# MAPLE SUGAR SAND

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BY

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# PREFACE.

The Province of Quebec, almost monopolizing as it does the output of maple products of the Dominion, may be said to be the centre of the maple syrup and sugar industry, with a result that the annual value of the products from this source amounts to a large sum. As maple sugar sand, an inevitable by- product of this industry, deemed of no particular value, and consequently discarded, was considered to contain malic acid, it was thought worthy of some study. Thus the present investigations were commenced in the spring of 1911 upon the recommendation of Dr. J.F.Snell, the object being to acquire some idea of the constituents of the material, with special regard to the content and isolation of malic acid.

The thanks of the writer are due Dr. Snell, not only for his suggesting the subject, but also for his generous aid given throughout the year in the way of valuable advice, besides privileges granted in the laboratory.

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Macdonald College.
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# INTRODUCTION.

At the outset it seems almost necessary that some explanation of the term "sugar sand" be made, for although this material is encountered by all those engaged in the maple syrup or sugar industry, yet for those not so associated some introduction is perhaps advisable.

When the process of evaporation of the sap from the sugar maple has reached a certain stage there is deposited a sand-like, gritty substance which gradually coats the evaporating pan as the process continues. As a rule this deposition does not commence until the sap has been concentrated to a thin syrup, when the point of supersaturation of some of the mineral salts is reached. Thus further evaporation results in their precipitation. Part of the material is deposited upon the sides and bottom of the evaporating vessel while the remainder, being in a finer state of division, is held in suspension in the thickening syrup. This substance thus separating out of the syrup is our "sugar sand", although it commonly receives other names as "malate of lime", "silica", or "niter", the last appellation being the most generally used. In these pages both sugar sand and niter will be used, but in either case the significance will be the same.

In almost all cases attempts are made to remove the niter, either partially or wholly. A rather crude method which is sometimes employed consists in simply allowing the syrup to settle, when the supernatant liquid is poured off. By this means, however, only partial removal is effected, as a considerable part of the niter remains long in suspension. In order to remove this portion more thorough measures are advised. Accordingly, the syrup is strained through felt, or cloth bags composed of flannel or some such material, a much more satisfactory method, specially when the syrup is to be used for making sugar, as otherwise a gritty product would result, due to the presence of the suspended niter. By these methods is obtained what one may call crude sugar sand or niter.

PREVIOUS WORK ON SUGAR SAND.

Very little attention has been paid to maple sugar sand if one is to judge from the amount of available literature dealing with the subject. In treating matters pertaining to maple syrup or sugar, writers have contented themselves with a mere mention of the subject, ~~and with the subject~~, and with the exception of the work of W.H.Warren, published in July 1911, after the writer had well begun the present investigation, no very definite attempt to study the material is on record.

Of the few analyses of the substance which are obtainable there are two of the crude niter, one of these being found in the report of the Indiana Experiment Station for 1899, and the other appearing in Bulletin No. 134, by A.H. Bryan, of the Bureau of Chemistry, U.S.Department of Agriculture. Although these two analyses reveal considerable differences, this is not to be wondered at,considering the difficulty in obtaining the crude niter in anything like uniform condition, owing to great possibilities of differences in moisture and sugar content, due to different methods and degrees of straining.

However, these analyses of the crude material showed that sugar sand was composed to a large extent of malate of lime,the figures being 33.75% and 40.10% respectively. Upon this point all are now fairly agreed,although in the Vermont Station Report for 1872 it was stated that niter was principally calcium tartrate, and Sy in the Journal of the Franklin Institute for 1908 says that some believe it to be a mixture of calcium malate and calcium tartrate. The results obtained by Warren (Journ. American Chem. Soc.,1911,p. 1210) show that the principal constituents of sugar sand are lime and malic acid, for in the sample which he had taken for analysis a calcium malate content of 68.64 % was found,while the next most abundant constituent,namely silica,was present to the extent of 7.74%. The sugar sand experimented with in this case, however, was not the crude kind reported on above,but had undergone the preliminary treatment of washing, a process removing most of the sugar.

Other than these above mentioned no investigations of maple sugar sand were discovered.

## ANALYSIS OF SUGAR SAND

Samples of niter,as they are obtained in the sugar bush by different farmers, are far from being in anything like uniform condition. Some farmers take great care to filter the niter carefully and thoroughly,allowing as much as possible of the syrupy liquid to drain off. The resulting niter, when allowed to dry somewhat, results in a sort of sugary,sand-like substance,easily handled,although with a slight hygroscopic tendency Samples of niter,however, are obtained in a far more liquid condition,as in cases where the syrup is not filtered or strained completely,or where removal of niter from the thickening syrup is effected by simply decanting the supernatant liquid. Thus there is left together with the niter in the bottom of the container a considerable amount of liquid,which amount would vary greatly.

It will be readily seen, then, that samples of niter from different places could be widely variant with respect to their content of water or sugar, so that analyses of such crude material would be of very little practical value,and altogether useless as far as comparative results are concerned. Thus is easily recognized the absolute necessity of bringing the crude sugar into some standard condition in order that useful analyses, capable of being intelligently interpreted, may be made.

**Material of Investigation**

In the present investigation experiments were conducted upon six samples of sugar sand coming from different parts of the Province of Quebec. They are briefly described below, while in a few cases the nature of the soil was learned to some extent.

Sample No.I.-From Argenteuil Co., light brown in color. High land, shallow, gravelly soil with limestone bottom.

Sample No.II.-From South Shefford Co., also light brown in color. High gravelly land.

Sample No. III.-From South Shefford Co., slightly darker in color. Land high, slate and loam.

Sample No. IV.-From South Shefford Co., dark brown in color, containing much syrup.

Sample No. V.- A mixture of niter from different parts of Shefford Co.; light in color.

Sample No.VI.-From Brome Co., very dark containing considerable syrup.

Although four of these samples have Shefford County as their source, yet they came from different farmers living some distance apart. The niters were all of a brownish color, some samples as Nos.IV and VI being noticeably darker than Nos II or V, due to the larger amounts of syrup contained. This was specially the case with No.VI which was in a more or less fluid condition, while the others, though tasting appreciably sweet, were comparatively dry, with a tendency to become hygroscopic, forming a slightly pasty mass.

Washing the Niter.

In order that they might be brought into some standard condition for analysis, these various samples of sugar sand were all washed with hot water until the taste of sugar had disappeared. This was effected by mixing the niter well in hot water, and then filtering through a Buchner funnel, the process being repeated. It was found that usually four such washings were sufficient to remove the sweet taste, although in the case of No.VI, which contained more syrup, the washings had to be repeated oftener. This may seem a very crude, inaccurate method, but it was found that the niter by this means was brought into a fairly uniform state.

By this process the sugar sand was found to lose about half in weight, as the results of a few measured washings of two varieties indicate:

| Sample | Wt. Before Washing | Wt. After | % Loss |
|---|---|---|---|
| No.I | 600 gms. | 270 gms. | 55 |
| " | 300 " | 147 " | 51 |
| " | 300 " | 147 " | 51 |
| " | 300 " | 146 " | 51.3 |
| | 1500 " | 710 " | 52.7 |
| No.V | 200 " | 101 " | 49.5 |
| " | 300 " | 142 " | 52.6 |
| " | 300 " | 143 " | 52.3 |
| " | 400 " | 188 " | 53 |
| | 1200 " | 574 " | 52.1 |

The washings obtained by this treatment of the niter were a dark-brown liquid containing principally sugars in solution. Lime, also, proved to be present, for the filtrate from the washing never failed to give a test for calcium. Such a solution, at first normally neutral, when left standing some time becomes distinctly acid, due to acetic acid fermentation which is readily set up, involving the liberal production of carbon dioxide.

The samples of niter used for analysis, after being washed, were dried in a moderately warm air-oven, then finely ground up and bottled. The material thus obtained was a fine, almost white, dry powder, without the hygroscopic tendency of the crude niter, and when examined under the microscope it appeared to be to a large extent crystalline. The average specific gravity was 1.80, the separate figures being as below.

| Sample | Specific Gravity. |
|---|---|
| No.I. | 1.81 |
| II. | 1.80 |
| III. | 1.83 |
| IV. | 1.79 |
| V. | 1.78 |
| VI. | 1.76 |

The sugar sand was then ready for analysis, and the following quantitative determinations were made on each sample.

1. Moisture.

2. Ash Determination, including the Analysis of Ash,

to determine the inorganic constituents of the niter.

3. Determination of Malic Acid.

Complete analyses of the niter were not made, As the principal constituent of interest is calcium malate, more attention was paid to the mineral analysis and to the determination of malic acid. Analyses in all cases were carried out in duplicate, the mean results being given.

Moisture.

As, during the preparation for analysis, the material was dried quite thoroughly before being bottled, it was found to contain but a small percentage of moisture. This was determined by heating to constant weight at 100 about 10 grams of niter.

| Sample | Moisture % |
|---|---|
| I | 0.21 |
| II | 0.69 |
| III | 0.69 |
| IV | 0.57 |
| V | 0.17 |
| VI | 0.11 |

Determination of Ash.

The residues of the moisture determination were heated in platinum dishes over Argand burners. As gentle a heat as possible was used until the organic matter was burnt off, leaving carbon only as carbonate. After being weighed from desiccators the samples were allowed to stand exposed to the air of the room for several days, and were again weighed in order that the increase in weight due to air-drying might be noticed.

| Sample | % Dry Ash | % Air-dry Ash | % Gain |
|---|---|---|---|
| I | 53.51 | 55.37 | 1.76 |
| II | 58.07 | 60.24 | 2.17 |
| III | 57.92 | 59.02 | 1.10 |
| IV | 58.18 | 60.15 | 1.97 |
| V | 57.00 | 58.67 | 1.67 |
| VI | 54.71 | 56.32 | 1.61 |
| average | 56.57 | 58.29 | 1.72 |

Analysis of Air-dry Ash.

In this analysis an examination of the inorganic constituents of the niter was made. The ordinary methods of procedure were followed, and were derived mainly from Bulletin 107 of the Bureau of Chemistry, U.S.Dep't. of Agriculture. As this ash contained carbonates, determinations of carbon dioxide were also included. The mean results of the analyses are shown below, the first table giving the components calculated as percentage of the air-dry ash.

| | No.I | No.II | No.III | No.IV | No.V | No.VI |
|---|---|---|---|---|---|---|
| carbon dioxide | 36.14 | 25.27 | 30.94 | 29.81 | 34.07 | 30.68 |
| carbon | | 2.09 | 2.49 | 2.40 | 2.29 | 2.23 |
| sand-silica | 11.14 | 30.81 | 22.24 | 24.98 | 18.15 | 24.54 |
| Mn O | 3.38 | 2.30 | 3.06 | 2.71 | 2.55 | |
| Ca O | 46.49 | 37.57 | 41.12 | 40.00 | 43.17 | 40.95 |
| Mg O | | | 0.47 | 1.40 | 0.76 | 1.56 |
| $P_2O_5$ | | 1.64 | 1.19 | 1.37 | 0.57 | 0.52 |
| iron | tr. | tr. | tr. | tr. | tr. | tr. |

When these figures are translated, and reckoned as percentage of niter we obtain the following:

| | No.I | No.II | No.III | No.IV | No.V | No.VI |
|---|---|---|---|---|---|---|
| $CO_2$ | 20.01 | 15.22 | 18.26 | 17.93 | 19.98 | 17.28 |
| Carbon | | 1.26 | 1.47 | 1.44 | 1.34 | 1.25 |
| Sand-silica | 6.16 | 18.55 | 13.74 | 15.03 | 10.65 | 13.82 |
| MnO | 1.87 | 1.38 | 1.80 | 1.63 | 1.49 | |
| CaO | 25.74 | 22.63 | 24.27 | 24.07 | 25.33 | 23.06 |
| MgO | | | 0.27 | 0.84 | 0.45 | 0.88 |
| $P_2O_5$ | | 0.99 | 0.70 | 0.82 | 0.33 | 0.29 |
| % Calcium in Niter | 17.76 | 15.62 | 16.75 | 16.61 | 17.44 | 15.91 |

A glance through these figures shows that,as far as the inorganic constituents are concerned, lime is the most important. There is considerable variation in the amount of sand and silica present, the mean value being 13.01 % of the niter. The percentage of Calcium gives a mean value of 16.7%,varying from 15.62% in NoII to 17.76% in No. I. Very little information regarding the nature of the soils is available,so it is difficult to say how the kind of soil influences the constituents of the sugar sand. As previously noted, however, the soil of Sample No.I was shallow with a limestone bottom, which fact may perhaps have something to do with the higher Calcium content found in that case.

Metals other than Calcium are seen to be present in very small amounts,so that it is safe to say that any organic acid such as malic acid, comprising a large part of the niter, would be present principally in combination with lime.

Later we shall have occasion to refer to some of these figures, specially to those relating to Calcium.

Malic Acid Content

As the value of the sugar sand depends entirely on the content of malic acid, the only organic acid present in any appreciable quantity, it is necessary to have an idea of the amount of that acid in the material.

The best results of the determinations of the malic acid value were obtained by a method based upon the same principle as that mentioned by Warren. Several other methods were tested,but failed to yield results agreeing as closely as that which is given below.

About 1 gram of niter is heated with 25 cc. of normal oxalic acid in a beaker over a water-bath for an hour and a half. The material is then filtered and washed, and the filtrate made up to 250 cc. Of this two 50cc. portions are taken. In one the total acidity is determined by titrating with tenth normal alkali. This gives the acidity, not only of the organic acid liberated by treatment with oxalic acid,but also that due to the excess of oxalic acid used.

It is then necessary to determine the excess of oxalic. This is done by neutralizing the other 50 cc. portion with ammonia,acidifying with acetic acid and precipitating the oxalic acid by calcium chloride. The precipitate of calcium oxalate is dissolved in sulphuric acid,and the oxalic determined by standard permanganate. When the acidity of the excess of oxalic is deducted from the total, that due to the organic acid is found

The results obtained with the six samples of nitre were as follows:

| | No.I | No II | No.III | No.IV | No.V | No.VI |
|---|---|---|---|---|---|---|
| Malic Acid | 62.08 | 53.70 | 54.45 | 51.19 | 58.60 | 51.84 |
| Reckoned as Malate, $C_4H_4O_5$ | 61.17 | 52.90 | 53.64 | 50.44 | 57.73 | 51.06 |

In the case of the two samples of crude nitre mentioned by Bryan in Bulletin 134, the malic acid contents are given as 20.86% and 27.97% respectively. These figures, compared with those above, may seem low, but it should be borne in mind that the niter analysed was in the crude condition, while the samples of the present work had been previously washed, losing in that operation about 50% in weight, due principally to solution of sugars, so that for comparison these results should be doubled. Warren, working on one sample from Vermont, obtained a value of 52.26%.

We may compare the results of the determination of percentage of Ca with the above figures, and estimate the amount of calcium malate in the niter:

(a) Calculated from the percentage of calcium, assuming the calcium to be all present as calcium malate;

(b) Calculated from the percentage of malic acid, assuming the malic acid to be all present as calcium malate.

The following figures are then obtained:

| | No.I | No.II | No.III | NO.IV | No.V | No.VI |
|---|---|---|---|---|---|---|
| % Calcium | 17.76 | 15.62 | 16.75 | 16.61 | 17.44 | 15.91 |
| Ratio $\frac{\text{malate}}{\text{Calcium}}$ | 3.44 | 3.38 | 3.20 | 3.04 | 3.31 | 3.21 |
| Calcium malate | | | | | | |
| (a) from Ca | 76.22 | 67.03 | 71.88 | 71.28 | 74.83 | 68.28 |
| (b) " malic acid | 79.67 | 68.91 | 69.87 | 65.73 | 75.25 | 66.56 |

We see that the ratio of malate to calcium is in all cases fairly constant, the average figure being 3.26. In pure calcium malate the theoretical ratio of malate to calcium is 3.29. When we compare the two sets of figures for the estimation of calcium malate in the nitre we see that they are in fairly good agreements for differences are certainly to be expected, as it is quite possible that neither the whole of the calcium is combined as malate, nor is all the malic acid in that form. There is the possibility of other salts of calcium being present, and of having other bases besides calcium combined with malic acid, and present to a very small extent However, these figures would lead one to believe that calcium and malic acid are the main constituents of maple sugar sand, and that the calcium and malic acid are almost wholly in the form of calcium malate.

ISOLATION OF MALIC ACID

We come now to what is perhaps the most important part of the consideration of maple sugar sand, namely the isolation of malic acid; for any commercial value which the nitre may possess will depend largely upon the ease with which this process may be performed.

There were two main methods in preparing malic acid, but as one proved to be much superior from every aspect, far more attention was devoted to it, in the trying of various modifications in order to obtain the maximum yield.

Lead Acetate Method

The first less important method is somewhat similar to that mentioned by some writers for the isolation of malic acid from mountain-ash berries, and involves treatment of the niter with excess of acid, generally nitric or hydrochloric. The niter is warmed with the acid diluted with several times its volume of water, and when well mixed ~~was~~ is finally filtered. To separate the malic acid from the excess of mineral acid used to liberate it, lead acetate is added to the filtrate when lead malate is precipitated. This salt, a white precipitate, fuses in the warm liquid to a gummy mass, but becomes crystaline and brittle on cooling. It is then well divided, and suspended in warm water, when hydrogen sulphide is passed into the liquid. The lead sulphide is then filtered and the filtrate after evaporation concentrates to a slightly yellowish syrupy mass. This does not crystalize in the open, but when left in a desiccator several days acid crystals are obtained.

This method seems a tedious one, involving too many operations permitting of considerable loss. For instance, the decomposition of the solid lead malate by means of hydrogen sulphide is very difficult to perform thoroughly, as it is hard to reduce the malate to a fine enough state of division to enable the gas to act upon it all. Small particles become coated with lead sulphide on the outside, which prevents the gas from acting upon the rest of the particles.

As for the acid itself derived from this treatment, it is liable to contain various impurities, due to incomplete removal of some of the reagents used. Thus the acid crystals may be contaminated with lead, due to incomplete action of the hydrogen sulphide, some of the lead malate passing into solution and remaining with the acid. That the acid obtained is impure in some way might be inferred from the melting point which in two cases was specially low, being at 90 degrees; while others, though being higher, were yet below 100°, the melting point of the pure acid.

Bimalate Method

This more important, and more practicable method of obtaining malic acid from niter involves first the isolation of the acid calcium salt,

$Ca(C_4H_5O_5)_2 \cdot 6H_2O$. This is obtained by treating the niter with half the acid required to liberate the free malic acid. Assuming the malic acid to exist in the form of neutral calcium malate in the niter, it is easy to find the amount of acid necessary, since it is possible to calculate the calcium malate content, as has been shown above. The reaction, for instance, with oxalic acid would be

$$2\ Ca\ C_4H_4O_5 + H_2C_2O_4 = Ca\ C_2O_4 + Ca(C_4H_5O_5)_2$$

Thus half of the calcium is precipitated as calcium oxalate while the rest goes to form the acid malate, or bimalate. From this salt malic acid may be obtained very easily, and it is largely due to the fact that calcium bimalate may be obtained in a fairly pure condition that this method is much superior.

The main question centred about the production of this acid salt, and considerable attention was devoted to this, in order to find out something about the various factors influencing the yield and to try to find what conditions favor the maximum production. We will first state the general method used, after which the influence of certain particular details of operation will be discussed.

General Method

A measured quantity of niter, usually 100 grams such as used for previous analyses, is gradually added with stirring to a dilute solution of acid, in a large beaker over a water-bath. The amount of acid used is calculated from the equation given above. The mixture is heated for an hour or more with frequent stirring, and then filtered on a Buchner funnel and washed. The filtrate is then concentrated until crystallization begins, and then cooled. Crystals of calcium bimalate separate out which are filtered off and dried, while the liquor is further concentrated to botain more crystals.

It was found that by this treatment the yield of bimalate was considerably less than the theoretical amount, so the plan was resorted to of treating the residue of the niter (obtained by filtering after treatment with the acid) with the mother-liquor from which the crystals were obtained. This mother-liquor is very strongly acid, and when this is allowed to act on the residue of the niter, which still contains some unattacked malate of lime, more calcium bimalate is liberated. This second treatment is precisely like the first, the conditions of temperature and time being kept similar in both. The mixture, as before, is filtered, and the residue well washed while the filtrate is concentrated and cooled, with the result that more crystals are obtained. This method of obtaining bimalate, then, resolves itself into two treatments, at a definite temperature, followed by several evaporations in order to secure the maximum yield.

| Exp't | Niter used | Acid used | Acid per 100 gm. | Temp. | Total Yield | Yield 1st Treatment | Yield 2nd Treatment | Final residue | % Ca in salt |
|---|---|---|---|---|---|---|---|---|---|
| A | No.1 | Oxalic | 28 gm. | 60 | 73.0 gm. | 54.4 | 18.6 | 51 | 9.53 |
| B | " | $H_2SO_4$ | 12.5 c.c. | 60 | 72.5 | 54.8 | 17.7 | 51.5 | 9.62 |
| C | " | HCl | 36.5 c.c. | 60 | 68.6 | 48.8 | 19.8 | 21.5 | 9.80 |
| D | " | $HNO_3$ | 28.5 c.c. | 60 | 74.5 | 57.7 | 16.8 | 20.5 | 9.87 |
| E | " | Oxalic | 28 gm | 80 | 70.3 | 44.7 | 25.6 | 56 | 9.56 |
| F | " | " | 28 " | 90 | 66.8 | 47.9 | 18.9 | 56 | 9.65 |
| G | " | " | 28 " | 50 | 72.6 | 51.9 | 20.7 | 55 | |
| H | " | " | 28 " | 70 | 71.7 | 45.2 | 25.5 | 53.5 | |
| J | " | " | 28 | 40 | 70.3 | 36.4 | 33.9 | 58 | |
| I | No.V | " | 28 " | 55 | 69.2 | 51.9 | 17.3 | | 9.74 |
| II | " | $H_2SO_4$ | 12.5 c.c. | 55 | 70.8 | 55.8 | 15.0 | | 9.72 |
| III | " | HCl | 36.5 c.c. | 55 | 63.2 | 50.3 | 12.9 | | 9.84 |
| IV | " | $HNO_3$ | 28.5 c.c. | 55 | 65.0 | 49.2 | 15.8 | | 9.81 |
| K | No.I | $H_2SO_4$ | 11 c.c. | 50 | 68.7 | 54.3 | 14.4 | 51.5 | 9.74 |
| L | " | " | 11 c.c. | 60 | 71.9 | 54.2 | 17.7 | 51 | |
| M | " | " | 11 c.c. | 70 | 65.7 | 50.1 | 15.6 | 52 | 9.69 |

Particular Methods.

Besides a few preliminary experiments sixteen quantitative determinations of the yield of calcium bimalate were carried out, and their results may be seen at a glance in the table on the preceding page.

It will be seen that tests were made with various acids, namely oxalic, sulphuric, hydrochloric, and nitric, to see what effect the kind of acid had upon the yield. Equivalent amounts of these acids were used, and diluted to about 400 c.c., while the time of treatment on the water-bath was 1¼ hours. The figures all refer to 100 grams of niter taken for each experiment.

As far as can be gleaned from the figures of experiments A, B, C, D, and I, II, III, IV, where experiments with the four acids were carried out under otherwise identical conditions, there is not much to choose between oxalic, sulphuric, and nitric, while when hydrochloric was used the yield was in each case smaller. Oxalic and sulphuric gave practically the same results, the differences between the figures being almost negligible, as there is necessarily a certain error entering into the various manipulations, such operations as filtering, drying, etc., and it is difficult to treat one experiment exactly like another in every respect. The yield from nitric acid treatment in D was better than those from the other acids, while in IV it fell somewhat lower. Other differences in the products, due to treatment with different acids will be mentioned later in the consideration of the quality of the salt itself.

Influence of Temperature.

Another important point looked into was that regarding temperature, to see at what temperature the greatest yield was possible. The experiments were made in 800 c.c. or 1000 c.c. beakers over the water-bath, and the temperatures were kept closely at the figures indicated by constant stirring, although of necessity, in some cases the temperature fluctuated several degrees from the figures at certain times. This, however, was unavoidable, and it may be said that the figures given represent very well the temperatures at which the experiments were conducted.

The following are a few figures in the solubility of acid calcium malate at different temperatures, from Iwig and Hecht. (Lieb.Ann.233,-1886-p. 166.)

| Temperature | Parts dissolved by 100 parts water. |
|---|---|
| 15° C. | 1.287 |
| 17 | 1.386 |
| 45 | 8.54 |
| 57 | 32.236 |
| 68 | 13.127 |
| 78 | 7.437 |

It will be seen that the temperature of maximum solubility of calcium bimalate is in the neighborhood of 60°C. It was found in the experiments that the greatest yield of calcium bimalate was obtained when the experiments were made near 60°C.

Let us look at the results of experiments A.E.F.G. H.J.

| Experiment | Temp. | Yield of Bimalate. |
|---|---|---|
| J | 40° | 70.3 |
| G | 50° | 72.6 |
| A | 60° | 73.0 |
| H | 70° | 71.7 |
| E | 80° | 70.3 |
| F | 90° | 66.8 |

In all these six experiments oxalic acid was used, while the other conditions were made as similar as possible. A glance at this table shows that the "optimum" temperature, or that at which the maximum yield is produced, is between 50° and 60°, the figures for these two temperatures exhibiting but little difference. However, as the temperature increases above 60°, the yield of bimalate falls off accordingly, while the figures for 40° show a decrease when compared with the result for 50°.

Experiments K.L. and M. are mainly to show the effect of temperature. In these sulphuric acid was used, in smaller amount than the theoretical, but in all three cases the same. Here again we see that the yield for 60° is higher than those for 50° or 70°, although, as before, the figure for 50 is better than for 70°. This conclusion, namely that the best temperature at which to conduct the isolation of calcium bimalate lies near 60°C., is what one would expect from the solubility figures given above, as a larger amount of the salt would be in solution and thus appear in the filtrate from the 60° treatment. It has been said that calcium bimalate is less soluble above 60°, on account of partial decomposition into the neutral salt and the free acid.

Again, the conclusion just referred to is borne out by the figures of the residues of the niter, which were weighed after being dried. The residue is principally calcium oxalate with a certain amount of silica, but would also contain a certain amount of bimalate which did not get in solution. From the solubility figures it is seen that this amount would vary with the temperature, and we notice that the residues vary inversely as the yield of the bimalate, the ~~maximum~~ minimum being that from the treatment at 60°.

Calcium Bimalate Crystals

Let us now examine the bimalate itself, to see what effect the various methods of treatment have upon its quality. Calcium bimalate separates in fine, well-defined, crystals, easily dried, containing six molecules of water of crystallization. The crystals are larger when the solution is allowed to cool slowly. As the filtrate from the treatment is colored brown, the crystals separating out are discolored to some extent. Accordingly in experiments I, II, III, IV, K, L, and M, a little animal charcoal (about 5 grams) was added to the mixture, with the result that the crystals were much better looking, being in most cases free from any colcration. In all cases, however, it was found that the crude crystals were not quite pure, and where sulphuric, hydrochloric, or nitric acids were used, these acids were found to be present, sulphates being found to a less degree. In all cases a trace of phosphoric acid was found, and this was increased from a trace to an appreciable amount in those cases where animal charcoal was made use of to take out coloring matter.

Calcium oxalate is insoluble, and calcium sulphate is much less soluble than either calcium chloride or calcium nitrate. Accordingly, since all of the calcium oxalate, and most of the calcium sulphate, is removed by filtering, one would expect the crystals of calcium bimalate separating out from a mother liquor containing either calcium chloride or calcium nitrate to be more contaminated than crystals derived from treatment of the niter with the other two acids. That this is the case may be inferred from the figures of the calcium content of the crude salt, which are included in the table of results. In pure bimalate the percentage of calcium is 9.66. The figures reveal a higher content of calcium in the salt obtained by the hydrochloric or nitric treatment, and this is what might be expected, as an admixture of calcium chloride or calcium nitrate would tend to raise the percentage of calcium. Again, where animal charcoal is used, the figures are slightly higher as the crude crystals are slightly contaminated with calcium phosphate.

Recrystallization

A few experiments were made in recrystallizing the crude bimalate, with the result that a much purer product was obtained in all cases. Two determinations of the calcium content from different samples gave 9.62 % and 9.65 %, while the ordinary qualitative tests failed to reveal the presence of any of the above-mentioned acids, including phosphoric acid, with the exception of a faint trace of chloride in one case where hydrochloric was the acid used. Recrystallization, then, is advisable, especially if malic acid is to be made. In fact it is almost necessary, as some of the bimalate crystals, notably the last crop, only obtained after considerable concentration of the mother liquor, are even more contaminated. If a pure malic acid is desired, recrystallization is essential, as impurities are much more easily removed from the bimalate than from the acid itself.

From this it will be seen that as regards the acids used in isolating the bimalate, the superiority of oxalic and sulphuric is demonstrated, with the advantage evidently lying with the former. As far as purity of product and yield are taken into account, nitric seems better than hydrochloric. However, in case of either of these two, it is impossible to concentrate the liquors to the same extent, as with the others.

This is only what may be judged from laboratory experiments, for on a larger scale, where cost of acid and other indirect matters such as choice of apparatus, have to be taken into account, the advantage of the oxalic method might be offset to some extent.

Malic Acid

From the acid calcium salt it is a simple process to obtain the free malic acid. The best method is to use oxalic acid. The recrystallized calcium bimalate is dissolved in water at 60°, and the theoretical amount of oxalic acid solution, heated to the same temperature, is added. The amount of acid used may be calculated from the equation:

$$Ca(C_4H_5O_5)_2 + H_2C_2O_4 = Ca\ C_2O_4 + \underbrace{2C_4H_6O_5}_{\text{malic acid}}$$

The mixture, after being heated, is filtered, and the solution tested for oxalic acid and for calcium, and if either is found to be present the corresponding(?) reagent is added, although it is better to have a slight excess of calcium than of oxalic. The solution, containing the malic acid is then evaporated to a thick syrup which crystallizes only with difficulty. This is effected best by drying the syrup well in a water-oven, and finally in a vacuum desiccator. After a few days the syrup will turn into a white crystalline mass with a tendency to take up moisture if left exposed, as malic acid is very hygroscopic.

By this method it was found that it is possible to obtain very nearly the theoretical yield of acid from the recrystallized salt. The greatest difficulty appears to be that of crystallizing the acid. However, it is quite probable that should a use be found for such an acid, in some cases crystallization would not be necessary, and that the syrupy acid would serve the purposes as well.

## OUTLOOK.

At present the demand for malic acid is very small, possibly on account of its scarcity and consequently high price. Accordingly, if it were possible to procure the acid in considerably larger quantities than are at present available, and at a more moderate cost, it is altogether likely that uses would be found for it— uses probably similar to those to which acids related to malic are put, such as tartaric, citric, etc. As the acid, if used, would in all probability be applied in connection with food or drug products, great care would have to be exercised, both in the preparation of pure calcium bimalate, and in the production of the pure acid itself, to remove traces of such substances as oxalic or other acids used in the process.

### Quantity of Niter Available.

The possibility, then, of making any use of malic acid from such a source as maple sugar sand would depend, not only upon the ease with which such laboratory methods as have been referred to could be carried on upon a larger scale, but also upon the amount of niter available. At the present time no really definite figures in this regard are at hand. One estimate that has been made is that from one thousand trees in one season it is possible to obtain from 15 to 20 pounds of dry, washed niter such as was used in this experiment, but it is difficult to say just how reliable this is. Niter has always been regarded as a waste product of no value, with the result that no special endeavors have been put forth to note the quantity deposited with any degree of precision. However, in the present maple season, 1912, investigations in several of the counties of this province are in progress regarding the available supply of niter, and it is hoped that some definite conclusions will be arrived at.

It is generally agreed by all those acquainted with the subject that the deposition of sugar sand is very variable, fluctuating in amount from year to year according to the time of sugar season, and differing considerably during the different sap runs of the same season. With regard to seasonal variation no satisfactory explanation has been found. Most observers, however, agree that the deposition of niter occurs in greatest quantity after an open winter, or in seasons when the sap is sweetest. The deposit is believed to increase somewhat as the season advances, but here again nothing definite is yet known.

In all cases, however, the quantity of niter obtainable from any one farmer is very small, so that much depends upon the proximity of the sources of supply and upon the facility with which it may be collected.

## SUMMARY.

The main points which have been brought forward in the foregoing pages may be briefly summarized as follows:

Maple sugar sand, brought to a uniform condition by washing until the sugars are mostly removed, consists to a large extent of calcium malate. Malic acid is present to the extent of 50-60%, while the calcium content is in the neighborhood of 17%, lime being the principal inorganic constituent.

The best method of isolating malic acid consists in first obtaining acid calcium malate. The maximum yield of this latter is derived from the use of oxalic acid, the operation being conducted at a temperature of 60 C.

Acid calcium malate, though slightly contaminated in the crude state to a degree varying with the acid used, may by recrystallization be purified, so that a fairly pure malic acid may be easily prepared from it.

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