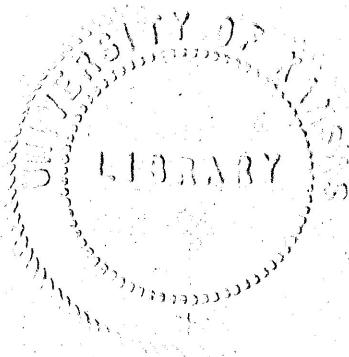


A STUDY OF PECTINS



by

Bertha Kitchell.

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A Study of Pectins. .

I. Introduction.

Pectin is understood by the great number of investigators, chiefly Tschirch and Fellenberg, to be that substance which is found in the sap or juice of fruits, gives a colloidal solution with water, is capable of being precipitated with alcohol, which is obtained either by ripening or chemical processes from the middle lamellae of the cell walls, and which leads under certain conditions to the formation of fruit jellies. It is closely allied with cellulose and with the gums and is considered by some as a step from one to the other. The occurrence of pectin is very wide. It is found in roots, rhizomes, stems, fruit, and even leaves. It may be found later that pectin occurs in all plants and in all plant parts. Some of the most prolific sources of pectin are rinds of citrus fruits, apples, pears, quince, cranberries, logan-berries, grapes, turnips, beets, and carrots.

The history of the work on pectins has been well covered up to 1914 in the "Historical Review" of W. D. Bigelow and H. C. Gore (Bulletin 94, U. S. Dept. of Ag-

riculture) and in Theodore Fellenberg's work on pectins.

In 1910 A. von Tschirch contributed a notable paper on "The Structure of Pectin" in which he demonstrated the location of the pectin in the plant. In 1914 came Theodore Fellenberg's contribution to the subject. Due to his investigations methyl alcohol was added as one of the constituents of pectin and he suggested that pectin was a methyl ester of pectic acid. He also gave the action of metallic salts on pectins and attempted to disprove the theory that protopectin is the calcium salt of pectin. In addition to this, Fellenberg made careful studies of the properties of pectin and pectic acid, a quantitative, if not very convincing, determination of the constituents of pectin, and a study of the value of salts in jelly-making.

L. E. Verdon (in J. Pharm. Chim. 5, pp. 347-53) gave the specific rotation of pectin from the roots of *Verbascum thapsus* L to be 123.76, and the specific rotation of the ash-free dried pectin of leaves of *Kalmia latifolia* to be 158.62. These were the first leaves to be studied for pectin. In a paper on "Pectins from Aucuba and from the Rind of Sweet Oranges", by V. Harlay (J. Pharm. Chim. 5, pp. 344-7), the specific rotation of the orange pectin was given as 176.6 and that from the aucuba as 217.3. These determinations were

made from the ash-free pectin, obtained by solution in water, precipitation with alcohol and hydrochloric acid, and purification by reprecipitation.

According to Edward Schneider, pectin prepared from apple marc by hydrolysis with hydrochloric acid yielded 35.87% pentosans and 45.83% galactan, the digestibility coefficient of the former being 88.69 while that of the latter was 76.78.

Altho the formula for pectin had been set forth by many of the older authors in various ways, Fellenberg did not feel justified in setting up a formula for pectin, because the substance itself had never been prepared in a sufficiently pure state and because the metal-pectin precipitates from whose analysis the formulae were derived could not be obtained as constants.

As yet pectin is one of the "great unknowns" of chemistry. Of what is it made up? That it is complex we know. Is it a cellulose or a hemi-cellulose, or does it more resemble the gums? Is there really a protopectin (as Tschirch calls the fore-runner of pectin), and if there is, what does happen when the protopectin of unripe fruit changes into the pectin of ripe fruit? Is pectin a methyl ester of pectic acid and is protopectin a calcium pectate? Is it possible to obtain an ash-free

pectin? Is it possible to get a quantitative separation of pectin from the fruit or root? Can we say that there is a galactan in pectin because mucic acid is obtained on oxidation with nitric acid? Are the pectins of various fruits and roots essentially the same or are they specific for different plants like the proteins? How does pectin differ from gelatin and can jellies be obtained from gums? If a jelly is a concentrated emulsion, what are the factors governing the production of a jelly? These and many more questions await solution.

II. Properties of Pectin.

The following comparisons can be made between the properties of celluloses, gums, and pectin. All three are alike in that they come from plants, roots, leaves, stems, or fruit; are carbohydrates of complex constitution; deflect the rays of polarized light to the right; form reversible colloids with water; leave an ash on ignition from which it is impossible to wholly separate them; and do not reduce Fehling's solution unless hydrolyzed. Gums and pectins are both precipitated by means of alcohol and both contain the phosphate radicle which might be important in the synthesis of the substances.

The hydrolysis products of the three substances

are somewhat similar in that they all give mono-saccharoses; but cellulose gives glucose, while the gums give arabinose and xylose, and the pectins give arabinose, mucic acid, and methyl alcohol. On hydrolysis with nitric acid cellulose gives a series of nitro-celluloses, while it is here that the pectin yields mucic acid.

Gums and pectins are precipitated by basic lead acetate. Pectin is also precipitated by copper sulphate, lead nitrate, neutral lead acetate, ferric chloride, and stannous chloride. The last three precipitate on long standing. Cellulose is dissolved by ammoniacal copper sulphate, stannous chloride in a solution of hydrochloric acid, and in solutions of cupric oxide in ammonia, and one made up of two parts of sulphuric acid to four parts of water.

The two characteristics which seem to be special for pectin are its solubility in sugar solution and its ability to form a jelly when its solution in sugar is concentrated.

III. Preparation of Pectin.

A. Pectin from Apples.

In the preparation of pectin, the Bourquelot and Herissey method was employed (Ibid. 6, 7, pp. 473, 1898).

Apple Extraction I.

2 kg. of apples were cored and ground to a fine pulp and then boiled seven times with 2-3 liters of 95% alcohol for two minutes. After each extraction the marc was expressed. There resulted 300 gm. of alcohol-moist marc. This was heated one hour at 110 degrees with 2,250 cc. of distilled water. (The high B. P. was reached by a boiling mixture made up of ammonia chloride and water in the proportion of 60 gm. of NH_4Cl to 100 gm. water.) The boiling was carried on in pressure bottles and at the end of the hour the pectin solution was expressed from the marc. The apples used were Kansas Jonathans, taken from cold storage, and the extraction was started on February 22, 1916. The filtrate was filtered several times thru a filter paper by means of a filter-pump until it was fairly clear; it was then precipitated with twice its amount of alcohol to which had been added hydrochloric acid in the proportion of 7 cc. of acid to 1,800 cc. solution or 0.39 cc. acid to 100 cc. of solution. The pectinous substance was pressed thru a cloth, kneaded out with alcohol until the acid reaction had disappeared; the alcohol was then boiled out and the pectin washed with ether and dried in an oven (water). The ash obtained from 0.29997 gm. was 3.85% of the pectin sample, using calibrated weights, a very small platinum crucible for ignition, and keeping

the air surrounding the balances dry. Fellenberg obtained 5.3 gm. under the above conditions, while at this juncture with the Kansas Jonathans less than a gram of pectin was obtained, with an ash content considerably above Fellenberg's, which was 0.25%, the lowest ever obtained. These differences might be due to the time of year that the extraction was made and the kind of apples used.

Apple Extraction II.

A second extraction of pectin from apples was made, using the same method and apples from the same box as those in the above extraction were taken from, but one week later. The apples had lost some of their moisture. In this case 304 gm. of alcohol-moist marc was obtained; 50 gm. of the marc was treated with 370 cc. of distilled water at room temperature, about 20° C., and allowed to stand for six days. The marc was then expressed, the solution filtered, and twice its volume of alcohol added. A precipitate of pectin was formed. The water was removed by boiling under reduced pressure and expressing. There was not enough pectin to weigh, but sufficient to identify its presence. It would have been interesting to compare the ash of the pectin obtained by this process with that of the pectin extracted

from the marc by boiling with distilled water.

Half of the remainder of this Apple Extraction II marc was boiled at 110° with distilled water under increased pressure and half with Lawrence city water, on February 16, 1916. (See foot-note)¹. The boiling was continued for one hour and the marc expressed. The thick solution obtained was a dark brown color, lighter in the case of the distilled water extract, and was but slightly deprived of its color by filtering. Centrifuging for twenty minutes at a high rate of speed removed about half of the suspension and coloring matter. But even after an hour's centrifuging all the impurities could not be separated from the colloidal solution of the pectin. The following experiments were performed to remove the color and turbidity from the solution of the city water extract.

(1) Reprecipitation with Alcohol.

In precipitation of the pectin with alcohol, twice the amount by volume of alcohol is used to one

1. Lawrence City Water (Bulletin No. 10, University of Kansas).

Mineral Analysis	Parts per Million.
Iron and Aluminum Oxides.....	14.0
Silica.....	37.4
Calcium.....	125.9
Magnesium.....	18.4
Sodium and Potassium.....	37.0
Chlorine.....	36.0
Sulphate.....	71.6
Free Carbon Dioxide.....	
Bicarbonate.....	429.0

part of solution, when about 900 cc. of solution is obtained from 200 gm. of marc. To every 100 cc. of alcohol, 0.59 cc. of concentrated hydrochloric acid is added. By using these proportions and reprecipitating the pectin, it was considerably purified and a pectin nearly white was the result. This seems to be the most efficient method of purifying, but it has the disadvantage, that when pectin approaches purity it becomes more soluble in alcohol and is more difficult to separate from the solution.

(2) Dialysis.

Dialysis, effected by placing pectin solution in a parchment bag and allowing a stream of water to run over the bag for an hour, did not reduce the color of the solution, which probably is due to a pectin-iron colloid.

(3) Lead Acetate Purification.

5 cc. of basic lead acetate (saturated) was added to 20 cc. of pectin solution. A hard jelly precipitate was formed. Dilute hydrochloric acid was added, which dissolved out the lead salt and left the pectin as a jelly. The jelly was filtered off, washed with water, alcohol, and ether, and dried. The pectin seemed to be as dark as before treatment.

(4) Cataphoresis Experiment.

Believing the impurity in the pectin solution to be a positive iron colloid and the pectin negative, it was thought that the pectin might be purified by cataphoresis, on the theory that the iron colloid would pass thru the parchment easily, more easily than the pectin and thus be attracted away from the pectin toward the negative pole. The pectin in a parchment bag was placed in a beaker of water and the anode placed in the parchment while the cathode was placed in the water. After an hour or two of cataphoresis the iron was partly deposited along the parchment and a slight test for it was obtained in the distilled water. The pectin in the parchment, when dried, was a lighter color than before cataphoresis had been performed. On reversing the current a precipitate of white pectin was observed on the cathode in the pectin solution. When the current was reversed for an hour, there was partial precipitation of the pectin in the vicinity of the cathode. When cataphoresis is carried on with the current unreversed, the water gives an alkaline reaction and the pectin solution a strongly acid reaction. The results obtained indicated that this iron colloid could be removed to some degree by cataphoresis.

(5) Purification with Absorbants.

Purified animal charcoal and talc were added separately to pectin solution, heated to boiling, and then centrifuged. In both cases small amounts of the solid remained in suspension, held by the colloid, but were it not for the talc and charcoal left in suspension the pectin solution would have been greatly purified, as the color of the brown iron colloid was removed. It might be that in certain proportions the animal charcoal purification would be found satisfactory.

The ash of the Apple II distilled water-extracted pectin gave from 0.2421 gm. of sample a percentage of 0.81, while with the Apple II city water-extracted pectin a sample of 0.39544 gm. gave an ash of 1.97%. Of course the accuracy of these ash determinations was impaired by the fact that such small quantities of the sample were employed.

B. Pectin from Turnips.

Pectin was obtained from young Texas turnips according to the Bourquelot and Herissey method, and from 2 kg. of ground turnips 330 gm. of alcohol-moist marc was procured.

Turnip Extraction I (with hydrochloric acid).

100 gm. of this marc was extracted at 110° under

increased pressure after 5 cc. of concentrated hydrochloric acid had been added. The final appearance of the marc was pinkish and the solution appeared to be less viscous than in the water extraction. 500 cc. of juice was obtained from 100 gm. of the marc with the acid extraction. The solution was centrifuged for half an hour and precipitated with twice the amount of alcohol. The precipitate was washed free of acid, washed again with ether and dried first on a porous plate, then in a water-oven. A light tan-grey powder resulted. This gave an ash of 1.6% from a sample of 0.475 gm. The entire amount of pectin obtained from the 100 gm. of marc was 2.34 gm.

Turnip Extraction II (distilled water extraction).

230 gm. of the turnip marc was extracted with distilled water in the above described manner and in this case 845 cc. juice was obtained and only 1.18595 gm. of pectin realized, showing how the presence of acid increases the pectin yield. A sample of 0.6306 gm. of this pectin gave 5.7% ash and a sample of 0.28088 gm. gave 3.9% ash. The color of this Turnip Pectin II was nearly white, a very light grey. On qualitative analysis of ash, the turnip pectin I gave a good test for iron and a tardy test for calcium. The city water apple extraction II pectin gave excellent tests for calcium and iron.

The distilled water apple Extraction II pectin gave no test for iron, but excellent tests for calcium and the phosphate radicle. The phosphate test was not applied to the other pectins as the test tried was on the purest sample.

As to the solubility of the pectins found, 0.82 grams of the pectin with 0.81% ash did not entirely dissolve to a bluish opalescent colloidal solution even in 1,200 cc. of water. On boiling, 0.1 gm. of the city water Apple II pectin dissolved in 40 cc. of sugar solution, but the distilled water Apple II pectin did not dissolve quite so readily. Acid aids greatly in the solution of pectin. The above data does not seem to collaborate all of Fellenberg's conclusions on the constitution of pectin.

IV. Fellenberg's Constitution for Pectin.

Fellenberg gives the following constitution for pectin with the constituents in the following proportions:

41.0%	arabinose	=	36.1%	araban
6.7%	methyl pentose	=	6.0%	methyl pentosan
54.8%	galactose	=	49.3%	galactose
<u>11.5%</u>	<u>methyl alcohol</u>	=	<u>11.5%</u>	<u>methyl alcohol</u>
			=102.7%	pectin.

He has pointed out some circumstances which would alter the calculation and diminish the 2.7% excess. Besides, he has calculated these determinations from ash-free pectin and his determination of the ash cannot be too accurate, as, for instance, in the case of the quince he could not have ashed more than 2 grams and any error in weighing or drying would count largely in calculating up to 100%.

Then there is a serious objection to his conclusion that because mucic acid was found on hydrolysis, a galactan was present, for the reason that galactose has never been found on the hydrolysis of pectin.

Fellenberg disagrees with the older authors who believed that protopectin was a calcium salt of pectin on the strength of the following experiments:

(1) He took the supposed protopectin and treated it with acetic acid and then hydrochloric acid, expecting to get equivalent amounts of pectin and calcium. On treatment with acetic acid most of the calcium was dissolved and the pectin remained unaffected. On further treatment with hydrochloric acid, some pectin was dissolved but only a slight amount of calcium which might have been occluded in the pectin and not bound up in its molecule. Because acetic acid dissolved up the most of the calcium but did not affect the pectin, Fellenberg

says that calcium and pectin cannot be in combination.

(2) He tried to titrate the supposed calcium pectate with tartaric acid and failed to get any results. It displaced no neutral pectin, thus lowering the acidity of the tartaric acid.

Fellenberg's proofs here do not seem to be sufficient. Take the first experiment. He dissolves the protopectin from apples by means of a sugar solution and then dissolves out the calcium from the so-called protopectin with acids leaving the pectin unchanged. It has been pointed out that pectin, obtained by the method Fellenberg used, was soluble in sugar solution, very nearly insoluble in water, and lost ash on treating with acids. It certainly is not sure that Fellenberg had protopectin here.

Then in experiment (2) he tried to titrate the neutral pectin substance containing calcium and was disappointed in not finding any amount of tartaric acid neutralized. If he expected tartaric acid to displace pectin, he would intimate that pectin was an acid; and he does say that pectin is a methyl ester of pectic acid. Calcium is probably not bound up with pectin as a basic radicle with an acid, but in some other way. Also it is not fair to treat with calcium alone when there is present in the ash also iron and phosphate radicles which

may be just as, if not more, intimately connected with the pectin.

Altho Fellenberg's proofs do not seem to disprove the calcium pectate theory, he does not add much to the theory that there is a protopectin at all. It seems very unlikely that there is from the following considerations:

The protopectin was distinguished from pectin by its insolubility in water and solubility in sugar solution, it has been shown that pectin agrees entirely with the so-called protopectin in these things. So far it has not been possible to remove the mineral salts from pectin without hydrolyzing it. Acid is used in extracting pectin from the marc, in making the cellulose which surrounds the pectin more permeable. Ripening may be merely the action of malic acid (in the case of apples) softening the tissues of cellulose so that pectin can be reached more quickly by a solvent, and the formation of sugar in the apple which dissolves the pectin more readily than does water. The over-ripening of the apple probably brings about the hydrolysis of the pectin. On treating turnip pectin with acid there is considerably less ash than on treating it with water. It might thus be that the pectin was in combination with metal radicles in the middle lamellae, that acid dissolved out these rad-

icles leaving pectin, and this substance richer in mineral might be called protopectin, and that less rich pectin; but it seems safer to say that there is no protopectin and that pectin occurs in the middle lamellae and acids, boiling water, or boiling alcohol releases it, and these solvents merely happen at the same time to dissolve up minerals, and that the minerals in the pectin of say ash 0.81% are due to occlusion.

V. Jelly-making.

It might be well before discussing the subject of jelly-making to give Miss N. E. Goldthwaite's definition of a jelly. "The ideal fruit jelly is a beautifully colored, transparent, palatable product obtained by so treating fruit juice that the resulting mass will not quiver, not flow when removed from its mold; a product so tender that it cuts with a spoon and yet so firm that angles thus produced retain their shape; a clear product which is neither syrupy, gummy, sticky, nor tough. Neither is it brittle and yet it will break and does this with a distinct cleavage which leaves sparkling characteristic faces."

To a physiological chemist a jelly is a concentrated emulsoid, but gelatin and agar-agar come under

this definition. As to the common fruit jelly it differs from agar-agar and gelatin in that its jellifying constituent is a carbohydrate and that sugar is necessary before jelly can be produced.

The impression gathered from Miss Goldthwaite's papers is that acid is a necessity in the making of jelly, and from the paper of Theodore von Fellenberg that a jelly, but not a very good one, can be obtained from sugar, pectin, and organic calcium salts, while an excellent jelly can be obtained from pectin, sugar, and pectin-free fruit juice. Miss Kate Daum, of the University of Kansas, has proved that acid in certain proportions removes the stickiness of jelly and makes it firm and clean to cut. An excess of acid produced viscosity. The following experiments were undertaken with pectin and sugar:

(1) 0.1150 gm. of turnip pectin was dissolved (imperfectly) in 10 cc. of city water, heavy in minerals, with 5 drops of 95% organic acid, and ten gm. of sugar. This was boiled 15 minutes and cooled. A delightful jelly, conforming to the Goldthwaite definition except in color resulted.

(2) A similar amount of turnip pectin to that used in (1) was boiled a similar length of time with 10 cc. of city water and 10 cc. of cane sugar. A good

jelly was obtained.

(3) 0.1 gm. of 0.81% ash-pectin was dissolved in 20 cc. of 25% sugar solution and boiled for 20 minutes. Here the water was distilled. A good jelly was obtained.

(4) 0.1 gm. of pectin was boiled with 40 cc. of 25% sugar solution and 5 drops of 95% oxalic acid for half an hour or more. The result of this was a dark brown viscous mass. A similar experiment with 10 drops of the acid was used and a still more syrupy mass was obtained.

The conclusions to be drawn are that a jelly can be formed with merely sugar and pectin as pure as could be obtained; that long boiling in the presence of acid (it might be the natural fruit acid) hydrolyzes the pectin, or the sugar, or both, and gives a viscous substance or a thick syrup; and that the presence of mineral salts in certain proportions seems salubrious.

As to the commercial possibilities of pectin, it can probably not take the place of gelatin, unless mixed with albumin, as albumin can coagulate pectin. Otherwise too much sugar would be necessary to make it jell for deserts and salads, as gelatin jells without the addition of sugar. Pectin is also too insoluble in water.

It is well known that jellies can be made from turnips, carrots, etc. Pectin is nearly white when obtained from turnips. Dried apple parings make a good source of pectin. Pectin is now put on the market as a concentrated acid liquid and promises a commercial future. The following preparation of pectin from a marc other than apple was carried out in order to throw light on the subject of whether jellies could be made commercially from the dried marc of carrots, turnips, beets, grape fruit, etc.

(1) Pectin from Grape-fruit Marc.

The first step taken in the preparation of grape-fruit marc was the removal of the fleshy mesocarp and the oily outer pericarp, leaving the pure white porous inner epicarp. (It is not necessary to separate the oily and waste parts if the pectin is finally to be precipitated with alcohol, since the alcohol would remove the oil, and the citric acid, etc. would remain in the aqueous solution of the pectin and not be precipitated out. However, if the marc is to be hydrolyzed and jelly made directly from it, the bitter principle would remain and interfere.) This white epicarp was ground and washed in bags with water until the bitter principle was removed. This was tested by taste. The soluble calcium salts were then removed with oxalic acid and likewise

the albuminous substances with tannic acid. The purified marc was subsequently boiled, expressed, and precipitated with 95% alcohol. A precipitate of pectin was formed at this juncture, but if the marc was allowed to dry to a horny mass, no pectin could be obtained without prolonged boiling with acids. Drying the pectin makes it harder to extract for the reason that it is packed so tightly in between the walls of cellulose. According to Bigelow, Gore, and Howard, if the marc is boiled with 2% hydrochloric acid for four hours, the pectin can be separated by the addition of alcohol. Pectin was also obtained from carrot, turnip, and beet marc before drying. The close of the semester prevented further experimentation, but it seemed assured that the preparation of jelly directly from the marc of the grape-fruit, carrot, and beet, even after thoro washing and drying, was a commercial possibility. A jelly was obtained from these substances using the freshly extracted juice.

The following is a brief resume of the contributions to the subject of pectins and general conclusions resulting from the experiments described in the foregoing pages.

Summary.

- (1) Tho Fellenberg obtained a pectin of ash

0.25% by the Bourquelot and Herissey method, the pectin of lowest ash content obtained by the same method here described was apple pectin with an ash of 0.81%. The pectin nearest to white in color was that of the turnip. Iron, phosphorus, and calcium were found in the ash. The ash of pectin extracted with city water contained about 2% more ash than that extracted with distilled water. Attempts to further purify by treatment with lead acetate, animal charcoal and talc with subsequent centrifuging, and by dialysis and cataphoresis, failed. Purification by reprecipitation with alcohol was effective but resulted in such a loss of pectin that the exact extent could not be determined. In the last step of the Bourquelot and Herissey method when the acid was washed out of the pectin with alcohol, this wash alcohol was not removed from the pectin by boiling off, but by absorption on a porous plate.

(2) Judging a substance insoluble in water when it is insoluble one part of substance to 500 parts of water, pectin is insoluble in water, as experiment showed that 0.8+ grams failed to completely dissolve in 1,200 cc. of water. Pectin is soluble in acid and sugar solutions. Judging from these facts and other considerations discussed, the conclusion was arrived at that there is

no protopectin and what was formerly considered protopectin was merely unextracted pectin.

(3) A jelly can be obtained from pectin and sugar alone, tho it is not as easy to cut or as tender as that jelly made with the additional use of acid. Jelly can be made aswell with the pectin of turnips as with the pectin of apples, and from the expressed juice of turnips as well as with the purified pectin. It seems assured that jelly could be made from the dried marc of grape-fruit, carrots, turnips, and beets as well as from the fresh marc.

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