TARTARIC ACID FROM TAMARINDS.

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I. INTRODUCTION.

Occurrence of Tartaric acid.

Tartaric acid occurs in the free state, or more often as acid potassium salt, and to a small extent as calcium salt, in association with oxalic, malic, citric and probably racemic acid in tamarinds, mulberries, sorrel, cucumbers and many other plants. It occurs in large quantity in the juice of the grape, which furnishes practically all that is found in commerce.

When the grape juice ferments the acid potassium salt is gradually deposited, partly as a crystalline crust on the sides of the vat, and partly with the 'lees' which consist of the yeast and the various suspended matters of the 'must' The crust is known as argol, and when recrystallised produces tartar, which by further recrystallisation is converted into 'cream of tartar' or commercial potassium hydrogen tartrate.*

The highest qualities of the tartar consist of nearly pure potassium hydrogen tartrate, thus the product from Messina contains 76 per cent of tartaric acid. As a rule a small amount of calcium tartrate is present and in some cases may be as much as 12 per cent. These high grade tartars are generally used for the production of 'cream of tartar' and the lees and lower grade tartars for the manufacture of tartaric acid.

The following figures give a general idea of the manner in which the composition of wine lees varies They are taken from a paper by Warrington in the J. Society of Arts for 1876, p. 370.

		Tartaric acid as			Total
		KHT.	CaT.		Tartaric acid.
Italian	33 samples	24·1	6·1	...	30·2 per cent
Greek	4 „	19·9	11·8	...	31·7 „
French	9 „	17·3	6·0	...	23·3 „
„	30 „	5·3	20·5	...	25·8 „
Yellow Spanish	59 „	8·7	18·2	...	26·9 „
Red Spanish	17 „	8·8	17·4	...	26·2 „

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* Thorpe's Dictionary of Applied Chemistry, Vol. V. 404.

The following mean values are given by Roux in his volume on "La Grande Industrie des Acides Organiques," 1912 :—

	Per cent of pot. hyd. tartrate.	Per cent of calcium tartrate.	Total per cent. calculated as tartaric acid.
French	23	3	20·2
„ (plastered)	10	20	20·0
Italian	28	5	25·4
Spanish	8	26	22·4

The lees derived from plastered wines, *i. e.* those in which baked gypsum has been trodden with the grapes as in Greece, Spain and the South of France, contain the bulk of the acid in the form of the neutral calcium salt. It will be noted that a 20 per cent content of tartaric acid is a low value for lees. The great bulk of the tartaric acid of commerce is manufactured from lees and not from high grade argols.

Outline of the European method of manufacture.

The powdered raw material, argol or lees, is mixed with water and hydrochloric acid and boiled. It is necessary in the case of some varieties of lees previously to heat the material with water in an autoclave under 4 — 5 atmospheres pressure for about 6 hours in order to facilitate the filtration of the material. The product from the autoclave is then treated with the requisite amount of hydrochloric acid, filtered, pressed and washed. The filtered liquor is nearly neutralised with milk of lime whereby the tartaric acid is precipitated as calcium tartrate. Excess of lime is avoided as otherwise ferric and aluminium hydroxides are precipitated with the calcium tartrate. The decomposition is completed by boiling with precipitated calcium carbonate, but the liquid should still be faintly acid.

The precipitate is washed several times with water. It is then mixed with water and decomposed with dilute sulphuric acid, a portion of the solution being tested at intervals with calcium chloride solution to ascertain when sufficient sulphuric acid has been added. The amount of sulphuric acid used is such that the final liquor contains 3 — 5 per cent of free sulphuric acid calculated on the tartaric acid present.

The precipitated calcium sulphate is washed in vacuum filters and the liquors evaporated in steam heated leaden pans, or in vacuum pans to crystallisation point, it is then run into a tub and continuously agitated by a mechanical stirrer to produce granular crystals, the mother liquor is reconcentrated, and a second and third crop of granules may be obtained. The final mother liquors are worked up for calcium tartrate.

The granules are redissolved, the solution heated with animal charcoal free from calcium salts, filtered, evaporated and crystallised in cylindrical leaden pans about 2 ft deep. The crystallisation is aided by sulphuric acid in which the acid is less soluble than in water.

Statistics.

The following figures for the year 1910 give an idea of the production of raw materials (argol and lees) in the three chief wine growing countries of Europe :—

France	...	12,000 tonnes.
Italy	...	20,000 ,,
Spain	...	10,000 ,,

France imports 3,000 tonnes and Italy exports 17,000 and Spain 8,000 tonnes and the U. S. A. import about 13,000 tonnes.

The chief manufacturing countries are the U. S. A., Germany and France.

Great Britain imports large quantities of both tartaric acid and cream of tartar, the quantities for 1910 are :—

Tartaric acid	2230 tons	...	value £ 203,365
Cream of tartar	4200 ,,	...	,, £ 307,000

and the bulk of both products is mainly used in the country as the exports for the same year were only 380 tons of tartaric acid and 100 tons of cream of tartar.

Uses.

The chief uses of tartaric acid are in the wine industry, in medicine and in the woollen dye house; also for calico-printing where it is a valuable mordant. It is also used as a substitute for citric acid in the manufacture of lemonade and mineral waters.

Tartaric acid in Tamarind.

The tamarind tree—*Tamarindus indica*—is very widely distributed in the Central Provinces and Southern India, and the fruits or pods are known to contain tartaric acid. The following analyses are to be met with in chemical literature:—

1. C. Muller (Pharm. Centralhalle 1882) gives the following figures for a sample of the pulp of E. Indian tamarinds:—

Total tartaric acid	10·9	per cent.
Citric acid	2·2	„
Water	27·0	„
Insoluble matter	16·2	„

2. D. Hooper (Agricultural Ledger 1907, No. 2. p. 13) gives the following composition of the fruits:—

Pulp 55·0, seeds 33·9, shell and fibre 11·1 per cent.

3. F. Adam (Z. Osterr. Apoth. V., 1905. *43,* 797 and 821. Abstr. in Chem. Central., 1905. ii, 1042) gives the following analysis of a 10 per cent. aqueous solution.

Total extract 6·25, invert sugar 3·85, total acid as tartaric acid 1·45, ash 0·35 per cent, and 90 per cent. of the total acids consist of tartaric acid, either as free acid or potassium hydrogen salt.

The same author examined the wine obtained from a mixture of tamarinds and sugar.

O. Remeaud (J. Pharm. Chim., 1906, (VI), *23,* 424; Abs. in Chem. Central., 1906, i, 1843) analysed two samples of commercial tamarind pulps and a sample of a pulp prepared from Indo-Chinese fruits collected at Saigon. The sample No. 1 was prepared by removing the outer shell and the nerves (24·35 per cent) the fibrous endocarp (7·76 per cent) and the seeds (37·07 per cent). The following numbers are given:—

	I.	II.	III.
Dry extract	62·83	73·04	73·04
Loss at 100	37·17	26·96	26·96
Ash	2·82	3·26	3·20
Total acidity as tartaric acid	11·73	15·34	15·89
Free tartaric acid	5·71	7·03	7·36
Pot. hyd. tartrate	6·05	7·34	6·58
Invert sugar	42·31	34·28	32·00
Sucrose	0·67	0·46	...
Pectin	0·35	...	1·38
$P_2 O_5$	0·25	0·38	0·28

These numbers refer to the pulp from the fruits, in other words the fruit after the removal of the seeds and husks. According to a statement in the Tropical Agriculturalist (Nov. 1905) the average annual yield per adult tree in British India is about 350 lbs. of pods which can yield about 200 lbs of prepared pulp.

The following table gives the imports of tartaric acid into India for the year 1914-1918.

Imports of Tartaric acid.

Year.	Quantity.	Value.
1914—15	37 tons.	£. 5,163.
1915—16	83 „	£. 16,804.
1916—17	93 „	£. 27,641.
1917—18	27 „	£. 8,521.

Assuming that 10 per cent. of pulp could be recovered as tartaric acid and that 90 tons is the usual quantity used in the country, 900 tons of pulp or nearly 1800 tons of pods would be required each year As 7 trees yield about one ton of pods, about 13,000 to 15,000 trees would yield the whole of the tartartic acid used in India.

Estimation of Tartaric Acid in Tamarind pulp.

The method adopted was that due to Goldenberg (Allen's Commercial Analysis Vol. I. p. 545).

1000 grams of pulp were boiled with water for 15—20 minutes when the whole mass was reduced to a slimy pulp, which was allowed to cool slightly and then strained through a cloth. The residual solid was again treated with water, boiled and strained and these operations repeated until the liquid was no longer acid. The mixed extracts were evaporated to about 450 c. c. and then made up to 500 c. c. in a graduated flask. The liquid was filtered through a dry filter paper and 250 c. c. of the filtrate heated with 10 c. c. of hydrochloric acid (20 per cent) and then boiled with 7 grams* of potassium carbonate for 20 minutes. After cooling the solution was made up to the original volume (250 c. c.) and then filtered through a dry filter paper, 150 c. c. of the filtrate was evaporated to about 15 c. c., 5 c. c of glacial acetic acid were added to the hot liquid and the whole stirred for 10 minutes when 10 c. c. of 95 per cent. alcohol were introduced. After standing for 10 minutes the alcohol was decanted through a filter paper, the residue washed twice by decantation and finally transferred to the paper and washed with alcohol until the washings were neutral to litmus.

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*Or sufficient to make the liquid neutral.

The crude potassium hydrogen tartrate so obtained was dissolved in hot water and titrated with 0·2 N sodium hydroxide solution using litmus paper as indicator. The sodium hydroxide had been previously standardised against pure potassium hydrogen tartrate.

Three samples analysed in the above manner gave the following results :—

	Wt. of tamarind used.	No. of extractions with boiling water.	Percentage of tartaric acid.
1.	100	4	14·9
2.	100	4	12·5
3.	100	4	13·8

II. PRELIMINARY EXPERIMENTS ON ISOLATION OF CALCIUM TARTRATE.

Four series of small scale experiments were made to ascertain the best method of treating the pulp in order to obtain an aqueous solution from which good quality calcium tartrate could be readily isolated.

The experiments were :—

1. Boiling with water in open vessels.
2. Boiling with water and hydrochloric acid in open vessels.
3. Heating with water in an autoclave at 135°.
4. Heating with water in an autoclave at 160°.

1. *Boiling with water.*

When the pulp is boiled with water for a few minutes a more or less gelatinous mass is produced, which it is impossible to filter. It is only with great difficulty that the mass can be pressed through cloth and there is a great tendency for the cloth to break. Even after two washings with water the mass has a slimy consistency.

2. *Boiling with water and hydrochloric acid.*

When a small quantity of the liquid obtained by boiling the pulp with water and straining through cloth is boiled with 10 to 15 per cent. of concentrated hydrochloric acid an appreciable quantity of a flocculent precipitate is formed. Smaller quantities of acid have no effect and it is extremely difficult to remove the flocculent precipitate by filtration.

If the tamarind pulp is boiled with a quantity of hydrochloric acid equivalent to the tartaric acid present, as ascertained by the previous analysis, the nature of the product is in no way different as far as pressing is concerned. The following results may be given, in which about four times the above mentioned quantity of hydrochloric acid was used :—

Table No. I.

No.	Weight of pulp in gms.	Water in gms.	Time of boiling in minutes.	No. of washings.	Concentrated hydrochloric acid in cc.	Weight of lime* in gms.	Weight of calcium tartrate obtained.
1	100	400	30	3	50	42	62 gms
2	100	300	30	3	30 + 20	46	60 ,,
3	100	300	30	4	30 + 20	48	49 ,,
4	100	300	30	3	50	...	45 ,,

samples 1 & 2 and 3 & 4 were taken from two different lumps from the same sack.

The hydrochloric acid was added in 1 and 4 after boiling and pressing, while in 2 and 3 30 c. c. were added before boiling and the other 20 c. c. were added to the washings while boiling.

All the washings were added to the main liquor and the whole neutralised with lime using litmus as indicator. The calcium tartrate was washed thrice by decantation, filtered, dried in a steam oven and weighed.

3. *Heating with water in an autoclave at 135°.*

The autoclave used was a small gun-metal one of about 6 litres capacity, provided with a steam inlet tube, a thermometer and safety valve. When steam heating alone was tried it was found that the water condensed so rapidly in the apparatus that it filled completely in a short time, hence external heating with a gas burner was used. In order to avoid the possibility of charring, a false bottom was introduced into the autoclave and the pulp was placed on this.

Three experiments were made at a temperature of 135—136° using 1250 grams of tamarind pulp and 2·5 litres of water. In one of the early experiments it was noticed that, when the material from the autoclave was pressed hot, a dark coloured

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*The lime used was afterwards shown to be impure and contained magnesia.

crystalline deposit was formed as the liquid cooled. This was recrystallised and examined and was found to be practically pure potassium hydrogen tartrate.

In these and subsequent experiments the autoclaved product was pressed and filtered hot and the liquid allowed to cool over night, the crystals of potassium hydrogen tartrate were then removed, the washings from the pressed pulp added to the mother liquor and the whole worked up for the preparation of calcicum tartrate.

The following process was adopted for the preparation of the calcium salt.

The acid liquid was heated to 90—100° and whilst mechanically stirred sufficient* milk of lime to neutralise the tartaric acid was added gradually. The stirring was continued for a further 15—20 minutes and the whole then allowed to cool and settle overnight. The calcium salt was thus obtained as a distinctly crystalline, granular precipitate, which did not cake when dried. It was washed several (4—5) times by decantation and then filtered and air dried.

TABLE II.

Weight of pulp 1250 grams. Water 2·5 litres. Temp. 135—136° Time one hour.

Exp. No.	Weight of KHT	Total liquid in litres	Tartaric acid* in liquid	Weight of Ca tartrate	Total tartaric acid calcd. from KHT + CaT.
5	32 grams	4·0	11·2 per cent	190 grams†	...
6a	29 „	4·6	12·3 „	223 „	12·2
6b	39 „	3·7	11·1 „	234 „	12·8

4. *Heating with water in an autoclave at 160°.*

The method was similar to that described for the experiments at 135° and Table III gives the result of four experiments.

TABLE III.

Experiment	Weight of pulp in grams	Time in hours	Weight of Calcium Tartrate dried at 100°
7	1000	2	170 grams.
8	1000	2	176 „
9	1000	1·75	172 „
10	2000	2	351 „

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*The tartaric acid was determined by analysis and after the neutralisation of the tartaric acid the liquid remained distinctly acid owing to the presence of other acids.

†Small amount of the liquor was lost.

In these experiments the liquid was removed by pressing the pulpy mass in cloth, and the solid cake was washed twice with hot water. The liquid so obtained filtered readily through paper and in this respect differed from the liquid obtained by simply boiling the pulp with water or hydrochloric acid.

The calcium salt was prepared by neutralising the *cold* solution with lime in the form of milk of lime. The addition of calcium chloride to the filtrate gave no further precipitate indicating the presence of no neutral potassium tartrate. This calcium salt was obtained in the form of a very fine powder which caked together when dry and which had a distinct gray colour.

The lime used in these experiments was subsequently found to contain appreciable amounts of magnesia, and when attempts were made to prepare tartaric acid from the calcium salt considerable difficulty in crystallising the tartaric acid was experienced and crystals of magnesium sulphate were also obtained.

In all the later experiments shell-lime was used.

Assuming that the calcium tartrate obtained in these experiments has a purity of 90 per cent. the yield of tartaric acid (in the form of calcium salt) is 9·3 per cent. of the weight of the tamarind pulp.

Table No. IV gives the result of a series of experiments made at 160° using about 1250 grams of pulp in each experiment.

TABLE IV.

Expt. No.	Weight of pulp in grams.	Time in hours.	Wt. of Pot. Hyd. Tartrate in grams.	Per cent of Tartaric acid in liquor.	Total acidity of liquor expressed as per cent of Tartaric acid.	Wt. of Calcium Tartrate in grams.	Total per cent of Tartaric acid obtd. i. e. KHT + CaT.
11.	1250	1·0	21 0	12·6	17·3	195	10·3
12.	1250	0·75	15·6	12·9	17·9	203	10·4
13.	1250	0·75	48·5	—	—	195	14·4
14.	1250.	1·0	39·0	11·2	—	212	12·2

Before carrying out larger scale experiments a series of analyses of liquors, obtained by simply boiling the pulp with water and also by auto-claving at 160°, were made in order to demonstrate that heating at 160°—170° for a comparatively short time did not destroy part of the tartaric acid present in the pulp and thus diminish the yield of acid which could be obtained.

TABLE V.

Sample of pulp.	Method.	Result of analysis. per cent. of Tartaric acid.
No. 1.	Boiling	12·4.*
„ 1.	Autoclaving	13·8.
„ 2.	Boiling	13 8.
„ 2.	Autoclaving	13·7.
„ 3.	Boiling	13·33.*
„ 3.	Autoclaving	15·33
„ 4.	Boiling	14·28.
„ 4.	Autoclaving	13·60.

As stated in the introduction in the manufacture of tartaric acid from lees the mass is sometimes autoclaved under 4—5 atmospheres pressure.

The cases of tamarind and lees are not however comparable as with lees all the tartaric acid present is in the form of salts, either the acid potassium or the normal calcium salt, but with tamarind pulp practically half the tartaric acid exists in the form of the free acid.

The experiments prove clearly that tartaric acid is not destroyed when the pulp is heated with water for two hours at 160°.

III. LARGE SCALE EXPERIMENTS ON THE PREPARATION OF CALCIUM TARTRATE.

The autoclave used for these experiments was a jacketted, cast-iron one of 60 litres capacity with an enamelled lining. The heating was accomplished by means of the steam jacket and of a steam inlet tube of copper leading into the middle of the mass of pulp and water. This was essential, as when the steam jacket alone was used, the interior of the mass was quite cool, even after 2–3 hours, owing to the low heat conducting power of the pulpy mass. In each experiment 40 lbs. of tamarind pulp were used and sufficient water to cover the pulp

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[*] These values are low owing to insufficient washing of the residue in order to remove all the potassium hydrogen tartrate.

(45 lbs). The mass was heated for 1 hour at 160—170° under a pressure of 55 to 60 lbs. The method of isolating the acid potassium and normal calcium salts was exactly the same as in the experiments described on p. 68.

After pressing in the screw press, the residual cake of fibre was removed, mixed with 2·2 lbs. of water in an enamelled iron jacketted pan and boiled for a few minutes, again pressed and the washing process repeated a 2nd and 3rd time. The 1st and 2nd washings were mixed with the main extract, after the potassium hydrogen tartrate had separated from the latter, and the whole worked up for calcium tartrate. The 3rd washing was used instead of water for extracting a fresh charge of pulp in the autoclave. The main liquor and the washings were all filtered hot by means of a small gun-metal filter press.

The results of a series of experiments at 160—170° are given in Table No. VI. The experiments were all made with the same tamarind pulp the total tartaric acid contents of which was found by analysis to be 15·3 per cent.

TABLE VI.

No. of Expt.	Weight of pulp in pounds.	Pressure in pounds.	Length of time of heating in hours.	Weight of pot. hyd. tartrate in pounds.	Weight of calcium tartrate in pounds.	Total Tartaric acid.
14	40	45—50	1·5	0·66	8·86	14·1 per cent.
15	85	55—60	1·0	2·28	15·25	12·5 ,,
16	80	55—60	1·0	2·19	14·0	12·3 ,,
17	80	55—60	1·0	2·14	14·5	12·6 ,,
18	40	55—60	1·0	1·27	8·0	14·1 ,,
19	30	55—60	1·0	1·14	6·0	14·5 ,,

Notes on the experiments :—

1. In experiments Nos. 15 to 17 the 80 lbs. of pulp were autoclaved in two separate lots, each washed separately and the liquors mixed and worked up in one lot for the preparation of the calcium tartrate.

2. In experiment No. 14 the temperature attained was only 140—145° and the calcium tartrate isolated was not of such good quality as in the other experiments.

3. The total percentage of tartaric acid in column 7 has been calculated on the basis of 100 per cent. purity of the isolated potassium hydrogen and calcium salts.

The products from experiments 15—19 were mixed and analysed with the following results:—

Potassium hydrogen tartrate	81·3	per cent.	purity.
Calcium tartrate	97·0	„	„

The potassium salt was distinctly crystalline and had a deep colour.

The calcium salt was granular and crystalline with a light fawn colour and showed no tendency to cake on drying.

4. In experiment No. 17 the evolution of gas was noticed. At the end of the given time the steam pressure in the jacket was not reduced and it was noticed that although the temperature remained constant the pressure in the autoclave rose to 150 lbs.

IV. REFINING OF THE POTASSIUM HYDROGEN TARTRATE.

An analysis of the crude crystalline product deposited as the clear liquid from the autoclave was allowed to cool showed a purity of 80 per cent.

123 grams of the crude product recrystallised from water gave 93 grams of yellow crystals and even after two further crystallisations the colour was not removed. Boiling the solution of the salt for some time with animal charcoal also failed to give colourless crystals, although the colour was appreciably improved.

A sample of 105 grams was boiled with water and the clear brown solution treated with 5 cc. of hydrochloric acid and 0·5 grams of potassium chlorate. The colour of the solution changed to yellow and on cooling 71 grams of crystals were obtained which were quite white when powdered; the mother liquid yielded another 5 grams of practically colourless crystals.

On a large scale 1650 grams of the crude tartar were crystallised from water, about 6 litres of water were used at a time and after the separation of the crystals the mother liquor was added to the residue and the operation repeated. 1200 grams of pale brown coloured crystals were obtained.

The recrystallised tartar was then boiled with two litres of water and 100 c. c. of concentrate hydrochloric acid and 12 grams of powdered potassium chlorate added. The clear liquid was decanted from undissolved tartar and allowed to cool when 210 grams of white crystals of pure potasium hydrogen tartrate were obtained. The residual tartar was treated alternately with 2 litres of boiling water and then with the mother liquor from a crystallisation and the process repeated until all the tartar had dissolved. In this way 1009 grams of pure colourless potassium hydrogen tartrate were obtained corresponding with a 61·2 per cent. yield on the weight of the original crude tartar.

V. PRODUCTION OF CRUDE TARTARIC ACID GRANULES FROM THE CALCIUM SALT.

The method adopted for the conversion of the calcium salt into free tartaric acid was as follows:—

A known quantity of commercial concentrated sulphuric acid was diluted with 4—5 times its volume of water in an enamelled jacketted pan, after mixing the temperature was raised to 75°C* and maintained at that temperature whilst the calcium tartrate was added in small quantities, the whole mass being kept well stirred by means of a bamboo pole. When nearly the theoretical quantity of calcium salt had been added the liquid was tested from time to time by taking 5 c. c. and mixing with 5 c. c. of a 20 per cent· calcium chloride solution, boiling and measuring the precipitate, if the quantity of precipitate was appreciable, more calcium tartrate was added and when the amount of settled precipitate was 0·25 the addition of the tartrate was stopped. In the last two experiments the addition of calcium salt was so adjusted that at the end the acidity due to the sulphuric acid was 2·5 to 3·5 per cent. of the total acidity. This was accomplished as follows:—Two standard solutions were prepared; the one of sodium hydroxide solution such that 1 c.c. of the solution was equivalent to 0·0797 grams of tartaric acid and the other of barium chloride containing 0·005 grams $BaCl_2$ per c.c. A sample was taken rapidly mixed with 50 c.c. of water and filtered. 10 c.c. of the filtrate was titrated with the standard sodium hydroxide solution and 25 c.c. with the barium chloride solution after the addition of hydrochloric acid; in the latter case the end point was taken when a drop of the barium chloride produced no further precipitate. If the number of c.c.s. required for the two titrations are respectively X and Y then the required amount of sulphuric acid is present when the ratio X/Y lies between the values 1 and 1·4.

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*If a temperature below 65° is used the decomposition is incomplete and if a temperature above 75° is reached charring occurs.

The stirring was continued for 30 minutes after the adjustment had been made and the hot mass was passed through a gun-metal filter press and the cake of precipitated calcium sulphate washed with boiling water. The washings were added to the main liquor until the sp. gr. of the washings fell below 4°B (=1·03).

The more dilute washings were used for working up with the next lot of calcium tartrate to be treated with sulphuric acid.

Table No. VII gives the results of several experiments.

TABLE VII.

Expt. No.	Weight in pounds of calcium tartrate taken.	Weight in pounds of sulphuric acid.	Weight of animal charcoal.	Weight of pot. ferrocyanide.	Weight of tartartic acid granules.	Yield of tartaric acid expressed per cent. of the theoretical.
20	1·76	0·75	8 grams	..	0·75 lbs	72·0
21	5·95	2·32	15 ,,	...	1·90 ,,	57·1
22	7·25	3·36	...	...	3·21 ,,	79·6
23	32·0	11·9	0·2 lb.	0·2 lb.	12·85 ,,	71·7
24	23·0	9·0	0·2 lb.	0·2 lb.	9·25 ,,	70·0

In experiment No. 22 no animal charcoal was used for decolorising the liquid and the resulting tartaric acid granules were not nearly so good a colour as in the other case. In experiment Nos. 23 and 24 potassium ferrocyanide was also used in order to remove iron present in the solution. The amounts of both animal charcoal and potassium ferrocyanide required to produce the best results were ascertained by taking small amounts (50 c.c.) of the tartaric acid solution and adding varying amounts (from 0·03 to 0·8 grams) of animal charcoal and 2 c.c. of 10 per cent solution of the ferrocyanide. In experiment No. 23 the liquid was filtered after the addition of the charcoal and again after the addition of the ferrocyanide in order to isolate the ferric ferrocyanide (Prussian blue) precipitate. In experiment No. 24, on the other hand, both reagents were added before the liquid was filtered. This was found more convenient as the filtration of the Prussian blue precipitate by itself was found to be very tedious* In No. 23 about 30 lbs of water were used for washing the cake

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*On the commercial scale the animal charcoal and potassium ferrocyanide would be added before the removal of the calcium sulphate, so that only one filter-pressing would be necessary.

of calcium sulphate. This cake weighed 41 lbs. when moist and after washing in the press was found to contain 1 per cent of tartaric acid. In No. 24 the cake contained about 1·5 per cent of tartaric acid.

The liquid which was water clear and of a very pale yellow colour was then evaporated until its sp. gr. was practically 1·24. In experiments Nos. 20 to 22 this was accomplished in glass vessels under reduced pressure, but in experiments Nos. 23 and 24 the small film evaporator described in this Journal Vol. 2, p. 209 was used, and the evaporation was carried out under a pressure of 100 mm. The inner tube was of lead* but the separator was of copper well tinned inside.

The concentrated liquid was then filtered to remove the calcium sulphate and again concentrated in the same apparatus under reduced pressure until the sp. gr. was 1·38-1·39†. It was then removed to a glass vessel and further concentrated under reduced pressure to the granulation point (sp. gr. 1·40). This point was readily ascertained by the appearance of granules in the evaporating liquor. The concentrated solution was then poured into a shallow vessel and left to crystallise over night. The granules were separated in a small porcelain centrifuge, washed with a little water and dried. The mother liquor and washings were again concentrated under reduced pressure to the granulation point and a second crop of granules obtained. The operations were again repeated until the mother liquor no longer gave crystals of tartaric acid.

Towards the end a certain amount of a slimy deposit was noticed, and as a rule not more than four crops of granules could be obtained. The granules isolated in experiments No. 23 and 24 were of quite good colour, and when analysed gave 99 per cent. purity.

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*After being used several times the evaporator did not work at all efficiently and on examination it was found that a fairly thick deposit of calcium sulphate had settled on the inner surface of the tube.

†Sp. grs. were all determind with hot liquors. The following numbers are of interest.

Baumé	Sp. gr. 15°/15°	Grams of Tartaric acid per litre.
4	1·03	18
14—15	1·11—1·12	130
17—19	1·13—1·15	190
25—30	1·21—1·26	
45—50	1·45—1·53	

The final mother liquors from these two experiments were united and then converted into calcium tartrate. The yield was 930 grams of good quality granular calcium salt.

VI. PREPARATION OF PURE TARTARIC ACID CRYSTALS.

For the purposes of recrystallisation 20 lbs. of good quality granules were dissolved in 12 lbs. of hot water and filtered whilst hot from the small amount of insoluble organic matter. 160 gr. of sulphuric acid was then added and the whole concentrated in a vacuum apparatus to granulation point (45-50° B) and then heated until quite clear and transferred to a hot earthenware crystallising vat. After 12 days the crystals were removed, centrifuged and washed. The mother liquor and washings were again concentrated under reduced pressure.

The first crop of crystals weighed 10·82 lbs. and consisted of about 45 per cent. of water clear prisms of the size of the commercial crystals. The remaining 55 per cent. were much smaller and had separated too quickly. The second crop of crystals weighed 3·08 pounds and was also of excellent quality but about 25 per cent. of the crystals were small.

The third crop of crystals weighed 1·1 lbs giving a total yield of 75 per cent. after recrystallisation.

This acid had a purity of 99·5 per cent. The crystals were quite white and when dissolved gave only a faint reaction for sulphuric acid.

VII. BY-PRODUCTS IN THE MANUFACTURE OF TARTARIC ACID.

The possibility of the manufacture of tartaric acid from tamarinds as a commercially sound undertaking would be considerably increased if any of the by-products could be utilised.

The by-products would be :—

1. Husks or shell. These could probably only be utilised for fuel.

2. Seeds.

In an article in the Journal of the Agri-Horticultural Society of India (1857, *9*, 1366) the statement is made that the seeds are rich in oil, but Hooper (Agricultural Ledger 1907, p. 16) has shown that the percentage of oil in the seed kernels is only 6·5, or 4·5 in the entire seed. No oil is obtained when the seeds are pressed.

On the other hand the seed kernals are rich in carbohydrates (63 per cent.) and albuminoids (18·1 per cent.) and are used in certain districts by the poorer classes as food and in others as cattle fodder.

The powdered seeds when boiled with water yield a glue or size which is used by wool weavers, saddlers and book binders.

It is extremely doubtful whether large quantities of seed could be disposed of for such purpose. It would probably be necessary to use them as fuel under boilers.

3. Sugar.

According to Remeaud the percentage of invert sugar in tamarind pulp is 34. The aqueous liquid left after the calcium salt has been removed should contain appreciable amounts of a reducing sugar. The percentage of reducing sugar in our samples varied from 20 to 25 per cent. and after autoclaving it was found that the amount was reduced to one half or one third.

Experiments were made by heating glucose with tartaric acid and water in an autoclave for 2 hours at 160°, when it was found that the amount of reducing sugar was diminished to an appreciable extent. Thus in one experiment, starting with 50 grams of glucose, 32 of tartaric and heating for 1 hour at 160° a black residue was obtained and only 28·4 grams of glucose could be detected in the solution. It is thus clear that although heating in an autoclave is necessary to facilitate the separation of the aqueous extract and the residue, it destroys appreciable amounts of the reducing sugars present and the fermentation of the mother liquors from the calcium tartrate precipitates would not be likely to pay.

4. The fibrous material left after removal of the tartaric acid with water.

Samples of the residue were dried and examined for ash and nitrogen. The ash varied from 3·03 to 3·39 per cent. and nitrogen from 1·71 to 2·07. The value of the material as a fertiliser is therefore extremely small and the only use to which it could be put would be as fuel under the boiler.

VIII. THE MANUFACTURE OF TARTARIC ACID FROM TAMARINDS AS A COMMERCIAL PROPOSITION.

Cost of Materials. The present prices in London for tartaric acid and potassium hydrogen tartrate are respectively 4·0 and 2·7 shillings per pound. The Calcutta price may be taken at the same value plus 10 per cent.

Tamarinds in Calcutta fetch about Rs. 5 per maund= Rs. 58—12—0 per 1,000 lbs.

The following figures gives a resume of the results based on the large scale experiments described in this paper.

1,000 lbs. of tamarind = 550 lbs. of pulp.

This pulp gives 15·0 lbs. of crude potassium hydrogen tartrate (p. 71) and from the crude product 9·2 lbs. of pure white potassium hydrogen tartrate can be obtained (p. 73) in addition 100 lbs. of calcium tartrate are produced (p. 71) and this salt yields 41·5 lbs. of tartaric acid granules (p. 74) and finally 31·1 lbs. of pure crystals (p. 76). In addition about 15 lbs. of calcium tartrate can be recovered from the mother liquors of the granules and crystals.

In producing these products the following chemicals are required :—

High grade lime free from magnesia at Rs. 60 per ton.

Sulphuric acid (80 %) at Rs. 8 per cwt.

Hydrochloric acid at ans. 6 per lb,

Animal charcoal at ans. 6 per lb.

Potassium ferrocynide at sh. 2/2 per pound London =Rs. 1—6—0 in Calcutta.

Potassium chlorate at ten pence per pound in London. =Rs. 1 in Calcutta.

The following table gives an idea of the relative values of the products formed and of the materials required in their production.

TABLE VIII.

Products obtained.	Rs.	A.	P.	*Materials required.*	Rs.	A.	P
9·2 lbs. Pot. hyd. tartrate	14	11	0	1000 lbs. Tamarinds	58	12	0
31·1 ,, Tartaric acid	72	13	0	25 ,, Lime	0	14	0
15·0 ,, *Calcium tartrate				48 ,, Sulphuric acid	3	7	0.
recovered say As. 10 per lb	9	6	0	†0.7 ,, Animal charcoal	0	4	0
				†0·3 ,, Pot. ferrocyanide	0	7	0
	96	14	0	1·5 ,, Hydrochloric acid	0	9	0
				0·15 ,, Pot. chlorate	0	2	6
					64	7	6

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*This would be used for producing more tartaric acid granules.

†These are the quantities which are used in the manufacture of tartaric acid from wine lees viz. 0·7 and 0·3 per cent. calculated on the weight of the moist calcium tartrate decomposed.

On the basis therefore that the manufacture is conducted in Calcutta, there would be a balance of roughly Rs. 30 per 1000 lbs of tamarinds treated. In a factory dealing with 130 tons of tamarinds per month the balance would be Rs. 8,736, which would have to cover all overhead charges including direction, scientific staff, labour, steam, power, depreciation and packing. An outside figure for these would be Rs. 3,500 leaving as profit Rs. 5,200 a month or Rs. 62,400 a year which on a capital of Rs. 2,00,000 would mean a profit of 31 per cent. or with a capital of Rs. 3,00,000, 20 per cent.

All these figures are based on the complete manufacture being located in or near Calcutta. It is clear that the price of tamarinds would be less at a centre, like Indore, where tamarinds are plentiful; on the other hand the cost of sulphuric acid at such a centre would be much higher probably as. 4 or 5 per pound. On further investigation of costs of materials in different localities it might be found to be more economical to produce the crude pot. hyd. tartrate and the calcium tartrate at a centre in the tamarind producing districts provided good lime is available, and to rail the dry salts to Calcutta for refining and conversion into tartaric acid. Although the weights of the salts would be relatively large when compared with the weight of the sulphuric acid viz. 115 to 48 the extra packing and higher freight for the sulphuric acid might more than compensate for this.

In Madras tamarinds fetch Rs 4 to 5 per 100 lbs. and the pulp Rs. 8 to 9 per 100 lbs. and in Indore the price of the whole fruit is sometimes as low as Rs. 1·5 to 2 per 100 lbs.

It should therefore pay to manufacture calcium tartrate from the fruit in Indore and rail the calcium salt to a centre where sulphuric acid is cheap and where efficient chemical supervision could be obtained for the conversion of the salt into tartaric acid.

IX. Summary.

The following is a brief summary of the conclusions drawn from the experiments described in the paper.

1. Tamarind pulp contains abont 12 to 14 per cwt. of tartaric acid, part of which is in the free state and part as potassium hydrogen salt.

2. The total imports into India are about 90 tons per annum and represent the produce of about 15,000 trees.

3. The acid can easily be recovered by the methods used in the production of tartaric acid from wine lees, provided the pulp is first heated for an hour with water at 160° in an autoclave. The whole of the acid cannot be recovered as pure tartaric acid, but about 6 per cent. on the weight of the pulp and in addition about 1·7 per cent. as pure pot. hyd. tartrate. A certain amount of the acid in the final mother liquors can be recovered as calcium tartrate, which can be worked up for tartaric acid.

4. Even with tamarinds at Rs. 5 per Bengal maund it would probably pay to manufacture the acid in Calcutta. A better plan would probably be to manufacture the calcium salt in Indore or in some other tamarind growing centre and rail the salt to Calcutta for conversion into the acid.

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