QUEBRACHITOL—A POSSIBLE BY-PRODUCT FROM LATEX.

BY

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During the past three years the Chemical Division of the Rubber Research Institute has devoted considerable attention to the non-rubber constituents of Hevea latex, and the possibility of employing these constituents as a new source of revenue for the plantation industry has arisen as a natural consequence of this work. A stage has now been reached when it is possible to report the progress that has been made in this direction with one of the non-rubber constituents, quebrachitol.

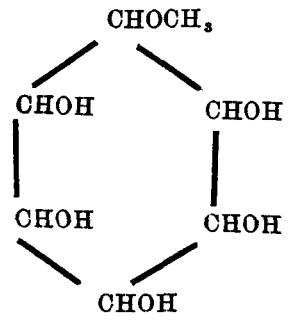
The separation of quebrachitol was an essential portion of our general examination of latex but the extension of this work to a scale considerably larger than that normally employed in the laboratory has had a dual object:—

(1) To obtain figures for the probable cost of production on a commercial scale.

(2) To prepare sufficient quantities of the pure material to enable potential consumers to explore the possibilities of the compound.

The presence of quebrachitol in latex has been reported by several observers and there is an extensive literature on the subject (see bibliography appended.)

Quebrachitol owes its name to its presence in the quebracho bark from which it was first isolated by Tanret in 1887(1). Chemically it is better described as *l*-methyl inositol and has the structure



Published figures for the melting-point vary from 186° to 191° but our experience shows that the pure compound melts fairly

sharply at 191°C. Tanret (loc.cit.) gives its optical rotation for the D line as —80° and its density at 0° as 1.54. The chemistry of the compound has not been by any means fully investigated and the only derivatives to which we have been able to discover any reference are:—

(1) Quebrachi-sulphuric acid and its salts (Tanret.loc.cit.).
(2) *l*-inositol, by hydrolysis of the methoxy group (Tanret. loc. cit.)
(3) penta-phosphoric derivatives (Bruni (2)) and
(4) quebrachityl penta-isovalerate, penta-laurate and penta-palmitate (Levi (3)). Perhaps its most striking property is its very high degree of solubility in water. We have determined the variations of solubility with temperature from 0° to 100°C. in order to effect better control of crystallisation. The results of these determinations are shewn in the graph (Figure 1).
(5) quebrachityl penta-acetate (Contardi, see Levi. loc. cit.)

A point of chemical interest which has emerged in this connection is that quebrachitol is appreciably more soluble than the corresponding unmethylated compound *l*-inositol. Thus at 12°C. the solubility of quebrachitol is about 39 per cent. by weight whereas that of *l*-inositol is only 30 per cent. by weight. This is contrary to the fairly general rule that methylation of a hydroxyl group reduces the solubility of a compound in water e.g. compare methyl alcohol with dimethyl ether and phenol with anisole.

Quebrachitol was first isolated from latex of *Hevea Brasiliensis* by de Jong in 1906 (4). Pickles and Whitfield (5) shewed that it was present both in latex and in rubber either as smoked sheet or Fine Hard Para. They give the total quebrachitol content of the latex as 0.5 per cent. de Vries, in his book " Estate Rubber " (6), reviews very briefly the literature on the subject and states that the amount present in the latex is practically constant at about 1.5 per cent. In another section, however, he states that the content may rise to 2.5 per cent. of the latex. Gorter (7) found 1.5 per cent. and Spoon (8) reports a variation throughout the year from 1.0 to 1.9 per cent. of the serum which is equivalent to approximately 1.5 to 2.5 per cent. of the latex. It will be seen that considerable difference of opinion exists and as many of the observers quote results without describing the method used a reasoned discussion of these divergences is impossible.

At present there is no really satisfactory method for the determination of quebrachitol and we advance the following reasons in support of this statement:—

(1) There is no method of precipitation available.

(2) The optical methods previously employed are invalidated by our lack of knowledge of other optically active compounds which may be present in latex.

(3) The great solubility of quebrachitol in water together with the presence of other soluble compounds such as sugars and potassium salts renders impossible its complete separation by crystallisation. The only figure which can be advanced with any confidence is the quantity of pure quebrachitol which can be prepared from a serum of known antecedents. In our experiments we have obtained a yield of 0.2 per cent. using dilute factory serum, which agrees with the figure of 0.5 per cent. found by Pickles and Whitfield for latex.

There is undoubtedly a small amount of quebrachitol remaining in the mother-liquors which are discarded but the recovery of this additional quantity is certainly impracticable and may be impossible.

In our earliest experiments we followed de Jong (loc. cit.) in obtaining quebrachitol by evaporation of the serum remaining after coagulation of latex with alcohol. The brown crystals thus obtained easily yielded pure quebrachitol when treated with decolourising charcoal in aqueous solution and then recrystallised. In later experiments we used normal serum from acid coagulation and found that the preparation of pure quebrachitol was again a simple operation although requiring rather more care than in the case of alcohol serum. The crystals obtained by cooling concentrated serum were initially separated by filtration and it was found impossible to effect complete removal of the somewhat viscous mother-liquor. Owing to this incomplete removal of the non-crystalline portion, two recrystallisations were necessary to obtain a fairly pure product. This was remedied by the use of a basket-type centrifuge for separation of the crystals from the liquid and the crude product thus obtained was light brown in colour and almost dry (water content 5 per cent.) and yielded almost pure quebrachitol after one recrystallisation only. By the kindness of the Socfin Company and the management of Bungsar Estate we were enabled to evaporate about 2000 gallons of serum and the experience thus gained permits us to put forward a tentative scheme for carrying out this manufacture on an industrial scale.

Raw Material. The raw material for the process is the residual serum from the normal coagulation of latex for sheet or crepe. The serum used in our experiments has been obtained from latex diluted to a content of 1.5 pounds of rubber per gallon, the original content of the field latex being approximately 4 pounds

per gallon. We have obtained a yield of pure quebrachitol equivalent to 0.2 per cent of the serum. In the literature, as previously indicated, are to be found figures which are considerably higher but all our calculations are based on our experimental observations and not on the published figures of other workers.

The quantity of this serum available is assumed to be 1000 gallons per day. A quantity of this order would be produced by an estate with a crop of 90,000 pounds of rubber per month.

Process.

(1) The serum is concentrated by evaporation to approximately one per cent. of its initial volume, the heat-coagulated proteins being removed by skimming.

(2) The concentrate is cooled to 0°C. and is maintained at this temperature until crystallisation is complete.

(3) The crystals are separated from the mother-liquor by means of a basket centrifuge, "whizzing" being continued until no further liquid is ejected.

(4) The resulting light brown crystals are dissolved in water (10 lbs. to 3 gallons) and boiled for 30 minutes with 10 per cent. of their weight of decolourising charcoal. The charcoal is filtered off and the operation repeated. The resulting decolourised solution is evaporated until crystals appear in the boiling solution and then allowed to cool and is maintained at 0°C. for not less than four hours at the end of which time crystallisation is complete. The crystals are separated by centrifuging and, when dried, have a melting-point of 187°—188°C. A further yield of very slightly inferior material is obtained by concentration and crystallisation of the mother-liquor.

(5) The liquid obtained from the centrifugal treatment of the original crude concentrate is evaporated further and allowed to crystallise. This crystallisation is very much slower than the original and it would be probably desirable to investigate the possibility of speeding up this separation by mechanical means. The crude material which is thus obtained is treated as under (3) and (4) above. The relation between the various intermediate products is clearly shown in the flow diagram Figure 2.

Costs.

Evaporation. The following data are assumed:—

Coal.	Cost at factory	$7 per ton.
	Calorific value	10,000 B. Th. Us. per ton.
Boiler.	Steam pressure	60 lbs. per sq. inch.
	Efficiency	60 per cent. (no superheater).

Evaporator. Triple effect with 90 per cent. efficiency.

Under these conditions the cost of removing 1000 gallons of water may be taken as $6 for steam alone. Since 1000 gallons of serum yields 20 pounds of pure quebrachitol this is equivalent to 30 cents per pound. From the flow sheet it will be seen that additional evaporation is required in other stages of the process e.g. during recrystallisation. The quantities of water to be evaporated in these operations, however, are very small and certainly do not amount to more than 2 per cent. of the main quantity of 1000 gallons. This figure of 30 cents is therefore taken as covering all the steam requirements of the process.

No absolutely accurate figures are available for the capital cost of the evaporation plant as this depends on the details of the construction and on the cost of transport to the site and of erection. From a study of various figures however it seems that £1,250 may be taken as a probable figure. Capital charges are calculated as 5 per cent per annum interest plus allowance for complete depreciation in ten years. The yearly output of the plant is calculated on the basis that it treats 1000 gallons a day for 47 weeks every year, allowing five weeks for repairs and annual overhaul. This is equivalent to 329,000 gallons of serum and a yield of 6580 pounds of quebrachitol per annum.

The minimum labour requirements of this plant would be three coolies per day, each working an eight hour shift at a minimum daily wage of 40 cents each. The annual labour cost would thus amount to $400.

From this section are omitted three items:—

(1) Water supply.

(2) Capital cost of steam boiler.

(3) Repairs.

The first depends on locality, the seconds depends on the existence or absence of a boiler for other purposes in the factory and the third could only be determined by experience. These figures are therefore omitted on the grounds that any figures advanced would be so tentative as to be useless. The costs under the heading of evaporation may therefore be summarised thus:—

	Per Annum.	Per pound of quebrachitol.
Steam		30 cents.
Capital Charges	$1,590	24 „
Labour	$400	6 „
Total ...		60 cents.

Refrigeration. Several different types of plant are available for this purpose and the cost of the various types might vary considerably. We have been informed on reliable authority that the operation could be satisfactorily performed in an apparatus consisting of an ammonia compression refrigeration machine with brine tanks and insulated vessels for containing the liquids to be cooled, at a capital cost of $1,800 and a daily consumption of two electrical units at four cents per unit. The labour involved in this process would be negligible and the costs may be summarised thus:—

		Per Annum.	Per pound of quebrachitol.
Capital Charges	...	$270	4.5 cents.
Current Consumption	...	$26	0.5 „
Total	...		5.0 cents.

Centrifuging. The costs under this heading comprise:—

(1) Capital charges on centrifuge.
(2) Power consumption.
(3) Labour.

The plant must be capable of treating each day about 140 pounds of crude concentrate and about 30 pounds of recrystallisation liquors. Owing to the necessity of absolute cleanliness when the pure product is being centrifuged it seems essential to instal a large machine for the crude and a small machine for the final product. These machines, complete with driving motors, would cost about £80 and £15 respectively and would require power of three-quarters and one-quarter horse power respectively. The labour charges may be taken as one coolie per day at 40 cents. Allowing 5 per cent. interest on capital, complete depreciation in 10 years and the same working time as previously we have:—

		Per Annum.	Per pound of quebrachitol.
Capital Charges	...	$120	1.5 cents.
Current Consumption	...	$98	1.5 „
Labour	...	$132	2.0 „
Total	...		5 cents.

Recrystallisation. The heat required for boiling and evaporating the recrystallisation liquors is extremely small compared with that required for the initial evaporation and is neglected. The cost

of centrifuging the final product has been allowed for under the appropriate heading and the items remaining to be considered are

(1) Capital charges on two stainless steel crystallising pans.

(2) Cost of decolourising charcoal.

(3) Labour charges.

Two pans of a suitable size constructed of " Staybrite " steel could be obtained for $700 and only half depreciation is allowed for in ten years.

The amount of decolourising charcoal required is 20 per cent of the weight of crude material treated, i.e. approximately 40 per cent of the weight of pure quebrachitol produced. For a yearly output of 6580 pounds, the consumption of charcoal will be 2630 pounds. The price of a suitable charcoal may be taken as £80 per ton, i.e. 30 cents per pound.

The labour requirements may be assessed at one coolie per day, i.e. at 40 cents per day.

	Per Annum.	Per pound of quebrachitol.
Capital charges ...	$70	1.0 cents.
Decolourising charcoal ...	$789	12.0 „
Labour ...	$132	2.0 „
Total ...		15.0 cents.

Details of Costs.

	Cents per pound.	Cents per pound.
Evaporating.		
Steam	30	
Labour	6	
Capital charges	24	
Total		60
Refrigerating.		
Current	0.5	
Capital charges	4.5	
Total		5

Centrifuging.

Current	...	1.5	
Labour	...	2	
Capital charges	...	1.5	
Total	...		5

Recrystallising.

Labour	..	2.0	
Decolourising charcoal	...	12.0	
Capital charges	...	1.0	
Total	...	15.0	15.0
Total	...		85

Summary of Costs.

	Cents per pound.
Steam ...	30
Current ...	2
Labour ...	10
Capital charges ...	31
Decolourising charcoal ...	12
Total ...	85

It should be pointed out that this figure for the cost of manufacture of quebrachitol is advanced here in a very tentative manner. It is intended merely to serve as a guide to the *order of cost* and *definitely not as an accurate estimate* upon which absolute reliance can be placed and to which a factory should be expected to work with precision. There is no evaporation plant of the correct type in operation in Malaya and estimates cannot therefore be based on observations made under working conditions. Factors which are at present incalculable have been necessarily disregarded. Thus no allowance has been made for repairs and maintenance and no figure can be advanced with any confidence. An estimate has been made for labour costs amounting to 10 cents per pound of quebrachitol produced. Charges under this head, particularly when dealing with native labour can only be determined with certainty as a result of actual practice on a works scale and it may well transpire that labour costs may amount to

20 or even 30 cents per pound thus bringing the total cost per pound of quebrachitol to 95 cents or 105 cents. Again one of the major items, evaporation cost, depends directly on the yield of pure product and an increase in yield by improvement in technique would be capable of effecting a not inconsiderable decrease in production cost. These figures have been based on the use of serum derived from the coagulation of latex of 1.5 pounds dry rubber content per gallon. From serum derived from latex of 2.0 pounds dry rubber content per gallon a higher yield of quebrachitol as a percentage of the serum could be obtained. Owing to the smaller quantity of serum produced in these circumstances and the retention of a higher percentage of the serum in the coagulum it is problematical whether the use of the more concentrated latex would yield as much quebrachitol as the more dilute, but the yield per 1000 gallons of serum treated would certainly be increased.

It was realised at an early stage of this work that evaporation would represent a very considerable proportion of the total cost of producing quebrachitol and attempts were made to isolate the compound by the precipitation of a solid derivative. Unfortunately all efforts in this direction were unsuccessful and evaporation appears to be the only possible method of separation.

The production of quebrachitol is obviously contingent on the creation of a market which will absorb the compound at an economic price and the material produced in our experiments has been devoted to this purpose. Small samples were taken to England when one of us (E.R.) proceeded on long leave and with the assistance of Mr. B. D. Porritt, Director of The Research Association of British Rubber Manufacturers, a number of chemical manufacturers were interested in the subject. During the last two months over ten pounds of the pure compound have been sent to Mr. Porritt by whom it has been distributed to various firms and at least three of these have shewn a very keen interest. We are unable, at present, to indicate for what particular lines of manufacture quebrachitol may find a use but the hope that there may be a market for it does not appear to us to be unreasonable. Two or three scientific workers of established position in the world of research have also expressed an interest in the chemical possibilities of the compound and have been supplied with small samples.

In conclusion it must be pointed out that we are not making a definite recommendation that plantations should engage in the manufacture of quebrachitol. The object of this paper is to report the effort that has been made to create a new

source of revenue from latex, which has so far given the following results:—

(1) It has been shown that quebrachitol can be prepared by a process of not unduly elaborate technique.

(2) Sufficient material has been produced to enable potential consumers to investigate its possibilities.

(3) Contact has been established with potential consumers and interested scientific workers.

(4) The laboratory results have been used as a basis for the calculation of the probable cost of manufacture on a commercial scale. The translation of costs from the laboratory scale to the full scale has been effected on paper only and it must be pointed out that further detailed calculations by professional designers of plant will be necessary before this translation is effected in fact.

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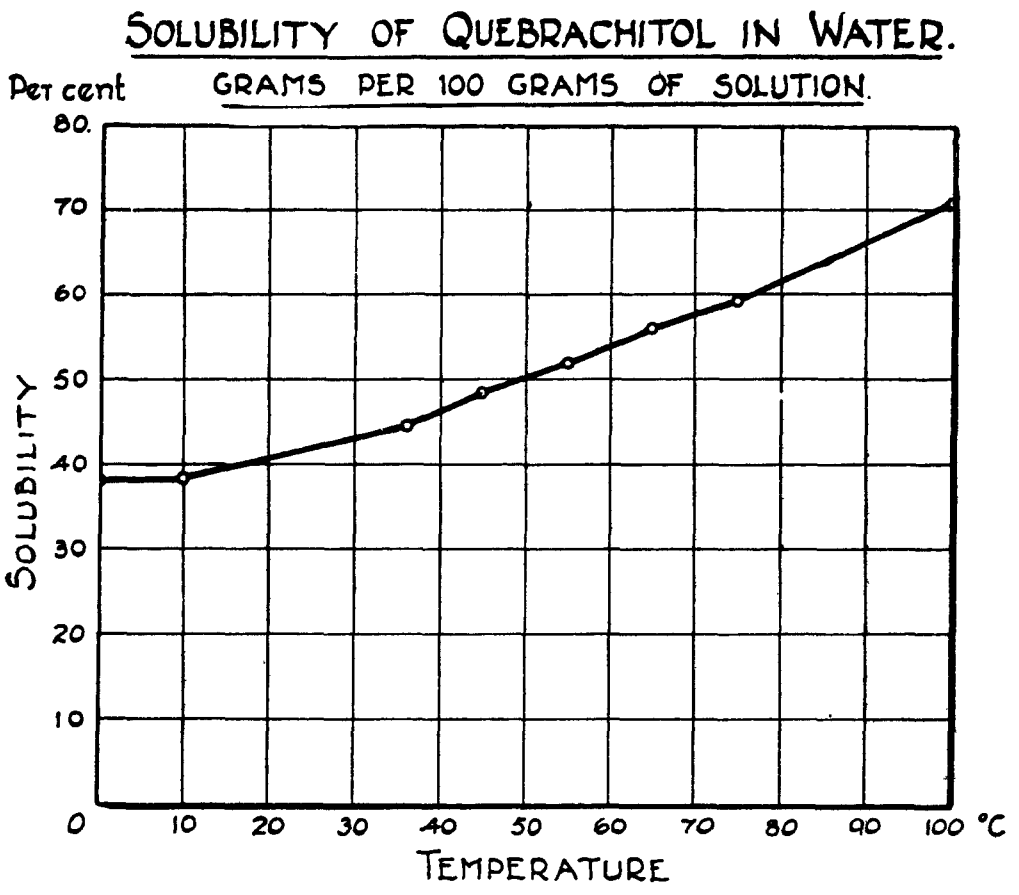
SOLUBILITY OF QUEBRACHITOL IN WATER.
Per cent
GRAMS PER 100 GRAMS OF SOLUTION.
SOLUBILITY
80.
70
60
50
40
30
20
10
0
10
20
30
40
50
60
70
80
90
100 °C
TEMPERATURE

FIG. 1.

FLOW DIAGRAM

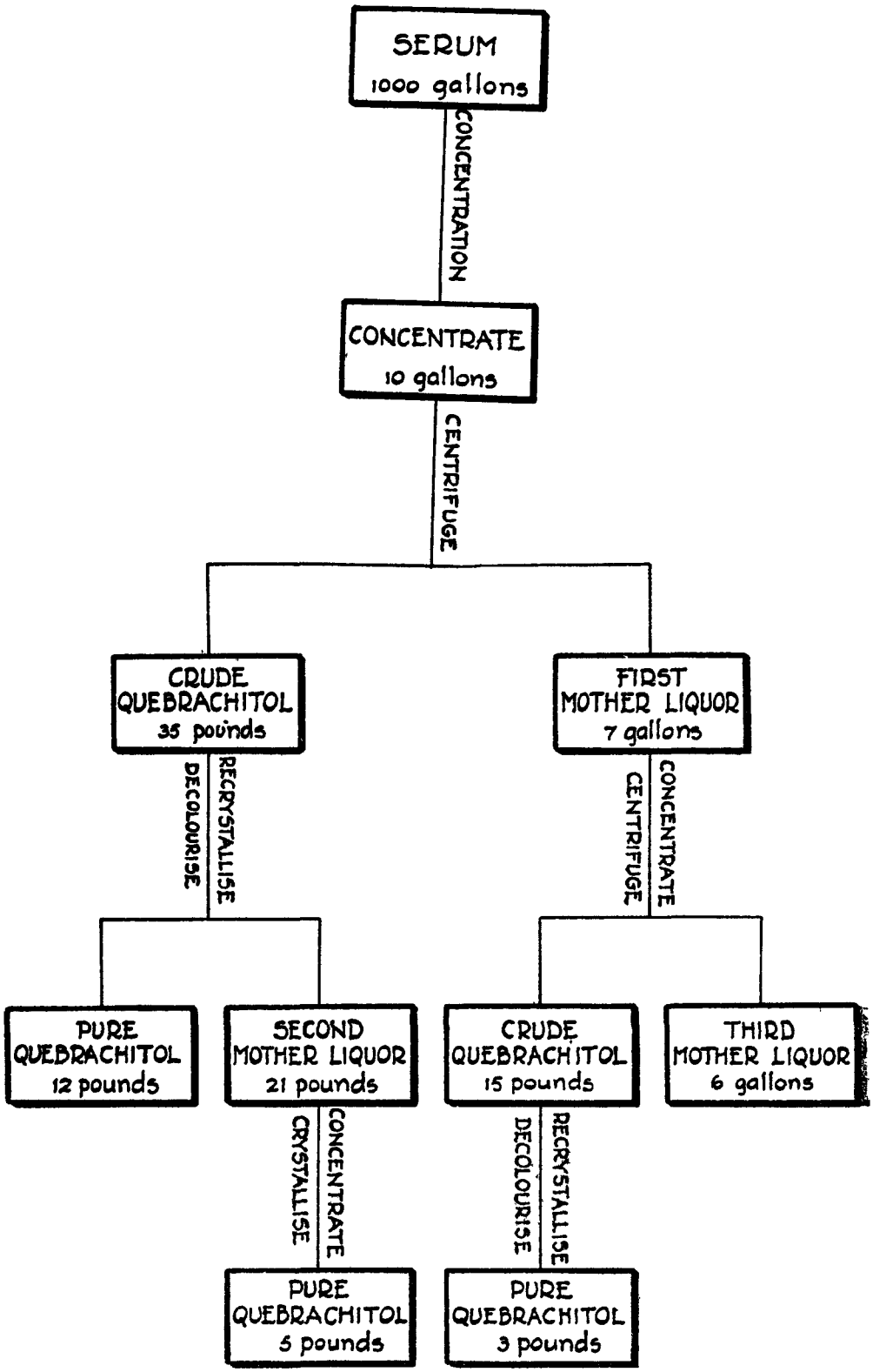

FIG. 2.