

ON THE CONSTITUENTS OF THE SAP OF THE "SILKY OAK,"
GREVILLEA ROBUSTA, R. BR., AND THE PRESENCE
OF BUTYRIC ACID THEREIN.

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[Read before the Royal Society of N. S. Wales, October 7, 1896.]

DURING last year, the author in conjunction with Mr. J. H. Maiden, carried out investigations on a deposit of Succinate of Aluminium, found existing in the timber of *Grevillea robusta*, R.Br. the results of which were communicated to this Society in a paper¹ read on the 6th November.

The occurrence of succinic acid in a deposit of this character appears to be extremely rare, and the origin of its formation was a matter for some consideration. As was pointed out at that time, it appeared probable, from the result of our inquiries, that the acid might have been formed by the alteration of malic acid, together with the formation of acetic acid, as a trace of the latter acid had been identified in the deposit. As it had not been possible at that time to obtain the sap from this tree, it was of course impossible to say whether malic acid was present or not, so the matter was allowed to remain open until the sap could be investigated. Special efforts were made to obtain, if possible, some of the sap, and it is to the kindness of Mr. W. P. Pope, Forester, in the Lismore District, of this colony, that I am indebted for the present material, he having collected and forwarded a small quantity of the sap for investigation.

Mr. Pope informs me that he obtained the sap by felling the tree, cutting it into lengths, which were then placed on their ends, so as to enable them to drain. He says that the sap would not run if the tree was merely cut into, or even if cut quite off, but

¹ On a natural deposit of Aluminium Succinate in the timber of *Grevillea robusta*, R. Br.

that it was necessary to cut the log into short pieces before the sap would run. The sap is thus obtained without much difficulty, but he thinks that the spring is the best time to procure it. The present sample was obtained during the month of February last. It will be noted that the method adopted by Mr. Pope to obtain this sap, is that by which the aborigines of the dry Western District of this Colony used to obtain a liquid from the roots of the "Mallee" trees to allay their thirst. The following extract will explain this:—"Looking as if they understood me, they therefore hastened to resume their work, and then I discovered that they dug up the roots for the sake of drinking the sap. It appeared that they first cut these into billets, and strip the bark and rind off, sometimes chewing it, then holding up the billet and applying one end to the mouth the juice drops out. We now understood for what purpose those short clubs, which we had seen the day before, had been cut."¹

The Organic Acid.

When received, the sap had a specific gravity of 1.0036 at 15.5°C. It was strongly acid to test paper, and had rather an unpleasant smell, indicating by its odour the presence of butyric acid. The determination of the acid was at once proceeded with. The total acidity determined by standard soda, 1 cc. = .0088 butyric acid, using phenol-phthalein as indicator, and after air had been drawn through the sap to remove CO₂ if present, was as follows:—10cc. of the original sap required 1.9 cc. of soda solution, or 100 cc. required 19 cc.; 50 cc. were then distilled almost to dryness, a small quantity of water added, and the remainder of the 50 cc. distilled over; 10 cc. of this distillate required 1.4 cc. of soda solution or 100 cc. required 14 cc., equal to .1232 gram. of butyric acid, so that by far the greater portion of the total acidity was due to this volatile acid, as it is not considered that the whole of the acid was obtained by this distillation. After the distillation of the 50 cc. had been thus carried out, a small quantity

¹ Mitchell—Three Expeditions, p. 197.

of dilute sulphuric acid was added to the residue in the retort, and again distilled. The amount of acid thus obtained was very small, and not greater than would probably have been obtained if water had been added instead of sulphuric acid. It appears from this result, that no volatile acid is present in combination, but that it wholly exists in the free state.

The distillate has a very marked odour of rancid butter, and when made alkaline with soda, evaporated to dryness, and treated with sulphuric acid and alcohol, the fruity odour given by the ethyl butyrate formed by butyric acid under this treatment was very marked.

To determine the rate of distillation of this volatile acid or acids, according to the method of E. Duclaux,¹ 50 cc. were distilled in portions of 10 cc. These were then titrated separately, with the result that the first 10 cc. required 1.8 cc. of soda solution, the second 1.4 cc., the third 1.3 cc., the fourth 1.1 cc.; and if we consider that the acid remaining in the retort would require at least 1 cc., we have the following percentages:—

1st fifth	=	27.27	per cent. distilled.
2nd „	=	21.21	„ „
3rd „	=	19.70	„ „
4th „	=	16.67	„ „
5th „	=	15.15	remaining in retort.
		100.00	

Now the rate of distillation for butyric acid does not differ very much from these percentages when we consider that only 50 cc. could be spared for experiment, while in the original determination 110 cc. were distilled in a retort holding 250 to 300 cc.

By adding together the first and second results as given in the table, of a distillation of butyric acid, so that they are represented as fifths instead of tenths, and so on throughout, we have the following figures:—

¹ Ann. Chem. Phys. [5] ii., 233.

1st	fifth	=	31.1
2nd	„	=	25.0
3rd	„	=	19.2
4th	„	=	13.9
5th	„	=	8.3

this represents 97.5 per cent. of total acids originally in the retort.

The characteristic feature of butyric acid, in distilling over in greater proportion in the first divisions of the distillate, is well marked in the results obtained from this sap, and it thus differs from acetic acid which gives less acid to the first portions of the distillate than to each succeeding one.

From a determination of the barium salt of a portion of the distillate from the sap, and weighing as BaSO_4 it was found that the percentage of barium sulphate was 79.2, while the theoretical quantity from barium butyrate is 74.91.

From the above results of the odour, the ethereal product, the rate of distillation, and the percentage of barium sulphate, it is apparent that the greater portion of this volatile acid is butyric acid, although the indications obtained by the result of the distillation, and also the barium determination, point to the presence of a small quantity of acetic acid.

The amount of fixed organic acid, other than the brownish humic-like material, is very small. Special effort was made to detect, if possible, the presence of malic acid, but the evidence obtainable from the small quantity of material received does not point to the presence of malic acid in the sap of *Grevillea robusta*. A very slight precipitate was obtained by adding alcohol to the prepared solution in which the absence of oxalic, tartaric, and citric acids had been determined. The usual tests with this precipitate pointed rather to the presence of succinic acid than to that of malic acid. As the acid is present in such small quantity much more material would be needed to satisfactorily determine it.

It is very evident, therefore, that the formation of the succinic acid found in the deposit in this tree, previously described, was

not from the alteration of malic acid, but rather that it was derived from the natural oxidation of butyric acid in the tree itself.

It is well known that all the fatty acids of the series $C_nH_{2n}O_2$, from butyric acid upwards, when oxidised by nitric acid yield succinic acid, together with other acids of the same series. Its formation from butyric acid is represented by the equation $(C_4H_8O_2 + O_3 = H_2O + C_4H_6O_4)$.¹ Many organic substances that are oxidised to butyric acid by nitric acid, generally yield succinic acid also, notably agaricic acid, from the Larch fungus (*Boletus Laricis*), which by oxidation with HNO_3 gives both acids.²

Normal butyric acid is widely distributed in the vegetable kingdom. It has been detected in croton oil, and other fatty vegetable oils; in tamarinds; in the fruits of the soap-nut tree, and that of the *Gingko biloba*, Linn.³ Iso-butyric acid also occurs in many vegetable substances. It occurs free in the flowers of the *Arnica montana*, as well as in the Carob bean (*Ceratonia siliqua*) and among the acids of croton oil.⁴

The presence of butyric acid in rotten potatoes was demonstrated in a paper read by Mr. J. R. Rogers⁵ in 1846, and from the method by which it was obtained, it must have existed as free butyric acid.

Although its presence in the vegetable kingdom is thus well authenticated, yet, I have not found that butyric acid has previously been detected in the sap of any tree.

I have no evidence as to the form in which the acid is present, whether as normal or as iso-butyric, but the odour is less unpleasant than that obtained from the decomposition of butter, so that if the sap is further investigated it may perhaps be proved to be iso-butyric acid.

¹ Watts' Dict. Chem., 1879 Edition, Vol. v., p. 453.

² Watts' Dict. Chem., (Morley & Muir) Vol. i., p. 87.

³ Roscoe and Schorlemmer—Treatise of Chemistry, Vol. III., pt. i., p. 591.

⁴ *Op. cit.* p. 599.

⁵ Pharm. Journ. Vol. v., p. 345.

In the report of the British Association for 1868, page 475, appears a paper by Alfred R. Catton, M.A., F.R.S.E., entitled "Report of Synthetical researches on Organic Acids." From his results he arrives at the conclusion that probably the whole of the volatile acids, and a considerable part of the fixed acids, are produced by the action of nascent hydrogen on carbonic acid.

Inorganic constituents of the sap.

The amount of total solids in 100 cc. of the sap was .5384 gram. On ignition .1842 gram. was removed. Of the remainder .2996 gram. was soluble in water, and .0546 gram. insoluble. The insoluble portion consisted of the phosphates of iron, magnesium and aluminium, and of magnesia, (the solution not being saturated by CO_2), not a trace of lime could be detected in this insoluble portion.

The soluble portion consisted of the chlorides of calcium, potassium, and sodium, a trace of sulphuric acid, but not phosphoric acid; nor could a trace of magnesia be found in this portion. The chlorine was estimated by titration with nitrate of silver (1 cc. equal .001 gram. chlorine). The alkalis were determined by estimating the chlorine in the dried mixture of their chlorides, and calculating their ratio. The calcium was determined as oxalate and weighed as carbonate.

The analysis of the inorganic constituents is as follows in 100 cc. of the sap:—

(a) Insoluble portion—				gram.
Phosphates of iron, magnesium, and aluminium = .0113				} .0546
Magnesia (MgO)...	...	...	= .0386	
CO_2 by difference	...	...	= .0047	
(b) Soluble portion—				
Chloride of Potassium (KCl)	...	...	= .1049	} .2998
Chloride of Sodium (NaCl)	...	...	= .0711	
Chloride of Calcium (CaCl_2)	...	...	= .1174	
$\text{SO}_3 = .0036$ equal to ? (Na_2SO_4)	...	...	= .0064	} .3544

The full analysis may be stated as follows, for 100 cc. of the sap, from which the percentage composition can be readily calculated.

Phosphates of Fe, Mg and Al.	...	=	·0113	gram.
Magnesia (MgO)	...	=	·0386	„
CO ₂ by difference	...	=	·0047	„
Chloride of Potassium (KCl)	...	=	·1049	„
Chloride of Sodium (NaCl)	...	=	·0711	„
Chloride of Calcium (CaCl ₂)	...	=	·1174	„
SO ₃ = ·0036 equal to ? (Na ₂ SO ₄)	...	=	·0064	„
Butyric Acid (by distillation)...	...	=	·1232	„
Organic substances, organic acids, etc.		=	·1842	„
Nitrogen	...		trace	„
Water	...		99·6982	„
				100·3600

The amount of chlorine in the soluble portion was found by titration to be ·167 gram. The results of the analysis give the chlorine with the potassium as ·0499 gram., with the sodium as ·0431 gram.; while the amount of calcium found requires ·075 gram. to form the chloride, or almost the identical amount left from the alkalis. The theoretical quantity of soda has been added to the SO₃ found, although it is not certain that it is present with that base, so a query has been placed before it. The presence of phosphoric acid is well marked, also the iron, good reactions being readily obtained for both forms. Nitrogen is present, but only as a trace.

Fehling's solution shows that the sap has slight reducing properties. The absence of lithia etc. was proved by spectroscopic investigation.

In drawing conclusions from the results of this investigation of the inorganic constituents, it appears evident that the calcium in this sap was present as chloride, or in its most soluble form, and not as generally supposed as a sulphate or as a phosphate, because, not a trace of lime was found in the insoluble portion of the ignited residue. Also that the alkalis were present as chlorides.

That the magnesia is not present as a sulphate or as a chloride, because no magnesia was found in the soluble portion of the ignited residue, nor sulphuric acid in the insoluble portion ; the small amount of sulphuric acid was found in the soluble portion and was probably present in connection with the alkalis, but of this I have no evidence outside the ready solubility of the sulphate, as only small quantities of cold distilled water, repeatedly applied, were used to extract the soluble portion from the ignited residue, no heat being applied.

It appears from numerous investigations and analyses of the ash of many plants, that the elements of this class most necessary to the growth of the tree, are sulphur, phosphorus, calcium, magnesium, potassium, iron, and possibly chlorine. All of these were found existing in this sap, while in addition we find sodium, and nitrogen, the former in fair quantity, the latter only in traces. No evidence was obtained as to the form in which the nitrogen was present, or with what constituent, but nothing was precipitated on boiling the original sap. The aluminium was found to be present in only very minute quantities, thus again confirming the inert character of this abundant element. It is thus the more remarkable that such a large deposit of aluminium succinate should have accumulated in the timber as described in the paper already referred to.

The general statement that calcium is present in the form of sulphate, phosphate, or carbonate, appears to be of too broad a character, and although no doubt correct in some instances, yet, it is not so in this sap. The chemical alteration and molecular arrangement of these inorganic salts within the cells of the growing tree, is no doubt different under altered conditions, and not always the same as theoretically supposed from information obtained by artificial cultures. In the estimation of the ash after incineration, we only arrive at the extreme stage of alteration, but we do not know all the changes that have taken place during the process, or what has been the order of the molecular alteration before the completed structure of the plant was obtained.



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