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STUDIES IN THE CHEMISTRY

of

C A R O B

A

INDUSTRIAL EXTRACTION OF SUGARS

From

CAROB

By

Aziz F. Abdul Karim

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INTRODUCTION

THE CAROB TREE.

Original home: The Carob tree* is said to have originated in Africa and was later grown in Egypt[1]. According to Alphonse de Condolle[2], its original home was around the eastern end of the Mediterranean, including the southern cost of Asia Minor and Syria, and perhaps Tripoli. Its cultivation began in historic times and was diffused by the Greeks in Italy and Greece and was carried by the Arabs west as far as Spain and Morocco[3]. According to Celsius[4], no tree is more frequently mentioned in the Talmud, where it is stated that its fruit used to be given as food to cattle and swine. Pliny and Theophrastus mention it as a native of Syria. In the New Testament it is identified with the "husks" eaten by the prodigal son in the parable Luke XV.16. By some it is taken to be the "Locusts" eaten by John the Baptist in the wilderness, whence the english names Locust-pods and St. John's Bread.

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*Also called: Caroubier (Fr.), Carruba (It.), Algaroba (Sp.), Kharrub (Ar.), Khirnuh (Per.), Yohannishbrot, (Ger.).

[1]Bustani - Da'irat Al-Maarif (Arabic Encyclopedia).

[2]The Origin of cultivated plants.

[3]L.H. Bailey, The Standard Cyclopedia of Horticulture, vol. II, pp.717-718.

[4]J. Kotto, The Cyclopedia of Biblical Literature, vol. I, p.403.

Name: In Arabic and Syriac, the tree derived its name "Kharrub or better Kharnub" from the resemblance of its fruit to a horn[1]. Similarly, by ancient Greeks such as Galen, Strabo and Aegineta the tree is called (Κεράτια) keratia i. e. little horns. According to Celsius Modern Greeks have converted the arabic name into (χάρουβα) Karouba and the Spaimards into Garroba and Algaroba[2]. The generic name Ceratonia Siliqua is due to Linnaeus.

Taxonomic Study: The tree belongs to Family "Leguimosae", sub-family "Coesalpinaceae", Genus "Ceratonia and species C. Siliqua Linn., of which species it is the only member. However, centuries of cultivation, selection and breeding, in different soils in the various regions of the Mediterranean basin, have produced a number of varieties with various characteristics which are propogated by grafting and budding. The tree is found as dioceious and as Monoceious or hermaphrodite. It is evergreen, grows to a height of about fifteen meters with a fine hemispherical comus or top, and about 10 meters in diameter of branches.[3]

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[1]Bustani - Da'irat Al-Maarif (Arabic Encyclopedia).

[2]J. Kitto - The Cyclopedia of Biblical Literature, vol. I, p.403.

[3]G. Post - Flora of Lebanon and Syria.

The stem is exogenous, large and woody, arboreous, erect and perennial. The branches are usually very short and break with ease. The leaves are of the alternate type, pinnately compound with three to five pairs of leaflets, usually four. These leaflets are oblong, obtuse or obonate, frequently retuse, with a reticulated venation, a coriaceous, leathery, texture and dark green in color on the upper surface and light green on the lower surface. Inflorescence is indeterminate, with short racemes solitary or clustered along the year old branches. The flowers are irregular, dioceous or polygamous, but not papilionaceous. The stamens are five on a top-shaped calyx having five dentiform deciduous segments. The fruit is a long, flat, leathery, indihescent, horn-like pod containing numerous brown, hard seeds embedded in pulp. This pulp has a pleasant sweetish flavor and a characteristic odor.

Distribution and adaptability: At present the tree is indegenous to all the coastal regions of the Mediterranean. Dr. Fairchild, in his book "Exploring for plants" says: "Carob forms one of the most picturesque trees with which the limestone cliffs of the Mediterranean are dotted". The tree hugs the seashore regions as it is easily injured by frost and severe cold. In this respect it is more resistant to cold than the orange and citrus trees but less than the olives. Its long

root system added to its small water consumption, makes it a strong draught resister. It thrives well in any soil and all localities where there is not much humidity. Its ability to stand abuse is described by J. Russell Smith in his book "The Crops a Permanent Agriculture". He says; "after having travelled through the carob districts of Spain, Portugal, and Algeria, I wonder that many of the trees can yield at all, so shocking is the treatment to which the soil has been subjected for centuries".

Present Status in Lebanon: In Libanon the tree is found almost always self-planted, scattered at random in rough, rocky and unplowed land. If by chance seedlings happen to appear in good soil, they are immediately uprooted or transplanted to border areas where they do not handicap the growth of other trees. It is not long ago since in various villages of Lebanon, a big landowner was willing to give to any fellah half ownership of the wild trees, that incidentally grew on his land, for merely budding them with good varieties. A large number of the trees that naturally grow on the rocky hills and mountains of Lebanon, and that give them an evergreen remarkable appearance, are up to the present wild, unproductive and annually pastured. "Iklim Al-Kharrub" is a district in southern Lebanon comprising about fifteen villages, was

so named due to the great abundance of the carob tree in that locality. Today you may find anything else more abundant there than carob.

Culture: From seeds the plant grows in one or other form of the wild variety. For greater production and better yield grafting is necessary. Three or four years after grafting the young tree is said[1] to yield from four to eight kilos of carobs. After six to eight years the yield is raised to about 50 kilos. When it becomes fully mature, and that is not in less than twenty years, it may yield up to 500 kilos, depending on the care and attention given to it.

In Lebanon due to the great neglect of the tree the yield rarely reaches the above figures. As a result of many conferences with several leading producers I was told that an ordinary carob tree yields about 100 kilos of carob, a very good tree yields 200 kilos, and an unusually good tree yields up to 300 kilos.

It may be worth mentioning that "Du Breuil gives the average yield at 100 kilos, in Southern France and mentions single trees in Valencia Spain that produce as high as 1380 kg.s".

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[1]Rothea - Caroubier et caroubes, Bull. de Sci. Pharmacol. 29, 369, 1922.

[2]L. H. Bailey - The Standard Cyclopedia of Horticulture, vol. II, pp. 717-718.

Production: Cyprus has been for a long time the leading producer and exporter of Carob. Sicily comes next and other producing countries are Italy, Spain, Algeria, Tunis, Palestine and Lebanon. Figures on the annual production of carob in Lebanon are to be looked upon with reservation. Government records on the subject are wanting, and reliable estimates are difficult as carob trees are in most cases grown helter-skelter in chance and irregular localities of the seashore regions. However, several leading dealers seem to agree on an approximation of fourty to fifty thousand tons of yearly production.

Varieties in Lebanon: Aside from the wild tree three cultivated varieties, noted for their high sugar content are found in Lebanon. The first is commonly called in Arabic "Khishabi" "خشابي" meaning woody, the second is "Mukaydsi" "مقيدسي". Probably from the original relation of the strain to Jerusalem, and the third is "Sandali" "صندلي". The Khishabi carob tree is characterized by its big, broad leaves, its long new shoots, and its high productivity. About 70% of the carob yield of Lebanon comes from here. Its ripe fruit is a long pod 20-30 cms. in length, 2.3 - 2.7 cms. in width and .8-1.2 cms. in thickness. It is hard, dark blackish in color, with

a smooth but twisted surface. The "Mukaydsi" carob tree is in general more resistant to climate and temperature changes. It has smaller and narrower leaves and far shorter new shoots. It is nearly half as productive as the Khishabi type. Its ripe fruit is a shorter pod 10-15 cms. in length, 2.3-2.6 cms. in width and 0.7-1 cm. in thickness. It is brownish bronze in color and has a smooth shiny surface. Its tenderness added to its higher sugar content makes it more delicious to eat, by the Lebanese Mountaneer as a carbohydrate foodstuff, than the other two varieties. The "Sandali" carob tree is very similar to the "Mukaydsi" tree. The strain could grow directly from the seed though in most localities in Lebanon it is budded on the wild variety. Its pod is 12-20 cms. in length, 2-2.5 cms. in width, and 0.6-9 cm. in thickness. It has a lighter brown color than the "Mukaydsi" pod, but a larger number of closely parked seeds. The "dibs" that is made from it is far superior in its color and taste to any of the other varieties.

Uses: All the parts of the carob tree are useful and are more or less utilized. Its heavy, hard, and strong wood with its natural mosaic appearance makes it serve very nicely for ornamental pieces of

furniture and inside finish of houses. Its leaves as also the bark are useful in tanning. A water extract of the green fruit, which is highly astringent in taste, is used for curdling milk in preparing a delicious native food product known as "Mikkayka".

The ripe fruit, with its high sugar content, has been used since olden times as a forage crop for pigs and swine. As a human food, it was always disesteemed and only eaten by poor people in cases of extreme necessity. Luke the evangelist was trying to show to what state of misery the prodigal son had reached by eating it. "In ancient pharmacopeas we find carob under the name of siliqua dulcis. It was administered as pectoral decoction. By the arabs it was highly looked upon as a medicine against Bronchitis[4]". As a meal it is eaten with avidity by all kinds of stock. During the last World War large quantities of carob were given as a regular food for the horses of the English Army in Palestine. Nowadays, large quantities of carob are annually used in the United States to flavor chewing tobacco.

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[4]Rothea - Caroubier et caroubes, Bull. de Sci. Pharmacol. 29, 369, 1922.

Roasted pods are used in some countries as coffee substitute. In Spain it is used in preparing a kind of cheap chocolate[1]. In most countries the greater quantity of carob goes to preparing syrups, molasses, fermented drinks, and alcohol. In Lebanon 90% of the carob used in the country goes to making "dibs", the rest goes mainly to the fermenting industries for making alcohol. In Italy it is claimed that they have developed an industrial method of extracting sugar (pure sucrose) from the pods[2]. It is not improbable that further research may put carob as a strong rival to cane and beet sugar; knowing that in the fruit of some of the good varieties we find double the percentage of sugar as we find in the best canes and beets.

It is said that carob seeds used to be the "carat" employed by jewellers in weighing silver and gold. At present they find a market as thickening gels in the textile industries and especially in calico printing[1].

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[1]G. Tagliani - Society of Dyers and Colourists, 14, 344, 1929.

[2]G. Oddo - Annali Di Chimica Applicata, 26, Fasc. 1, 1936.

Preservation: Two things have to be guarded against in the preservation of carobs. First, the various kinds of parasites that penetrate the fruit and start the destruction of the pod rendering it often completely useless. Second, moisture which if above 15% helps in starting fermentation. Combating the parasites, according to Rothea, could be effectively accomplished by furmigation with either carbon tetrachloride or chloropierin in a dose of ten to twenty grams per cubic meter and a contact of 24 to 48 hours. Dessiccation to 60° or 70°, on the other hand, besides taking care of the factor of moisture, also helps very much in killing the parasites.

Composition of Pod: Reinsch and Volcker reported as early as 1864 the presence of glucose, gum, albumin, tannin, pectin, chlorophyll, fat and starchy materials. Around 1892, Heckel and Schlagdenhaufen found, 18% glucose, 32% sucrose, gum, tannin, pectin albumen and 34% cellullese. Muntz in his work "Composition chimiques des Caroubes", gave the following figures:

16.3%	.....	water
4.3%		nitrogenous matter
14.3%		glucose
30.1%		sucrose
0.54%		fat
32.1%		other different carbohydrate material and cellulose
2.2%		mineral matter or ash.

Around 1900 M. Balland started a thorough study of carobs of the various producing countries. The results of his analysis appeared in "Journal de Pharmacie et de Chimie" en 1904. His researches constituted the most complete work on the subject up to that time. Some of his figures are given in Table I.

Between 1920 and 1930 several European as well as American chemists made a large number of analyses on carobs of different varieties and districts. Chiefly noted among these are Rothea, Condit, Jaffa, Albro, Walton, Sanchez, Nater. Some of their results are attached in Table II, for comparison and reference.

Around 1933, a group of Italian chemists, Oddo, Algerino, Ribon, and de Fonzo, stimulated by the idea of advancing an industrial method for extracting crystalline sugar from carobs, made analysis of 46 different samples that came from all districts of the Mediterranean basin and vicinity. Their work besides being the most recent and most complete on the subject is done by modified analytical methods adapted to the complex composition of carob. Selected representations of their results are given in Table III.

TABLE No. I.

Place of Sample	Moisture	Nitrogenous Matter.	Fat	Sucrose	Reducing Sugars	Starchy and other carbohydrate material	Cellulose (crude)	Ash
Algeria	13.00	5.08	0.50	30	1	39.87	9.10	2.25
	9.200	6.02	0.55	21.74	21.36	28.43	10.5	2.20
Cyprus	11.00	5.60	0.40	28.57	14.53	29.70	8.10	2.10
Crete	12.00	5.74	0.35	8.2	26.04	37.74	7.85	2.08
Greece	10.8	6.86	0.50	29.4	10.28	30.70	9.5	1.96
Mersine	12.3	6.3	0.60	27.1	12.75	26.95	11.8	2.2
Portugal	11.8	5.74	0.50	15.76	21.00	34.05	9.15	2.00

TABLE No. II

Analyst	Place		Moisture.	Reducing Sugars.	Sucrose	Crude Protein	Nitrogen free extract	Fat	Cellulose	Ash
Jaffa and Albro	California (entire pod)	Minimum	9.12	3.25	6.39	3.26	26.99	1.00	4.98	1.67
		Maximum	19.81	18.69	41.56	15.22	43.57	3.82	17.42	3.46
		Average of 8 samples.	13.28	11.08	19.44	6.75	39.80	2.17	9.29	2.57
	" Pods without seeds	Minimum	3.70	3.00	7.02	2.02	24.48	.82	3.14	1.76
		Maximum	24.70	20.54	43.62	7.18	48.36	4.02	15.31	3.87
		Average of 17 samples.	11.50	11.24	23.17	4.50	36.30	2.37	8.78	2.72
Rothea	France entire fruit.	Minimum	12	8.5	29.4	3.00	24.57	0.25	4.8	2.50
		Maximum	19.5	11.0	34.67	4.35	30.7	0.42	7.82	4.07
Noter	? ?		-	19.62	23.46	2.1		0.25	19.5	
Sanchez	Valencia		15.9	7.94	32.78	4.06	26.15	0.49		2.57

TABLE No. III

	Prpvince		Seeds	Moist-ure	Glucose F.	Glucose A.A.	Sucrose F.	Sucrose A.A.	Starch (soluble)	Cellu-lose	Pro-tein	Fat	Ash
1.	Portugal	(Algarve)	12	-	10.8	11.8	21.2	21.1	-	3.5	-	-	-
4.	Spain	(Valencia)	13	11.11	9.7	9.3	23.5	24.0	-	3.6	3.48	-	-
8.	"	(Mallorca)	14.9	11.73	6.5	6.5	18.5	17.7	-	3.84	3.I	0.48	1.47
11.	Morocco	(Tetuan)	14.0	14.08	9.7	11.05	18.9	20.2	3.69	3.3	-	-	1.97
13.	Algeria	(Algeri)	10	13.94	9.8	10.0	16.5	16.4	1.15	3.2	3.8	-	1.94
14.	"	(")	24	-	9.2	10.0	17.7	18.4	-	5.7	-	-	-
15.	Tripoli	(Tripoli)	9.9	14.04	10.6	11.0	18.2	19.3	1.15	3.7	3.7	-	1.62
19.	Italy	(Pacecc)	5.6	17.27	7.9	8.2	25.3	25.9	-	3.7	4.2	-	1.64
28.	"	(Bari)	5.6	-	11.6	13.2	19.1	20.1	0.82	3.6	-	-	-
31.	Greece	(Retimme)	12.7	-	6.9	7.00	22.3	23.1	-	4.09	-	-	-
33.	"	(Canea)	11.05	12.26	7.18	8.05	25.59	24.34	-	4.05	3.6		
30.	Cyprus	(Limassol)	9.5	-	8.7	8.9	17.5	18.4	0.95	3.8 m	-	-	-
40.	"	(daAlessandria)	9.4	-	7.7	8.0	17.3	17.3	0.99	3.3	-	-	-
41.	Lebanon	(Beirut)	6.9	-	8.4	8.1	26.6	26.0	-	3.36	-	-	-
42.	"	(")	8.4	12.52	8.6	8.6	24.4	24.1	-	3.36	3.48	-	1.57
43.	Turkey	(Stambul)	7.4	10.19	8.6	8.8	21.0	22.5	1.42	-	3.72	-	-
44.	Palestine	(Haifa)	6.7	11.95	7.6	8.5	18.7	19.7	-	3.1	4.1	-	1.47
45.	"	(Beitgemal)	10.9	-	6.1	6.2	19.9	19.6	0.2	3.69	-	-	-
46.	"	"	18.8	-	6.2	6.8	19.1	20.1	-	5.4	-	-	-

From Table III, a few points are worthy of observation.

1. The percentage of seeds in cultivated varies between 5 to 15%, reaching a maximum of about 26% in the wild ones.

2. Most carobs are richer in sucrose than in glucose although that is not always the case.

3. Carob is richer in sugar content than canes and beets. The percentage of total sugar in some of the good varieties is twice as high as in the best canes and beets.

4. Samples number 41 and 42 represent the two common carob varieties that are found in Lebanon. Number 41 is the "Mukaydsi" variety and Number 42 is the "Khishabi variety". The two varieties record the highest percentage of total sugars among all the 46 samples analysed. Such a fact is highly encouraging and is of outstanding importance in a study aimed at utilizing carob for its sugar contents.

THE PROBLEM

The carob tree is a highly productive tree that does not need much agricultural attention. It thrives well in those areas of Lebanon that are rocky and suitable for nothing else. Besides value of its crop, encouraging its plantation, (1) saves those slopes that are suffering erosion with every shower of rain, (2) utilizes the wasted natural soil resources, and, (3) converts the barren seashore hills to evergreen groves of picturesque appearance.

However, these considerations do not appeal very much to our poor fellah. His attention is focused around those crops that give him a sensibly good revenue. The carob tree would not receive more of his time or care until he is convinced that he can get a crop that will find a better market than the one it has been having up to the present time.

I have already mentioned the fact that about 90% of the carob produced in Lebanon goes to making "dibs". This is a thick, dark and opaque syrup made by concentrating on direct fire and in a very crude way, a water extract of the crushed pods. It is locally used by the poor mountaineer as a sweet foodstuff. It is cheap,

and its market is poor, as it lacks all of the marketable qualities that characterize commercial syrups and molasses. Its chief drawbacks are: (1) Its unattractive opaque black color

(2) Its rank taste,

(3) the lack of uniform consistency.

As a first attempt to study the industrial possibilities of carob, I have limited my investigation to trying to improve this old and native product, with the idea of presenting it to the market as a syrup of standard quality, of attractive color and of a characteristic pleasant taste.

I hope, however, that the chemistry department and specially Professor H. W. Close, will keep up this interest in carob, and will help to extend more rigorous research to the various problems, scientific or technical, that it presents. Carob analysis has already revealed industrial potentialities that are highly promising. A scientific study of such potentialities, will not only be received with gratitude by our fellah and our government, but also by every person who loves his country, who likes Lebanon, and who likes to see that every bit of its soil, rock and hill contributes and adds to its natural beauty and to the comfort and happiness of its people.

EXPERIMENTAL PART

The experimental part includes six main operations: crushing, extraction, classification, decolorization, concentration and keeping. Exhaustive study of each of these operations and of the many factors that enter into every one of them is beyond the time that I could put on my problem. The little that was done is given in the following pages of this paper.

CHAPTER I

C R U S H I N G

Carob would not have presented a crushing problem of its own had it not been for the fact that the sugar in the pulp has the consistency of thick molasses. When the pod is crushed it becomes very sticky, cakes and looks like vulcanized rubber. Its sticking to parts of grinding machines interfered with several attempts at simple and successful crushing.

The first trial in grinding carob was done with a small laboratory grinding mill, having a sieve of 7mm mesh, and run by a directly connected electric motor of ½ H.P., 110-220 volts, 60 cycles and a single phase and 1125 R.P.M. Although this mill was used for grinding many substances that are much harder than carob, it was found unsuitable for grinding the latter for three main reasons. First, carob pulp stuck tightly between the knives of the mill and offered great resistance to the running of the motor. This necessitated stopping the motor and cleaning the mill after grinding of every half a kilogram of carob. Second, the seeds were crushed and mixed with the rest of the pod. This meant, aside from the loss of the seeds which have their own separate market, the introduction

of many foreign substances, of gelatinous and colloidal nature, into the sucrate material of the pod. Third, the crushed product was so finely ground that its particles packed together, on the addition of water. This preventing uniform, rapid, and free diffusion of the water through the pulp during the extraction period. As a result extraction of the sugars from the various layers was unequal and incomplete.

The second machine that was tried was a hand run Olive seed crusher of semi-industrial size. It has movable spikes that are adjustable to give three different sizes. Through the two larger sizes, carob pods passed out practically unchanged. Through the smallest, however, the seeds were crushed and mechanical difficulties due to sticking were quite pronounced. So this machine was also inadequate for grinding carob.

Finally, resort was taken in a centrifugal meat chopper of 1 cm. mesh, directly connected to electric motor of 1.1 K.W., 110-190 volts, 324 R.P.M. and 3 phases. Except for its frailty for carob, it worked very nicely. The knife blades of a central, circular, moving disk, rotated the pods against a vertical cylindrical surface having a large number of elongated openings with sharp

edges projecting inward. The carob pods were directly chipped out leaving no chance for their packing in and introducing the usual sticking troubles. The seeds went out this time not only uncrushed but were also centrifuged away from the pulpy material, because of their greater weight. This served as a simple practical method for their seperation from the other constituents of the pod. However, the size of the particles was still finer than necessary and packing during extraction, though less than before, was still an unresolved problem. As no other grinding machines were available, and changing the sieves of the ones we have for others of larger meshes was practically impossible, with the facilities that were at our disposal, I had to manage the work with the least equipment that we have gotten. Hence, the packing problem was partially remedied by occasional stirring during the extraction period.

CONCLUSION:- Crushing carob for the purpose of extracting its sugar*, could be satisfactorily done by a chopper similar to the one I used. The mill,

however, has to be of a stronger make, connected to a more powerful motor, and has to have sieves of larger mesh about 1.5-2 cms.

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*In grinding Algaroba to be used as a meal for animals Ben Williams of the Hawaiian Commercial and Sugar Company suggests heating the beans to a temperature of 600 to 800°F., by superheated steam in a rotary kilm. This converts the sugars which are found in a state of molasses to a solid and dry substance that can be easily crushed. However, such a procedure cannot be applied in our case as high temperatures introduce color troubles which are, already and without heat, quite serious.

CHAPTER II.

E X T R A C T I O N

Aim: To find the proper conditions under which the maximum quantity of sugar, found in carob, could be economically extracted.

Factors studied: The variable factors that were taken into consideration were four: (1) Temperature (2) Proportion of solvent to carob (3) Time of extraction, (4) Number of extractions.

The solvent factor, on the other hand, was kept constant, taking it for granted that no other solvent could economically compete with water in a work such as the one I was undertaking.

1. **Temperature.** G. Oddo, who is credited for a good deal of work on carob, has found that more sugar is extracted at 30°C than at 75° - 90° C.[1] W. Kroner and H. Kothe have found

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[1] Annali di Chimica Applicata 26, Fasm. 2, 1936.

that pure glucose solutions are discolored at high temperatures and that the discoloration was related to the PH of the solution.[2] Morover, if comparison is permissible and could be carried at all to sugar extraction from canes, Muller Von Czernicky has found that there exists no difference between cold and hot masceration[3].

As a result of my work, extractions at temperatures higher than 80°C, were found objectionable from three points of view: (1) High temperature developped an undesirable darkening in the color of the extract. (2) It introduced more gummy and non-sugar material into the extract, causing it to become more impure and more troublesome to clarify. (3) It added the fuel expense involved in heating the water used for extraction.

All the above considerations definetly define the factor of temperature and puts room or low temperature extraction as being more advantageous than and preferable to high temperature extraction.

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[2]Jour. Ind. Eng. Chem. 31, 248, 1939.

[3]Archif Voor de Java Sukerindustrie 174, 1899.

2. Proportion of water to carob:

Preliminary work on extraction with water to carob weight ratios of 4:1 and 5:1 and an extraction period of 1,2 or 3 hours gave the following results:

TABLE IV

Proportion of water to carob	Time of extraction in hours	Color of extract Lovibond units.	Temperature of extraction	Total sugars as invert.
4:1	3	-	17°C	12%
5:1	1	-	17°C	9%
5:1	2	-	25°C	11%
5:1	2	-	16°C	10.5%
5:1	2	5 Y, 1.3R	17°C	-
5:1	2	5 Y, 1.4R	18°C	-
5:1	2	4.6 Y, 1.3R	13°C	-
5:1	2	5 Y, 1.5R	15.6°C	-

The extracts, as seen from Table IV, had their sugar content fluctuate between 9-12%, and their color vary between 4.6-5 Yellow and 1.3-1.5 Red. Being of that dilution and of that light color they showed no difficulties in subsequent operations, of filtration, clarification and decolorization. So, work was directed

next, at getting more concentrated solutions. In accomplishing that, the first thing that was tried, was the possibility of extraction by multiple diffusion batteries, a procedure that is commonly applied in sugar extraction from beets.

500 grams of crushed carob was put in a thin linen bag and allowed to diffuse with 2 liters of water for three hours at room temperature (16°C). The diffusion juice was then drawn off and poured upon 500 grams of fresh carob in a second bag. Here also diffusion went on for three hours after which the enriched juice was drawn off and poured on 500gr. of fresh carob in a third bag. After another three hours the concentrated juice was drained off and tested for its color and ease of filtration and decolorization. In the meanwhile, two liters of water were poured over the residue of Bag I and allowed to diffuse for three hours then drained and added to bags II and III successively. A third similar extraction with one liter of water followed the previous two. The results are shown in detail in Table V.

TABLE V.

Number of Extraction	Vol. of water added to Bag I.	Extract recovered from Bag I and put on carob in Bag II.			Extract recovered from Bag II and put on carob of Bag III.			Extract recovered from Bag III.			Extract recovered from 2nd. extraction of Bag III and put on fresh carob in Bag IV.		
		Vol. of Juice.	Baume Density (M145)	Equiv. Brix Degree.	Vol. of Juice	Baume Density (M145)	Equiv. Brix Degree.	Vol. of Juice.	Baume Density (M145)	Equiv. Brix Degree.	Vol. of Juice.	Baume Density (M145)	Equiv. Brix Degree.
First	2000cc	1500	8	14.4	1090	13	23.5	650	18	32.8			
Second	2000cc	1940	2	3.6	1860	5	9	1850	9	16.2	1360	15	
Third	1000cc	960	0.5	1	950	1	1.8	940	2	3.6			

The 650cc. of the most concentrated extract was found to contain about 30% of total sugar, and to have the following color: 30 Y, 7.5 R, 2 B. On defecation with $Ca(OH)_2$ at 40°C, its color got practically black, it filtered very slowly, and it was not possible, with any reasonable quantity of carbon to decolorize it. The 1850cc of juice recovered from the IInd. extraction of Bag III, when put over a fresh quantity of carob in Bag IV, was found to have a deeper color* than the 650cc solution of the first extraction, though the percentage of sugar in the former was still less than that of the latter. Obviously, in the second extractions coloring material was increasing faster than sugar. If work were extended similarly into the third extractions, until the percentage of sugar was near that of the first extraction, the situation would probably be worse than that of any of the previous cases. Such a complicated system

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*Its actual color was not determined as the tintometer did not posess slides of deeper color.

of extraction with so many disadvantage was soon discarded as being economically inapplicable.

3. Time of Extraction.

The second attempt at getting a concentrated extraction juice was done by decreasing the water to carob ratio from 4:1 to 2:1. This ratio could not be reduced any more as with it the amount of water was just enough to cover the carob after it had absorbed a good deal of the solvent and gotten swollen. While studying the various properties of the new extract, the influence of the time factor or the rate of extraction was also noted and recorded.

500 gr. of carobs was mascerated with one liter of water for three hours at room temperature. The juice was then drained off. The partially extracted residue was, after rinsing with water to remove any juice hanging to it, again mascerated with one liter of fresh water. After an elapse of two hours a 200cc sample of the juice was taken and tested. The rest of the juice was removed after another hour and also tested. The results of the various tests on the three extracts are shown in Table VI.

TABLE VI.

	First Extract	Second Extract after 2 hours.	Second Extract after 3 hours.
Temperature of extraction	26°	25°	25°
Volume of juice received in cc.	600	200	800
Density of juice (Water-phal's balance).	1.0810	1.0176	1.0192
Equivalent Brix degrees	19.6	4.5	5
Acidity of the juice*	2	0.4	0.55
Color (In Lovibond units	20 Y, 4.5 R, 1.5 B.	4.6 Y, 1.4 R, 0.6 B.	4.6 Y, 1.5 R, 0.6 B.
Percentage total sugar (as reducing) by volume of juice.	17.79	4.13	4.72

*Measured in number of ccs. necessary to neutralize 25cc of juice to phenolphthalein color.

Discussion of results:

1. Sugar: Most of the sugar found in carob is extracted during the first extraction, most of what remains is extracted during the first two hours of the second extraction, while about 0.6% only, is extracted during the last hour (third hour) of the second extraction. The third extract was tasted and did not taste sweet so it was decided not to use it.

2. Color: The greater part of the coloring material came into solution in the first extraction. However, although the color of the second extract after two hours was nearly the same as after three hours, coloring material continued coming into solution in the third fourth and fifth extraction and long after the residue had been exhausted from all its sugar.

3. Filtration: No filtration difficulties were involved even in the most concentrated extract.

4. Number of Extractions: From what has been said, it is clear that with two extractions of three hours duration each most of the sugar in carob comes into solution. However, if the first and second extracts were combined together for further treatment, they would constitute a dilute solution containing only from 10-12% sugar.

With the idea of trying to limit the number of extractions to two, measures were directed at getting a more concentrated second extract,

before combining it with the first. This was accomplished by two ways: (1) In the second extraction the carob to water ratio was changed from 1:2 to 1:1. This was possible here as no appreciable quantity of the solvent was absorbed by the carob during extraction. (2) The juice obtained from the second extractions was used once as a solvent for the second extraction of another batch. The resulting extract contained now from 8-10% sugar, and when combined with first extracts gave a fairly concentrated solution containing from 14-15% sugar.

The residues that remained after the second extraction were not totally exhausted, and contained a very small percentage of sugar. However, no further endeavor was attempted at extracting that small quantity of sugar for two reasons: (1) The residues were intended to be used as cattle food and a small quantity of sweet material, besides increasing the nutritive value of the meal, it would make it more palatable and appetizing to the animals. (2) The solutions produced from further extractions, aside from containing a larger proportion of coloring material than sugar, were

were too dilute and the expenses involved in evaporating the extra amount of solvent, are greater than the actual value of the sugar extracted.

Conclusion: Two extractions at room-temperature and of three hours duration each would suffice to extract most of the sugar found in carob. In the first extractions the ratio of carob to water is 1:2 and in the second 1:1. The juice obtained from the second is, for economy, better used as a solvent in second extraction of another batch.

CHAPTER III.

C L A R I F I C A T I O N.

Aim: To free the turbid impure juice, so far as is practicable, from all non-sugar constituents, both dissolved and suspended; without spending too much on clarifying agents and without alteration or precipitation of the sugars themselves.

Clarifying Agents: Preliminary work using several chemical as well as physical clarifying agents such as: lead acetate, lime, alumina, calcium carbonate, magnesia, diatomaceous earth, has shown that lead acetate and lime were the two best defecants for the turbid carob juice. Although lead acetate removed more of the foreign constituents including the coloring matter, than lime, its use as a promising commercial defecant was soon given up because of its expense and more, because of its poisonous character and the difficulty involved in its complete seperation from the clarified juice.

Defecation with lime had early revealed

the following facts: when used in small quantities, the acids, gummy matter, albumen and suspended impurities were imperfectly precipitated and the sediment or much settled very slowly. With the use of larger quantities of lime the impurities were easily precipitated and settled quickly, but in that highly alkaline medium part of the sugars were precipitated with the impurities and part, especially the reducing sugars, were decomposed imparting to the clear juice a very undesirable dark color during evaporation in later operations.

So the experimental work that was done next, aimed at determining the amount of lime that was necessary to precipitate as much of the foreign materials as possible without attacking the sugars.

Experimental: Two 1:2 first extracts, having the following properties, were defecated with different quantities of dry powdered $Ca(OH)_2$.

	Extract I.	Extract II.
Density of the juice	1.081	1.0844
Equivalent Brix degree	19.6	20.4
Acidity	2	2

	Extract I.	Extract II.
Total sugar	17.8	18.51
Color	20 Y	20 Y
	4.5 R	4.5 R
	1.5 B	1.7 B

50cc. portions of Extract I were pipetted into each of five 100cc. volumetric flasks and treated with the quantities of lime indicated in the table below. 100cc. portions of Extract II were pipetted into each of six 100cc. volumetric flasks and treated also with the quantities of lime shown in the table below. All flasks were shaken with the $Ca(OH)_2$ and put in a warm water bath at a temperature between 45-55°C*, for one hour. The solutions were

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*According to Geerlings, the destructive action of lime on reducing sugars is greatly hastened and increased at high temperature and in an alkaline medium. Consequently, if defecation is carried out at temperatures higher than 55°C., the calcium salts of the reducing sugars undergo spontaneous decomposition changing the clear-juice on evaporation to a carbonaceous mass having a very acid reaction due to formic acid.
I had experience of this phenomenon in one of my preliminary experiments on defecation.

H.C. Prinsen Geerligs:- Cane Sugar and its Manufacture 153, 1909.

taken out of the bath, shaken vigorously, and cooled to room temperature. Then all the flasks were left to settle overnight. The next day the solutions were filtered from mucky substances, the much washed and then filtrates were made up to 250cc. 50cc of each of the diluted juices was taken and hydrolyzed for 5 minutes with 10cc of HCl, (sp.gr. 1.103) at 70°C for determining its total sugar. The solutions were immediately cooled, neutralized with 20% NaOH solution and made up to 100cc. Sugar was then determined by a modified Fehling's procedure* using methylene blue as an indicator. The results are shown in Table VII.

TABLE VII.

Extract I.			Extract II.		
Number of Flask	Weight of $Ca(OH)_2$ used in defecating 50cc. juice	Percentage of sugar in defecated juice.	Number of Flask	Weight of $Ca(OH)_2$ used in defecating 100cc juice	Percentage of sugar in defecated juice.
1	80 mg.	17.8	1	200mg	18.5
2	90 "	17.75	2	220mg	18.5
3	100 "	17.7	3	240mg	18.55
4	110 "	17.8	4	260mg	18.5
5	120 "	17.8	5	280mg	18.45
			6	400mg	18.5

*A. O. A. C. Methods of Analysis, 4th. ed. P. 477-478, 1935.

Observations and Discussions:

(1) The 80 mg. of $Ca(OH)_2$ that was used in flask (1) of Extract I, was a little more than the exact quantity of lime that is necessary to neutralize the acidity of the solution, the latter being 75 mg.

(2) During the filtration of the defecated juices, from the various stoppered flasks, a distinct change in color was observed. From a clear brown color the filtrates developed a dark bluish black color, especially on the surface of the solution. A similar phenomenon was also observed when the filtrates were shaken vigorously with air, however, here, the dark bluish color did not persist very long and with standing for sometime the solutions, nearly reassumed their previous brown color.

(3) The color of the defecated juices decreased gradually with increasing quantity of lime. Solution (1) of Extract I had the darkest color while solution (6) of Extract II had the lightest color. Moreover this last solution did not show change or darkening in its color, on exposure to air, during filtration as all the rest.

(4) Up to 0.4% of lime, the sugars were not yet

affected and the solutions showed the same percentage of sugar, after defecation, as in the original juices.

In view of the fact that: (1) Increasing the quantity of lime had hitherto been removing more of the coloring matter and given a juice of lighter color (2) Increasing the alkalinity of the medium had made it more unfavorable for a color change to take place on exposing the defecated juices to air, and (3) the Sugar content of the juice had not decreased so far; work was extended to see to which extent would increasing the percentage of lime continue to improve the color of the defecated juice without affecting the sugars.

Experimental: Fresh 1:2 first extract having the following properties was used for defecation:

Density of the juice	1.0818
Equivalent Brix degree	19.8
Acidity 1.8cc	
Total sugar.....	18.65
Color.....	20 Y
	4.4 R
	1.5 B

100cc portions were defecated with different quantities of dry $Ca(OH)_2$ between 45-55°C, for one hour. The solutions were then allowed to cool and settle overnight. Next morning all solutions were filtered, precipitates washed, alkalinity neutralized by 0.1N HCl, and the sugar was determined after hydrolysis as before. The results as well as the quantities of lime used are given in Table VIII.

TABLE VIII.

Number of flask.	Weight of $Ca(OH)_2$ used in defecating 100cc. juice.	Percentage of sugar found in the defecated juice.
1	400mg.	18.4
2	500mg.	18.36
3	600mg.	18.30
4	700mg.	18.25
5	800mg.	18.04
6	900mg.	17.83
7	1gr.	17.60
8	2gr.	16.65

Observations and Discussions:

(1) The defecated juice was clear in all the 8 cases.

(2) 4.5cc of 0.107 N HCl was necessary to neutralize the alkalinity of 50cc. of juice No.1.

(3) The color got darker, this time, with increasing quantity of lime. The difference between samples 1, and 8, is seen by a color determination of the juice after it had been filtered and made up to

250cc.

Color of No.1	5.5 Y.	1.5 R,	0.5 B.
Color of No.8	20 Y	3.3 R	0.5 B.

(4) Changing color on exposure to air was not seen even in the first sample.

(5) Sample No.1, with 0.4% lime had this time, a decrease of 0.25% sugar, while according to results obtained before (Table VII) no decrease in the sugar content of the defecated juice was noted with the same percentage of lime. Moreover, up to 0.7% $Ca(OH)_2$ the percentage of sugar decreased at the rate of 0.05% per 100 mg. of $Ca(OH)_2$. From 0.8% lime and on the sugar content steadily decreased at a rate between 2 to 4 times the previous one.

Further work was done for two purposes.

(1) Investigating more carefully the range lying between 0.3-0.7% lime with the idea of ascertaining where, within that range, sugar started decreasing, color started increasing and color change on exposure to air ceased to exist.

(2) To see if an increase of lime, within these limits, where the quantity of sugar decomposed is small, means greater removal of the undesirable, mucky, nonsugar substances.

Experimental: The extract that was used in the experiments outlined below had the following properties:

Density of the juice	1.0798
Equivalent Brix degree acidity	2cc.
Total sugar	18.04
Color	24 Y 4.3 R 0.6 B

100cc. portions of this juice were defecated with different quantities of lime between 45-55°C for 1 hour. The defecated juice was then tested for its color, density, alkalinity, percentage sugar. The muck was washed from any sugar, dried and weighed. The results are given in Table IX.

TABLE IX

Tests on the Defecated Juice

No. of Sample	Weight of $Ca(OH)_2$ added	Color.	Density 31°C	Alkalinity.	Percentage Sugar.	Weight of muck.
1	300	10.5Y,1.5R	1.0787	1.6cc	18.0	0.3520
2	350	10Y 1.4 R	1.0789	3	17.94	-
3	400	10Y 1.4 R	1.079	4.2	17.94	0.4140
4	500	12Y 2.2 R	1.079	6.2	17.94	0.4780
5	600	17Y 3.2 R	1.0794	7.9	17.85	0.5332

Discussion of Results:

1. Sugar: Regarding the percentage of sugar in the

defecated juice, the new results seemed to confirm the results given in Table VII, that is, the use even of 0.5% lime had no influence on the sugar content of the solution.

2. Impurities precipitated: The continuous increase of the weight of the muck up to 0.5% lime, indicated that more impurities were being thrown down without any sugar precipitating with them.

3. Color: The color of the defecated juice changed on exposure to air in samples 1 and 2, thus confirming what was previously observed. With samples 3,4 and 5 changes in color ceased but samples 4 and 5 were darker in color than 3.

We can safely say, now, that up to 0.4-0.5% lime the amount of sugar remained practically unchanged in the defecated solution. However, if considerations of color, alkalinity, and presence of calcium salts in the clarified solution would outweigh the extra amount of impurities precipitated then defecation with the smaller percentage of lime, i.e., would be preferable to any higher quantity. Decision on such question had to be postponed until after the significance of each of the above factors

had been studied in connection with the decolorization and concentration operations that came next.

At this point work was conducted on decolorizing and concentrating the defecated juice to a thick syrup of about 65° Brix density. Such a work brought out two important points:

First, the defecated juice being quite on the alkaline side in its reaction had to be neutralized before treated any further. This was necessary for four reasons: (1) The various kinds of decolorizing carbons were not effective in an alkaline medium. They worked a little better in neutral solutions and best in acidic ones. (2) Evaporating an alkaline juice under partial vacuum and even at temperatures lower than 70°C. showed excessive foaming which prevented smooth and successful evaporation. (3) The alkaline juice developed during concnetration colored decomposition products that made the color of the solution far worse than its original color before decolorization. (4) The presence of calcium salts in the final syrup gave it an undesirable bitter taste.

Thus being convinced of the necessity of neutralization several chemicals were used for accomplishing that. These chemicals with the various problems and difficulties that arose as a result of their use are as follows:

1. Acetic Acid: Kept calcium salts dissolved in the juice. Developed humus brown black color on evaporation.
2. Carbon Dioxide: Bubbled through the juice to neutrality to phenolphthalein did not throw any precipitate. On evaporation calcium carbonate as well as other calcium salts came down gradually and continuously during concentration until the solution became a thick syrup that could not be filtered.
3. Tartaric Acid: Eliminates most of the calcium as tartrates. On evaporation continuous deposition of insoluble incrustations was noted even when the syrup was about 65° Brix in density. The syrup retained a foreign unpleasant taste of tartrates and had a comparatively darker color.
4. Phosphoric Acid: Accurate adjustment of the reaction of solution was necessary to precipitate most of the calcium as phosphate. Incrustations were also observed here, but the final syrup was of a brighter and lighter color than that gotten with other neutralizing agents.

Second, neutralizing the juice was not enough for effective decolorization. Excess acid could not be added directly on the alkaline juice for the

various calcium salts, i.e. carbonate, tartrate or phosphate, become more or less soluble in an acidic medium. This required filtration of the calcium precipitates from the neutralized juice before the addition of the required quantity of acid for helping good decolorization. However, after the decolorization of the juice the extra acid had to be neutralized with lime before proceeding to concentration.

Having gone so far I started doubting the advantages and merits of defecation. The introduction of 0.4 - 0.5% lime into the juice, although no doubt, removed as impurities a fraction of a percent of the total dissolved solids, but also meant the introduction of so many additional operations which needed more or less expensive chemicals, new equipment, as well as technical experienced personnel to supervise and direct the work of the whole system.

With the idea of ascertaining whether defecation with lime justified, in the quality of syrup produced by its use, the introduction of so many operations that complicated very much the whole scheme, comparative experiments on clarification with lime and other clarifying agents, intended to give light on this point, were carried out next. The results seemed to be more in favor of disposing

with defecation. The experiments in detail will be given in the next chapter in connection with decolorization and concentration.

CHAPTER IV.

DECOLORIZATION AND CONCENTRATION.

Aim: By decolorization we sought the removal, from the clarified juice, of the greater part of its coloring material, plus a good deal of the non-sugar impurities that were still retained in the juice and that could be absorbed by the decolorizing chars. By concentration we seek to evaporate from the decolorized solution, under proper conditions, enough of the water to get a clear syrup of bright golden yellow color.

Factors studied: The factors that were more or less taken into consideration are:

A. In Decolorization:

1. Dilution of the juice and its influence on the case of decolorization.
2. Effect of the method of clarification and clarifying agents on decolorization.
3. Intensity of the color of the clarified juice.
4. Reaction or acidity of the clarified juice.
5. Temperature of decolorization.
6. Kind of decolorizing char used and its fineness.
7. Percentage of char needed for satisfactory decolorization.

B. In Concentration:

1. Temperature of evaporation
2. Color changes during concentration.
3. Quantity of syrup produced with respect to:
   (a) Its density, (b) color, (c) clarity, (d) taste, (e) liability to crystallize on standing (f) liability to darken on keeping.

It is worth mentioning, however, that

(1) these two operations (i.e. decolorization and concentration) had to be studied together for it was only by the proper adjustment of the factors affecting the first to those interfering with the second that efficient and economical conditions for the working of the whole system could be formulated.

(2) Isolation and seperate control of each of the various factors mentioned above was not attempted, except in few cases where industrial considerations or time available permitted it. The influence of a factor or several together was observed and carefully followed through all the various operations to the final syrup. Outlined description of the experiments performed will come next.

Experimental:

I. The following experiments were made on a dilute 2 hours, 1:5 extracts.

1. 800cc. of juice were defecated with 7cc. of milk of lime of 15°Bc density. Muck was allowed to settle for one hour and a half, solution filtered, carbon dioxide bubbled through to very slight alkalinity (10cc. juice took 0.1cc of 0.107 N HCl to discharge the color of phenolphthalein). The $CaCO_3$ precipitated was filtered and five 100cc portions of the clear filtrate were treated respectively, with 0,1,2,3, and 4cc. of 0.107 N HCl, and with 1 gr. of Nuchar each, for 20 min. at room temperature. The decolorized solutions were filtered and their color determined.

Result: All solutions were of the same Col N. The slight difference in the acidity of the five solutions was not enough to show any measurable difference in their color. So in order to avoid much dilution of the juice the influence of acidity on decolorization was studied next with a more concentrated solution of H_3PO_4. H_3PO_4 was chosen because after decolorization the acidity of the solution could be easily neutralized and phosphate removed by lime.

2. Another extract was defecated at 40°C with 15°Bi milk of lime until a sample of the filtrate gave no precipitate with a 20% testing solution of sucrate of lime. The solution was then filtered

from muck and tested for its color and alkalinity:

color of solution before defecation 5 Y, 1.4 R

color of solution after defecation 5 Y, 0.9 R

alkalinity of solution: 3cc. of 0.107 N HCl was required to neutralize 25cc. of juice to phenolphthalein and point.

500cc of the clear defecated juice were neutralized with 0.67 N H_3PO_4. The color of the neutral solution was measured and it came to be 2.4 Y, 0.4 R. 100cc portions of this solution was decolorized with 1% Nuchar at 17° C for 20 minutes and with different quantities of 0.67 N H_3PO_4. The results are given below:

TABLE X.

Percentage Nuchar	Time of decoloration.	Temperature of decolorat	cc.of 0.67N H_3PO_4 used.	Color of decolor. solution.
1%	20 min.	17°C	0	0.6 Y
"	" "	"	1	0.2 Y
"	" "	"	2	0.1 Y
"	" "	"	3	0

3. A new extract having a color of 4.6 Y and 1.3 R was divided into four portions:

The first portion was decolorized directly and without clarification with 1% Nuchar at 80°c and

for 15 minutes. The resulting solution was colorless.

The fourth portion was defecated at 40°C with milk of lime, muck filtered, solution neutralized with 0.67 N H_3PO_4 and precipitate formed filtered. The neutralized solution was then acidified (4cc H_3PO_4/100cc juice) and decolorized with 1% Nuchar at 80°C for 15 minutes. The solution was filtered, excess H_3PO_4 neutralized with lime, the $Ca_3(PO_4)_2$ formed filtered and resulting solution* evaporated on direct fire to a thick syrup. The color of the syrup was 20 Y, 12 R.

4. A new extract was brought to a boil with 1% filter acid, stirred for 10 minutes and then filtered.

500cc. of the clear filtrate was decolorized with 1% carbon at 80°C for 20 minutes. The solution was then filtered and after its color was determined, it was evaporated on direct fire to a thick syrup.

color of clear juice	5 Y, 1.5 R
color of decolorized juice	0.3 Y
color of Syrup	30 Y, 7.5 R

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* Its color was not determined because it meant nothing after the many dilutions that the solution had suffered.

1300cc of the same clear filtrate was acidified with H_3PO_4 as in (3) decolorized as usual and its color determined. The acid was then neutralized with lime, filtered, and solution concentrated to 750cc. Its color now was determined. Then it was further concentrated to 250cc and again its color determined. Here the concentrated solution was decolorized with 1% Nuchar and then concentrated to a syrup. The color changes that were noted during concentration are given below.

TABLE XI.

Volume of juice	Color before decolorization.	Color after decolorization.
1300	5 Y, 1.5 R	0.1 Y
750	1.2 Y, 0.3 R	---
250	12 Y, 2.4 R	3 Y, 0.6 R
Syrup	29 Y, 7 R	

II. The following experiments were made on 1:2 extracts of an average color of 22 Y, 4.8 R, 1.5 B, and of a sugar content fluctuating between 18 to 19%. A number of these experiments are analogous to those previously done and described under I, in connection with the more dilute extracts. So detailed description of the various common and usual

operations will be avoided this time as being unnecessary repetition.

1. Juice was defecated with 0.4% powdered lime, between 50-60°C. Alkalinity of solution was neutralized with I N HCl to the end point of Bromthymol blue (about pH 6). 100cc. samples were then treated with different quantities of 1 N HCl and decolorized with 2% carbon. The results are tabulated below:

TABLE XII.

Color of original solution after defecation 5 Y, 1.2 R.

Percentage carbon.	Time of decolorization.	Temperature of decolorization.	ccs. of 1N HCl added.	Color of decolorized solution.
2%	30 min.	70° - 80° C.	0	1 Y, 0.2 R
"	"	" "	1	0.5 Y, 0.1 R
"	"	" "	2	0.4 Y
"	"	" "	3	0.3 Y
"	"	" "	4	0.2 Y
"	"	" "	5	0.1 Y

Conclusion: At constant temperature, percentage char, and time, the greater is the acidity of the solution the better would its decolorization be.

2. Juice was defecated with 0.4% lime. Alkalinity of solution was neutralized with CO_2 to

phenolphthalein end point. Solution was then decolorized at room temperature with 2% Nuchar, filtered and clear filtrate was then concentrated on a water bath and in partial vacuum at 70°C, to half its original volume. Calcium carbonate precipitated during concentration was filtered, and clear solution treated with 0.5% Nuchar filtered and concentrated to a thick syrup.

Syrup produced:

Density: 65° Brix

Color: 24 Y, 3.2 R

Taste: Good

Crystallization on standing: No

Deposition or settlings on standing: slight

3. Juice defecated with 0.4% lime. Alkalinity neutralized with H_3PO_4. Neutralized solution decolorized with 2% Nuchar at room temperature, and for one hour. Then concentrated in partial vacuum to one-fourth the original volume. Precipitate thrown down during concentration was filtered and clear filtrate further concentrated to a syrup.

Syrup produced:

Density: 62° Brix

Color: 25 Y, 3.5 R

Taste: acceptable

Crystallization on standing: No

Settlings on standing: Much.

4. Juice defecated as before, alkalinity neutralized with tartaric acid, in soluble tartrates filtered and solution decolorized with 2% carbon. Decolorized solution was then concentrated, with several intermediate filtration, under partial vacuum to a syrup.

Syrup produced:

Density: 70 Brix

Color: 26 Y, 3.5 R

Taste: Bitter and unpleasant

Crystallization: Big and much

Settlings: much.

5. Juice was heated with 0.2% Super-cel to about 95°C for about 10 minutes. Then it was filtered and clear filtrate divided into four portions. Two were treated with Darco Grade S,51 at two different temperatures and the other two with Nuchar C P.F, R 2804. The results are given below:

TABLE XIII

Kind of Char.	Percentage char	Time of decolorization.	Temperature of decolorization.	Color.
DARCO	2%	15 min.	21°C	1.1 Y, 0.1 R
	"	"	80-90°C	1.2 Y, 0.3 R
NUCHAR	2%	15 min.	21°C	1 Y
	"	"	80-90°C	1 Y, 0.2 R

Conclusion: (1) Of the two kinds of decolorizing chars, which were available, Nuchar which was finer and more fluffy than Darco worked better. So it was used in all later experiments.

(2) Decolorization is preferable at room temperature than at temperature above 80°C.

6. Juice was treated with 0.2% Super-Cel, mechanically stirred for 30 min., and then filtered. The clear solution was decolorized with 2% carbon for 30 min. and at room temperature. Clear filtrate was then evaporated in partial vacuum between 45-50°C to a thick syrup.

Syrup Produced:

Density: 80 Brix

Color: 25 Y, 4 R

Taste: Good

Crystallization on standing: Yes

Settlings on standing: No

7. Juice clarified with super-cell, to clear solution 0.05% tartaric acid was added and then decolorized with 2% Nuchar at room temperature. Solution was concentrated in partial vacuum between 45°-50°C to a syrup:

Syrup Produced

Density: 65°Brix

Color: 20 Y, 2.5 R

Taste: Good

Crystallization on standing: No

Settlings on standing: No

8. Juice clarified with Super-cel, decolorized with 2% Nuchar, at room temperature and left over night. Decolorized solution was concentrated in partial vacuum at 70°C until reduced to its ⅓ its original volume. Then decolorized again with 1% carbon and concentrated further to a syrup.

Syrup Produced:

Density: 70° Brix

Color: 23 Y, 3 R

Taste: Good

Crystalization on standing: No

Settlings on standing: No

9. Juice clarified with Super-Cel, decolorized with 2% Nuchar and left over night. Solution concentrated in partial vacuum at 70°C to a syrup:

Syrup Produced:

Density: 70°Brix

Color: 20 Y, 2.4 R

Taste: Very good

Crystallization on standing: No

Settlings on standing: No.

10. Juice clarified with Super-Cel at 50°C, decolorized at room temperature with 2% Nuchar with mechanical stirring for one hour. (Color of decolorized solution = 1 Y).

(olor of decolorized solution = 1 Y). Solution concentrated to one-third its original volume then treated with 1% Nucha and left over night. Then concentrated further to a syrup:

Syrup produced:

Density: 70° Brix

Color: 10 Y, 1.3 R (very nice color)

Taste: Very good

Crystallization on standing: No

Settlings on standing: No.

Discussion of Results:

1. The concentrated juice presented no difficulty in removing enough of its color for preparing it to the concentration operation.
2. Defecation removed more coloring matter from the more concentrated and more colored juice (i.e. 1:2 extract), than from the dilute and light colored juice (i.e. 1:5 extract).
3. Decolorizing two solutions, one clarified by defecation and the other by Super-Cel, with the same percentage of carbon gave a product of lighter color with the former than with the latter. Leaving aside all complications that are associated with defecation*, what seemed a point in its favor now, was more than compensated for by the

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* See page 46.

intense deep red color developed in the defecated juice during concentration.

4. With the same percentage of carbon the greater is the amount of coloring matter absorbed by the char. However, the disadvantages involved in either keeping the acid after decolorization or in precipitating* it from the solution, made it preferable to minimize the amount of acid added or better to dispose of using it altogether. Acidity

5. As previously indicated, the effectiveness of a char is directly connected with its state of subdivision or fineness, that was shown by the difference, in the decolorizing power, between Nuchar and Darco.

6. Two decolorizations, at room temperature, one, with two percent carbon, applied at the beginning to the juice before concentration and the other, with one percent carbon, applied to the thin syrup, are preferable to a single decolorization, with the same total percentage carbon, applied either to the thin juice or to the thin syrup.

The second decolorization was not only effective in removing a good deal of the coloring matter developed during concentration but helped also in precipitating any foreign substances that were thrown down from the concentrated juice. Hence it contributed

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*See pages 44-46.

to the improvement of both the color and clarity of the final syrup.

7. Evaporation of carob juice on direct fire could not produce a light colored syrup even (1) if decolorizing measures were taken to start concentration with a colorless solution. (2) With several intermediate decolorizations effected on the thin syrup. Discoloration specially of concentrated juices, was too quick to be advantageously controlled by any number of decolorizations.

8. Under partial vacuum the juice could be concentrated to a thick syrup of 80° Brix or even more, without danger of appreciable decomposition or discoloration, if the temperature of evaporation is kept at 70° or below.

9. Crystallization of sugar from the syrup on standing is directly connected with the acidity of the juice used in making the syrup as well as with the concentration of sugar in the latter. If the desired syrup should have a Brix density below 70° Brix there is no need for the presence or addition of any acid, if on the other hand the syrup that is desired to prepare should be of a density above 70° Brix slight addition of some non-objectionable acid such as H_3PO_4 that will help to hydrolyse disaccharides during concentra-

tion will help to prevent the formation of crystals.

10. The very large number of syrup samples that were prepared by different methods under different conditions of extraction, clarification, decolorization and concentration, and that were of different color shades, clarity and thickness at the time of their preparation, showed one outstanding thing in common and that was a tendency to darken with time until they reach a dark red color which they all approached as a limit. This part was of utmost importance as it clearly meant, that after we had met and overcome all difficulties that confronted the simple preparation of a presentable syrup, and we had gotten a syrup of the desired qualities and color we see that it does not keep.

So attention was directed finally toward trying to see what kind of a phenomenon was responsible for this color change. This is taken in the next chapter.

C H A P T E R V.

THE DARKENING PROCESS.

Aim: (1) To ascertain the mechanism of the darkening process, i.e. whether it is a photochemical or oxidation phenomenon or both.

(2) To try to determine the type of compounds to which the substrate and catalyst belong.

I. **Mechanism:** Sane, non-parasitic, and freshly crushed pods were used in the following experiments:

A. 20cc. of a 1:2 extract was added to a series of 7 tubes, and each was preserved by few drops of an alcoholic solution of thymol.

1. Tube 1, was left aerobic and in light
2. Tube 2, " " " " " darkness
3. Tube 3, " " " + trace of Na_2S
4. Tube 4, " " " + 1 cc. fresh lemon juice.
5. Tube 5, " " closed + $Na_2S_2O_4$*
6. Tube 6, " " anaerobic by bubbling CO_2 and closing tightly and left in light.
7. Tube 7, was left anaerobic as in 6 but left in darkness.

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*buffered by some Na_2HPO_4.

Results:

1. Tube 1, the control, started deepening in color from the beginning and in one week got appreciably dark.
2. There was no difference between tubes 1 and 2 and between 6 and 7, showing clearly that light has no effect on the darkening phenomenon.
3. Tube 3, did not show any darkening for two weeks after which it slowly darkened.
4. Tube 6, showed even after two months very slight change in its color. Whereas tube 4, at the end of the same period was yet lighter in color.
5. Tube 5, remained unchanged even after four months.

Conclusion: These experiments prove conclusively that the darkening is an oxidation phenomenon. Among all the reducing agents used, lemon juice seemed to be quite effective and at the same time applicable to industrial operations. From this it appears that the best way to preserve the color of syrup obtained as prescribed previously is to add some concentrated lemon juice (lemon juice concentrated under reduced pressure), to the syrup and keep the whole thing in hermetically sealed bottles.

B. Two 1:2 extracts were prepared, in one case as usual and in the other case under anaerobic

conditions (by continuous bubbling of CO_2 during the extraction period). Both extracts were clarified by some Super-Cel and centrifuged in air free, closed bottles.

Result: Color of two extracts identical 16 Y, 2.2 R.

Conclusion: This goes to show that during maceration no measurable color change takes place and this precaution during extraction is thus seen to be unnecessary.

II. Substrate:

The nature of the substance or substances which undergo this change in color has not been determined, but by analogy to other such phenomena in the plant kingdom, one assumes that this substance belong to the tannoids. The following experiment seems to speak for such a hypothesis:

The ordinary 1:2 extract when treated with 0.4% lime and shaken very vigorously in air, darkens or rather blackens in color. On the other hand when the same extract is treated with excess of neutral lead acetate and the solution filtered, then treated with H_2S to precipitate excess lead, then H_2S is removed by aeriation and to the resulting solution lime is added as before and shaken no color change takes place.

III. Catalyst:

A. 1:2 extract was immersed in boiling water for 15 minutes, cooled and then treated with 0.4%

lime and shaken vigorously, a dark black color was produced. Addition of H_2S or $Na_2S_2O_4$ to the darkened solution brought it back to its original color.

B. A trace of KCN was added simultaneously with 0.4% lime to a 1:2 extract and solution shaken vigorously. No dark color was developed.

Conclusion: (1) Experiment A seems to show that the catalyst is not an enzyme in the usual sense. (2) Experiment B seems to indicate that the catalyst is a heavy metal which is bound by the cyanide.

A more thorough study of the nature of the substrate and catalyst found in carobs will be left for future research.

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BIBLIOGRAPHY

M. Balland - Analyses de Caroubes de differente promenance - Journal de Pharmacie et de Chimie. 19, 569, 1904.

C. F. Bardorf and J.A.B. Ball - The Elements of Sugar Refining. 1925.

G. Bianca. Il Carrubo Monagr. Storico. Agra. L'Agricultura italian. 7, 1881.

Bonzouc, Dela Motte et Riviera - Da Caroubier et de la caroube. Recueil de Medicine Veterinaire 1877-1878.

M.C. Charaux: Sur la Manne du Caroubier et le Sucre retire de cette Manne. Identite de ce sucre avec la Pinite ou Methyl-d-inosite. Bull. Soc. Chimie Biologique. 10, 597, 1922.

J. Condit. The Carob in California - Bull. Coll. Agr. Univ. Cal. 309, 431, 1919.

Alphonse de Condolle - The Origin of Cultivated plants.

Ed. Curot. Le Sucre dans l'alimentation des animaux 1905.

D. Fairchild - Exploring for plants, pp.99, 238-9, 1930.

T. R. Hodgon - The Composition of Locust Bean Seeds, Analyst, 46, 366, 1921.

M.E. Jaffa and F.W. Albro - Nutritive value of the Carob bean. Cal. Agr. Exp. Sta. 309, 441, 1919.

Klaproth - Du Sucre de Caroubier - Men - Acad. Royale, Berlin, 1904.

F. Kryz. The Seed Content and edible portion of the Carob fruit. Z. Nahr. Genussom, 39, 353, 1920.

W. Kroner and H. Kothe - Discoloration of Dextrose Solutions. J. Ind. Eng. Chem. 31, 248, 1939.

Muntz - Composition chimique des Caroubes.

M. Neuhauer - St. John's Bread as raw material for industrial alcohol - Ind. Eng. Chem. News Ed. 11, 140, 1933.

Y. Nikaido - Beet-Sugar Making and Its Chemical Contro. 1909

G. Oddo - Estrazione Industriale del Saccararosio Cristallizzato dalle Carrube Nota II. Annali di Chimica Applicata. 26, Fasc. 1, 1-10 1936.

G. Oddo, A. Algerino, and E. Ribon - Analizi delle Carrube ditutto il bacino del Mediterraneo e adiacenze. Controllo et modificazioni dei Procedionenti d'Analisi. Nota III, Sull'estrazione del Saccarosio cristallizzato delle Carrube - ibid. 26 Fasc. 1, 11-19, 1936.

G. Oddo, A. Algerino, and E. Ribon - Studio sulle Carrube di tutto il bacino del Mediterraneo e Adiacenze: descrizione dei Campioni. Nota IV Sull'estrazione del Saccarosio cristallizzato dalle Carrube. 26, Fasc. 2, 56-65, 1936.

G. Oddo, A. Algerino, and E. Ribon. Studio delle Carruba di tutto il bacino de Mediterraneo e adiacenze: Resultati ottenuti nell'anallisi chimica, Nota V Sull'estrazione del Saccarosio cristallizzato dalle Carrube - 26, Fasc. 2, 65-69, 1936.

G. Oddo - Fermentazione Alcoolica del Mosto e del Melasso di Carrube - Nota VI - ibid.: 26. Fasc. 2, 70-78, 1936.

G. Oddo, A. Algerino e Antonio - Identita dello Zuccharo cristallizzato estratto della carrube (Ceratonia Sil) et dalla algarroba de Peru (Prosopis horrida, incruis pallida ace) Col Saccarosio della Canna da Zucchero et della barbahietola. Nota VII - ibid: 26, FAsc. 3, 1936.

H.C. Prinsen Geerligs - Cane Sugar and Its Manufacture. 1909.

Reinch e Wigger's Handbuch der Pharmakognosie.

G. Rimuni - Manufacture of Alcohol from carobs and utilization of hyproducts - Atti congresso naz. Chim. pura Applicata, 2, 1926, 995.

A. Rogers. Industrial Chemistry a manual for the student and Manufacturer. vol. II, Sugar.

Rosenthaler. Ueber einen Bestandteil des Unreifen Joannisbrotes. Arch. Pharm. 1903.

Rossi. Extraction dell'Alcool dalle Carruba - Ann. Schol. Sup. Agric. Portieri - Napoli, 1881.

Rothea - Caroubier et Caroubes. Bull. de Sci. Pharmacol. 29, 369, 1922.

Rothea - Caroubier et Caroube. Bull. de Sci. Pharmacol. 29, 443, 1922.

Jose V. Sanchez - Chemical Investigation of Spanish Carob Beans. Anales. Soc. espan. fis. Quin. 32, 165, 1934.

W. W. Skinner. Methods of Analysis, A.O. Ac. IVth Ed., 1935.

J. Russell Smith - The Crops a Permanent Agriculture (1929) Chap. VI, The Carob, pp.45-61.

G. Tagliani - The Application of the Locust bean in the Textile Industry, and especially in Calico Printing - Society of Dyers and Colourists, 14, 344, 1929.

G. P. Walton - A chemical and structural study of Mesquite, Carob, and honey locust beans. U.S. Dept. Agr. Bull. 1194, 1, 1923.

F. W. Zerban and L. Sattler. Analysis of sugar Mixtures containing Dextrose, Levulose, Maltose, and Lactose. J.Ind. Eng.Chem. 30, 669, 1938.

G. Post. Flora of Syria and Lebanon - Carob.

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