutes. In order to clarify the meaning of the term “jelly units” assume that 10 lb. of albedo are to be extracted under the above conditions. 353 lb. of sugar may be added to each lb. of the 2.727 lb. of pectin obtained and yield jellies of strength 50. The 2.727 lb. of pectin obtained from the 10 lb. of albedo will require approximately 963 lb. of sugar. Thus by multiplying the jelly units by the weight of albedo used in the extraction, the total quantity of sugar that the resulting pectin will support is obtained. Now according to the method of making jellies previously reported the pectin-acid-sugar solutions were boiled so that the resulting jellies contained 69.4% sugar. Therefore each 100 lb. of sugar added will make 144 lb. of jelly. 963 lb. of sugar will make 1387 lb. of jelly. By multiplying jelly units by the factor 1.44 the total weight of jelly is obtained.

THE EFFECT ON THE YIELD AND JELLYING POWER OF PECTIN OF VARYING THE HYDROGEN ION CONCENTRATION OF THE EXTRACTING MEDIUM BY THE ADDITION OF TARTARIC ACID, WHILE MAINTAINING THE BOILING PERIOD CONSTANT AT 20 MINUTES.

This series of experiments was started before the above series was finished and it looked very much as if the optimum jelly units would be obtained at a boiling period of 20 minutes but when the data were completed it was found that the optimum occurred at 30 minutes. In these
experiments the boiling period was maintained constant at 20 minutes and not at the optimum of 30 minutes. However this will have no bearing upon the ultimate goal of these experiments; namely, the determination of the hydrogen ion concentration at which the extracting medium must be regulated in order to produce a pectin of optimum jelly units.

The pectins were prepared by extracting 25 g. portions of lemon albedo as previously described except that the hydrogen ion concentration of the extracting medium was varied from a pH of 4.64-1.78 by the addition of normal tartaric acid, varying in amounts from 0-1000 cc., while the boiling period was maintained constant at 20 minutes. The hydrogen ion concentration of the extracting medium was determined potentiometrically on separate samples prepared by extracting 5 g. of albedo with a proportional amount of water and acid, boiling for 20 minutes and quickly cooling.

The data are presented in Table II and Figures IV, V and VI.

**TABLE II.**

Data Showing the Variation in Jelly Grade, Yield and Jelly Units of Pectin with Hydrogen Ion Concentration of the Extracting Medium, Boiling Period Maintained Constant at 20 Minutes.

<table>
<thead>
<tr>
<th>Tartaric Acid Added cc. 1.0 N</th>
<th>pH Ext. Medium</th>
<th>Jelly Grade</th>
<th>Yield %</th>
<th>Jelly Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>4.64</td>
<td>312</td>
<td>14.1</td>
<td>44.0</td>
</tr>
<tr>
<td>5</td>
<td>4.02</td>
<td>383</td>
<td>13.8</td>
<td>52.9</td>
</tr>
<tr>
<td>23</td>
<td>3.30</td>
<td>358</td>
<td>18.9</td>
<td>67.7</td>
</tr>
<tr>
<td>55</td>
<td>2.90</td>
<td>358</td>
<td>24.4</td>
<td>87.4</td>
</tr>
<tr>
<td>100</td>
<td>2.62</td>
<td>354</td>
<td>26.3</td>
<td>93.1</td>
</tr>
<tr>
<td>182</td>
<td>2.40</td>
<td>360</td>
<td>30.0</td>
<td>108.4</td>
</tr>
<tr>
<td>315</td>
<td>2.20</td>
<td>334</td>
<td>31.9</td>
<td>106.5</td>
</tr>
<tr>
<td>535</td>
<td>2.00</td>
<td>334</td>
<td>33.0</td>
<td>111.2</td>
</tr>
<tr>
<td>1000</td>
<td>1.78</td>
<td>342</td>
<td>30.8</td>
<td>105.3</td>
</tr>
</tbody>
</table>

The jelly grade of the pectins was determined as previously stated. The results are presented in Table II and in Figure IV. In Figure IV jelly grade is plotted against the hydrogen ion concentration of the extracting medium. The resulting curve reaches an optimum point at a pH of 4.02 and again at a pH of 2.40. A sharp break
in the curve occurs beyond a pH of 2.40 due to hydrolysis of the pectin.

When no acid is added to the alcohol used in the precipitation of the pectin the resulting curve will have but one optimum point, namely, at a pH of 2.40. When acid is added to the alcohol the curve will have two optimum points, one occurring at a pH of 2.40 and the other somewhere between a pH of 2.40 and the pH of the distilled water extraction, depending upon the amount of acid added to the alcohol during the precipitation of the pectin. The variation in the jelly grade of the pectins, as shown in the curve in Figure IV, is not only due to the hydrogen ion concentration of the extracting medium but also to the acidity of the alcohol used in the precipitation of the pectin. Nevertheless it is quite evident that a
better grade of pectin is obtained than when acid is not used.

In Figure V the yield of pectin is plotted against the hydrogen ion concentration of the extracting medium. The optimum yield occurs at a pH of about 2.0 and corresponds very closely to the optimum yield obtained by extracting at a constant pH while varying the time of boiling. The yield of pectin depends upon the hydrogen ion concentration rather than upon the titratable acidity of the extracting medium as will be shown in the succeeding experiments.

In Figure VI jelly units are plotted against the hydrogen ion concentration of the extracting medium reaching an optimum value at a pH of approximately 2.15. In a previous experiment it was found that the optimum value was obtained when the albedo was extracted for 30 minutes so that in order to obtain the greatest amount of jelly from a given weight of albedo it must be boiled 30 minutes at a pH of 2.15.

The jelly unit depends upon the pH of the extracting medium rather than upon its titratable acidity as will be shown later.

THE EFFECT ON THE YIELD AND JELLYING POWER OF PECTIN OF VARYING THE HYDROGEN ION CONCENTRATION OF THE EXTRACTING MEDIUM, BY THE ADDITION OF HYDROCHLORIC ACID, WHILE MAINTAINING THE BOILING PERIOD CONSTANT AT 20 MINUTES.

In this series of experiments the pectins were extracted from the albedo in a manner similar to that described in the preceding experiments. The boiling period was of 20 minutes duration and the hydrogen ion concentration of the extracting medium was varied from a pH of 4.64-0.29 by the addition of varying amounts of normal hydrochloric acid instead of the tartaric acid previously used. An equivalent amount of normal hydrochloric acid
was added to each liter of 90% alcohol used in the precipitation of the pectin instead of the tartaric acid previously used. Data, similar to that tabulated in the previous experiments, were accumulated and are presented in Table III and Figures VII, VIII, IX, X, XI.

### TABLE III

Data Showing the Variation in Jelly Grade, Yield and Jelly Units of Pectin with Hydrogen Ion Concentration of the Extracting Medium, Boiling Period Maintained Constant at 20 Minutes. Pectins Extracted with Hydrochloric Acid.

<table>
<thead>
<tr>
<th>Hydrochloric Acid Added cc. 1.0 N</th>
<th>pH Ext. Medium</th>
<th>Jelly Grade</th>
<th>Yield %</th>
<th>Jelly Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>4.64</td>
<td>316</td>
<td>14.93</td>
<td>47.2</td>
</tr>
<tr>
<td>4.4</td>
<td>3.80</td>
<td>260</td>
<td>14.95</td>
<td>38.9</td>
</tr>
<tr>
<td>11.3</td>
<td>3.20</td>
<td>320</td>
<td>21.26</td>
<td>68.0</td>
</tr>
<tr>
<td>18.3</td>
<td>2.60</td>
<td>360</td>
<td>27.90</td>
<td>100.4</td>
</tr>
<tr>
<td>35.4</td>
<td>2.00</td>
<td>346</td>
<td>32.86</td>
<td>113.7</td>
</tr>
<tr>
<td>94.8</td>
<td>1.40</td>
<td>240</td>
<td>34.10</td>
<td>81.8</td>
</tr>
<tr>
<td>306.0</td>
<td>0.80</td>
<td>108</td>
<td>31.40</td>
<td>33.9</td>
</tr>
<tr>
<td>1000.0</td>
<td>0.29</td>
<td>...</td>
<td>14.00</td>
<td>...</td>
</tr>
</tbody>
</table>

In Figure VII the jelly grade of the pectins is plotted against the hydrogen ion concentration of the extracting

**FIGURE VII**

![Figure VII](image-url)
medium. Curve 1 represents the results of this series of experiments where hydrochloric acid was used in the extraction, and Curve 2, the results of the previous series of experiments where tartaric acid was used in the extrac-

**FIGURE VIII**

<table>
<thead>
<tr>
<th>Yield - Per Cent</th>
<th>c.c. Acid - Normality 1.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>35</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td></td>
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<tr>
<td>25</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td></td>
</tr>
</tbody>
</table>

**FIGURE IX**

<table>
<thead>
<tr>
<th>Yield - Per Cent</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>35</td>
<td>0.0</td>
</tr>
<tr>
<td>30</td>
<td>0.5</td>
</tr>
<tr>
<td>25</td>
<td>1.0</td>
</tr>
<tr>
<td>20</td>
<td>1.5</td>
</tr>
<tr>
<td>15</td>
<td>2.0</td>
</tr>
</tbody>
</table>

| 10               | 2.5|
| 5.0              | 3.0|
| 4.5              | 4.0|
| 4.0              | 5.0|
tion. The difference between the two curves from a pH of 4.64 to 2.40 is evidently due to the nature of the acid used in the precipitation of the pectin and not to the conditions of the extraction. Using hydrochloric acid in the alcohol lowers the ash of the pectin much more than does tartaric acid. It has been shown that a certain amount of a salt may increase the strength of jellies while a too small or a too great amount may decrease their strength. This perhaps is the explanation of why the curve representing the hydrochloric acid extraction at first decreases with an increase in hydrogen ion concentration while in the tartaric acid extraction the curve increases then decreases. Had no acid been added to the alcohol during the precipitation of the pectin the two curves would have been almost identical. This was found to be the case in the preliminary experiments not reported here.

The important point in connection with these curves is that the jelly grade eventually increases, reaching an optimum value at a pH of 2.40 in each case regardless of the nature and quantity of the acid used in the extraction. An increase in the hydrogen ion concentration of the extracting medium beyond a pH of 2.40 results in a decrease in the jellying power of the pectin.

In Figures VIII and IX the yield of pectin is plotted against acid added to the extracting medium and the

![FIGURE X](image-url)
hydrogen ion concentration of the extracting medium respectively. In both figures Curve 1 represents the results of the hydrochloric acid extraction and Curve 2 the results of the tartaric acid extraction. It is readily observed from the curves in these two figures that the yield of pectin, or hydrolysis of protopectin, depends upon the hydrogen ion concentration rather than upon the acidity of the extracting medium.

In Figures X and XI jelly units are plotted against cc. of acid added to the extracting medium and the hydrogen ion concentration of the extracting medium respectively. In both figures Curve 1 represents the results of the hydrochloric acid extraction and Curve 2, the results of the tartaric acid extraction.

Since the jelly grade and yield of pectin depends upon the hydrogen ion concentration of the extracting medium rather than upon its titratable acidity, the product of the jelly grade and yield (jelly units) should also depend upon the hydrogen ion concentration. A perusal of the curves in Figures X and XI shows the jelly units are at the same optimum value at a pH of approximately 2.15 regardless of the nature of the acid used in the extraction. This means that by extracting a given weight of albedo at a pH of 2.15 more jelly is obtained from the resulting pectin

**FIGURE XI**
than is obtained by extracting at any other hydrogen ion concentration.

DISCUSSION

A method of extraction for the production of a powdered pectin of high jelly units is given below. This method is based on the data presented above.

The directions are for a 25 lb batch of pectic material. Run 1500 lb of water, containing sufficient acid to adjust the hydrogen ion concentration of the extract to a pH of approximately 2.15, into a tank provided with steam coils. Heat the solution to the boiling point and dump in 25 lb of pectic material (dry basis). Boil exactly 30 minutes, then run the batch into a water jacketed tank containing 1000 lb of water. Should the 1000 lb of water be at a temperature of 20° C, the resultant temperature of the mix will be below 68° C. since the tank and the water in the jacket will absorb some heat. This sudden cooling of the extract will immediately slow up the hydrolysis of the pectin. Circulate water through the jacket and agitate the mix until it is below a temperature of 30° C. Clarify the cooled extract by means of a filter press using filter cell as a filter aid. The clarified extract may then be treated by any of the known methods for the recovery of the pectin.

The quantities of water cited above are for a pectic material containing about 34% extractable pectin. The ratio of water to pectic material should be considerably reduced if the pectic material contains less pectin as it undoubtedly will.

By following the above procedure practically all the pectin is recovered in one extraction. Although the jelly grade of the pectin is not the highest possible under these conditions, yet the yield times the jelly grade will result in the greatest possible number of jelly units. Therefore more jelly may be obtained from the pectin from the 25 lb of pectic material, under the specified conditions of extraction, than from that obtained by altering the boiling period or hydrogen ion concentration of the extracting medium.
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SUMMARY

1. The jelly grade of a pectin reaches an optimum value when the pectin is extracted at a hydrogen ion concentration of approximately 2.40. This optimum point is independent of the titratable acidity of the extracting medium and of the nature of the acid used. Extractions at hydrogen ion concentrations greater than that represented by a pH of 2.40 results in a sharp decline in the jellying power of the pectin, indicating a hydrolytic action on the pectin.

2. The jelly grade of a pectin decreases as the time of boiling during extraction increases. Boiling from 5-15 minutes results in a sharp decline in jelly grade; boiling from 15-30 minutes has scarcely any effect upon the jelly grade of the resulting pectin; boiling from 30-60 minutes sharply decreases the jelly grade and boiling from 60-180 minutes the decrease in jelly grade is more gradual and is a straight line function of the time of boiling.

3. The yield of pectin depends upon the hydrogen ion concentration at which the pectin is extracted rather than upon the titratable acidity. Increasing the hydrogen ion concentration beyond a pH of 4.0 results in a sharp increase in the yield of pectin. With tartaric acid the maximum yield is obtained at a pH of 2.0; with hydrochloric acid the optimum point occurs approximately at a pH of 1.45. Increasing the hydrogen ion concentration beyond these points results in a sharp decrease in the yield of pectin, indicating that the pectin is hydrolyzed and that some of the hydrolytic products are insoluble.

4. The yield of pectin also depends upon the time of boiling during extraction. Boiling from 5-60 minutes the yield increases rapidly; boiling from 60-120 minutes the increase is not so pronounced while boiling longer than 120 minutes results in practically no increase in yield above that obtained by boiling 120 minutes.
5. Regardless of the amount and nature of the acid used, a pectin of maximum jelly units is obtained when it is extracted at a hydrogen ion concentration of pH 2.15. When the hydrogen ion concentration is greater or less than that represented by a pH of 2.15 there is a sharp decline in jelly units.

6. A pectin of maximum jelly units is obtained when the extraction is accomplished by boiling 30 minutes. A boiling period shorter or longer than 30 minutes results in a decrease in jelly units.

7. The greatest possible quantity of jelly, therefore, is obtained when the pectin is extracted from the pectic material at a hydrogen ion concentration of pH 2.15 by boiling 30 minutes.

8. A method of extraction is given whereby the above principles are taken into consideration.
1. Tarr, Lester W.
   No. 134, Tech. No. 2 (1923).
2. Tarr, Lester W., and Baker, George L.
   No. 136, Tech. No. 3 (1924).
3. Tarr, Lester W.
   Fruit Jellies, No. 3, Jelly Strength Measurements, Del. Agr.
4. Myers, Philip B., and Baker, George L.
   No. 144, Tech. No. 7 (1926).
5. Myers, Philip B., and Baker, George L.
   Fruit Jellies, No. 5, The Rôle of Pectin, 1. The Viscosity and
   Bull. No. 149, Tech. No. 8 (1927).
6. Tschirch, A.
7. Chodnew, A.
   Pectin, Pectinsäure und Metapectinsäure, Ann. Chem. Pharm.
   51, 355-395 (1844).
8. Payen
   Rec. Sav, Etrange 9, 148 (1846).
9. Fremy, E.
   5 (1848).
10. Norris, F. W., and Schryver, S. B.
    The Pectic Substances of Plants. III The Nature of Pectinogen
11. Fellenberg, Th. von
12. Devaux
    Lineana, Bordeaux (1903).
13. Haynes, Dorothy
    The Gelatinization of Pectin in Solutions of the Alkalies and
    the Alkaline Earths, Biochem. Jr. 8, 553-83 (1914).
    Decarboxylation of Polysaccharide Acids: Its Application to
    the Establishment of the Constitution of Pectins and to their
15. Smolenski, K.
16. Weisner, Julius
17. Mangin, L.
    Sur Les Composés Pectiques, Jr. Bot. 7, 37-47; 121-131; 325-
    343 (1893).
18. Sucharipa, R.
    Protopectin and Some Other Constituents of Lemon Peel, J. A.
    C. S. 46, 146 (1924).
19. Poore, Homer D.
20. Norris, F. W.  

21. Gaertner, Hermann  

22. Wilson, C. P.  
The Manufacture of Pectin, Ind. Eng. Chem., 17, 1065 (1925)

23. Conrad, Carl M.  

24. Hardy, Frederick  
The Extraction of Pectin from the Fruit Rind of the Lime (Citrus Medica Acida), Biochem. Jr. 18, 283-90 (1924).

25. Farnell, R. G. W.  
The Pectin Substance of Sugar Cane Fiber, Intern. Sugar Jr. 26, 630 (1923).

26. Mehltitz, Alfred  

27. Bigelow, W. B., and Gore, H. C.  

28. Goldthwaite, N. E.  

29. Caldwell, J. S.  

30. Carré, Marjorie H.  

31. United States Patents:
   1,077,714 (1913) Food product consisting of a jelly base.
   1,082,682 (1913) Food product.
   1,235,064 (1917) Electro osmotic purification of gelatinous substances.
   1,304,166 (1919) Food product and its method of manufacture.
   1,365,000 (1921) Food product.
   1,365,001 (1921) Food product and process of making same.
   1,380,572 (1921) Process of producing pectin.
   1,385,525 (1921) Process of extracting pectin.
   1,386,224 (1921) Production of pectous substances.
   1,393,660 (1921) Pectous material and process of making the same.
   1,398,339 (1921) Act of making jams, jellies, and marmalades of fruits.
   1,410,920 (1922) Pectic substance and process of making the same.

32. Hunt, C. H.  

33. Magoon, C. A., and Caldwell, J. S.  
34. Schryver, S. B., and Haynes, Dorothy
   The Pectic Substances of Plants, Biochem. Jr. 10, 539-547
   (1916).

   The Pectic Substances of Plants. Part II. A Preliminary
   Investigation of the Chemistry of the Cell Walls of Plants,

36. Sucharipa, R.
   Experimental Data on Pectin-Sugar-Acid Gels. J. A. O. A. C. 7,
   57 (1923).

37. Fellers, Carl R.
   The Extraction of Apple Juices in the Manufacture of Jelly,

38. Lüers, Von H., and Lochmüller, K.
   Die Messung der Gelierkraft von Frucht-pectonen, Kolloid-
   Zeitschrift 42; 154-163 (1927).

39. Rooker, William A.
   Fruit Pectin, Avi Publishing Co., Inc. (1928).

40. Wilson, C. P.
   Relation of Chemistry to the Citrus Products Industry, Ind.
   Eng. Chem. 20, 1302-1307 (1928).

41. Myers, Philip B., and Baker, George L.
   Fruit Jellies No. 6, The Rôle of Pectin, 2. The Extraction of
   Tech. No. 10 (1929).