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# An investigation of the effects of sugar, acid and pectin on the quality of gels

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AN INVESTIGATION OF THE EFFECTS OF SUGAR, ACID AND PECTIN  
ON THE QUALITY OF GELS.

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Reginald K. Stratford

Thesis Submitted For The Degree of Master of Science  
Massachusetts Agricultural College.

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## INTRODUCTION

Review of Literature.---The study of pectin bodies has extended over almost a hundred years, and yet today very little is known about their composition, structure or chemical properties; the terminology is anything but clear and much of the work is of a contradictory nature. A systematic classification of the work already done on the pectin bodies is needed before any new work can be attempted. There are several excellent reviews on the early study of pectins, two of the most exhaustive being Green (1896), and Bigelow, Gore and Howard (1905).

An attempt is made in this thesis to divide the review under headings of different pectin bodies and so make the first step towards simplifying the study of any particular pectin, this was found to be a very difficult thing to do. The writer does not at the present time feel in a position to explain many of the apparent contradictions without first acquainting himself more fully with every angle of the subject.

Experimental Work.---The simple method of determining pectin by precipitating with alcohol has been considered by many to be at best a crude experiment as there is no doubt but that the precipitate includes many pectin-like bodies which have not the power to form gels under the usual conditions followed in jelly-making. This fact, coupled with various methods of extraction and the possibility of a large variety of pectins accounts, to some extent at least, for the inability of many investigators to produce gels of the same consistency under seemingly similar conditions with any degree of regularity.



With the knowledge of these difficulties in mind the following experiments were conducted and a standard for the study of the gel powers of pectins was established. With the aid of this standard it will now be possible to study much more accurately the effect of various methods of extraction and the gel qualities of pectins from different sources together with a number of other closely related problems.

Opportunity is taken here to express my gratitude and appreciation to Dr. C. A. Peters for his help and advice throughout the work, and to the Staff of the Department of Chemistry for the aid given me during the progress of the investigation.



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REVIEW OF LITERATURE

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### Nature and Occurrence of Pectines

As early as 1825 Braconnot found substances widely distributed throughout the plant kingdom which he extracted from the roots of several plants, especially those of the turnip and carrot, the bulbs of the onion, and from the stems, leaves and fruits of herbaceous plants and trees. To this substance, feebly acid, he gave the name of pectin (pectic acid). Braconnot was so impressed with the constant occurrence of this substance in his research that he regarded pectins as one of the principal constituents of all plants.

About this time or a little earlier Payen (1822) extracted from the root of *Ailanthus glandulosa* a peculiar vegetable jelly which was closely related to, if not identical with, Braconnot's pectic acid.

Vanquelin (1829) obtained a substance from carrots which he called pectin (pectic acid) and studied some of its chemical properties.

During the next ten years Fremy and Mulder added much to our information as to the chemical peculiarities of pectin.

Fremy (1840) in a paper discussed some of the changes in the cell wall of various fruits. The fruit becomes less acid on ripening and the cell walls thinner. The presence of an insoluble mother substance of pectin-forming material, later named pectose, existing in the cells of unripe fruits, is suggested as a result of





experiments on fruit marc. In these experiments the marc in boiling water yielded only small quantities of pectin, but with dilute acid gave it in abundance. The author was very careful to distinguish between pectose and cellulose, though he was unable to separate the two.

Poumaredé (1839) denied the existence of pectic acid in the plants. He considered pectin as an organized tissue and pectic acid as a reaction product. Later Poumaredé and Figuier (1846) considered pectin and "legnin" (cellulose) to be identical, and they continued to deny the existence of pectic acid in the plant.

Chodnew (1844) brought forward the theory that pectin bodies exist combined with calcium in beet marc, and described an experiment in which beet marc was allowed to stand with dilute hydrochloric acid. When the marc became soft and translucent on washing, it regained its opacity and harshness upon adding a very little lime water. The author also noted that pectins disappear during the ripening of fruits. He suggested that pectins may form malic acid upon disappearance.

Payen (1846) pointed out that in certain plants pectic bodies exist in combination with the metals of the alkalies and alkaline earths, chiefly potassium and calcium.

Frémy (1859) pointed out a method for distinguishing between cellulose and the various pectic bodies. This method consisted in treating the tissue with ammonia-cupric sulphate (Schweitzer's reagent). This reagent dissolves pure cellulose while the group of pectic bodies remain apparently unaffected, though really much modified, insoluble cupric pectate being formed.



Stude (1864) claimed that pectin bodies existed in the plant as calcium pectate, and that pectose did not exist.

Until the memoir of Magnin (1892-93) appeared the whole group of pectin compounds was ill defined. He arranged them in two series, those of neutral and those of feeble acid reactions. In each there are probably several members varying in solubility from absolute insolubility to complete solubility in water, the intermediate bodies exhibiting gelatinous stages.

Tollens (1895) suggested that pectin in the plant may not have acid characters, but may exist as a lactone, and at the same time Cross (1895) considered that pectin may be ligno-cellulose free from incrusting material.

Pectose and pectin are the two extremes of the neutral series. Pectose is insoluble in water and closely associated with cellulose in the substance of the membranes while the latter is soluble in water and forms a jelly under favorable conditions.

In the acid series the two most noteworthy members are pectic and meta pectic acids, the former generally existing in the membrane in combination with the metals of the alkaline earths, especially calcium when, in the free state, it is insoluble in water. Meta pectic acid is insoluble in water without forming a jelly. The two series are closely related to each other, for by the action of heat, acids and alkalies, the various members of each can be prepared from pectose.

Tschirch (1907) published a paper dealing particularly with staining methods employed in studying the pectins in plant tissue and the solubility of pectin matter in sugar solutions.



Bridel (1907) derived pectins from Honeysuckle, *Lonicera xyloslenom*, L.; snow berry or wax berry, *Symphoricarpus racemose*, L.; and black bryony, *Tamus communis*, L. About the same time Harley (1906) obtained pectins from aucuba and from the rind of the sweet orange. The pectins were all found to have practically the same properties except a slight difference in color and rotatory power.

Fellenberg (1914) found that in barely ripe, fresh fruit there occurs protopectin (pectose) and a very little pectin, but no pectic acid or methyl alcohol, while in decayed fruit the protopectin has disappeared, but pectin is still present and pectic acid and methyl alcohol exist in excess.

Oden (1917) demonstrates the presence of insoluble or almost insoluble acid substances in various plant tissues by a method based on the change in the electrical conductivity of an aqueous suspension of the tissue. This change occurs on the addition of a small amount of ammonium hydroxide, forming readily dissociated ammonium salts with the acid pectin substances. These pectin substances, besides acting as binding material for plant tissues, constitute a means for regulating the content of H and OH ions in the circulating fluids, and maintaining the cell contents in a slightly acid condition. They form a reserve of insoluble acid, which is nevertheless readily available for the neutralization of any alkaline substances brought into contact with the cell.

Hornby (1920) investigating the pectin substances of cattle foods found them to vary greatly in different foods. Using Fellenberg's method of determining pectin, the author was able to show that methyl pectate varies in different parts of the plant. As a result of his investigation he showed that pectin material goes far to make up the



remaining per cent composition of foods after the water, pectin, ether extract, soluble carbohydrates, fiber and ash have been determined.

### Methods of Extraction and Preparation of Pectins.

#### Pectin

Frémy (1840) prepared pectin from fruit juices by first boiling to coagulate the albuminous matter, then filtering and purifying by repeatedly precipitating with alcohol and dissolving in water. The resulting body was white and soluble in water.

Chodnew (1844) prepared pectin from pears and apples. They were ground up, boiled in water and the juice filtered first through linen and then through paper. The clear filtrate was precipitated with alcohol and the precipitate washed with alcohol and ether, and squeezed out. Upon standing the pectin substance lost its gelatinous character and became like woody fiber.

Frémy (1847) published two methods for the extraction of pectin; one by boiling a fruit marc or a root marc with malic or citric acid, and another consisting of precipitating a ripe fruit juice with alcohol.

Andrlik (1894-95) discussed the action of dilute hydrochloric acid on beet marc, and prepared a pectin body by water extraction, precipitating it with alcohol. He found that the longer





the acid acted on the beet marc the more insoluble in water was the pectin produced.

Bourquellet and Hérissey (1898-99) studied the extraction of pectin with hot water.

Pellet and Métillon (1906) determined that there was no difference in the extract of pectin matter digested in the cold either with water or alcohol.

Miss Goldthwait<sup>e</sup> (1909-10) after trying various methods of isolating pectin matter, outlined by different experimenters, adopted the following method: --- A given volume of fruit juice was added, drop by drop, to an equal volume of alcohol, by means of a separatory funnel. The mixture was allowed to stand over night in a cold place and the jelly-like mass of pectin material was separated from the liquid by filtering through very fine cotton cloth stretched tightly over the mouth of a flask. The liquid was worked out of the mass with a spatula. Repeated resolution in water and precipitation in alcohol improved its purity. The pectin so obtained was very stable, nearly colorless, transparent solid of insipid taste.

Ball (1915) followed substantially the same method of earlier investigators in extracting pectin from carrots, only he treated the water extract with oxalic acid to precipitate the calcium, and separated the pectin by addition of an equal volume of alcohol.

McNair (1916) obtained pectin from lemon rinds using Fellenberg's method, which, briefly, is as follows: --- The rinds are boiled with several changes of alcohol, the filtrate heated in an autoclave for one hour at  $110^{\circ}\text{C}$ . in the presence of water, filtered and precipitated by a double volume of acidified alcohol (removing



alcohol with acid and ether) and dried in a vacuum desiccator.

The preparation of pectin bodies from various sources is described in detail by Schryver and Haynes (1916), and the only important difference from previous methods outlined is the use of a warm .5 per cent solution of ammonium oxalate to extract pectinogen from the fruit residue after the expression of the juice.

Caldwell (1917) outlines a method for the preparation of pectin for commercial or home jelly-making. Briefly describing this method, - the pectin is extracted from the apple marc with successive additions of boiling water, and the solution concentrated by successive freezings. The concentration is finally completed by evaporating the residue at about 70°C. This thick solution can be preserved by precipitating the acid with calcium carbonate.

Magoon and Caldwell (1918) claimed their method of preparing pectin decreased the cost of production. The solids and most of the coloring matter are precipitated by the addition of a small amount of commercial alum to the aqueous extract made basic with ammonia. The pectin is precipitated from the clear filtrate by the addition of magnesium sulphate crystals. The precipitate is filtered and washed free of magnesium sulphate with cold water.

Hunt (1918) precipitated pectin from a water solution with ammonium sulphate. He found pectin so prepared compared very favorably with pectin precipitated by alcohol.



### Pectic Acid

Bracconot (1825) published a paper giving a method for the extraction of pectin (as pectic acid) from roots containing starch. The method consists in pulping the roots, washing with water to remove sugar, then boiling the marc with dilute hydrochloric acid, and washing and heating the starch free and sugar free marc with very dilute potash or soda. Finally the addition of hydrochloric acid precipitates pectic acid as a jelly.

Vanquelin (1829) worked on the carrot, obtaining pectin from the juice by boiling in order to clarify, then precipitating with alcohol. From the marc he obtained pectin (as pectic acid) by boiling with dilute caustic potash and precipitating with calcium chloride, -or better, barium hydroxide, -filtering, treating the filtrate with sulphuric acid and then with potassium hydroxide, and finally precipitating with hydrochloric acid.

Fromberg (1843) boiled beet marc with sodium carbonate in order to extract the pectin as the sodium salt of pectic acid, and precipitated the acid by the addition of an excess of hydrochloric acid to the solution.

Chodnew (1844) prepared pectic acid from white beets, and some other material, as follows: --- The marc was boiled with dilute potassium hydroxide from a quarter to half an hour. The solution was filtered first through a cloth and then through paper, the pectic acid precipitated from the filtrate by hydrochloric or nitric acid, and finally with alcohol, and the precipitate pressed out by hand. The precipitated pectic acid gradually lost its gelatinous property and became like woody fiber.



### Metapectic Acid

Chodnew (1844) prepared metapectic acid by boiling pectin with potassium hydroxide. While Frémy (1847) prepared it by boiling with a dilute acid and later (1859) by boiling beet marc with milk of lime.

Scheibler's (1868) method of extracting metapectic acid was as follows: — Beet pulp was washed and macerated in cold 85 per cent alcohol. The pressed out residue was thrown into boiling water, the alcohol boiled out, potassium hydroxide added until a strong alkaline reaction was obtained, and the solution heated for a long time on a water bath. The product was then filtered, saturated with carbon dioxide, concentrated by evaporation, filtered and the filtrate acidulated with acetic or hydrochloric acid. The pectic acid was then precipitated with alcohol and finally the concentrated aqueous solution was poured into a small high cylinder, a little alcohol was added and the mixture allowed to stand for several weeks. During that time a precipitate of metapectic acid was formed which carried nearly all the ash.

### Metapectin

Ullik (1895) obtained metapectin from sugar-free beet marc by the following method: — The marc was allowed to stand several days with a one per cent solution of hydrochloric acid, then pressed out and the filtrate concentrated at the lowest possible temperature. Alcohol was added and the resulting gelatinous precipitate, after filtering, was





dissolved in water and digested for one hour with a one per cent hydrochloric acid solution at 60°C. The mixture was filtered and two precipitates were formed on fractional precipitation of the filtrate with alcohol. The first was metapectin and the second parapectin.

### Parapectin

Frémy (1847), boiling pectin with water, obtained parapectin and also found that by boiling pectin a long time with acids he obtained parapectin.

Ullik (1895) obtained parapectin by fractional precipitation with alcohol of his solution containing metapectin (p.



## Properties of Pectin Bodies

### Pectin

Frémy (1840) extracted pectin which proved to be difficult to burn quantitatively on account of its ash, which retained carbon dioxide. Better results were obtained when the lead salt was prepared and burned. Boiling the pectin with water increased the amount of lead that would combine with it, which Frémy called an increase of "saturation capacity".

Chodnew (1844) from pears obtained a pectin which was soluble in water, easily powdered when dry, neutral in reaction and gave no precipitate with calcium chloride, barium chloride or with ammonium hydroxide. Lead acetate, basic lead acetate, copper sulphate, lime water and potassium hydroxide gave gelatinous precipitates. This pectin contained 8.5 to 8.7 per cent ash. Pectin from the apple was also studied, and was found high in ash but was largely freed from it by precipitating with alcohol from an acid solution.

Frémy (1847) found the properties of pectin to be, neutral, soluble in water, insoluble in alcohol, not colored by iodine, not precipitated by neutral lead acetate and inactive to polarized light.

Scheibler (1879) obtained a water soluble body with a rotatory power of over  $+200^{\circ}$  from beet marc previously extracted with alcohol.

Weisberg (1888) confirms the view of Scheibler that gelatinous hot water extract from beet marc, exhausted by alcohol, was a pectin.



Wohl and Van Niessen (1889) considered that pectins of beet marc were insoluble in water unless rendered soluble by hydrolysis, and to be slowly changed to soluble forms by hot water, and much more rapidly by acids and alkalies.

Herzfeld (1891) obtained from ripe oranges an inactive pectin, which was, however, precipitable by neutral lead acetate, distinguishing it from Frémy's pectin.

Magnin (1892-93) gives as the properties of pectin, that it dissolves in water giving a viscous liquid, very difficult to filter which soon forms a jelly. This is the body Frémy found in ripe fruits, and it exists in many mucilages. It gives no precipitate with neutral lead acetate, but is thrown down by the basic acetate in the form of white flocks. If boiled for several hours in water it is converted into an isomer, parapectin, which is precipitated by the neutral acetate. Further boiling with dilute acids convert it into metapectin which is precipitated by barium chloride.

Bourquellot and Hérissey (1898) found that a one per cent solution of pectin from gentian root was gelatinized by lime water, sodium hydroxide followed by hydrochloric acid, neutral and basic lead acetates, ferric chloride, magnesium sulphate, and ammonium sulphate, but not by sodium sulphate. The pectin was not reducing and was dextro rotatory  $[\alpha]_D^{20} = +82.3$ . Acidified water extracted a more dextro rotatory body  $[\alpha]_D^{20} = +145.3$ .

Bourquellot (1899) later defined pectins as substances which dissolve in water, yield mucic acid, and are coagulated by lime water, baryta water and by pectase. The solutions were optically active contrary to the results of Frémy ( $[\alpha]_D^{20} = +82.3^\circ$  to  $194^\circ$ ).



Javillier (1899) with quince pectin found it was strongly dextro rotatory  $[\alpha]_D^{20} = +188.2^\circ$

According to Pellett and Motillon (1906) in the presence of either lead subacetate or alcohol, the pectins appear to be inactive optically, but the aqueous solution alone is polarized. The rotation may amount to as much as  $0.5^\circ$  on a normal weight of pulp.

Goris and Crete (1910) considered the error in optical rotation of pectins to be due to the presence of organic salts. To this compound, which may be made by various chemical means from protopectins, is due the jellying of fruit juices. It is a reversible colloid, is not coagulated by  $\text{AgNO}_3$ ,  $\text{HgCl}_2$ ,  $\text{Co}(\text{NO}_3)_2$ ,  $\text{NiSO}_4$ ,  $\text{FeSO}_4$ ,  $\text{ZnSO}_4$ ,  $\text{MnCl}_2$ ,  $\text{CaCl}_2$ ,  $\text{SrCl}_2$ ,  $\text{BaCl}_2$  nor the alkaline salts. Boiling pectin, sugar and fruit juice produces a jelly, and if calcium salts are substituted for the fruit juice a jelly is formed, which is different from protopectin and pectic acid.

Schryver and Haynes (1916) obtained a substance they called pectinogen, which, when kept in an alkaline solution at room temperature, readily undergoes conversion into another substance, also acidic in character, which is precipitated from its alkaline solution by acids as a gel. The authors named this substance pectin. It differs from pectinogen in that it is insoluble in water, and that a soluble solution of its sodium salt gives a gelatinous precipitate with calcium chloride.





### Pectic Acid

Braconnot's (1825) preparation of pectic acid had a feebly acid reaction to litmus and was slightly soluble in hot water. The filtered liquor did not precipitate on cooling, and barely reddened litmus. It was, however, coagulated by alcohol, by metallic salts and even by sugar. The dried transparent leaflets were slightly swelled by cold water. A potassium salt of pectic acid was separated by precipitating it from a water solution with alcohol, allowing the alcohol to extract coloring matter and excess of alkali. This potassium salt was very soluble in water, yielding 15 per cent of potassium calculated from its sulphate ash. Its water solution was coagulated by salts, alcohol and sugar and gave precipitates with solutions of salts and heavy metals. An ammonium salt was obtained which possessed properties similar to those of the potassium salt.

Braconnot (1833) separated a pectin (pectic acid) from oak bark with a solution of alkali which was not precipitated by organic acids, but was readily thrown out of solution as a jelly by a trace of mineral acid or alkali earth salts.

Mulder (1838) considered that pectic acid, prepared by dissolving in alkali and precipitating with acid, differed from pectin only in its higher ash content.

Frémy (1840) found that pectic acid dissolved in dilute potassium hydroxide would no longer precipitate on adding acid, the salt of the metapectic acid having been formed. From the free metapectic acid neutral lead acetate precipitated a salt much richer in lead than the lead salt of pectic acid. The free acid



had an acid taste and was deliquescent. Long standing with potassium hydroxide reduced the acid to still greater "saturation capacity", and a more acid taste. Chodnew (1844) found that dilute acids effected a similar change in pectin and pectic acid. Frémy considers the above facts to be due to a hydration of the original pectin.

Chodnew (1844) prepared pectic acid which was colorless and easily powdered. It was obtained nearly free from ash by repeatedly precipitating with alcohol from a water solution made slightly acid with nitric acid. It yielded one per cent ash on burning, which consisted chiefly of iron phosphate. It was insoluble or only slightly soluble in hot water, but readily dissolved in alkali to a clear solution.

Magnin (1892-93) gives the reactions of pectic acid as follows: --- It is insoluble in water, alcohol and acids; forms soluble pectates with the alkalies and insoluble ones with the metals of the alkali earths. It dissolves in solutions of alkaline salts such as the carbonates of sodium and potassium and most organic ammoniacal salts, forming with them the double salts which gelatinize more or less freely with water. Its solutions in alkaline carbonates are mucilaginous and difficult to filter, while when oxalate of ammonia is the solvent it is perfectly fluid and filters readily.

Ullik (1895) found pectic acid to have a high rotatory power, about  $[\alpha]_D^{20} = +186$  to  $300^\circ$ , and to form easily soluble alkali salts, dialyzing readily, while the other salts are insoluble and gelatinous.



Fellenburg (1914) found that pectic acid does not form a jelly on boiling with sugar and pectin free fruit juice except when the enzyme pectase is present. In a later paper (1918) the author found that pectic acid is sparingly soluble in hot water, giving colloidal solutions which are flocculated by salts.

### Pectinogen

Schryver and Haynes (1916) designated a substance, pectinogen, which is obtained by the extraction of a vegetable pulp with ammonium oxalate and precipitating with alcohol. On treating with absolute alcohol and drying in air, pectinogen is converted into a granular powder. It dissolves in water very slowly, as a considerable amount of imbibition of fluid must occur before dispersion takes place. It forms viscous, somewhat opalescent solutions, which are distinctly acid to phenolphthalein. Pectinogen rapidly undergoes a change when it is kept at room temperature in an alkaline solution. A freshly prepared neutral solution (by caustic alkali) gives a precipitate with either acid nor dilute calcium salt. If, however, it is made alkaline a change is indicated by the fact that both the above reagents will, after a short time, yield a bulky gelatinous precipitates when added to the solution. There is little doubt that pectinogen is rapidly converted into another acid, pectin, the rate of change being very rapid.

Frémy (1840) found that from the free meta pectic acid, neutral lead acetate precipitated a salt much richer in lead than the lead salt of pectic acid. The free acid had an acid taste and was deliquescent.



### Metapectic Acid

Frémy (1840) found that from the free metapectic acid, neutral lead acetate precipitated a salt much richer in lead than the lead salt of pectic acid. The free acid had an acid taste and was deliquescent.

Chodnew (1844) on the other hand, studying the properties of metapectic acid, found that it was not deliquescent in the air and formed no soluble salts with calcium or barium.

Magnin (1892) states that metapectic acid has an acid reaction; is freely soluble in water, forming soluble salts with all bases especially calcium and barium, which precipitate pectic acid. Metapectic acid warmed with an excess of alkali takes on a yellow color. This body and its compounds approach the gums in their composition.

Ullik (1895) obtained metapectic acid which was white weakly acid mass, precipitated by barium chloride and lead acetate and of strong rotatory power  $[\alpha]_D^{20} = +167.4^\circ$ .

### Parapectic Acid. (Pectin)

Weisberg (1907) published an article in which he discussed the presence of both leve and dextre rotatory parapectic acid in decomposed beet pulp. The more decomposed the pulp the more leve rotatory parapectic acid was present.





### Metapectin

Frémy (1847) by boiling pectin with a dilute acid obtained metapectin which only differed from pectin and parapectin by being slightly acid and precipitable by barium chloride.

### Parapectin

Frémy (1847) by boiling pectin with water obtained parapectin, which differed from pectin in being precipitated by neutral lead acetate.

Ullik (1895) working with parapectin found it to be an amorphous white substance precipitated by lead acetate, but not by barium chloride, showing a rotation of  $[\alpha]_D^{20} = 123.8^\circ$ .

### Pectose

Frémy (1847) considered pectose to be a substance analogous to starch.

Magnin (1892-93) considered the actual properties of pectose not formerly well known, and difficult to ascertain. The material was so closely associated with cellulose that it could not be prepared pure. The reagents separating it from cellulose converted it into either pectin or pectic acid.

Fellenberg (1914) writes of pectose, better called pectopectin, which exists in unripe or barely ripe fruit, but



not in over ripe or rotten fruit, is an insoluble substance and is not calcium pectinate. Acids do not split it into pectin, though this may possibly be accomplished by hydrolysis. As no reducing sugar is formed on the reduction of protopectin to pectin there is no glucoside present. Protopectin does not form a jelly when cooked with sugar and pectin free fruit juice. Protopectin when heated with water and acidified alcohol forms pectin, the methyl ester of pectic acid. It is converted directly into pectic acid, and methyl alcohol by sodium hydroxide in the cold.



## Constitution and Products of Pectin Bodies

Bracconet (1825) on treating a pectic acid solution with nitric acid, obtained oxalic acid and a white powder which was treated with ammonia to separate it from calcium oxalate. The ammonia solution acidulated gave a granular crystalline substance which he believed to be mucic acid.

Frémy (1840) stated that pectins did not yield sugar on hydrolysis.

Chodnew (1844) gives the combustion figures for pectin from apple marc as, carbon, 43.70 and 43.70; hydrogen, 5.63 and 5.41; oxygen, 50.67 and 50.8. Pectin formula is given as  $C_{28}H_{21}O_{24}$ . The author also prepared and dialyzed the calcium, barium, sodium and silver salts, obtaining the formula  $C_{26}H_{20}O_{23}$ , from the combustion of the purified product.

Scheibler (1868) published two papers of much interest in which the formation of sugar from pectin was described. Metapectic acid hydrolyzed, yielding crystallizable sugar, which he called arabinose. Later the sugar was found to be the same whether prepared from beet marc or gum arabic.

Herzfeld (1891) considered pectins as a combination of arabin and galactin, not separable by known means and recognized by yielding furfural on the one hand and mucic acid on the other.

Magnin (1892-93) claimed that metapectic acid acted upon by sulphuric acid, splits into a dextro rotatory crystallizable sugar, apparently identical with arabinose and a little known organic acid, indicating by its behaviour some relationship to the group of glucosides.



Ullik (1895) separated up to 90 per cent of mucic acid from pectic acid, but he noted that the pectic acid from different sources and prepared by different methods behaved very differently in regard to yield of mucic acid, some giving as high as 80 per cent and still others no mucic acid whatever. Those yielding the highest per cent mucic acid showed the highest rotatory power and on hydrellysis passed over principally into galactose, while those showing low per cent of mucic acid gave almost altogether arabinose. He found that metapectin yielded 20 per cent mucic acid on oxidation, while parapectin gave no mucic acid but yielded with phloroglucin and hydrochloric acid an intense color reaction, denoting pentoses or pentosans.

Trempe de Hass and Tollens (1895) found that the relationship of hydrogen and oxygen in pectin bodies was nearly one to eight as required by the carbohydrate formula, and that the pectic bodies, which they studied, contained no complex which gave rise to dextrose, but complexes were present which yielded pentose sugars and galactose on hydrellysis with acids.

Tollens (1895) in a later paper says that pectin bodies may probably be regarded as glucosides, since the acid reaction, combination with bases and slightly higher oxygen-hydrogen ratio of extracted pectins, indicate the presence of carboxyl groups.

Bourquellot and Heunsey (1898) found that the pectin from gentian root yielded mucic acid and arabinose like that from beet mure.

Votocek and Sebor (1899) obtained from beets, by treatment with alkali, an arabic acid which they determined to be not a homogeneous compound. Other evidence that arabic acid was a mixture





of similar substances was that varying quantities of arabinose and galactose were obtained by hydrolyzing the acetylation product. The original acid was not regained, but the products possessed different rotatory powers and contained different proportions of the groups which give rise to arabinose and galactose. A very pure glucosazone was obtained from the hydrolyzed product of the arabic acid, so that three complexes may be present, araban, galactan and glucosan.

Widtsoe and Tellens (1900) reported arabinose, xylose and fucose in gum tragacanth, which Gerard had found to be 60 per cent pectin.

Bauer (1901) was able to obtain various sugars from pectins from different sources, - galactose from pear pectin, xylose from apple pectin, and other sugars not positively identified from orange peel.

Weisberg (1907) observed that the pectin of the beet, by the action of alkali of lime, is converted into metapectic acid and the soluble salts of this acid. The pectin contains two components, - an araban which yields furfural on distillation with sulphuric acid and is oxidized to oxalic acid by the action of nitric acid, and a galactan which on oxidation with nitric acid gives mucic acid.

Wilhelmi (1909) by treating the water extract of beet pulp with milk of lime obtained by precipitation a dextro rotatory pectin substance leaving a levo rotatory substance in the alkaline filtrate. Three precipitates were obtained from the filtrate by treating it with carbon dioxide, oxalic acid and ammonium oxalate. The author considered it probable that these three precipitates indicated the presence of a sugar compound, an organic acid or lactone and lastly Scheibler's metapectic acid. The calcium precipitate of dextro-rotating substances was treated with hydrochloric acid to neutrality,



the precipitate yielding a levo rotatory solution, which with an excess of hydrochloric acid polarized to the right, (hydrolysis to arabinose). The author believes the substance producing this effect to be levo parapectic acid (Weisberg) which is a transition product yielding arabinose. The calcium precipitate consists of two fractions, one soluble in hydrochloric acid. The soluble fraction did not change on long heating, did not reduce Fehling's solution, and gave no tests for pentoses or mucic acid. This he regarded as a pectin from which the arabinose yielding group (L. parapectic acid) is split off. The fraction insoluble in hydrochloric acid gave a reaction for pentoses and mucic acid. In conclusion the author considers the hypothetical pectose of the beet to be without doubt a lacton or an anhydride of parapectic acid.

Schryner and Haynes (1916) studied the combustion numbers of pectins obtained from turnips, strawberries, rhubarb stems, and apples and found (with the exception of the apple pectin) the percentage ash free composition to be, C. 41.93, H. 5.17, O. 52.90, which agrees with the formula  $C_{17}H_{22}O_{16}$ . The authors found that pectinogen on distillation with hydrochloric acid yields furfural in such a quantity as to indicate that one pentose group is contained in each complex of seventeen carbon atoms.

Ehreich (1917) published a paper on the constitution and technical importance of pectins. He divides crude pectin from the beet root into two constituents, one a levo-rotatory araban  $-174^{\circ}$  to  $-121^{\circ}$ , and the other, the main constituent, a dextro-rotatory calcium magnesium salt of pectic acid having a specific rotation of

$+150^{\circ}$  to  $+155^{\circ}$ . The author discusses the action and products of these two substances in detail and concludes that his results would indicate that natural pectin of vegetable cell membrane must be



regarded as the calcium magnesium salt of a complex anhydro-arabino-galactose, methoxytetragelacturonic acid.

Fallenberg (1918) found that when a pectin extract is treated with sodium hydroxide a schism of methyl alcohol takes place to the extent of 7 to 11 per cent, and the pectin is converted into pectic acid. Pectin is soluble in water and various preparations yielded furfuraldehyde, corresponding to 35 to 46 per cent of arabinose and 8 to 10 per cent of methylpentose.

#### Determination of Pectin Bodies

Weisberg (1907) points out that the furfural method for the determination of pectin cannot be relied upon in the presence of sugars or other organic material. But the pectin may be determined in the diffusion and in the carbonated juices by means of subacetate of lead, clarifying in one experiment with subacetate of lead, and in another experiment heating to 90 to 95° C. with an excess of it. The difference in polarization gives the quantity of metapectic acid.

Royal and Nestornitz (1914) suggest a method for the determination of pectins, in products of sugar manufacture, by determining the araban and galactan present, the sum of these two groups giving the pectin content. For the former the phloroglucinol method of Tollens and Kruger is suggested, based on the formation of furfural and the conversion of this into araban content by means of suitable calculation factors. For the latter Crydk's method (Z. ver deut Zuckerind, 37, 153, 1887) is employed by which galactan is converted into mucic acid.



Fellenberg (1916) outlined a method for the determination of pectin in spices by the estimation of methyl alcohol. This is a method based on liberating the methyl group ( $\text{CH}_3$ ) as methyl alcohol and determining the methyl alcohol calorimetrically. Wash 1 to 2 gms. of the sample first with boiling, 95 per cent alcohol, then transfer the contents of the filter to a flask while hot; treat with 5 cc. of a 10 per cent sodium hydroxide solution, then 2.5 c.c. dilute sulphuric acid (1 - 4) and distill fractionally three times. The distillate is treated with 1 c.c. alcoholic sulphuric acid, and 1 c.c. 5 per cent potassium permanganate solution. Treat comparison solutions, containing .5 mg., .1 gm., 3 gm. of methyl alcohol at the same time. After two minutes treat each of the mixtures with 1 c.c. of an 8 per cent oxalic acid solution, 1 c.c. concentrated sulphuric acid and 5 c.c. magenta sulphuric acid. Compare colorations obtained after lapse of one hour. The pectin content of the sample is ten times that of the methyl alcohol.

In 1917 Fellenberg published a modification of his method (see above) to include the determination of lignin as well as pectin.

McNair (1916) found that it was possible to determine the amount of pectin present in a solution by the use of a refractometer.

Campbell (1920) in determining pectin in fruit juices, used 10 c.c. of filtered juice and 180 c.c. alcohol, adding the juice drop by drop from a pipette, with vigorous stirring. It was filtered immediately, dissolved in boiling distilled water, evaporated to dryness, heated two hours at  $70^\circ \text{C}$ . in vacuo, weighed, ashed and reweighed. The loss in weight multiplied by 10 equaled the percent of pectin.





### Jelly Formation

Tschirch (1908) experimented with currants. He concluded jelly as due to a pectin and sugar solution or a combination of pectin and sugar. Without sugar he could obtain no jelly.

Miss Snow (1909) determining the effect of sugar and temperature on fruit juices concluded from her results that the density at which a good product is formed varies with different fruit juices, but seems to be nearly uniform for each fruit, and is not effected by the amount of sugar used. The desired density was obtained at a lower temperature and in less time with a large amount of sugar. The smaller the amount of sugar the longer the period of boiling required.

Miss Goldthwaite (1909) found that good fruit jellies invariably gave the methyl alcohol test for pectins, which seemed to indicate that pectin in the formation of jelly does not undergo any deep seated change, but rather that the phenomenon of jelly-making is more nearly physical than chemical. Pectin and acid are necessary to the formation of gels and Goldthwaite found that in the absence of either of these a jelly could not be produced, while it seemed that the quantity of sugar required varied in proportion to the pectin present.

Physical constants of hot juices ready to jell were found to be substantially: boiling point  $103^{\circ}\text{C}$ , and sp. gr. 1.28.

Robertson (1909) considered the formation of gels may be analogous in some instances to emulsification and may, therefore, be dependent on surface tension phenomena.



Goldthwaite (1910) in another article described the making of jelly from a large variety of fruit juices. A great variation was found in the amount of pectin present in different fruits, but by boiling the fruit juice down and adding more acid fair jellies were obtained even from fruits very low in pectin. Miss Goldthwait considered a very frequent cause of failure in jelly-making to be due to the use of too much sugar, while the percentage of inversion of the sugar seemed to have something to do with the production of good jellies, but to what extent was not known.

Haynes (1914) working with pectins from limes together with a little lemon pectin, studied the rate of precipitation of pectins by alkalies and alkali-earths, and after giving an excellent review of the history dealing with the theory of gelatinization, draws the following conclusions:

(1) The rate of gelatinization of pectin is not determined by the rate of diffusion, nor by the rate of surface adsorption of the alkali or alkali earths producing gelatinization.

(2) It can be expressed as a velocity equation determined by the concentration of the reacting substances, when the initial concentration of pectin is constant.

(3) It is, therefore, regarded as determined by the rate of chemical reaction, - the substitution of H by OH, K, etc.

(4) That the reaction of this kind takes place is supported by the fact that the constitution deduced for compounds of the alkalies and alkaline earths is strikingly analogous to that of the corresponding compounds of the mono and di-saccharides. Similar molecular compounds with salts are probably also formed.



(5) Gelatinized pectin forms solid solutions with alkaline earths, which may be compared with the solids of lime and cane sugar.

Fellenberg (1914) obtained very different results from Tschirch. He found that a purified pectin and sugar solution gave no jelly. Pectins from various fruits, and in varying quantities, when added to a sugar solution, resulted in syrups only. He concluded, therefore, that the formation of jelly is due to other certain substances than pectin and sugar, certain salts being necessary, and that it is possible other parts of the fruit juice play active roles in jelly-making.

Ball (1915) studying the action of pectase (pressed from the leaves of *Syringa vulgaris*) on a 2 per cent pectin solution explained the coagulation of pectin thus: --- Pectic acid is produced by the action of pectase on pectin. If electrolytes are absent the mixture remains liquid, but if any ions are present partial precipitation of colloid takes place. At first these colloidal particles will be free from one another, but as the action of pectase proceeds a semi-solid reticulum is built up. If electrolytes are present a large amount of clumping together of the particles takes place, and a suspension is formed with a consequent diminution of viscosity. A maximum viscosity will be reached when the rate of gel formation becomes insufficient to counterbalance the clumping effect.

McNair (1916) testing the viscosity of pectin sugar and acid found:

(1) That all three substances tested, when in aqueous solution, independently increase the viscosity of distilled water.



(2) That mixtures of any two or all three of the substances result in an increase in viscosity greater than the viscosities independently.

(3) That jelly will form when acid, pectin and sugar are in solution of a certain concentration.

(4) That jelly will form from a solution of 3 gm. per cent pectin and 65 gm. per cent sugar.

(5) The viscosities of the separate substances are not additive.

(6) The increase in viscosity may be due to the presence of the hydrogen ion.

(7) That sugar may have two functions, viz., that of a dehydrating agent and by increasing viscosity.

Fellenberg (1918) experimenting with fruit jellies, indicates that these owe their existence to the combined presence of pectin, sugar and salts.

Barker (1918) found that by removing the free acid of a pectin solution by neutralization with calcium carbonate he could preserve the pectin without jellification taking place.

Campbell (1920) obtained the following results on the relation of pectin, sugar and acid in the manufacture of commercial jelly.

(1) A pectin content of 1.25 per cent produces a fine commercial jelly; whereas 1.0 or .75 per cent of pectin produces a delicate quality resembling home-made jelly.

(2) An acidity of .3 per cent (as sulphuric acid) is necessary to produce a good quality gel, the minimum being .27 per cent and the maximum .5 per cent.





(3) An excess of sugar produces a soft gel while an insufficient amount results in a tough product.

### Pectase

Bertrand and Maleore in 1894 discussed the effect of the ferment pectase on pectin, and the wide distribution of that enzyme in plants. It is especially abundant in leaves and it has been possible to prepare it from that source. It can only coagulate pectins in the presence of alkaline earth salts, forming salts of pectic acid. In acid fruits it is present in the soluble form, but its action is inhibited by the free acid.

Bourquellet and Herissey (1898-99) found that a one per cent solution of pectin from gentian root was gelatinized by a solution of pectase in forty minutes. They found the soluble ferments produced by *Aspergillus niger* partially hydrolyzed the pectose in gentian root converting it into pectin. Pectin was hydrolyzed (rendered non-coagulable) by diastase from malt, but not by saliva or emulsin. The ferment which dissolves pectin they called pectinase. Pectase and pectinase added together to a pectin solution caused a coagulation, then solution similar to the effects of rennin and trypsin on casein.

Ball (1915) see jelly formation, p. 28.



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EXPERIMENTAL WORK

--- 0 ---



## PREPARATION AND STANDARDIZATION OF MATERIALS

Pectin

Source of Pectin.----Several pounds of fresh apple pumace were obtained from the Horticultural Department of the college. The pumace was thoroughly dried by spreading it out in a steam drying oven for three days at a temperature of about 70°C. The dried material was then ground at the Experiment Station in the same manner as cattle feeds, and stored in an air tight bottle. This sample, together with an equal amount of commercially dried and ground apple pumace furnished Dr. J. B. Lindsey by W. W. Carey & Son, Lyonsville, Mass., were the sources of pectin used. As no difference could be seen in the extracted pectin from these two sources they were used interchangeably throughout the following experiments.

Method of Extraction and Preparation of Pectin.---

Reviewing the work of earlier investigators it was observed that almost without exception they adopted different methods of extracting and preparing pectin material. A few of the later methods showing particularly the variations in the procedure are as follows: Miss Goldthwaite (1909) precipitated pectin from different juices by running the juice drop by drop into an equal volume of alcohol, allowing the mixture to remain over night and filtering off the excess alcohol through a piece of linen. Shryver and Haynes (1916) extracted pectin material from various sources by treating the marc used with a warm .5 per cent solution of ammonium



oxalate then precipitating the pectin with alcohol. Magoon and Caldwell (1918) treated the water extract of beet marc with commercial alum and ammonia to clarify the liquid and then precipitated the pectin from the clear filtrate with magnesium sulphate. Hunt (1918) precipitated pectin material from a water extract of a beet marc with ammonium sulphate.

Some work was done on the last two methods, but very poor results were obtained due possibly to the rather vague outline given. For the general study of gel formation the more complicated methods of extraction were considered unnecessary, and it was found advisable to work out a simple method of preparing the pectin material.

The necessity for eliminating or reducing as far as possible factors that would influence the gel properties of pectin were considered. It has been known for a long time that long heating would reduce or destroy the gel properties of pectin, though to the writer's knowledge nobody has ever done any very careful work on it. It has been shown by Bigelow, Gore and Howard (1905) that six hours boiling with water under a reflux condenser with change of water at the end of every hour does not completely remove all pectin from apple pulp. Therefore three separate extractions were made, and the pulp heated in all about nine hours. A fourth extraction was tried, heating the pulp three hours longer, but very little pectin was obtained and it was not thought worth while to extract a fourth time.

A number of attempts were made to filter large quantities of the alcohol precipitate of pectin by suction through filter paper, muslin, linen, and by hand through linen, but it was found to be an almost impossible undertaking without the aid of a filter press, particularly as a very large amount of the pectin material was required.





To overcome this difficulty the following method of pectin extraction was adopted in which the pectin material was not precipitated by alcohol, but the liquid extract was concentrated at a low temperature, the very fine precipitate being allowed to settle out from the pectin solution over a period of time. This pectin solution was used with excellent results in place of pectin precipitated by alcohol.

The detailed method is as follows: --- One hundred grams of apple pumace were weighed out on an ordinary balance, transferred to a 1000 c.c. beaker with 800 cc. of added water, and the material heated for three hours in a water bath. The juice was then pressed out by hand through a piece of rough toweling. The residual pumace was treated twice again in the same manner to remove most of the pectin material.

The three filtrates (about 1500 c.c.) were mixed together and filtered twice through a piece of very fine muslin. The resulting liquid, which was thick, turbid brown and gummy, was placed in a 10 inch evaporating dish and reduced in volume from 150 - 200 c.c. in an electric drying oven at a temperature of 70°C. The solution was then placed in a 2 liter bottle and allowed to stand a week or ten days. It was meanwhile preserved from bacterial, yeast, or mold growth, by the addition of a small quantity of chloroform, which was found to be a satisfactory preservative. The pectin solution did not vary during the two months either in per cent pectin or per cent of acid. More than that the texture of gels made from the pectin under similar conditions did not vary during the two months. Shryver and Haynes (1916) used chloroform and toluene to preserve their pectin solutions, and found it satisfactory. While no experiments were run comparing the gels made



from pectin solutions with and without chloroform, still it was noticed that after boiling there was no trace of chloroform left in the gel.

About twenty extractions were made, and it was found that after the liquid had stood for about two weeks a half inch of fine precipitate settled to the bottom of the bottle, leaving about 6 inches of the clear brown liquid on top which was syphoned off. After determining the per cent pectin in this solution, measured quantities of it were used in all the experiments.

Determination of Pectin.---The method of determination of pectin material outlined by Campbell (1920) was followed. The pectin from 5 c.c. of the clear solution was precipitated by 90 c.c. of a 95 per cent solution of alcohol. The juice was added drop by drop to the alcohol from a pipette with vigorous stirring. The precipitate was then transferred to a Gooch crucible, which had been previously prepared with a thin layer of asbestos, dried and weighed. The loss in weight multiplied by 20 equalled the per cent ash free pectin. Checks were obtained to .015 gms.

Grams of pectin obtained from 5 c.c. solution per cent pectin:

Whole mixture before fine precipitate settled out.	.1953 gms.)	} 4.0%
	.2051 " )	
Clear upper mass after fine precipitate settled out.	.1774 gms.)	} 3.5%
	.1775 " )	

These figures go to show that alcohol will coagulate the very fine precipitate at the same time that it precipitates the pectin.

The dried pectin from the clear solution contained 2.72 per cent ash.



Determination of Acidity.---Goldthwaite (1909-10)

found that the acidity of a fruit juice could best be determined by running the fruit juice to be tested into a measured quantity of N/10 NaOH, using phenolphthalein as an indicator. This method was found to be entirely satisfactory for pectin liquids, and the following procedure was adopted.

To 10 c.c. of N/10 NaOH were added 5 drops of phenolphthalein, and the clear concentrated solution of pectin was run in drop by drop from a burette until the end point was reached. From this the per cent acidity was determined, and expressed as per cent H<sub>2</sub>SO<sub>4</sub>, which is the method of expression used by Campbell (1920) and other investigators.

Example of determining acidity and expressing it as

H<sub>2</sub>SO<sub>4</sub>:

10 cc. N/10 NaOH requires 26.31 c.c. of pectin solution

10 c.c. N/10 NaOH = .049 gms H<sub>2</sub>SO<sub>4</sub>

∴ per cent acidity as H<sub>2</sub>SO<sub>4</sub> =  $\frac{.049}{26.31} \times 100 = .186$

An experiment was run to see if the actual acidity of the pectin solution would vary by increasing the volume with distilled water. There was no difference in the actual acidity. The results were the same as those obtained by Goldthwaite (1909-10)

Sugar

Twenty-five pounds of the best quality granulated sugar, from the Revere Sugar Refinery, was purchased through a local dealer on January 31, 1921.



### Acid

Fourteen grams of citric acid, c.p., were dissolved and made up to 100 c.c. with distilled water. This solution was standardized against a N/1 NaOH solution, phenolphthalein being used as an indicator.

After a solution had been prepared for about a week mold growth was noticed, so a little chloroform was added which seemed to keep the acid in perfect condition.

### OUTLINE OF METHOD ADOPTED FOR DETERMINING THE STIFFNESS OF GELS.

The adoption of the following method for determining the stiffness of gels was made only after the various influencing factors had been studied so that the reasons for much of the detailed procedure will be found in the following section of the thesis. This method was followed in all cases except where otherwise stated.

It was found possible and at the same time desirable to do all the work in test tubes as it saved time and permitted a much larger number of experiments to be conducted at one time, which made the work of comparison much easier.





Details of Procedure. --- A definite quantity of sugar was weighed out accurately to 1 c.g. and transferred to a test tube. The cubic centimeters of pectin solution required were added very slowly from a burette, and from a graduated 1 c.c. pipette, enough 2.N citric acid was run in to make up the acidity to .3 per cent (expressed as  $H_2SO_4$ ). Water was then added to bring the volume up to 10 c.c. and the material thoroughly mixed together with a stirring rod. This solution was placed at once in an oil bath, having a temperature of 115 - 120°C. for exactly ten minutes. The solution was then stirred continuously to insure complete mixing of the materials and to prevent boiling over or bumping. After standing at room temperature for 24 hours the gels were removed carefully with a piece of flat galvanized iron, about 1 c.m. wide and 18 c.m. long, rounded at the end so that it could reach to the bottom of the test tube. It was found possible after a little practice to remove these gels without injuring their form in the least.

The gels were then classified according to the following scale.

- |                               |                                |
|-------------------------------|--------------------------------|
| 1. No gel                     | 5. Good gel (Commercial jelly) |
| 2. Poor gel                   | 6. Stiff gel                   |
| 3. Soft gel                   | 7. Very stiff gel              |
| 4. Fair gel (Household jelly) |                                |

It was difficult at first to establish any kind of a comparative standard that could be carried from day to day, and an attempt was made to devise some kind of a mechanical method for determining the stiffness of gels. This was found to be a separate problem, and it was not until the very excellent description of Goldthwaite (1915) was adopted for 4, Fair gel



(Household jelly) that it was possible to build up the required range without the application of a mechanical tester. Her description of a good fruit jelly is as follows: --- "By jelly is meant, <sup>a</sup> - mass will quiver not flow when removed from its mold; a product with texture so tender that it cuts easily with a spoon and yet so firm that the angles thus produced retain their shape; a clear product that is neither syrupy, gummy, sticky, nor tough; neither is it brittle and yet it will break and does this with a distinct beautiful cleavage which leaves sparkling characteristic faces."

As the gels become stiffer the distances between the numbers increases (Table V), and it was found possible to use  $1/2$  or even  $1/4$  to signify about where the gel stood between the two numbers.

Example.---Materials needed to make 10 c.c. of a gel containing 1 per cent pectin, .3 per cent acid and 100 gms. sugar to 100 c.c. solution, containing pectin, acid and water.

<u>From Table IV</u>		<u>Actual Amounts</u>	
Sugar,	6.17 gms.	Sugar,	6.17 gms.
Solution,	6.17 c.c.	Pectin sol.(3.5%)	2.86 c.c.
-----		Citric acid (2.N)	.25 c.c.
Total volume	10 c.c.	Water,	3.06 c.c.
		-----	
		Total volume	10. c.c.

Attention may be drawn here to the fact that in all the following work the per cent pectin and acid are not based on the amount of solution used, but on the total volume of the gel solution containing pectin, sugar, acid and water before being heated (sp. gr.= 1).



This relationship was adopted because it made comparisons easier, tending to simplify the whole study of pectins.

#### FACTORS INFLUENCING THE CONSISTENCY OF GELS.

It is agreed by many investigators, Caldwell (1917), Goldthwaite (1909-10) and others, that heating pectin material for a long time destroys its gel properties. In one experiment the pectin extract was heated 72 hours, the alcoholic precipitate at the end of that time giving 87 per cent of the original pectin material present. If long heating does destroy the gel powers, which was not tried at this time, then the alcoholic precipitation is no means of determining the gel powers of pectins and possibly not of pectin.

The real method then for determining the gel-forming powers of pectins would seem to be, to make gels from them and compare their texture, assuming that a stiffer gel indicated more pectin or a pectin of greater gel-forming power.

It was, therefore, considered that before any investigational work could be conducted that a gel standard was necessary, and before this could be established it was essential to know something of the factors influencing gel formation, - enough at least to be able to control them.



After considerable preliminary work it was found that the following factors influenced the consistency of gels, when pectin, sugar and acid were first mixed together in the cold:

1. Time of heating.
2. Temperature of bath.
3. Per cent acid.
4. Concentration of sugar.
5. Per cent pectin.

Time of Heating.---The practice of boiling the solution of pectin, sugar and acid to a definite boiling point or specific gravity, Snow (1909), Goldthwaite (1909-10), Campbell (1920), was considered to be the reason for at least some variations in the production of uniform gels. If there is an action of the acid on the sugar or on the pectin, and the action varies with the time of heating, such a method of boiling to a definite temperature will give a gel product which may be influenced by several interdependent factors, the extent of which is unknown. An attempt is made later to indicate what some of these factors may be.

To eliminate as far as possible any reaction that may take place, due to long boiling or high temperature, the shortest time was selected at which even the most concentrated sugar solutions could be mixed and dissolved. It was found that ten minutes was the shortest time with constant stirring that would insure complete solution of the sugar together with the dissolving of any little particles of gel material that are sometimes formed when the solution is first heated. That this time is not too short to make good





gels out of a normal amount of materials can be seen from the data in Table I.

The failure of some of the sugar to dissolve between 5 - 7 minutes heating accounts to some extent for the poorer gels.

At this time an attempt was made to measure the difference in evaporation between 5 and 10 minutes boiling, but the amount lost was so small it could not be measured.

TABLE I<sup>+</sup>Time of Heating

Pectin, 1%. Temperature 115-120°. Acid, 0.3%.							
Time, minutes	5	6	7	8	9	10	
Sugar to 100 c.c. sol. gms.							
70	1 <sup>+</sup>	1	1	1	2	2	
75	1	1	2	2	2	3	
80	1	2	2	2	3	3	
85	3	4	4	5	5	5	
100	4	4	5	5	5	5	
115	4	4	4	4	4	4	
130	4	4	4	4	4	4	
150	2	2	2	2	2	2	

<sup>+</sup> The quality of the gels are indicated by numbers. (See page 38 for original assignment of numbers.) Number 4 indicates a good household gel while 5 a good commercial gel.



Temperature of Bath.---It was found that the temperature of the boiling gel solution varied with the quantity of the sugar and, to a small extent, with the amount of pectin used. The boiling point varied anywhere from  $101^{\circ}$  -  $110^{\circ}\text{C}$ .

That the temperature of the bath has an effect on the consistency of the gels was brought out in a series of experiments in which various amounts of sugar were heated with pectin and acid for 10 minutes at different temperatures, varying about  $5^{\circ}\text{C}$ . from each other. The figures given in Table II represent in general the extreme of temperature within which it was attempted to keep the gas heated oil bath. For the most part the temperature remained at a point midway between the extremes.

TABLE II<sup>+</sup>

Difference in Temperature

Pectin, 1%. Time, 10 minutes. Acid 0.3%.

Temperature of bath, Deg. C.	100-05	105-10	110-15	115-20	120-25	125-30
Sugar to 100 c.c. sol. gms.						
70	1	1	2	2	2	2
75	1	1	2	2	3	3
80	3	3	4	4	5	5
85	3	4	4	5	5	5

+ See page 38 for reference to symbols.  
4 indicates a good household gel while  
5 a good commercial gel.



The data shows that the higher temperatures make stiffer gels which may be due to the longer boiling of the solution as a higher temperature would bring the solution to boiling in much less time than a lower temperature. This is further indicated by the fact that the last 10 degrees made no difference in the consistency of the gels. It was found, however, that between the temperatures of 120 - 130°C. it was almost impossible to keep the solution from boiling over. Therefore to insure a sufficient and yet constant temperature, 115 - 120°C. was chosen for all the experiments.

Acidity of Solution.---The amount of acid in the original pectin solution must always be known. (The acidity of the clear pectin solution used was .186 per cent, expressed as per cent H<sub>2</sub>SO<sub>4</sub>). Knowing the quantity of pectin solution to be used the amount of acid added was calculated and enough 2.N citric acid added to make the acidity .3 per cent of the total volume of the gel solution (page 37).

It can be seen from the following table that .3 per cent acid is necessary for the production of the best gel whether the pectin used is 1 or 2 per cent or if the sugar is 80 or 160 gms. Any amount of acid over that even up to 1.8 per cent did not alter the consistency of the gel. No experiments were conducted to find out what the effect of long boiling with varying quantities of acid would be on the quality of gels. Campbell (1920) found that boiling fruit juices to a definite boiling point, the range of acidity was as narrow as .27 - .5 per cent (as % H<sub>2</sub>SO<sub>4</sub> ).



TABLE III  
Effect of Acidity

Time, 10 minutes. Temperature, 115 - 120°

Pectin 1% Sugar 80 gms. to 100 c.c. sol.		Pectin 2% Sugar 80 gms. to 100 c.c. sol.		Pectin 1% Sugar 120 gms. to 100 c.c. sol.	
Acidity	No. Gel <sup>+</sup>	Acidity	No. Gel.	Acidity	No. Gel
.04	1	.08	1		1
.1	1	.1	1	.1	1
.2	2	.2	2	.2	1
.3	5	.3	5-6	.3	2
.4	5	.4	6	.4	2
.6	5	.6	6	.6	2
.8	5	.8	6	.8	2
1.0	5	1.0	6	1.0	2
1.2	5	1.2	6	1.2	2
1.4	5	1.4	6	1.4	2
1.6	5	1.6	6	1.6	2
1.8	5	1.8	6	1.8	2

+ Explanation of numbers on page 38.





Concentration of Sugar and Volume of Solution, - Sugar.

As the final volumes of all the solutions were to be made up to 10 c.c. it was necessary to find the increase in volume of water on addition of varying amounts of sugar. To 100 c.c. of water 10 gm. quantities of sugar were added, and the increase in volume noted. (See Table IV, second column.) As the volume of the solution approached 200 c.c. it gradually increased on the addition of 10 gms. of sugar, but this increase was so small, only 1 c.c., it was not considered necessary to make allowance for it. The quantity of sugar used, therefore, was based on the grams of sugar required to 100 c.c. of a solution containing pectin, acid and water, and it was found that 5 gms. variation of sugar would influence the consistency of gels enough to record. From the figures in column two it was easy to calculate the grams of sugar required to make 10 c.c. of solution of 5 gm. per cent variations and this is given in column three.

Solution.---Column four, Table IV, gives the cubic centimeters of solution containing pectin, acid and water, required in addition to the sugar to make 10 c.c. of gel solution. For an example of the volumes of the various constituents that go to make up 10 c.c. of solution see page 39.

THE HISTORY OF THE UNITED STATES

The history of the United States is a story of growth and change. It begins with the first settlers who came to the shores of the Atlantic coast in the early 17th century.

As the colonies grew, they developed their own institutions and customs. The struggle for independence from Britain was a natural result of this process.

The American Revolution was a turning point in the nation's history. It led to the creation of a new government based on the principles of liberty and justice for all.

The Constitution of the United States was drafted in 1787 and has since served as the foundation of the nation's government.

The history of the United States is a story of progress and achievement. It is a story of a nation that has grown from a small group of colonies to a great power.

The American dream is a dream of opportunity and success. It is a dream that has inspired millions of people to build a better life for themselves and their families.

The history of the United States is a story of resilience and strength. It is a story of a nation that has overcome many challenges and emerged as a more united and powerful people.

The American spirit is a spirit of freedom and democracy. It is a spirit that has guided the nation through its history and will continue to guide it in the future.

The history of the United States is a story of hope and possibility. It is a story of a nation that has the potential to create a better world for all its people.

The American dream is a dream that is within the reach of every person. It is a dream that is worth fighting for and worth believing in.

1111

TABLE IV

Volume Relations of Dry Sugar and Liquid in 10 c.c. of Gel.

Sugar to 100 c.c. sol. gms.	Total Volume of 100 c.c. Water and Sugar	Sugar Required for 10 c.c. gel sol. gms.	Volume of liquid necessary to make 10 c.c. when sugar is added. c. c.
50	131.0	3.82	7.63
55		4.09	7.42
60	137.2	4.37	7.29
65		4.67	7.13
70	143.4	4.88	6.97
75		5.12	6.82
80	149.6	5.35	6.68
85		5.57	6.55
90	155.8	5.78	6.42
95		5.98	6.29
100	162.0	6.17	6.17
105		6.36	6.04
110	168.2	6.54	5.95
115		6.71	5.84
120	174.4	6.88	5.74
125		7.02	5.64
130	180.6	7.20	5.54
135		7.35	5.44
140	186.8	7.49	5.35
145		7.64	5.27
150	193.0	7.77	5.18
155		7.90	5.10
160	199.2	8.03	5.02
165		8.16	4.95
170	205.4	8.27	4.87
175		8.39	4.79
180	211.6	8.51	4.72
185		8.61	4.65
190	217.8	8.72	4.59



Varying Amounts of Pectin.---By determining the per cent pectin in the original solution it was found possible to measure through a burette the cubic centimeters necessary to give the grams of pectin required for an experiment. The per cent pectin is the per cent compared with the final volume of the solution after sugar, pectin, acid and water have been mixed together and before it is boiled (p.46) . A variation of only .1 per cent pectin is noticeable in the character of the gel. Tables showing the effect of varying quantities of pectin and sugar follow under the general head, "A Standard for Gels."

#### THE INFLUENCE OF PECTIN AND SUGAR ON THE QUALITY OF GELS.

In order to determine the gel powers of pectin from a single source with varying amounts of sugar and pectin, keeping the amount of acid constant, a series of experiments were conducted in which the ingredients were mixed, heated and allowed to stand for 24 hours when they were examined for consistency.

The following table shows the influence of .1 per cent variation of pectin from .3 - 1.6 per cent, and the influence of 5 gm. variations of sugar; using sugar in amounts corresponding to 60 - 150 gms. in 100 c.c. of solution. The lowest gel limit



for the range of pectins remained constantly at 65 gms. of sugar, while the upper limit of gels increased from 115 gms at .3 per cent pectin to 145 gms. of sugar at 1.6 per cent pectin. The range of the stiffest gels (numbers 3 to 7 1/4) also increased from 95 - 105 gms. of sugar as the amount of pectin increased.

As the per cent of pectin increased it became hard to classify the pectins for stiffness by the method adopted so that any work with pectin solutions above 1.6 per cent was not included in the tables. The range from .3 - 1.6 per cent pectin was considered wide enough for the study of variations in the gel producing powers of pectins.





TABLE V<sup>+</sup>

Character of Gels with Varying Amounts of Pectin and Sugar

Pectin % Sugar to 100 c.c solution gms.	Temperature, 115-120°C. Time, 10 minutes. Acid, .3%. <i>Volume</i>													
	.3	.4	.5	.6	.7	.8	.9	1.0	1.1	1.2	1.3	1.4	1.5	1.6
65	1 1/2													1 1/2
70	1	1 1/2	1 1/2	1 1/2	1 1/2	1	2	2	1	4	4	5 1/2	5	5
75	2	2	3	3	3	3	3 1/2	4 1/2	5	5	5 3/4	6	6	6
80	2	3	3	4	4	4	5	5 1/2	5	5	6	6 1/2	6 1/2	6 1/2
85	2	3	3 1/2	4	4	5	5	5 1/2	5	5	6	6 1/2	6 1/2	6 1/2
90	3	3 1/2	4	4 1/2	4 1/2	5	5 1/2	5 1/2	6	6	6 1/2	6 3/4	6 3/4	7
95	2	3	4	4 1/2	5	5 1/2	5 1/2	6	6	6	6 1/2	6 3/4	6 3/4	7 1/4
100	2	3	4	4 1/2	4 1/2	5	5 1/2	6	6	6	6 1/2	6 3/4	7	7
105	2	3	4	4	4	5	5 1/2	6	6	6	6 1/2	6 3/4	7	7
110	2	3	3	4	4	5	5 1/2	6	6	6	6 1/2	6 3/4	7	7
115	2	2	3	3	4	4 1/2	5	5 3/4	6	6	6	6 1/2	6 1/2	7
120	2	2	3	3	4	4	5	5 1/2	6	6	6	6 1/2	6 1/2	7
125	1	1	2	2	3	4	4	5	5	5	5 1/2	6	6	6 3/4
130	1	1	2	2	3	4	4	4 1/2	5	5	5 1/2	6	6	6 1/2
135							2	4	4	4	5	5 1/2	6	6 1/2
140							1	2	3	3	4	5	5 1/2	6 1/2
145							1	1	1	1	2	2	3	4
150								1	1	1	1	1	2	2

+ Quality of gels indicated by numbers. See page 38.



CHART I

Influence of Sugar and Pectin on the Consistency of Gels.

Very Stiff Gel - 7

Stiff Gel - 6

Good Gel - 5

Fair Gel - 4

Soft Gel - 3

Poor Gel - 2

No Gel - 1

1.6  
1.4  
1.2  
1.0  
0.8  
0.6  
0.4  
% Pectin:  
Stiffest Gels

51  
140 Grams Sugar to  
100 c.c. Sol.

140  
130  
120  
110  
100  
90  
80  
70

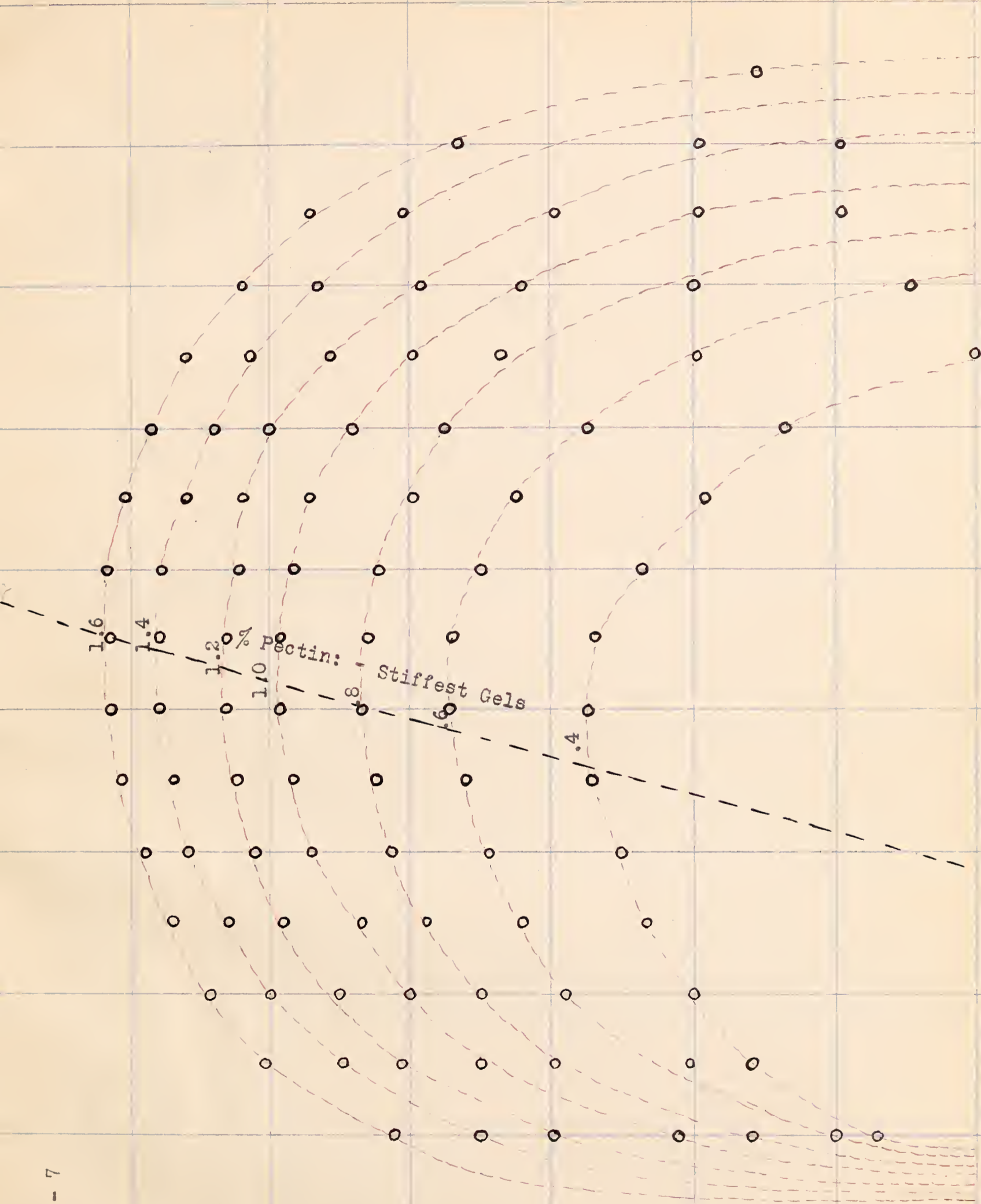
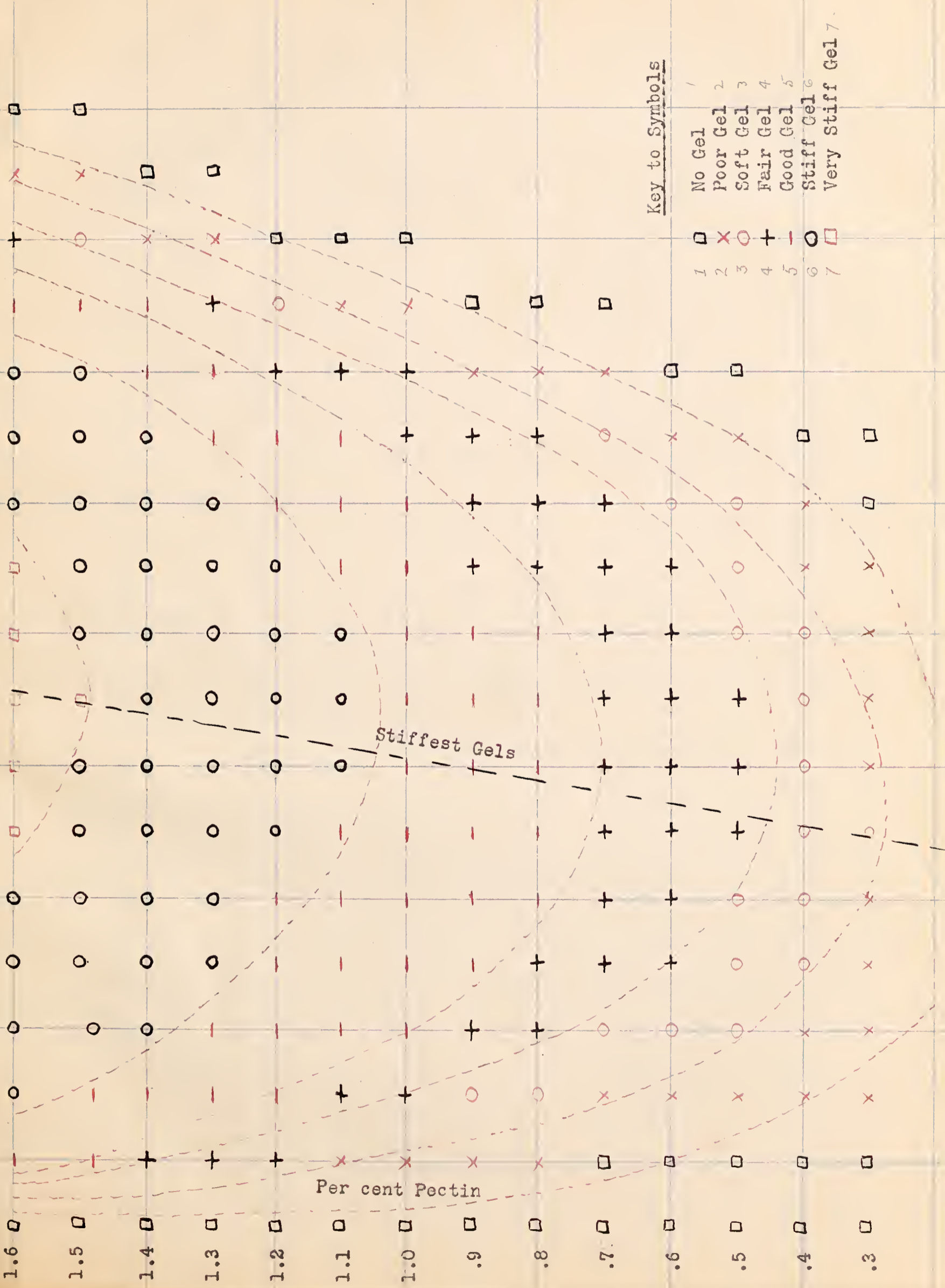




CHART II

Areas of Various Gel Consistencies.



Key to Symbols

- 1 No Gel
- 2 Poor Gel
- 3 Soft Gel
- 4 Fair Gel
- 5 Good Gel
- 6 Stiff Gel
- 7 Very Stiff Gel



Referring to Chart I, experiments have been carried through with every .1 per cent variation in pectin. The odd numbers have not been included in the chart and the results only of the even per cents of pectins are given. Each experiment with a test tube is indicated on Chart I by "O". The chart shows the curves of pectin solution when 5 gm. variations of sugar to 100 c.c. of solution and the arbitrary gel stiffness are plotted against each other. While these areas, of necessity, are not sharply defined still the chart serves to bring out more clearly the information contained in Table V, - the sharp lower end point of the gels, the general increase in the sugar required for the stiffest gel and the extended end points varying with the per cent pectin at the upper limit of the gels.

In addition it is seen that with each pectin concentration there are two points of the same gel consistency below the point of the stiffest gel, one with less and one with more sugar. For example, with a 1 per cent solution the same gel consistency can be made with either 85 or 120 grams of sugar.

Considering the left hand side of the chart which covers the curves of pectins containing less sugar than will produce the stiffest gel, the graphs show that as the amount of pectin is increased the amount of sugar necessary to make a gel of the same consistency is decreased. In other words, gels of the same consistency can be made by various combinations of sugar and pectin. For an example of this let us state a set of combinations in the region of good gels, taking only the left-hand side of the chart, - a 1.6 per cent pectin will make a good gel with 75 gms. sugar to 100 c.c. of solution; a 1.4 per cent pectin with 77 gms. of sugar; a 1.2 per cent pectin with 85 gms., and a 1.0 per cent with 102 gms. of sugar.





Chart II brings out this last fact still more clearly. Here the results of every .1 per cent of pectin are given. The sugar and pectin are plotted against each other and the chart divided into areas which are marked with different symbols. Each area includes the greatest possible number of variations of sugar and pectin that will, under standard conditions, produce gels that can be grouped or classified under the seven different headings given.

It should be possible, therefore, in practice to control the quality of gels with varying quantities of sugar and pectin so that a uniform quality of gel can be obtained within a range of at least .6 - 1.5 per cent pectin and 70 - 140 gms. of sugar to 100 c.c. solution.

#### THE INFLUENCE OF HEATING ACID IN VARIOUS COMBINATIONS ON THE QUALITY OF GELS.

In ordinary experience a large amount of sugar is considered detrimental in the production of a good fruit gel, such mixtures remaining as a syrup. This was found to be the case in all the previous experiments, and it was not until some experiments were conducted with gels containing over 150 gms. of sugar to 100 c.c. solution that it was observed that, when the acid was heated first with sugar and water before the pectin was added, good gels could be obtained regardless of the large amount of sugar in solution. This discovery led to the development of the data in Table VI in an attempt to find the cause of this unusual phenomenon.



TABLE VI

Heating with Acid.

Pectin, 1%. Temperature, 115-120°.

Series	Sugar and Water		Pectin Solution		Sugar, Pectin Acid		Solution to 100 c.c. sol.		
	Acid %	Time of heating min.	Acid %	Time of heating min.	Acid %	Time of heating mixture min.	A 75 gms.	B 100 gms.	C 160 gms.
0					.3	15	4	5	2
1					.6	15	4	5	2
2					.6	30	4	4	1
3					.6	60	2	2	1
4	.6	10	0	0	0	5	3	4	4
5	.6	25	0	0	0	5	3	4	4
6	.6	55	0	0	0	5	1	4	4
7	.3	10	.3	10	0	5	3	3	4
8	.3	25	.3	25	0	5	3	2	4
9	.3	55	.3	55	0	5	1	1	4
10	0	5	.6	10	0	5	3	4	2
11	0	5	.6	25	0	5	1	3	2
12	0	5	.6	55	0	5	1	3	1
13	0	5	0	10	.6	5	1	3	3
14	0	5	0	25	.6	5	1	3	3
15	0	5	0	55	.6	5	1	1	2



Five separate lots of experiments were run in which the sugar, acid and pectin were heated in various combinations. Each lot was divided into three series which were heated for 10, 30 and 60 minutes respectively. Each series was made up of three test tubes of gel containing 75, 100 and 160 gms. of sugar to 100 c.c. solution. The experiments were arranged in this way so that the effect of long heating of different combinations of pectin, sugar and acid, could be seen on gels containing a low, medium and large amount of sugar. The results obtained do not show conclusively the reason for the variations noted, still they serve as an indication of the causes, and at the same time open up a field for further investigation.

In all the work outlined in the table, the volume of the solutions was made up to 10 c.c. before heating together for the last 5 minutes. This was done so that there would be no variations in the concentrations of the solutions due to long boiling.

Acidity of .6 per cent was used in these experiments as it was considered that whatever variations were due to the acid would be more pronounced if .6 per cent rather than .3 per cent acid were used. Series 0 was used as a check to determine whether there was any difference between .3 and .6 per cent acid. When the gels were heated for 15 minutes no difference was observed.

From a study of the series 1 - 2 - 3 of the table, in which pectin, acid and sugar, were being heated together, it can be seen that long heating or an excess of sugar (160 gms.) will interfere with the formation of a good gel.

On the other hand where the sugar and acid are first heated together, series 4 - 5 - 6, the pectin added and the solution heated for 5 minutes, good gels are obtained with an excess of sugar. In 6A, only, where 75 gms of sugar were used there was no gel.



Series 7 - 8 - 9, where the acid was divided and the pectin and sugar solutions were heated separately the same length of time, indicates that some other factor enters into the production of a good gel, where the sugar is in excess, besides the simple destruction of the pectin by the acid with long heating.

The above indication is brought out still more plainly by series 10 - 11 - 12C, where the sugar is heated without any acid, and where the pectin solution contains all the acid, and poor gels are obtained. This would indicate that not only are the gel properties of pectin destroyed by long heating with an acid but in concentrated sugar solutions a certain amount of hydrolysis of sugar is necessary for the production of a good gel.

The production of "soft" gels, obtained in series 13- 14 - 15C, where the sugar and pectin are heated separately and the acid added before heating together for 5 minutes, might be explained by the increased gel powers of the pectin because the pectin was not heated with the acid, or by the fact that the pectin does not interfere with the action of the acid on the sugar when the acid is heated for only 5 minutes with the pectin and sugar.

In summing up the results of these experiments it would appear that there are a number of factors that influence the quality of gels.

(1) The hydrolysis of the sugar is desirable in concentrated sugar solutions, but where there is only a small amount of sugar in solution too much hydrolysis results in a poor gel. This would indicate that some balance was desirable in the solution between twelve and six carbon sugars or else there is some relationship necessary between the twelve carbon sugars and the solution of pectin. If it were simply a case of hydrolysis good gels could be obtained even with low amounts of sugar, but this has not been found to be the case.





(2) The gel properties of the pectin are destroyed by long heating with an acid, due possibly to the hydrolysis of the pectin. This fact of course has been known for a long time. As far back as 1840 Frémy observed that the gel properties of pectins were destroyed by heating.

(3) Comparing series 1 - 2 - 3C, where sugar, pectin and acid are heated together for varying lengths of time, with series 7 - 8 - 9C where the sugar is heated with .3 per cent acid and the pectin heated with .3 per cent acid, the solutions being kept separate except for the last 5 minutes, it may be concluded that the pectin must in some way interfere with the action of the hydrolysis of the sugar, or the hydrolysis of the pectin may be more rapid in the presence of a sugar solution with long heating.

(4) A study of series 13 - 14 - 15C would indicate that when the pectin and sugar are heated for a very limited time with .6 per cent acid the pectin does not interfere to the same extent with the hydrolysis of the sugar when the sugar solution is concentrated (150 gms.)

(5) When 100 gms. of sugar are used to 100 c.c. of solution the quality of the gel is less effected by various combinations than at either extreme of sugar concentration.

As has been said before these results are not conclusive. They only show the presence of an interesting factor or factors, and some very careful analytical work will have to be done before any definite conclusions can be drawn.



## SUMMARY

(1) A method of extracting pectin has been developed which interferes to the least possible extent with the quality of the original pectin.

(2) A procedure for handling and determining the gel properties of pectin is given in detail. The procedure was found to be reliable and a great amount of time and material were saved in conducting the experiments.

(3) The following factors were found to influence the quality of gels: --- variations of 5°C. in temperature; one minute variations in time of heating; 5 gm. variations of sugar to 100 c.c. solution; 0.1 per cent of pectin; acidity from 0 - .3 per cent.

(4) A table and two charts have been developed which show the influence of 0.1 gm. variations of pectin ( .3 - 1.6%) with 5 gm. variations of sugar to 100 c.c. solution (64 - 150 gms.). The table may be used as a standard to study pectins from various sources and the effect of different methods of extraction and preparation on the gel qualities of pectins.

(5) The effect of heating acid, sugar and pectin in various combinations has been studied, and it has been found that good gels can be obtained with large amounts of sugar where the sugar and acid are first heated together, the pectin added and the solution heated for only a few minutes.



## CONCLUSIONS

- (1) It is possible by controlling the factors of heat, temperature, sugar, pectin and acid to produce gels of the same consistency at any time.
- (2) The practice of boiling gel solutions to a definite temperature does not seem to be advisable when the stiffest gels are desired.
- (3) Contrary to the usual belief good gels can be obtained from a solution of apple pectin containing a high concentration of acidity when the pectin and acid are not heated together for a long time.
- (4) With gel solutions ranging from .3 - 1.6 per cent pectin the sugar limits are from 65 - 145 gms of sugar to 100 c.c. solution when sugar, pectin and acid are all heated together for 10 minutes.
- (5) As the amount of pectin is increased the amount of sugar necessary to make the stiffest gels increases so that gel formation seems to be due to a ratio of sugar and pectin rather than the arbitrary amounts of three substances.
- (6) The concentration of the sugar can be so regulated that the same quantity of gels can be produced with pectin solutions of various strengths by regulating the amount of sugar to be used by the amount of pectin in the solution.
- (7) There seem to be several factors entering into the production of good gels.
  - (a) A certain amount of inversion of sugar seems to be necessary, but only where there is an excess of sugar in the solution.



(b) The gel powers of pectin are destroyed by long heating with an acid.

(c) Where the concentration of sugar is great in the solution the presence of pectin at a high temperature seems to interfere with the action of the acid on the sugar.

(d) With less heat the pectin in concentrated solutions of sugar does not seem to interfere to such an extent with hydrolysis of the sugar so that better gels are produced.





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