STUDIES IN THE CITRUS-FRUIT SERIES

No. I

STUDIES IN
LEMONS AND ORANGES

BY

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P R E F A C E

This report is based on work, commencing October 1944, carried on some orange and lemon fruits of Lebanon. In its first part I claim to present no pioneer research in the chemistry of citrus fruits, save the collection of new data concerning their composition in this country.

In the second part, again, I merely endeavour to answer a simple and practical question: "Can the citrus waste products of this country be utilized for the production (among other by-products) of citric acid and pectin ? " The problem, of course, is here studied from its chemical aspects only, and hence no complete and satisfactory answer should be sought for. Nevertheless, this issue is important; so important, in my opinion, as to justify even an attempt at its solution through a study of the chemistry of citrus products.

Consequently, in preparing this paper, special care has been taken to refer every topic to its literature, without undue reproduction of methods of analysis, theories of reactions, etc., which facts are easily accessible through indicated references.

In acknowledgement, I wish to thank the personnel of the Chemistry Department for their kind cooperation, and particularly Prof. N.D. Constan for placing his private laboratory at my disposal and kindly supervising my work.

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George I.H. Hanania.

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GENERAL INTRODUCTION

THE CITROUS FRUITS

These fruits[1], which were first mentioned in history (about 2000 B.C.) to have existed in China[2], are now botanically classified under the family "Rutaceae" as genus "Citrus". Thus they are normally spoken of as "Citrus Fruits". They are berries of the hesperidium type, and consist of a "rind" (comprising the epicarp, hypoderm and most of the mesocarp), that encloses "segments" consisting of the inner mesocarp, endocarp and seeds[3]. Of this genus only two species are studied in this paper:

1. Orange - Ar. برتقال, Fr. Orange douce, It. Arancio dolce, Sp. China, Ger. Apfelcine.
   Citrus sinensis (Osbeck) or C. Aurantium var. sinensis (Engl.).

2. Lemon - Ar. ليمون حامض, Fr. Citron, It. Limone, Sp. Limon, Ger. Limone.
   Citrus limonia (Osbeck) or C. Medica var. limon (L.).

The history of the citrus fruits in the Near East is rather obscure. In Palestine oranges, lemons and citrons were commonly grown about 250 B.C. - 50 A.D.[4], and it seems plausible that from there they spread into the neighbouring countries: Italy, Spain, Lebanon, Syria, Egypt etc.. However, a stage of dormancy must have hovered over the Near East, for plantations remained meagre until the present century, when citrus fruit growing was abruptly revolutionized, particularly in Palestine. To give an idea of the present status of citrus production in the Near East, some data on citrus exports are plotted in graphs (fig. 1) for Palestine[5], Lebanon[6] and Egypt[7].

1- In this paper subscript numbers refer to footnotes, while numbers in brackets refer to bibliography.
2- Palestine Trade Catalogue - Govt. of Palestine, Jan. (1943).
3- For details of structure refer to Winton p. 682.
4- Supra footnote 2.
5- Based on figures obtained from Dept. of Statistics, J'lem.
6- " " " " " Bull. Econ. (1941).
7- " " " " " Dept. of Economics, A.U.B.

A natural consequence of this increased production in Palestine was the dawning of a by-product industry there. For Lebanon, this obviously was not the case; and although conditions in the future will depend on a number of unforseen economic factors, the discussion of which is irrelevant to the nature of this work, it may still be confidently ascertained that it is natural for a miniature by-product industry to arise in this country at least as a supplement to its citrus production.

CHEMISTRY OF THE CITRUS FRUITS

Research field in Citrus Chemistry comprises two main divisions: the first we may call the "academic", referring to the study of the composition and pure chemistry of citrus oils, pectins, vitamins and the like; and the second the "applied" or practical utilization of chemical principles in the field of citrus products, of which preservation of juices, squashes, pulp and peels; canning; manufacturing jellies, jams, marmalades, citric acid, pectin, alcohol, acetone, essential oils, cattle fodder..... are some examples.

This dualism, if we may so call it, characterises most of our modern problems of science; and yet, in its final stage, it always culminates in a greater whole: a synthesis of the academic and the applied. A particularly striking example of that is Citrus Chemistry, where the exclusive specialization in the study of terpenes, pectic substances and vitamins on the one hand, and the very many industrial enterprises of the above mentioned by-products on the other, are being slowly linked together and synthesized into the more important whole, Food Chemistry.

The antiscurbatic value of citrus fruits was perhaps the first incentive towards the study of their chemistry, and long series of papers on that and other vitamins and compounds of biochemical interest were and are still being published in the Biochemical Journal[8]. Later, interest in the essential oils and pectins of the citrus fruit rinds developed, and again the story of that is a long series of papers in the chemical literature[9]. The story of the by-product industry,

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8- Refer to Bioch. J. 25, 888, 1081 (1931); 26, 865 (1932); 27, 279 (1933); 28, 1153 (1934); 29, 275 (1935).. etc...
9- cf. (23), (24), (27), (28), (29), (30), (16)....etc..

however, extends over a longer period; and although its development was less organised, an attempt at sketching some of its main features is presented later in this paper.

In consequence of the forementioned dualism, this paper may seem to have been severed into two unrelated topics; part I (the analytical) corresponding to the academic, and part II (dealing with by-products) to the applied. However, despite an apparent lack of a final synthesis, this work is not discontinuous; for the second part receives merit only as a derivative of the results obtained from the first. This is the logical unity that binds both parts.

TABLE 1.

COMPARATIVE ANALYSES OF ORANGES (Citrus sinensis)

		FRUIT							JUICE				
		Wt.	Peel	Seed	Marc	Water	Protein	Ash	Vol.	Solids	Citric Acid	Sugars Total	Sucrose
		g.	%	%	%	%	%	%	cc.	%	%	%	%
California	Min.	124	14	0	20	82.17	0.91	0.41	55	9.80	0.92	7.65	4.00
	Max.	250	35	3	32	88.57	1.41	0.53	98	13.88	1.72	10.78	5.12
Sicilian	Min.	120	27	1	16	77.52	--	--	% 43	9.38	1.78	2.23	--
	Max.	137	34	2	23	83.78	--	--	51	13.27	2.56	2.66	--
Palestine	Min.	73	30.9	-	13.7	---	--	--	26.2	10.1	1.05	4.9	0.5
	Max.	343	47.6	-	25.5	---	--	--	45.2	14.8	3.96	9.2	4.1
Lebanon	(Av.)	179	29.6	1.2	12.0	82.6	1.10	0.51	cc. 54	12.15	1.56	8.2	4.1

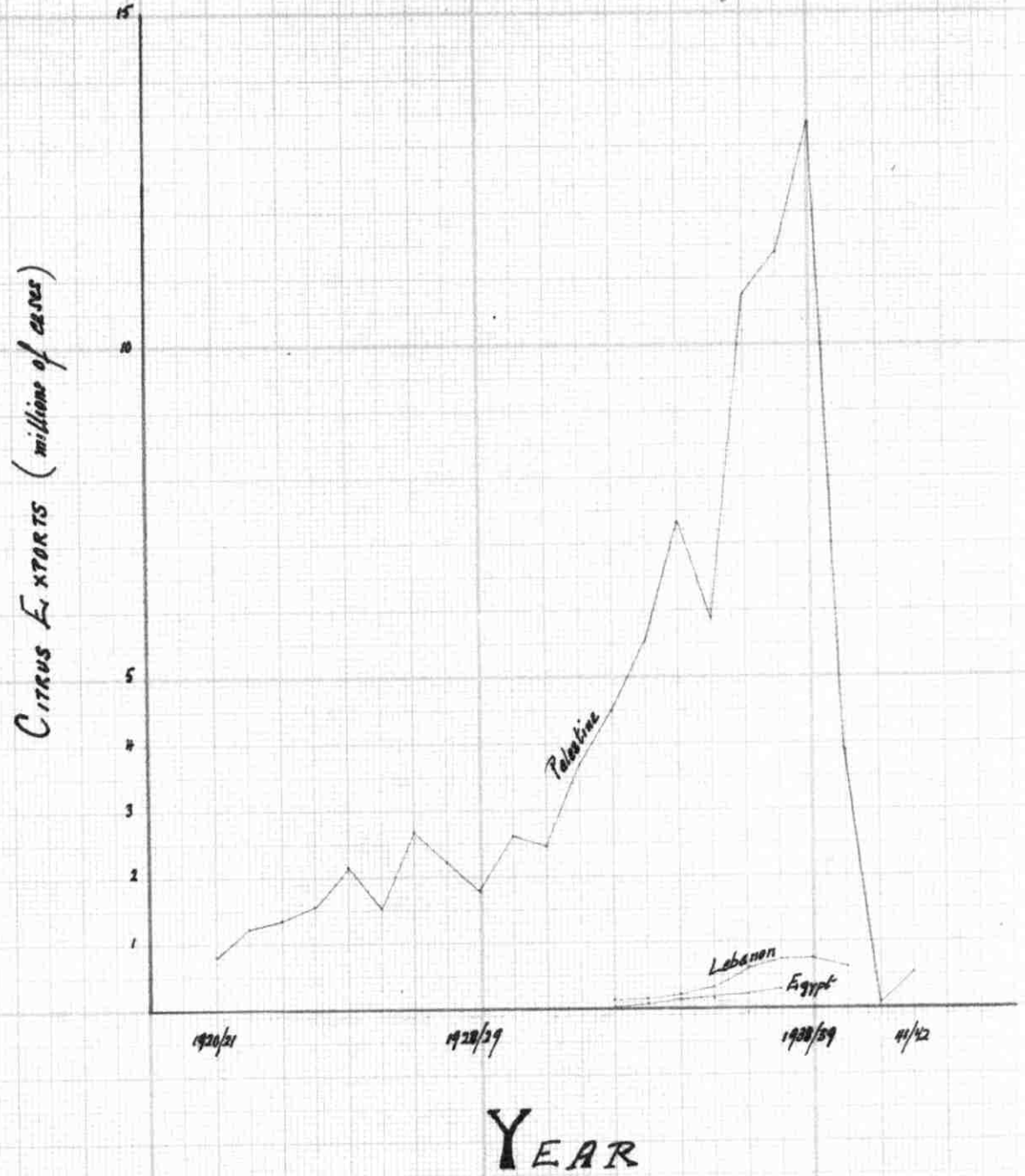
CITRUS EXPORTS (millions of cases)
15
10
5
4
3
2
1
Palestine
Lebanon
Egypt
1920/21
1928/29
1938/39
41/42
YEAR

TABLE 2.

COMPARATIVE ANALYSES OF LEMONS (Citrus Limonia)

		FRUIT							JUICE				
		Wt.	Peel	Seed	Marc	Water	Protein	Ash	Vol.	Solids	Citric Acid	Sugars Total	Sucrose
		g.	%	%	%	%	%	%	cc.	%	%	%	%
Californie	Min.	80	13	0	13	77.93	0.69	0.42	23	9.08	5.74	1.20	0.35
	Max.	170	50	3	38	88.54	1.14	0.78	95	13.20	8.40	3.60	0.58
Sicilian	Min.	115	35	1	16	78.12	--	--	34	9.90	6.51	0.07	--
	Max.	128	44	3	23	83.65	--	--	44	13.38	7.21	0.96	--
Lebanon	(Av.)	163	26	1.2	14.2	76.6	0.88	0.65	54	11.79	6.14	0.90	0.41

TABLE 3.

VARIATION IN THE COMPOSITION OF ORANGES

	FRUIT							JUICE				
	Wt.	Peel	Seed	Marc	Water	Protein	Ash	Vol.	Solids	Citric Acid	Sugars Total	Sucrose
	g.	%	%	%	%	%	%	cc.	%	%	%	%
December	158	28.9	1.2	11.8	81.0	0.98	0.50	42	9.88	1.86	7.6	4.3
February	187	30.1	1.4	12.1	84.3	1.09	0.48	58	11.82	1.48	8.3	2.8
April	192	29.8	1.0	12.1	82.5	1.23	0.55	62	14.75	1.33	8.7	5.3

TABLE 4.

VARIATION IN THE COMPOSITION OF LEMONS

	FRUIT							JUICE				
	Wt.	Peel	Seed	Marc	Water	Protein	Ash	Vol.	Solids	Citric Acid	Sugars Total	Sucrose
	g.	%	%	%	%	%	%	cc.	%	%	%	%
November	155	15	1.2	10.8	72.0	0.60	0.50	42	11.78	6.81	0.24	---
February	174	27	1.05	13.4	79.5	1.12	0.71	59	11.50	6.01	0.91	0.37
April	161	35	1.3	18.5	78.2	0.94	0.74	61	12.11	5.59	1.54	0.45

TABLE 5.

COMPOSITION OF PARTS OF ORANGE (April)

	Fraction of orange	Water	Protein	Acid*	Sugars Total	Ash
	%	%	%		%	%
Peel	29.8	74.4	1.6	-	-	0.60
Marc	12.1	69.8	1.5	-	0.8	0.51
Juice	56.8	91.1	0.3	18.3	8.7	0.31
Seed	1.0	63.2	13.2	-	-	0.98

TABLE 6.

COMPOSITION OF PARTS OF LEMON (April)

	Fraction of lemon	Water	Protein	Acid*	Sugars Total	Ash
	%	%	%		%	%
Peel	35.0	70.9	2.02	-	-	0.62
Marc	18.5	76.3	1.16	-	0.22	0.58
Juice	35.1	88.1	0.40	85.6	1.54	0.27
Seed	1.3	51.2	11.55	-	-	1.05

* cc. 0.1 N NaOH.

VITAMIN C

The determination of Vitamin C (ascorbic acid) in the orange and lemon juices was considered of primary importance, and, this special paragraph is, therefore, devoted to its discussion. No attempt at forwarding a prelude, to serve as background, will be adequate for such an important topic; and hence Rosenberg's survey of its history, chemistry and physiology is recommended instead (10).

The problem to be faced was very simple: fresh fruit juices could be analysed for Vitamin C very easily by direct titration with 2,6-dichlorophenolindophenol in an acidic medium (Tillman's method), for it had been proved by many workers in the field that interference of foreign reducing agents is negligible if the titration be conducted rapidly (35), (42), (43). Two modifications of this method were compared[9] and used interchangeably, as they showed no appreciable discrepancy in results. The following are the results compared with those obtained for Palestine:[10]

Vitamin C in Citrus Juices (mg 100 cc)

	ORANGES		LEMONS	
	Palestine 1935-6	Lebanon 1944-5	Palestine 1935-6	Lebanon 1944-5
Dec.	50	50	48	49.0
Jan.	56	54	51.5	50.0
Feb.	49	52	52	49.8
March	55	50	41	42.5
April,	50	47	-	38.7

9 - Govt. Central Labs., J'lem. and cf. (43).
10- cf. (43).

DISCUSSION OF RESULTS

On examining tables 1 - 7 one can make the following remarks on the various results obtained:

Oranges: In general, weight and composition compare favourably with the average. Volume of juice seems to be low, and also, though to a lesser extent, its acidity. Total solids are medium but sugars rise above the average. During its ripening period[11], the analysed orange seemed to increase in weight, volume of juice and total solids content. The slight decrease in acidity is not normal (17). Total sugars increased gradually, but no fixed relation between the amounts of sucrose and invert sugar was apparent[12]. Vitamin C content compares favourably with that of Palestine's fruit but is slightly lower.

Lemon: The size of the fruit compares favourably with the average, yet its peel content is rather low. Sugars and total solids are medium, but volume of juice rises above the average, while citric acid content falls below. During its ripening, the lemons weight and juice increased regularly, but the abnormal increase in peel content was surprising. The fall of citric acid content to 6 % by February is also disappointing. For sugars, the increase was less than that in oranges but again at no fixed rate. Vitamin C content is fair all during the season except in April when it falls considerably.

For the pectin yields refer to the chapter on "Pectin".

CONCLUSION

In the light of the foregoing discussion one may sketch the following characteristics of the analyzed fruits:

Oranges: are of fair size and average composition, the sugar content being slightly excessive. During their ripening they behave rather normally, and their Vitamin C content does not fall considerably.

Lemons: are rather mediocre in size, peel content and citric acid content. Though quite juicy their Vitamin C content is not high, particularly in April. During their ripening, the citric acid content falls to 6 % by February but the peel improves.

11- Tests of (22) passed.
12- cf. (14) p. 693

In conclusion, then, the following remarks might serve to sum up the analytical part of this work:

1 - The analysed fruits are, at their best, of average composition.

2 - For Vitamin C, both oranges and lemons are good sources, but in April lemons become considerably poorer.

3 - For citric acid, the lemons are rather poor , except during the early part of the season.

4 - Considering the rough nature of this work, the conclusions drawn above represent rough estimates; hence the possibility of more accurate analysis or the existence of fruits of better quality.

P A R T II

B Y - P R O D U C T S

PRELIMINARY

This second part of the work pertains to the "applied" branch of citrus chemistry in compliance with the argument of the General Introduction. To survey this branch, however, would necessitate a study of the citrus by-product industry since its birth in Italy during the eighteenth century. It is not the intention of this note to do so. Reference to present conditions would, perhaps, suffice. For Italy, Smith (34), Sereni (33) and Braverman (18); for America, Will (38) and later Wilson (41); and for Palestine, Braverman (19) and Viteles (36)... give accounts of the present industry with its scopes and possibilities. The extent of the industry at present becomes obvious from the following list of by-product industries:

1 - Preservation:	whole fruits, juices, syrups and pulps; candied peels.....
2 - Canning:	fruits, peels...
3 - Dehydration:	juices, whole fruits...
4 - Citric Acid:	and calcium citrate.
5 - Pectin:	syrup and powder. Also pectates.
6 - Oils:	of lemon and orange, essences...
7 - Fermentation Products:	alcohol, acetone, vinegar, wines...
8 - Jellies, jams	and marmalades.
9 - Wastes:	cattle fodder, fuel...

At present, this country faces no acute problem for citrus waste production*; and yet the choice of citric acid and pectin for these studies was partly founded on their deficiency here during the war. But, as the coming two chapters will expose, this choice was also founded on their interesting chemistry.

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* cf. p. 2 of thesis.

Chapter 1

C I T R I C A C I D

1. HISTORICAL

Citric Acid ($C_6H_8O_7.H_2O$)[1] is no novelty of our age. As far back as 1776 Retzius had distinguished it from tartaric acid, and in 1784 Scheele had obtained it in crystalline form, yet not until 1857 were its properties and tribasicity well established by Liebeg[2].

The story of the manufacture of citric acid, however, does not run parallel to the story of its chemistry. The Italians had long ago developed a home industry out of the transformation of lemon and lime juices into the "citrate of lime", and that they recently developed into a citric acid industry[3]. Several other countries, like France, America, South Africa, Spain and Palestine also developed that industry. In America (California) although the first serious attempt at manufacturing citric acid came towards the end of the last century, it was not until 1921 that that developed into a successful industry, of which a good account is given by Wilson (39). It was also maturing in France around that period, and Roux (11) gives a comprehensive account of its present status there.

Palestine, of course, faced the problem only recently; and the rather successful attempts at manufacturing citric acid were, no doubt, mainly supported by the present war[4] (19), (36). In Lebanon, however, no such attempts have yet been reported even during the war. It was the study of the reasons for that failure that led to this work.

Other than citrus fruits, two main sources of citric acid may be mentioned:
1 - Synthetically from dichloroacetone.... (lab. procedure).
2 - By fermentation of sugars. This latter method is slowly rivalling the old process and has overwhelming literature[5].

1- Refer to Remington's "Practice of Pharmacy" p. 943; or Hutchinson's Encyclopaedia p. 426. Also (11) p. 291.
2- ibid. p. 291.
3- cf. p. 13 of thesis.
4- cf. Palestine Trade Catalogue, 1943, and (31).
5- U.S.P. 1936982 (1934); Ger. P. 619977 (1935) and 679847 (1939); J. Ind. Eng. Ch. 26 (1934); J.Indian Eng. Ch. Soc. Ind. Eng. News 3, 64 (1940) and 5, 201 (1942); Bioch. Z. 307, 293 (1941); Ann. 503, 63 (1933); Ann. Chim. Appl. 24 (1934); Arch. Microbiol. 5 (1934); Pishchevaya Prom. 1, 28 (1941)....

2. PROBLEM

Citrus cull fruits exist in this country due to mechanical or physical injury, partial decaying, freezing, shape defects, etc. (26) and as such they constitute the raw material for the manufacture of citric acid from their juices. The natural question to be asked would then be: Is it possible to utilize the cull fruits of this country for an efficient production of citric acid ? And the answer to that comprises the two logical steps in a scientific study of the problem:

(a) a critique of the various already adopted manufacturing processes as applicable to the present conditions here.

(b) The formulation, in the light of the above mentioned critique, and based upon laboratory experiments performed, of a modified and simple method for the preparation of citric acid on a technical scale.

3. DISCUSSION AND CRITIQUE

Five different methods for the manufacture of citric acid from citrus juices were studied, those being by Wilson (39), Roux (11), Cruess (5), McNair (7) and Warneford-Hardy (37); and every step in the process is analyzed by itself in the forthcoming discussion. Let us first enumerate the principal phases in such a manufacturing process[6]:

a) Extraction of the juice.
b) Saturation of the juice and precipitation of the citrate.
c) Decomposition of the citrate and formation of dissolved citric acid.
d) Concentration of this solution, and granulation of the acid.
e) Purification and recrystallization of the acid.
f) Treatment of the mother-liquor.

a) Extraction: To obtain the juice from the lemons all five methods had to be modified into the use of a hand, electrically driven, squeezer. Varying amounts of fresh lemons (not exceeding 15 kg a batch) were used, and it was found most handy to pass the freshly extracted juice through coarse muslin in order to free it from seeds, pulp and some mucilage. Storing the juice at this stage allows fermentation to set in[7], and

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6- cf. (11) p. 309.
7- cf. (5) p. 605.

destroy the gummy material that makes freshly pressed juice so difficult to filter (while very little citric acid is lost on condition fermentation does not proceed too far). For Beirut weather in winter a standing of 60 hours was found quite satisfactory, at the end of which period the juice would have separated into three layers: clear solution in the middle, mud in the buttom and mud plus soft pulp at the surface. At this stage it was found convenient to siphon out the clear juice; that undoubtedly leaves an appreciable amount of the acid in the mud and pulp residues totalling 10 - 17 %[8] of the total acid content of the juice. These are therefore boiled with a little water and filtered, either by letting it stand, and decanting as before, or through the use of filter aid. Thus it is possible to eliminate altogether, or use very little of, the summach for coagulation[9] or filter aid for speeding filtration[10].

b) Precipitation: This reaction presents no difficulty. The best recommendations are for the use of lime water and calcium carbonate; but the simple use of powdered calcium carbonate only proved efficient and precipitated a pure product that settled easily, thus allowing speedy filtration through siphoning.

c) Decomposition: The general plan here offers no chance for discrepancy, the process being the formation of a citrate paste and its decomposition with 20 - 25 % H_2SO_4 using 2 % excess acid for better precipitation[11]. Washing by decantation was found to eliminate the trouble of filtration although the use of a Buchner funnel is anyway very simple.

d) Concentration: This is the critical stage in the process for large firms use concentration in vacuo, and, due to cost and lack of machinery at present, this is not possible here. On studying the problem it was found possible to evaporate this solution at a temperature not exceeding 60° and on condition the amount of free (excess) sulphuric acid does not exceed 0.15 %[12]. For higher temperatures and higher concentrations of H_2SO_4 the solution darkens very much and as much as 6 % of the citric acid could be lost through decomposition. Even under the most favourable conditions, however, a yellowish colouration will inevitable develop. The intervening filtration of $CaSO_4$ that crystallizes out as concentration proceeds, need not be done more than twice, the second being at sp. gr. 1.300 (determined by a hydrometer and representing the concentration beyond which

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8- Determined as by (11).
9- cf. (7).
10- cf. (39).
11- cf. (11), p. 314.
12- Determined according to (3) p. 606.

citric acid begins to crystallize). Solutions too dark-coloured had to be decolourized with animal charcoal (1 - 2 % by weight), but this, if done to the very concentrated solution, would be extremely difficult to filter, hence its use ought to be anticipated. Beyond sp. gr. 1.300 concentration is followed even more carefully (temperature about 55°) until granulation sets in. The above mentioned modification is more tedious than vacuum concentration, but its merit is the elimination of the use of vacuum pans altogether.

e) Purification and Recrystallization: The citric acid having been allowed to crystallize as prescribed by all five methods, its washing can be effected in a Buchner funnel rather than in a centrifuge. Redissolving and concentration then follow the above modifications; however, this simplified procedure makes it necessary only to decolourize the solution with charcoal. Excess acid (sulphuric) would have already been taken care of before concentration and cations like copper, lead, tin, iron and nickel[38] do not exist here as the work was carried out in no metallic container. Very little $CaSO_4$ was encountered at this stage and if produced (again before sp. gr. 1.300) it was easily filtered. Crystallization follows as above.

f) Mother Liquor: Varying grades and colours of mother liquors result depending upon conditions of experiment and nature of juice. For a single preparation performed it is best to mix, decolourize and evaporate for another granulation. It is not necessary nor worth while to repeat further crystallizations.

4. EXPERIMENTAL

As a consequence of the foregoing discussion the following procedure is recommended for the preparation of citric acid on a semi-technical scale, the amounts being for 15 kg. of lemons as prepared in this laboratory:

15 kg. lemons (about 125 in number) are sliced each in two halves and the juice extracted. The whole mass is filtered through coarse muslin, giving about 5 l. of juice which are conveniently stored in a 5 l. round-bottom flask for three days. The remaining pulp, marc and seed mixture is soaked in 400 cc. water, boiled for 15 minutes and let stand. At the end of three days, 4 l. of clear juice can be siphoned out of the middle layer of the juice in the flask. The pulp

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38- ibid. p. 607 and (39).

is again filtered through coarse muslin, giving about 350 - 400 cc. liquid to be added to the mud remaining in the flask. This mixture is next filtered through fine muslin; or, alternatively, a little filter aid is added, let stand for a while, and then the supernatent liquid is decanted and added to the clear juice. The result is about 4.5 l. of juice.

These are heated in a 10 l. container to about 70°, agitated by an electric stirrer, and 225 g. powdered calcium carbonate[14] are added cautiously until frothing (due to effervescence) becomes mild, after which addition is speeded. Decomposition is completed within 30 minutes, and towards the end the addition of calcium carbonate should cause no visible reaction. This is let stand over an electric heater until the temperature exceeds 95°.

During this time the calcium citrate would have settled to the bottom, and the supernatent liquid can, therefore, be easily siphoned out. Boiling water is used to wash the precipitate into a large sized Buchner funnel, and there two other washings (200 cc. boiling water each) leave behind a clear white powder. The yield on dry basis would be about 400 g. calcium citrate, probably containing excess calcium carbonate.

For the decomposition reaction the wet powder is made into a thin paste in a 2 l. beaker with about 500 cc. water, and is heated never beyond 60°. Then, while the electric stirrer agitates the solution, 735 cc.[15] of H_2SO_4 (containing 300 g. per l.) are slowly added, the reaction taking an hour for completion, at the end of which the solution would have to be heated to 55° again. A check on the amount of excess H_2SO_4 may be conducted[16] at this stage. After letting stand for another hour the solution can be very conveniently filtered by suction and washed twice with hot water and twice with cold (50 - 60 cc. each) the washings being added to the filtrate.

Altogether, there will now be about 1.5 l. of citric acid solution to be evaporated. This is done slowly in a water bath at 60° until the density becomes almost 1.2 (the volume about 800 cc.). If the solution had not, by now, developed a colour darker than yellow, it is simply filtered from any crystallized calcium sulphate. Otherwise approximately 10 g. of animal charcoal are added, the mixture stirred, and after 15 minutes filtered as before.

14- Assuming the juice to contain 7 % acid, to ensure excess.
15- Based on the amount of calcium carbonate added.
16- cf. (11) p. 314 and 363.

Concentration is continued in a one l. beaker at a bath temperature of 55°, with intervening inspection of the specific gravity. For this, a hydrometer kept in a 50 cc. measuring cylinder serves well for the routine. Nevertheless, at sp. gr. 1.300 (determined at the temperature of the solution), the solution is filtered from any calcium sulphate precipitating, by slight suction; too strong suction often pierces the filter paper because of the density and viscosity of the solution.

The filtrate is further concentrated (in a 600 cc. beaker) at 50 - 55° very carefully, until the surface of the solution gets covered with minute crystals. At this, the granulation point of citric acid, the flame is put off and the solution left to cool in its water bath overnight and then in the refrigerator for another two days. During this period crystals of citric acid form and stick to the sides of the beaker to such an extent that breaking the beaker often becomes an easier job of getting the crystals than scratching them off the glass.

These crystals are now dissolved in about 250 cc. of water, decolourized with 3 - 4 g. animal charcoal, filtered, and evaporated cautiously as before. When citric acid crystallizes the mixture is again left in the bath and then the refrigerator. The same procedure is followed for removing the crystals, which are washed with very little water, pressed between filter paper and dried at 35 - 40°. This represents the first crop.

Next, the two mother liquors plus washings (adding to about 750 cc.) are treated with 9 g. charcoal, filtered, concentrated and crystallized as before. This is the second crop. A third crop might be obtained from the resulting mother liquors depending upon the volume and quality at this stage.

The above procedure ought to give the following results:

First crop	= 83 g.
Second "	= 66 g.
Third "	= 32 g.
Total acid obtained	=181 g.

But, considering the juice to have contained 6% acid, theoretical amount of acid present = 225 g.

Therefore yield = 71 % ..... first crop = 32.55 %
second " = 25.88 %
third " = 12.55 %

Or yield on juice basis = 4.26 %.

5. CONCLUSION

This chapter produced a simplified laboratory procedure for preparing citric acid from 15 kg. of lemons. Using three crystallizations about 71% of the acid in the juice could be obtained in pure form (tested by pharmaceutical standards). For small scale operations this might be considered a practicable procedure but the manufacture of citric acid on a large scale is not recommended for two reasons:

1. Citric acid content of the analyzed lemons was rather low.

2. This method gives, at its best, 71% of the acid only.

Chapter 2

P E C T I N

1. DEFINITION AND PROBLEM

The problems of citric acid and pectin arise from a study of different parts of the same fruits, hence they are closely associated and supplementary. The latter, which is the object of our studies in this chapter, is the more complicated and delicate of the two, because three different aspects of the problem are possible, those being:

a- Studies in the chemistry of pectins (composition and properties),
b- " " " production " " (mainly from apples and citrus refuse),
c- " " " application" " in the making of:
(1) jellies....
(2) pectates (15), protective colloids.....

This intimates that pectins may be defined either in terms of their constitution, or in an empirical fashion. We shall adopt the latter for its simplicity and in order to be consistent with the nature of our problem; and, consequently, shall define the term "pectins" as representing those vegetable products extracted from fruits by suitable means, which, in association with acid, or the acid juices of fruits, form jellies[1].

Ever since their discovery by Braconnot in 1825, pectins have, of course, been the subject of very thorough physical and chemical research, to survey which this report is not competent. Nevertheless, it may be stated that as a result of the works of Ehrlich, Fellenberg and Schneider in Germany; of Campbell, Eranfoot, Hardy, Morris, Nanji and Norman in England; and of Hooker, Norris, Olsen and Sucharipa in America[2].... we now know that pectins are polysaccharides, more complex than starches but less than glucose, of varying composition depending upon origin, and yielding on hydrolysis: arabinose, galacturonic acid and methyl alcohol. Variation among pectins is believed to be due to differences in molecular size, degree of esterification of the galacturonic acid units, and amount of accompanying "ballast" material such as pentosans[3].

1- cf. (5) p. 1.
2- For details of references see (5) p. 94.
3- cf. (5) p. 5.

The nature of pectins is thus neither simple nor well established yet; and we therefore shall confine our studies to the possibilities of obtaining pectin from our lemons and oranges, having in view

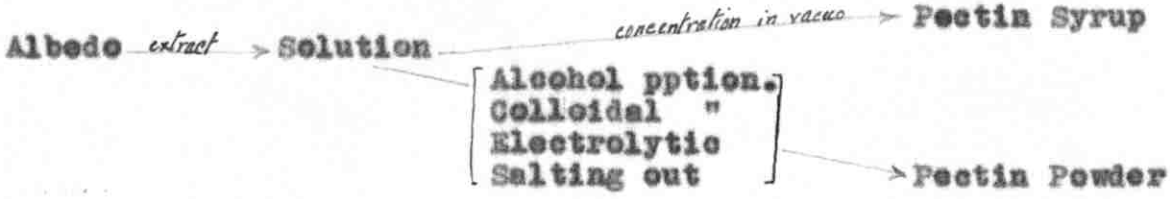
1- testing the various already adopted methods for preparing pectin in its production from lemon and orange peels on a small scale,

2- utilizing the product in making jellies,

3- establishing the practicability or futility of work on pectins in this country.

2. THEORETICAL

The chemistry of the preparation of pectin being rather an obscure topic, it was considered of importance to summarize the various adopted procedures before submitting the results of the experiments performed. For that, the following sketch may serve to shorten an otherwise very lengthy discussion:



The first step is thus an extraction, which must be preceded by leaching in order to have sugars and other undesired substances removed. The extract may now be concentrated in vacuum (otherwise the pectins are hydrolysed and decompose) to produce the commercial pectin syrup or jelly stock, and Rooker (9) describes this process in great detail. Alternatively, pectin may be precipitated from solution in the form of a powder according to one of three principles:

1- Salting-out with a very soluble electolyte.

2- Precipitation from a solvent in which it is insoluble.

3- Precipitation by neutralizing its negative colloidal charge either electrolytically or through the addition of an electrolyte of opposite charge.

The product will always contain foreign substances like pentosans, minerals, etc., and its purity may be determined from its calcium pectate yield or its jellying power (with reference to a conventional standard). The work carried out here is given in the next paragraph.

3. EXPERIMENTAL

Preparation of Pectin: In the preparation of pectin solution from pomace the procedure adopted was modified as follows: the dried peel[4] was passed through a meat mincer, leached twice with water and then left in cold water overnight. The next day, after draining, the pulp was extracted with water acidified with 1% tartaric acid three times, using one hour extraction periods at 95 - 100° [5]. The combined extracts were centrifuged (using keiselguhr) to give a clear pale yellow solution. From this solution pectin powder was prepared in four ways:

1- Salting-out - using magnesium sulphate[6]. Here it was found difficult to control the saturation point, remove the excess salt completely and also to filter the solution rapidly.

2- Colloidal precipitation - using aluminium hydroxide (40) but not removing the excess electrolyte. This method was found quite simple particularly when the pH of the solution (and hence its viscosity) was controlled. However, the product was coloured, had a taste and a rather high ash content.

3- Colloidal precipitation with subsequent elimination of electrolyte - using aluminium hydroxide and removing it with alcohol containing 10 % concentrated HCl as prescribed by Wilson (40). The product in this case was much purer and had a lower ash content.

4- Alcohol precipitation - using equal volumes of solution and alcohol and then purifying the coagulum with alcohol again (3) (5). The result was a pure product, the best of the lot in quality but still contained some starch.

The yields from the various methods were analyzed according to the Carre-Haynes method modified by Hinton[7] and are given in Table 8.

4- Using dried peel was found to eliminate the possibility of rotting. Also cf. (9) p. 17.
5- Reasons for this choice as optimum conditions are found in (23) and (32).
6- cf. (3) p. 347.
7- cf. (5) p. 8.

Jellying Tests: The conditions of formation of pectin-sugar-acid jellies have already been exhausted by Tar[8] and Myers and Baker[9] in America, and Ogg[10] in England; Cruess (3) and Hinton (5) also devote chapters to the discussion of their nature, preparation and effects of various factors (like pH) on them.

Such work carried in this laboratory may seem trivial in comparison, and therefore only the part that deals with the jellying tests as criteria of the purity of pectins shall be included here.

For the jellying test the following modification of the standard (32) was adopted: a constant amount of sugar, 62 gr., and 0.3 gr. citric acid were used. The minimum amounts of the various pectins necessary for causing a jelly point to appear on cooling the solution when boiled to a weight of 100 gr., were recorded (Table 8).

Table 8.

Yields of Various Pectins

	Method of Precipitating Pectin	Ash %	Yield of Ca Pectate %	Jellying Test Min. amount of Pectin gr.
Lemon	Salting-out	15.54	78	---
	Colloidal pption	11.85	90	1.74
	Colloidal pption and alcohol	5.10	97	1.60
	Alcohol pption.	3.92	97	1.55
Orange	Salting-out	14.86	81	---
	Colloidal ppt.	10.21	91	1.70
	Colloidal ppt. and alcohol	4.13	97	1.58
	Alcohol pption.	3.84	101	1.52
Standard*		2.76	98	1.50

8,9- Bull. Del. Agric. Exp. Sta. No. 134, 142, 149, 160, 168, 187.
10- Dissertation, University of Cambridge.

* Pectin powder, Fruit Growers Exchange, Califarnia.

4. DISCUSSION AND CONCLUSION

Of the methods tested for the preparation of pectin from lemon and orange albedo, the last two gave satisfactory results as indicated by their ash content, calcium pectate yield and jellying power. It should be remarked, however, that the ash content is not considered so far a criterion of the purity of a pectin; as a matter of fact Table 8 shows no definite relation between ash content and calcium pectate yield. The method of colloidal precipitation with subsequent elimination of electrolytes seemed to have been the more tedious operation of the two, but it had at least three advantages over the other (alcohol precipitation):

1- Volume of liquid encountered was smaller. This has obvious advantages in large scale manufacturing, but even here filtration was more speedy.

2- Aluminium sulphate, ammonia, alcohol and concentrated HCl were needed in relatively small amounts, hence the decrease in expense.

3- The electrolyte could not be lost by evaporation, and hence the operation was less delicate. It could also be recovered by crystallization quite easily.

Nevertheless, if alcohol (or any other such precipitating agent like acetone) be easily available and cheap, and its recovery be controlled, by careful operation, then its method would have the advantage of yielding a product of better quality.

At this stage the investigation had to stop and the choice between the two methods remained undecided pending the publication of further information on the subject.

In conclusion, then, we may summarize this chapter as follows:

1- The analyzed lemons and oranges gave both good yields of pectin, that of oranges being slightly superior.

2- Pectin may be prepared successfully from the fruits either by colloidal precipitation (with subsequent elimination of electrolyte) or by precipitation with alcohol.

3- Further investigation in this field is worth while.

4- A personal opinion of the writer is that electrolytic precipitation should also be seriously considered, as it will surely come into use one day.

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