taken at the end of four days. In the regulation of sewage filters practical comparative results may be obtained in a much shorter period. In sewage laboratories where only rough tests are required, the room temperature may be used, in which case eight days may be taken as the standard time of incubation but, as in the case of the 37° tests, practical results may be had in much shorter periods of time.

The amount of methylene green used should be one cc. of a solution containing one-half a gram per liter. Larger amounts of this, as well as of methylene blue, have a slight antiseptic action.

4. The comparison of the relative putrescibility by dilutions of sewages and effluents is a very valuable test of the various methods of sewage treatment. It not only tests the work accomplished by purification plants but gives data as to the amount of dilution necessary to prevent foul odors in the final disposal of a sewage or effluent which enters a stream or other body of water.

REFERENCES.

1. Spitta, 1903. Weitere Untersuchungen über Flussverunreinigung. *Archiv. f. Hyg.*, XLVI, p. 64.
2. Spitta and Weldert, 1906. Indikatoren für die Beurteilung biologisch gereinigter Abwässer. *Mitteilungen aus der Königlichen Prüfungsanstalt für Wasserversorgung und Abwässerbeseitigung zu Berlin*, VI, p. 160.
3. Phelps and Winslow, 1906. On the Use of Methylene Blue in Testing Sewage Effluents. *American Public Health Association, Papers and Reports*, Vol. XXXII, Part II, p. 7. Also 1907 *Jour. Infect. Diseases, Supplement No. 3*, p. 1.
4. Johnson, Copeland and Kimberly, 1905. The Relative Applicability of Current Methods for the Determination of Putrescibility in Sewage. *American Public Health Assoc., Papers and Reports*, Vol. XXXI, Part II, p. 80.
5. Clark and Adams, 1908. Studies in Incubation Tests. *Journal of the American Chemical Society*, Vol. XXX, p. 1037.

MOUNT PROSPECT LABORATORY,
BROOKLYN, N. Y.

CONTRIBUTION ON THE CHEMISTRY AND PHYSICS OF JELLY-MAKING.

By N. E. GOLDTHWAITE.

Received February 18, 1909.

The object of these experiments has been to determine as exactly as possible the conditions necessary for the formation of fruit jellies. These conditions are doubtless well known to the manufacturers of fruit products, but diligent search of chemical literature has failed to disclose articles dealing directly with the subject in hand.

Bigelow's admirable review¹ of the work done on

the chemistry of pectin bodies, emphasizes the fact that as yet little has been definitely ascertained concerning the constitution and function of these compounds. The experimental results indicate in general that these pectin bodies are carbohydrates. Herzfeld¹ regarded them as combinations of araban and galactan, and Tollens² has suggested that they may be glucosides.

Though the constitution of these bodies is so far from being determined, yet their fundamental physical characteristic—that of forming jellies under certain conditions—has long been well known practically. Our quest in the present work is to find the conditions under which this gelatinizing power best manifests itself, *i. e.*, the conditions under which pure fruit jellies of the best texture are formed. Bigelow's arbitrary method for making jellies³ by boiling together equal parts of fruit-juice (more or less diluted with water) and of cane-sugar, for 20 minutes, does not, in our experience, necessarily yield jellies of a uniformly good texture. By a jelly of good texture we mean one obtained by so treating fruit juice that the resulting mass will quiver, not flow when shaken—one which can be cut easily with a spatula, the angles so produced preserving their shape when a piece is isolated, and yet one which is not tough.

I. Method of Procedure.—Since the present work was begun in September, 1908, the jellies so far investigated have been made from fall fruits only. In extracting the juices for these jellies any unsound portion of the fruit was removed and the sound portion cut into small pieces if possible. The fruit so prepared was barely covered with cold distilled water (about 1 liter, or less, to 2 kgs. of prepared fruit) and the whole brought slowly to the boiling point and kept simmering until the fruit was thoroughly cooked. The mass was then removed to a filter made of a double fold of cheesecloth and allowed to drain completely. It was found that the pulp remaining on the filter could be again boiled up with water (the least amount possible) and that the resulting juice would make a good jelly. This was particularly true in the case of grapes, even the fourth and fifth extractions making an excellent quality of jelly—a quality better than that made from the first extraction because potassium acid tartrate crystals did not appear in it as is usual in the case of jelly from grapes.

¹ *Zts. Ver. d. Zuehr. Ind.* **41**, 295, 667 (1891).

² *Ann.*, **286**, 292 (1895).

³ *Jour. Am. Chem. Soc.*, **23**, 347. *Bureau of Chem., Bull.* **66**, 50.

¹ *Bureau of Chem., Bull.* **94**, 67–87.

Naturally, considering the nature of our problem, we followed no set method for making our jellies, but varied our methods within wide limits, *e. g.*, we varied the acidity of the fruit juice from a neutral condition to 0.669 per cent. of acid; the amount of sugar used from none to 2 volumes per 1 volume of juice; the time of boiling sugar with juice from the whole time of cooking to the last five minutes only. The total time of cooking was always limited to the time when we obtained a good jelly test, *i. e.*, when a portion of the hot liquid would jelly as it was dropped from a cold metal spatula.

II. Necessary Constituents of Jelly. (a) Pectin.—Braconnot, who first investigated pectin, pointed out¹ that very palatable jellies could be produced from the alkaline pectates which he isolated from carrots by treating the latter with alkalis. He made jellies by dissolving these alkaline pectates in water, heating with sugar and then adding a small quantity of a mineral acid.

Although the jelly-maker never handles directly such alkaline pectates or even pectin itself, yet it has long been recognized that the first essential constituent of a fruit juice for making jelly is this latter body—pectin. Its presence in a given juice is readily ascertained by adding to a portion of the juice an equal volume of alcohol, shaking and cooling; a gelatinous precipitate filling a considerable portion of the total volume of the liquid indicates pectin. Good jelly-making consists in so controlling conditions as to cause this pectin to be precipitated evenly throughout the total volume of liquid allowed it. That it can be precipitated by alcohol, various metallic salts, acids and sugar was discovered by Braconnot.

(b) Acid.—The second essential constituent of fruit juice for making jelly is acid. This fact may be proved in a twofold manner. First, negatively, *e. g.*, when the acid of a primarily good jelly-producing juice is neutralized, no jelly can be made from the resulting juice although it contains plenty of pectin; second, positively—if a juice which contains pectin, but which in its natural condition will yield no jelly, be acidified properly, a good jelly may be produced.

Negatively, the necessity of acid in a jelly-making juice was proved as follows: A given quantity of crab-apple juice was divided into three equal portions. Of the first portion an excellent grade of jelly was produced, using an equal volume of sugar, boiling the juice 10 minutes before the addition of

the sugar and 20 minutes thereafter, *i. e.*, till the jelly-test was obtained. To the second portion of juice a sufficient quantity of N/10 NaOH was added to just neutralize the acid present, and then an attempt made to make jelly as above. Result, a dark colored thick, fruit syrup which never gave any signs of forming a jelly, but from which cane-sugar crystals were slowly deposited. To the third portion of juice sufficient N/10 NaOH was added to neutralize half the acid present, the subsequent treatment corresponding to the above. Result, a thick fruit syrup which never showed any signs of jelly formation although at the end of four months pectin could be precipitated abundantly by the addition of alcohol.

Experiments corresponding to the first and second of these cases were carried out with grape juice, with exactly analogous results. That the juices contained plenty of pectin is evident from the fact that in their natural state they easily yielded jellies.

These experimental results are summed up in Table I:

Experi- ment No.	Kind of fruit.	Sp. gr. of juice.	Per cent. of acid in juice (calc. as H ₂ SO ₄).	Proportion of cane sugar to juice by vol.	Time of boiling.		Texture of jelly.
					Before adding sugar.	After adding sugar.	
5	Crab-apple	1.043	0.550	1:1	10	10	Excellent
6	Crab-apple	1.043	0.000	1:1	10	10	Syrup
7	Crab-apple	1.043	0.275	1:1	10	10	Syrup
126	Grape	1.025	0.313	1:1	30	10	Excellent
127	Grape	1.025	0.000	1:1	30	10	Syrup

Nos. 5 and 126 represent respectively crab-apple and grape juices in their natural condition from which excellent jellies were easily prepared. Nos. 6 and 127 represent these same juices after neutralization from neither of which could jelly be made. Though No. 7 represents only a half-neutralization of crab-apple juice yet this also refused to yield jelly. It should be noted that the low sp. gr. and acidity of the grape juice used in these experiments is due to the fact that this juice was composed of the later extractions of the pulp. On account of this low sp. gr. a considerably longer time for boiling was necessary, but for reasons shown further on, this preceded the addition of the sugar.

Positive proof concerning the necessity of acid for the formation of jelly may be cited as follows: Sweet apple, pear and peach juices contain an abundance of pectin as is evident from the alcohol test, yet under ordinary conditions it was found impossible to produce jellies from these juices.

¹ *Ann. de Chim. et. de phys.* [2], 28, 173 (1825); *Ibid.* [2], 30, 96.

However, addition of an organic acid to each juice so modified conditions that a very fair jelly could be made as shown in Table II:

TABLE II.

Experi- ment No.	Kind of fruit.	Sp. gr. of juice.	Natural % of acid in juice.	Acid- ity of juice after addition of H ₂ SO ₄ .	Propor- tion of cane- sugar by vol- ume.	Time of boiling.		Texture of jelly.
						Before add- ing	After add- ing	
80	Sweet apple	1.042	0.098	0.098	3/4 : 1	10	20	Syrup
110	"	1.042	0.098	0.308	"	20	7	Fair jelly
111	"	1.042	0.098	0.395	"	20	7	Good jelly
112	"	1.042	0.098	0.552	"	20	7	Very good
117	"	1.037	0.098	0.675	"	20	10	Fair jelly
106	Pear	1.047	0.284	0.284	"	20	10	Syrup
100	"	1.047	0.284	0.405	"	20	10	Syrup
105	"	1.047	0.284	0.511	"	20	10	Good jelly
150	Peach	1.033	0.311	0.311	"	20	10	Syrup
151	"	1.033	0.311	0.575	"	20	7	Fair jelly

Examination of this table shows that the texture of these jellies was best when the acidity corresponded to about 0.5 per cent. for juices whose sp. gr. was about 1.04. It is interesting that this acidity and sp. gr. correspond in general to those of crab-apple juice, the best natural juice for jellies so far investigated in these experiments. Increasing the acidity of these juices beyond about 0.5 per cent. seemed to impair the texture of the resulting jelly, as is evident from No. 117.

III. Discussion.—It appears then that through this addition of an organic acid to a fruit juice containing naturally little acid, jellies can be made if these juices contain pectin. However, the flavor of the fruit is generally changed; the sweet apple jelly so made tasted much like that made from sour apples, the tartness of course increasing with increasing percentages of acid; the flavor of the pears, in pear jelly, was fairly well preserved, while in peach jelly the peach flavor was completely destroyed. Repeated experiments, varying the percentages of acid were made in an endeavor to preserve the peach flavor, but success was not attained in this respect, though a jelly of fair texture could be produced. From experiments testing the relative merits of tartaric and citric acids in connection with the use of one or the other to acidify a fruit juice, the balance of favor seemed to be with the former. Both texture and flavor of jellies made by its use were superior to those in which citric acid was used. Nos. 151 and 152 in Table V represent tests in which tartaric acid was the acid added, while in Nos. 153 and 154 citric acid was used. The method of making Nos. 151 and 153 corresponds, like-

wise Nos. 152 and 154. There was no question concerning the superiority of Nos. 151 and 152, *i. e.*, the jellies made by the help of tartaric acid.

That a mineral acid like hydrochloric can be substituted for an organic acid was demonstrated. While this is interesting from a chemical standpoint, it naturally would not be recommended in the preparation of fruit jellies for food.

In determining the acidity of fruit juice better end-reactions were obtained when the juice was titrated into the *N/10* alkali (using phenolphthalein as an indicator) rather than the reverse as is usual. In the case of grape or plum juices no indicator was necessary, but the titration was best carried out titrating the *N/10* alkali into a definite volume of the juice (well diluted) and taking as the end-reaction that point at which the pink color of the liquid just merged into green.

That no acid disappears as such in the preparation of jellies was proved by the following experiments: Crab-apple juice (100 cc. acidity = 0.532 per cent.) was made into jelly using an equal vol. of sugar. The resulting unskimmed jelly was dissolved in distilled water, diluted to 500 cc. and the acidity again determined. The acidity of this dissolved jelly was found to be 0.107 per cent., or, if calculated in terms of the original volume of juice (100 cc.) it equaled 0.535 per cent. This is identical with the original acidity (0.532 per cent.) within the limits of experimental error.

Experiments substituting lime-water and also calcium salts as a precipitant of pectin in making jellies from sweet fruit juices were carried out. However, good jellies have not so far been obtained by this method.

It was found that glycerin could be used in place of sugar in the making of crab-apple jellies. The jellies so made were of excellent texture and of fair taste and they had remarkable keeping qualities.

When glycerin and sugar were used simultaneously with peach juice, a fair jelly was produced, but from this sugar subsequently crystallized out. These crystals were remarkably large and perfect.

IV. Sugar in Jelly-making.—That so-called jellies can be produced by merely boiling down fruit-juices is well known. Naturally the flavor of such a jelly is decidedly fruity, but in texture it is very tough. The making of such jellies requires a large amount of juice, *e. g.*, we found to make one glass of such apple jelly required a volume

of juice sufficient for six glasses when made with sugar. Ordinarily, sugar is cheaper than fruit juice, so from the standpoint both of palatability and of economy (possibly also of digestibility) jellies made with sugar are preferable.

(a) *Amount of Sugar.*—The proportion of sugar to juice is a somewhat difficult one to decide. Experimental results indicate that it depends more upon the proportion of pectin present in a juice than upon any other one factor. It seems probable that in the actual practice of making jellies poor results are very likely to occur through the use of too much sugar, and this because of the relatively large quantities of water that have been used in extracting the fruit juices. Through using these relatively large quantities of water the jelly-maker is deceived regarding the actual volume of fruit juice, hence the use of an overabundance of sugar. Fruit juices which have required little water for their extraction, apparently will utilize a larger proportional amount of sugar than those that necessarily have been much diluted with water. Some of these statements will be made clearer from the following records of experiments:

TABLE III.

Experiment No.	Kind of fruit.	Sp. gr. of juice.	% of acid in juice (calc. as H_2SO_4).	Volume of juice, cc.	Proportion of cane-sugar to juice by volume.	Time of boiling.		Amount of jelly formed, Grams.	Texture of jelly.
						Before adding sugar, Min.	After adding sugar, Min.		
1	Crab-apple ¹	1.0375	0.350	300	$\frac{3}{4}$: 1	5	15	237	Tough
2	"	1.0375	0.350	300	$\frac{3}{4}$: 1	5	12	316	Good
3	"	1.0375	0.350	300	$\frac{3}{4}$: 1	5	10	474	Excellent
4	"	1.0375	0.350	300	1 : 1	5	9	553	Too soft
120	Grape	1.066	0.487	300	$\frac{3}{4}$: 1	0	30	266	Tough
121	"	1.066	0.487	300	$\frac{5}{8}$: 1	0	30	281	Fair
122	"	1.066	0.487	300	$\frac{3}{4}$: 1	0	23	382	Good
123	"	1.066	0.487	300	1 : 1	0	20	473	Very good

Note in each of these two series of experiments that with an increasing proportional amount of sugar, the volume of jelly produced constantly increases. Note also that the texture of the grape jelly improves with increasing volume of sugar, while in the case of the crab-apple the best jelly is that in which proportion of sugar to juice is as $\frac{3}{4}$: 1; increasing this proportion of sugar impairs the texture of the jelly. An explanation of these facts concerning the texture of the jelly is suggested when we consider that we are here dealing with a grape juice of high sp. gr. and of comparatively high acidity, but with a crab-

¹ Both the low sp. gr. and acidity of this crab-apple juice are explained by the fact that it was the fourth extraction of juice.

apple juice of low sp. gr. and of low acidity, hence this grape juice is able to utilize a larger proportional amount of sugar than the crab-apple juice can.

It may also be noted here that as the proportion of sugar in grape juice increases (and consequently the volume of jelly as shown) the crystals of acid potassium tartrate naturally deposited from this jelly decreased. Possibly the increased volume of jelly from a given amount of juice accounts for this, inasmuch as this increased volume of jelly means a less concentration of the potassium acid tartrate contained in it. This behavior of grape jelly is interesting especially when taken in connection with what has been previously remarked concerning making it from other than the first juice extraction. That too great a proportion of sugar to juice (depending on the sp. gr. and acidity of the latter) impairs the texture of the jelly, is emphasized in Table IV.

TABLE IV.

Experiment No.	Kind of fruit.	Sp. gr. of juice.	% of acid in juice (calc. as H_2SO_4).	Proportion of cane-sugar to juice by vol.	Time of boiling.		Texture of jelly.
					Before adding sugar, Min.	After adding sugar, Min.	
115	Sweet apple	1.037	0.675	$\frac{3}{4}$: 1	20	15	Very good
170	"	1.037	0.675	1 : 1	20	10	Good
171	"	1.037	0.675	$1\frac{1}{2}$: 1	0	15	Poor
172	($\frac{1}{2}$ of 171)	...			..	15	Poor
173	($\frac{1}{2}$ of 171) + equal vol. of juice	...			..	20	Very good
174	Sweet apple	1.037	0.675	2 : 1	0	15	Very poor

The texture of No. 115 was very good, but increasing the proportion of sugar beyond the proportions used in this experiment resulted in a deterioration of the texture of the jelly. Nos. 171–172 and 174 are striking examples of the use of too great a proportion of sugar. Nos. 171 and 174 were a very poor quality of jelly; pectin was precipitated in lumps throughout the mass, not in a continuous, semi-firm substance as in a good jelly. Subsequent boiling of 171 (*i. e.*, 172) served only to darken the product, but not to improve its texture. However, upon the addition to 171 of an equal vol. of juice (No. 173) and upon further boiling, a jelly fully equal in texture and taste to No. 115 was produced. Evidently then, in making fruit jellies, close attention must be given to the proportion of sugar used. Too little renders the jelly tough, too much (*i. e.*, more than the proportion of pectin present in the juice will warrant) greatly impairs the texture and flavor of the jelly. This latter fact may account more than any other for jelly failures.

TABLE V.

Experiment No.	Kind of fruit.	Sp. gr. of juice.	Natural per cent. of acid in juice (calculated as H ₂ SO ₄).	Per cent. of acid in juice as used.	Weight of juice. Grams.	Proportion of cane sugar to juice by volume.	Weight of cane-sugar. Grams.	Before adding sugar. Min.	After adding sugar. Min.	Time of boiling.	Temperature at which jelly test was apparently observed.	Sp. gr. of hot jelly.	Wt. of jelly + skimmings.	Texture of jelly.	Per cent. of cane-sugar found in fruit juice = d.	Per cent. of cane-sugar put into jelly = e.	Total per cent. of cane-sugar in jelly = d + e.	Before inversion.	After inversion.	Saccharimeter readings.	Temp. at which saccharimeter readings were taken.	Per cent. of cane-sugar found in jelly = s.	Per cent. of cane-sugar un-inverted = $s/(d+e)$.	Per cent. of cane-sugar inverted = $100 - s/(d+e)$.	Crystallization of cane-sugar at surface of jelly.
100	Pear	1.047	0.295	0.405	317	3/4:1	190.5	20	10	103.0°	1.28	340.0	Syrup	7.71	56.00	56.00	19.11	-13.39	20.0°	48.50	86.60	13.40	Slight		
101	"	1.047	0.295	0.522	316	3/4:1	190.5	20	10	103.0°	1.28	338.4	Thin jelly	7.71	56.59	56.59	20.00	-13.03	21.0°	49.48	87.43	12.60	None		
102	"	1.047	0.295	0.669	316	3/4:1	190.5	20	10	103.0°	1.28	344.2	Poor jelly	7.71	55.34	55.34	15.50	-12.78	20.0°	42.20	76.25	23.75	"		
103	"	1.047	0.295	0.669	261	1:1	253.0	20	4	103.0°	1.30	419.5	Fair jelly	7.71	60.30	60.30	23.61	-13.47	21.0°	55.55	92.12	7.88	Much		
104	"	1.047	0.295	0.669	263	1:1	253.0	0	20	103.0°	1.285	419.5	"	7.71	60.30	60.30	6.04	-12.38	22.0°	27.70	45.93	54.07	None		
110	Sweet apple	1.042	0.100	0.308	312	3/4:1	190.5	20	7	103.0°	1.27	346.4	Fair jelly	7.71	55.00	62.71	24.30	-11.20	22.0°	53.30	85.00	15.00	"		
111	"	1.042	0.100	0.395	314	3/4:1	190.5	20	7	103.0°	1.27	345.9	Good	7.71	55.00	62.71	21.60	-11.20	22.0°	49.30	78.45	21.55	"		
112	"	1.042	0.100	0.552	315	3/4:1	190.5	20	7	102.5°	1.25	356.0	Very good	7.71	53.50	61.21	20.40	-11.16	22.0°	47.40	77.43	22.57	"		
113	"	1.042	0.100	0.552	314	3/4:1	190.5	0	26	103.0°	1.26	342.0	Good	7.71	55.70	63.41	2.40	-11.00	23.0°	20.20	31.85	68.15	"		
114	"	1.042	0.100	0.552	256	3/4:1	150.0	10	13	103.0°	1.27	263.0	Very good	7.71	57.00	64.71	14.00	-10.94	24.0°	37.80	58.41	41.59	"		
120	Grape	1.066	0.487	0.487	316	1/2:1	95.0	0	30	104.0°	1.26	266.5	Tough	7.71	35.00	35.00	-0.30	-10.37	24.0°	15.25	43.57	56.43	Slight(?)		
121	"	1.066	0.487	0.487	318	5/8:1	127.0	0	30	103.0°	1.26	281.0	Fair	7.71	45.00	45.00	+2.46	-11.15	24.0°	21.30	47.33	52.67	None		
122	"	1.066	0.487	0.487	320	3/4:1	190.5	0	23	103.0°	1.26	382.0	Good	7.71	49.00	49.00	5.90	-10.64	24.0°	25.06	51.14	48.86	"		
123	"	1.066	0.487	0.487	319	1:1	253.0	0	20	103.0°	1.26	473.0	Very good	7.71	53.00	53.00	9.64	-11.22	23.0°	31.56	59.54	40.46	"		
124	"	1.066	0.487	0.487	298	1:1	239.0	15	4	104.0°	1.30	434.0	Very good	7.71	55.00	55.00	18.38	-12.48	23.0°	46.48	84.70	15.30	Slight.		
130	Plum	1.033	0.623	0.623	254	1:1	215.0	0	27	103.0°	1.26	365.0	Good	7.71	59.00	59.00	12.60	-9.25	23.0°	33.00	56.00	44.00	None		
131	"	1.033	0.623	0.623	254	1:1	215.0	10	10	103.0°	1.26	370.0	"	7.71	58.10	58.10	23.35	-9.90	23.0°	50.18	85.05	14.95	Slight		
140	Medium sour apple	1.041	0.257	0.257	259	1:1	210.0	0	22	103.0°	1.27	362.0	Good	7.71	66.00	58.66	20.90	-12.10	21.0°	49.40	84.21	15.80	"		
141	"	1.041	0.257	0.257	259	1:1	210.0	0	18*	103.0°	1.27	344.0	Good	7.71	66.00	61.66	20.00	-11.77	21.0°	47.50	77.03	23.00	None		
142	"	1.041	0.257	0.428	259	1:1	210.0	12	13	103.0°	1.28	344.0	Very good	7.71	61.00	61.66	20.00	-12.6	21.0°	48.80	79.11	20.88	Slight		
150	Peach	1.033	0.311	0.311	259	3/4:1	159.0	20	10	103.0°	1.29	253.8	Syrup	7.71	62.41	65.21	31.82	-12.18	19.0°	65.18	100.00	0.00	Some		
151	"	1.033	0.311	0.575	259	3/4:1	159.0	20	7	103.0°	1.29	263.7	Fair	7.71	60.30	61.11	26.05	-11.05	18.0°	55.63	91.03	9.00	"		
152	"	1.033	0.311	0.575	259	3/4:1	159.0	0	29	103.0°	1.28	273.1	"	7.71	57.22	60.02	12.35	-11.18	19.5°	35.05	58.41	41.59	None		
153	"	1.033	0.311	0.600	259	3/4:1	159.0	20	7	103.0°	1.28	267.7	Thin jelly	7.71	59.40	60.20	27.30	-11.71	17.5°	56.20	93.35	6.65	Some		
154	"	1.033	0.311	0.600	259	3/4:1	159.0	0	32	103.0°	1.28	266.4	"	7.71	60.00	62.80	16.80	-11.60	18.0°	42.07	67.00	43.00	None		

* Hard boiling.

* Hard boiling.

(b) *Inversion of Sugar.*—It has been pointed out by Bigelow¹ that the amount of inversion of sugar in jellies and jams varies in general with the length of time of heating, the content of acid, and also the nature of the acid. Experimental data further substantiating these statements are tabulated in Table V.

A word of explanation concerning the data in this table should be given here.

The specific gravity of the juice in each instance was determined by means of a hydrometer. The acidity of the juice either before or after adding more acid was determined as already indicated.

The percentage of cane-sugar put into the jelly was calculated from the weight of sugar added and the total weight of jelly and skimmings obtained. Unfortunately it was necessary to weigh the jelly itself hot.

The percentage of cane-sugar found in the jelly was calculated from the direct and invert readings according to Clerget's formula $S = 100(a-b)/(144 - t/2)$. Polarizations were made upon normal weights of the juices and half-normal weights of the jellies, all the results being calculated to normal weights. Solutions were clarified and inverted according to the method elaborated by Sherman.²

Examination of this table shows, as we should expect, that the percentage of inversion of sugar

That the percentage of acid in the juice affects this inversion is evident from a comparison of Nos. 100-102 (note discrepancy in 101); Nos. 110-112; and No. 150 with No. 151 and No. 153. In these instances the time is generally identical.

That the nature of the acid also affects somewhat the amount of inversion is illustrated by comparison of Nos. 151-152 with Nos. 153-154, the acid added to the two former being tartaric, and to the two latter citric.

The amount of this inversion that is desirable, in order to produce jellies of good texture, is a point more difficult to decide than the proportional amount of sugar to be used. Examination of the table shows that crystallization of cane-sugar occurred more readily generally, from the jellies in which inversion was least. However, in every case, this crystallization always occurred at the surface of the jellies and in none of the cases had any care been taken to protect these jellies from the air, as is ordinarily done, by paraffining the surfaces. Hence, there was every opportunity for evaporation from the surface of these jellies and the consequent formation of crystals.¹ That the sugar should not be boiled sufficiently long with the juice to insure practically complete inversion, is quite probable from the following experiments, as shown in Table VI.

TABLE VI.

Experiment No.	Kind of fruit.	Sp. gr. of juice.	% of acid in juice (calc. as H_2SO_4).	Wt. of juice. Grams.	Sweetening constituent.	Proportion of sweetening constituent to juice by volume.	Wt. of sweetening constituent. Grams.	Time of boiling. Min.	Temp at which jelly-test was apparently observed.	Sp. gr. of hot jelly.	Texture of jelly.
160	Crab-apple	1.043	0.550	103	Cane sugar	$\frac{3}{4} : 1$	66.5	0 10	103°	1.27	Excellent
161	Crab-apple	1.043	0.550	103	Fructose		66.5	0 10	103°	1.24	Syrup
162	Crab-apple	1.043	0.550	103	Equal wts. of } } <i>d</i> -glucose and fructose		34.8 <i>d</i> -glucose 34.8 fructose	0 10	103°	1.26	Good (at first)
163	Crab-apple	1.043	0.550	103	Cane sugar	$\frac{3}{4} : 1$	66.5	8 2	103°	1.28	Excellent
143	Sour apple	1.041	0.257	103	Fructose	$\frac{3}{4} : 1$	62	0 20	104°	1.275	Syrup

is vastly influenced by the time the sugar and juice are boiled together, *e. g.*, compare No. 103 with 104; Nos. 112-113 with each other; No. 123 with 124; No. 130 with No. 131; No. 151 with No. 152; and No. 153 with No. 154. Note in these comparable cases that the proportional amounts of sugar and the acidity are identical.

¹ Bureau of Chem., Bull. 66, p. 52.

² Organic Analysis, p. 91.

That jellies can not be made through substituting fructose for cane-sugar is evident from Nos. 161 and 143, as only a thin syrup resulted in these cases. Corresponding experiments (not

¹ In other cases not cited in the table but within the writer's previous practical experience—cases in which such jellies as currant, red raspberry, and blackberry were paraffined as soon as they had set, no crystallization of cane sugar occurred even after a lapse of two years. In these cases a very small amount of inversion had probably taken place, since the sugar had been boiled with the juice not to exceed five minutes.

tabulated) substituting *d*-glucose for cane-sugar resulted apparently in a good firm jelly; however, *d*-glucose shortly began crystallizing from this jelly and soon could be seen throughout the mass. No. 162 in which equal weights of fructose and *d*-glucose were substituted for cane-sugar (representing a condition of complete inversion) resulted very similarly to the case in which *d*-glucose was used alone, *i. e.*, *d*-glucose crystallized out. No. 163 in which cane sugar was boiled with the juice for only two minutes finally showed evidence of cane-sugar crystals on the surface.

From all the foregoing results two things are apparently evident: First, some inversion of cane-sugar is desirable; second, an inversion approaching completeness is undesirable, see No. 162. So far as our researches now extend it seems better not to boil sugar and juice together from start to finish in jelly-making, but rather to add the sugar so that it may be boiled with the juice for a period not to exceed one-half the total time of cooking. However, we wish to investigate this point further.

Some experiments regarding excessive cooking of an over-diluted juice have been carried out. Results seem to show that the texture of the jelly may be greatly impaired in this way. This also demands further investigation.

V. *Physical Constants*.¹—In connection with our work it seemed desirable to determine whether or not there is a boiling point or a definite specific gravity of the boiling jelly indicative of that condition at which a good jelly may be formed on cooling. Although it was impossible to determine these points with absolute accuracy yet reference to Tables V and VI shows a remarkable coincidence among these physical constants. Boiling points were observed by suspending a thermometer with the bulb in the boiling liquid, and specific gravities were observed by means of a hydrometer floated in the hot liquid which had been transferred with as great rapidity as possible to a glass cylinder previously heated with boiling water. That these boiling points and specific gravities coincide so nearly, even though we are dealing with different fruit-juices and very different proportions of sugar, is worthy of notice.

VI. *Artificial Jelly*.—That the essential substances for the formation of a jelly of good texture

have been indicated in the foregoing is probable from the success attending the attempts to make jelly from an artificial fruit-juice. For this purpose it was necessary to isolate pectin. Pectin was obtained from crab-apple, grape, sweet apple, and peach juices. The isolation of this pectin was a difficult matter and the methods indicated by different experimenters¹ were tried. The following modification of their methods was finally adopted as the one giving the best results: a given volume of the cold, filtered (previously boiled) fruit-juice was added drop by drop by means of a separatory funnel to an equal volume of alcohol, stirring constantly; the mixture was allowed to stand over night in a cold place and then the precipitated jelly-like mass of pectin was separated from the liquid by filtering off through very fine cotton cloth stretched tightly over the mouth of a 4-liter jar. The liquid was worked out of the mass of pectin by means of a spatula. Repeated re-solution and re-precipitation of the pectin improved its purity. The pectin so obtained was a very stable, nearly colorless, transparent solid, of insipid taste. Its principal reactions in solution were tried and correspond to those given by Braconnot, Fremy and others.

Jelly of excellent quality was easily made from this pectin by preparing a 1 per cent. solution of it in a 0.5 per cent. solution of tartaric acid, heating to boiling, then adding a 3/4 volume of sugar and boiling until the jelly-test was observed. The total time of boiling did not exceed 15 minutes. Jellies made as above were nearly colorless, but were excellent in texture and taste. When a few cc. of grape-juice were added to the pectin solution the color of the jellies was very pleasing. That these jellies were not made directly from fruit-juice would not be suspected from taste or texture. Jellies equally good were made in this way from the pectin from sweet apples, crab-apples, and peaches. This last fact would seem to indicate that the pectin of peaches does not differ materially, at least from a practical standpoint, from that of other jelly-making fruits.

It may be of interest to add that pectin was extracted from jelly (the jelly being previously dissolved in an equal volume of water) by the method used for extracting pectin from fruit juices. This pectin apparently corresponded in its physical and chemical characteristics with that extracted directly from fruit-juices. Good

¹ We understand that some work (unpublished) on these points, also on the relation between the proportion of sugar used and the amount of jelly produced, has already been done by Miss Jenny Snow, of the University of Chicago.

¹ Chodnew, *Ann.*, 48, 56. Fremy, *Ibid.*, 64, 383.

fruit jelly invariably gives the alcohol test for pectin. These facts would seem 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.

VII. Summary.—1. The essential constituents of a jelly-making fruit-juice are, first, pectin; second, acid.

2. A desirable accessory constituent is cane-sugar. Too much sugar is likely to be used in jelly-making with a consequent deterioration of the quality of the jelly. The amount of inversion preferably produced in this cane-sugar is yet undetermined.

3. Over-dilution of fruit-juice should be avoided, since this leads to the use of too much sugar; probably the extra boiling thus rendered necessary also impairs the texture of the jelly.

4. The physical constants of hot juice ready to jell on cooling are, substantially, boiling point 103°C. , and specific gravity 1.28.

5. Jelly is readily made through boiling pectin with acid, water and sugar.

6. Jelly-making seems to consist in so controlling conditions by means of acid and sugar and boiling as to cause the pectin to be precipitated in a continuous mass throughout the volume allotted to it.

RESEARCH LABORATORY OF THE
DEPARTMENT OF HOUSEHOLD SCIENCE,
UNIVERSITY OF ILLINOIS.

[CONTRIBUTION FROM THE BUREAU OF CHEMISTRY, DEPARTMENT OF AGRICULTURE.]

A STUDY OF THE FATTY ACIDS OF FISH OILS.

By L. M. TOLMAN.

Received April 2, 1909.

This study was undertaken several years ago in connection with an investigation of the cod-liver oils and related fish-liver oils, part of the results of this work being published in the *Journal of the American Chemical Society*, 28, 387-395 (1906). The oils used in this study were prepared for us by the Bureau of Fisheries, Department of Commerce and Labor, so that their exact history and purity were known. The oils selected for this especial work were a sample of Norwegian cod-liver oil, American cod-liver oil, a pollock-liver oil, a hake-liver oil, a ling-liver oil, a dog-fish liver oil, a trout-liver oil and a seal blubber oil. These were chosen as they formed a series of oils representing fish closely related to the cod

fish widely separated from the cod, and a fresh water fish whose habits of food were entirely different, while the sample of seal blubber oil gave an oil from a warm-blooded animal which largely subsists upon fish. In addition, a sample of linseed oil and one of corn oil were examined in order that a comparison could be made between the highly saturated vegetable oils and the highly unsaturated fish oils. The following table (I) gives a description and analysis of the oils enumerated:

TABLE I.—DESCRIPTION AND ANALYSES OF FISH OILS.

Description of sample.	Sp. gr. 15.6°C.	Index of refraction.	Iodin number.	Hexa-bromid. Per cent.	Saponification No.	Solid acids. Per cent.	Free acids. Per cent.	Unsaponifiable matter. Per cent.
2447 Cod.....	0.9265	1.4810	165.7	46.6	178.1	5.70	0.47	
15600 Cod.....	0.9274	1.4805	168.0	34.0	188.6	15.55	0.28	0.91
14261 Pollock....	0.9245	1.4795	150.9	42.7	...	15.99	0.95	
14304 Hake.....	0.9254	1.4812	158.2	30.3	178.1	13.58	0.56	0.76
11556 Ling.....	0.9224	1.4784	143.4	30.2	183.1	14.42	0.91	
15604 Dog fish...	0.9220	1.4786	153.3	37.2	180.3	18.52	0.65	3.20
16780 Trout.....	0.9275	1.4801	154.8	35.1	189.4	7.01	1.69	
15608 Seal.....	0.9246	1.4776	143.8	19.5	191.1	9.96	0.64	0.13

These oils, as will be seen from the results given in this table, do not show a very wide variation in the chemical and physical characteristics. Considering the chemical analysis alone, all of the oils would come within the limits allowed or found in our experiments for cod-liver oil, except the seal and dog fish oils, which are somewhat different in the amount of unsaponifiable matter; and and yet it would be difficult to select a more varied lot of oils as far as the source is concerned. In the study of the unsaturated acids, the halogen compounds, especially the bromin compounds, were used as the basis for the separation of the unsaturated fatty acids. After a careful consideration of the various methods, and after experimenting to a considerable extent with the oxidation with dilute permanganate, as suggested by Hazura, it was decided that the formation of the insoluble brominated acids gave more information as to the composition of the fatty acids than any other of the methods which have been applied. As the methods used in separating the saturated and unsaturated acids and the determination of the iodine numbers are in a sense empirical methods, it is necessary at least to name them, and in some cases to give the method employed in detail.

The Hanus method was used for all of the iodine absorption determinations and accounts for the fact that the results on this determination are somewhat higher than the older figures which are