XV. *On the nature and combinations of a newly discovered vegetable acid; with observations on the malic acid, and suggestions on the state in which acids may have previously existed in vegetables.* *By* M. Donovan, *Esq.* *Communicated by W. H. Wollaston, M. D. Sec. R. S.*

Read June 1, 1815.

Having often observed the sour disagreeable taste of the berries of the Sorbus (or Pyrus) Aucuparia, it occurred to me that the juice might contain an acid of a peculiar nature, and I resolved to submit it to a strict examination. I was not at that time acquainted with the fact, that these berries had already occupied the attention of Scheele, and that this philosopher had pronounced their acid to be the Malic.

Some preliminary experiments showed me that the juice occasioned a precipitation in acetate of lead and nitrate of silver; but it produced no change in lime water, barytes water, sulphate of copper, nor, although it might be expected from its very astringent taste, did it affect sulphate of iron.

A quantity of the juice was poured into a solution of sugar of lead; a curdy and somewhat heavy precipitate appeared, which was separated by filtration: this, from its solubility in acetic and dilute nitric acid, I judged to be malate of lead. The filtered liquor was red, and perfectly transparent, but after a few hours, I observed a powder deposited at the bottom, and as I saw no sufficient reason for its appearance, it attracted my attention. To the naked eye it looked like a coarse powder; but, when examined by the microscope, proved to be composed of amorphous crystalline grains. With this small quantity of powder I made some trials, which ended in exciting farther curiosity. It was probable, that the precipitate which remained on the filter might be made to furnish more grains, and accordingly, after edulcorating the mass, I caused boiling water to pass through it. After two hours I examined the different washings; those made with cold water remained as at first, but those with boiling water had become white and turbid, from the suspension of a subtile powder. In several hours after, the cloud had disappeared, and displayed an abundant and beautiful formation of slender prismatic crystals, which glistened with silvery splendor at the bottom of the vessel. The mass which remained on the filter had become hard, was much diminished, and was very dense.

I accounted for the production of crystals by supposing that the precipitate, whatever might be its composition, was insoluble in cold water, but soluble in very large portions of boiling water, and hence the crystalline deposition on cooling. Experiment, however, showed, that the residual hard mass, even when levigated, boiled with water, and filtered, would no longer afford crystals on cooling: and this was a sufficient objection to my supposition; for, if one portion of the compound be soluble, why not the whole?

I observed, that even when the precipitate newly obtained, was washed with portions of cold water until it no longer altered vegetable colours; yet the first, second, and sometimes the third washing with boiling water would, after the deposition of the crystals, immediately redden litmus. An opinion now suggested itself, which the following trials greatly strengthened.

In order to obtain the acid of the saturnine precipitate, the latter was boiled with dilute sulphuric acid: the liquor became red and transparent, while the sulphate of lead subsided to the bottom. Imagining that I had now obtained the acid in a state of sufficient purity, although coloured with adhering vegetable matter, I thought to separate the sediment by filtration, but was disappointed: for the liquor came through very turbid, notwithstanding that the supernatant liquor had been transparent. It was apparent, therefore, that the sulphuric acid being in too small a quantity, had displaced but a part of the vegetable acid, that the latter dissolved the remaining part of its own combination with lead, and deposited it when the solution touched any thing cold, thus producing the turbidness. After some hours, the turbidness in the filtered liquor subsided, forming a stratum on the bottom of the vessel, over which lay a number of crystals.

The theory of the crystalline formation in the washings of the precipitate now became obvious. It appeared that when the saturnine compound was washed with cold water, no other effect than edulcoration was produced: but that hot water partially decomposed the mass into a super and a sub-salt, the former of which being soluble in boiling water, filtered through, but on cooling, deposited crystals of the neutral salt, while free acid was left dissolved in the liquor. The first washing contained most free acid, and therefore suffered least of the neutral salt to crystallize.

The red acid liquor, as has been stated, contained much lead, and this it was necessary to separate. The most unexceptionable method appeared to be the transmission of sulphuretted hydrogen through the clear liquor. This was accordingly done, after having heated the acid liquor so as to redissolve the crystals and sediment. The resulting sulphuret of lead was filtered off, and the clear fluid was boiled for a length of time, to expel the superfluous gas.

Supposing now that I had obtained the pure acid, I began to form various conjectures as to its nature; in the midst of which I discovered, that the berries of the Sorbus Aucuparia had already occupied the attention of SCHEELE, and that he had pronounced their acid to be the malic. There was indeed a great coincidence of properties between the two acids: malic acid is red, when evaporated to dryness it deliquesces, its combinations with potash, soda, and ammonia are deliquescent; such were also the properties of the acid under consideration. Yet I had never understood that malate of lead could be made to afford crystals: an experiment on this head, therefore, became necessary.

The juice of nearly ripe apples was saturated with potash, and the solution when filtered, was mixed with solution of acetate of lead: the precipitate was collected on a filter. This after being edulcorated was washed with boiling water, as before. In sixteen hours, crystals, precisely the same as the berries had afforded, were deposited, although less in quantity.

The production of crystals in both these cases, seemed to show that the acid of both fruits was the same: yet there was one difference. The precipitate remaining on the filter, after the action of boiling water, was, in that produced from apples, soft and pasty; but that obtained from the Sorbus berries was hard and dense. It became therefore necessary, to discover what would be the habitudes of malate of lead obtained by other means.

Scheele showed that the primary action of nitrous acid on sugar is to form malic acid. I therefore heated together equal weights of these substances, until the effervescence ceased. The brown residue was diluted with lime water, and when the oxalic acid that might have been formed, was in this manner separated, the remaining acid substance was saturated with potash. Acetate of lead was added, and the malate of lead thus formed was collected and edulcorated.

It now remained to ascertain whether this malate possessed the property of crystallizing, like that prepared from apple juice. I accordingly poured on it different portions of boiling water which were received in different vessels: the washings were all of a brownish yellow colour, from a small quantity of malate of lead held dissolved. At the end of 48 hours this salt was all deposited in the state of a brown subtile powder, but there was no formation whatever of crystals. On the surface of each washing was an iridescent pellicle of some lustre, which I found to be characteristic of the malic acid. This experiment, as Scheele directs, was made with weak nitric acid; I repeated it with an acid of considerable strength, but after sixty hours there was not one crystal.

It deserves attention, that the matter which remained on the filter in these two experiments, after washing with boiling water, were as soft and pasty as when first collected; whereas the salt of lead obtained from the berries of the Sorbus, had grown dense, hard, and was much diminished.

The saturnine compound that had been formerly obtained from the berries, when partially decomposed by sulphuric acid, afforded crystals on cooling: in order to ascertain if the malate of lead obtained from sugar would do the same, I repeated the process on it, but obtained no crystals. These experiments were made under almost every possible circumstance with the same results.

I next precipitated all the lead from the remaining malate; the malic acid thus obtained, was again mixed with acetate of lead, and the precipitate treated with boiling water as before: but the results were the same. From this malate of lead the acid was again separated, and the same process as before was four times repeated: but notwithstanding nearly all the foreign matter was thus separated, no crystals formed.

SCHEELE found that the gooseberry contains nearly equal parts of citric and malic acids. I thought it necessary to examine if this fruit would afford crystals. SCHEELE's process for separating the acids is as follows. The juice is to be evaporated to the consistence of honey, the pure acid to be separated by alcohol, and the alcohol to be finally evaporated. The residuum is to be dissolved in water, saturated with carbonate of lime; the solution is to be filtered, and boiled so as to separate the citrate of lime. The remaining brown solution is malate of lime: the salt is to be precipitated by alcohol, redissolved after edulcoration, and the solution is to be precipitated with acetate of lead.* All this I followed; but after treating the malate of lead with boiling water, I obtained no crystals.

The raspberry was found by SCHEELE to contain the same

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* CRELL's Chemische Annal. 1785, vol. ii. 292.

acids. I examined this fruit in a similar manner, but no crystals were produced.

Vauquelin detected malic acid in a variety of plants, but in none so abundantly as the Sempervivum Tectorum. In the juice of this plant, it is united to lime in the state of a supersalt.*

Malate of lead was formed by pouring solution of acetate of lead into the filtered juice of this plant. The precipitate, when washed with boiling water, deposited on cooling, the the same subtile powder as usual, but no crystals. Nor were any obtained when the malate was partially decomposed by sulphuric acid, in the manner already described.

Scheele found that the berries of the Sambucus Nigra, contain the malic acid unmixed with any other. I therefore examined their very mucilaginous juice, but could not produce crystals.

As in my experiments on apples I had obtained crystals, I wished to try what effect the vinous fermentation might have on their juice. The process was repeated with cyder, but I was surprised to find, that although a malate of lead was obtained, the property of forming crystals had been destroyed.

From various conjectures it appeared possible, that the berries of the Sorbus while very young, might perhaps contain a malic acid that would furnish few or no crystals. In the beginning of August (1812) the berries being still green, I made an infusion of them, which after filtration afforded a precipitate with acetate of lead. Boiling water produced no crystals, nor did the mass become hard as on former occasions.

Seven varieties of malic acid had now been examined,

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* Annales de Chimie, Tom. xxxiv. 127.

which when united to lead would not afford crystals. In the two latter cases it was surprising that those acids which in other trials afforded abundance, would now afford none. That the juice of the green berries was real malic acid, was proved by the following properties.

1. The acid, when separated from the juice, was of a crimson colour.

2. When evaporated to dryness, it soon deliquesced.

3. When rendered solid, and acted on by nitrous acid, some crystals of oxalic acid appeared.

4. The acid formed deliquescent salts with potash, soda, and ammonia.

5. Its combinations with lime and lead possessed their proper characteristics.

The acid of very young sour apples was combined with lead, and the compound treated with boiling water: the washings deposited much more crystals than mature apples would have done.

The truth was now manifest. Beside the malic, there is another acid formation, which in different fruits is formed at different periods, and which has hitherto escaped observation: and I consider the preceding details by no means redundant, inasmuch as they establish one decided difference between the two acids. Many others will shortly be stated.

The first step towards confirming the difference, was to obtain the new acid in a state of purity: and after numerous attempts, I found that the only way to obtain it pure, was to separate it from the crystals. The process is indeed complex and difficult.

The berries of the Sorbus Aucuparia are to be collected when first they have arrived at maturity. After sufficient bruising in a Wedgewood mortar, they are to be subjected to strong pressure in a linen bag. If collected at the most favourable time, they will afford nearly one half their weight of juice, S. G. 1077. This after due subsidence is to be strained, and mixed with filtered solution of acetate of lead. The precipitate is to be collected on a filter, and in order to separate any uncombined colouring matter, it should be washed with cold water. A very large quantity of boiling water is to be poured on the filter, and allowed to pass through the precipitate into different glass jars. After some hours, the washings become opaque, and at length deposit crystals of singular lustre and beauty. Those which have been formed in the colourless washings are to be alone retained; they are to be separated by the filter, dried in the air, and preserved for a farther process.

The original mass remaining on the filter, from which the crystals have been obtained, being now hard and brittle, is incapable of affording any more, without undergoing a new operation. It is to be boiled for half an hour with a little more dilute sulphuric acid than is sufficient to decompose the salt; when cold it is to be filtered. The filtered liquor is to be mixed a second time with acetate of lead; the precipitate washed, as before, with boiling water, and the crystals selected from the colourless washings only. The remaining mass again grown hard, is to undergo the process of decomposition with sulphuric acid, combination with lead, and the formation of crystals: and after all, it will be found that the crystals of all the processes will be inconsiderable when collected.

The whole of the crystalline product being dried, is to be boiled for half an hour with 2.3 times its weight of sulphuric acid, S. G. 1090, supplying water as fast as it evaporates, and taking care to keep the mixture constantly stirred with a glass rod. The clear liquor is to be filtered off, and poured into a tall glass jar of small diameter. While still hot, a stream of sulphuretted hydrogen is to be transmitted through it, and when all the lead has been precipitated, the fluid is to be filtered off, and boiled in an open basin, until the discharged vapour no longer blacken paper impregnated with acetate of lead.

The theory of the process is obvious. When acetate of lead is added to the juice, malate of lead and the combination of the new acid with lead precipitate; the latter is decomposed by boiling water into a super and a sub-salt; the supersalt is held in solution, but as the liquor cools, the neutral compound deposits itself in crystals, and the first washings contain most free acid. When boiling water is no longer able to overcome the attraction of the latter portions of acid to oxide of lead, no more crystals can be formed. We then apply the stronger power of sulphuric acid, we obtain the free vegetable acid, and proceed as at first. When all the crystals are collected, such a quantity of sulphuric acid is added as will be *nearly* sufficient to decompose them: this is so done in order completely to exclude the sulphuric acid, which without this precaution would be exceedingly difficult to effect. The undecomposed portion of the crystals dissolves in the vegetable acid newly extricated: but, if in the boiling, the fluid were not continually stirred, a mass would be formed in the bottom so hard as to resist decomposition. If the liquor after filtering were allowed to cool, the neutral salt would crystallize; it must therefore be used hot. The stream of sulphuretted hydrogen passing through so high a column of fluid soon separates the lead, while the pure vegetable acid is liberated, contaminated indeed with a little sulphuretted hydrogen. This gas does not disappear completely by boiling, for the acid retains the odour, be it ever so long boiled; exposure for a few days in an open vessel dissipates it completely.

In preparing this acid, it is not necessary, as it is in the process for malic acid, to saturate the juice of the berries with potash, at the commencement of the process: for of the two compounds formed after the mixture with acetate of lead, the malate dissolves in the evolved acetic acid in preference to the other. The colouring matter, which adheres obstinately to the malate of lead, is very apt, when extricated during the washing with boiling water, to tinge the otherwise perfectly colourless crystals, which form as the liquor cools. This is a great inconvenience, for the colouring matter cannot be washed away, even by cold water, without decomposing a quantity of the salt: hence the only remedy is, to reject all the crystals formed in the coloured washings, and to reserve those only that are of a pure whiteness. The crystals are of so delicate a fabric that they must be separated by the filter. When dried on paper, by exposure to air, they form a white brilliant flake of a silver lustre, resembling well-prepared acetate of mercury, but still more beautiful.

As to the amorphous crystalline grains which first attracted my attention, the following experiment elucidates the theory of their formation. A quantity of the pure acid obtained by the above process, was boiled for some time on an excess of carbonate of magnesia. The liquor after filtration was found to restore the original colour of reddened litmus, and to render green the tincture of cabbage. An acetate of lead was formed by boiling solution of super-acetate on carbonate of lead. This solution was mixed with the former, and the precipitate was collected by the filter.

Notwithstanding the evident excess of magnesia existing in one solution, and the necessary neutrality of the other, yet the filtered liquor was found strongly to redden litmus paper. We are not to suppose that the two salts evolved a free acid during their mutual decomposition. As much oxide of lead was liberated from the acetate, as was necessary to the neutrality of the acid eliminated from the compound with magnesia; the solution would therefore have retained all its ingredients in a state of neutrality, except that which originally contained an excess of magnesia. But the new salt of lead at the moment of its formation, was decomposed by the water present into a super and a sub-salt: the excess of acid being not only sufficient to saturate the redundant magnesia, but also to leave a portion free in the solution. This liquor, after an hour, deposited a quantity of crystalline grains, and after that, the acidity increased. Hence appears the reason of a crystallization in the original liquor: a super-salt is formed, which after a while deposits the neutral salt in a crystalline form.

This acid appearing from what has been already stated, as well as from what will be hereafter detailed, to be of a peculiar nature, it became necessary to give it a name. After some consideration I bestowed on it one, which, although not unexceptionable, is sufficiently accordant with the general analogy of chemical nomenclature, and which has received the approbation of some competent judges. Until a better name be devised, I have called it the Sorbic Acid.

To establish its peculiar nature, I have examined its combinations with certain bases, but have confined myself to those of which the analogous combinations amongst the malates had been already examined by SCHEELE. The sorbic and malic acids not having been distinguished by that philosopher, it seemed that here the distinction ought particularly to be established: and the standard of comparison must necessarily be whatever had been ascertained of the malates by their discoverer.

Sorbic acid, when perfectly pure, is a transparent, colourless, and inodorous fluid, soluble in alcohol, and in any proportion of water. When evaporated, it forms an uncrystallizable solid mass which deliquesces: when subjected to distillation, the liquor which passes over, shows no traces of acidity. Its acidity is such that it causes even a painful sensation on the organs of taste. It is not much altered by being kept in an uncombined state. I have had it for more than a year in a corked phial, and at the end of that time, no other change was produced than the separation of a tenuous coagulum, small in quantity, as the acid was very pure, but it is more abundant when the acid is impure. When mixed with malic acid, as in fruits, this acid is the first to disappear, while the other retains its properties long after the commencement of decay in the plant.

A quantity of malate of lead obtained from Sempervivum Tectorum was boiled with sorbic acid and a little water; the whole, from being colourless, became somewhat brown. The liquor was then filtered, and the turbid liquor which came through, was heated until it became clear; it was then suffered to rest. As it cooled, it let fall a powder, but when this was filtered off, the liquor remained clear, and in an hour a great profusion of crystals was let fall. The mass which remained on the filter contained some gritty particles.

Thus it is evident, that malate of lead was decomposed by sorbic acid, which could not happen unless the latter were a distinct substance. The malate was only partly decomposed, the oxide of lead united to the excess of sorbic acid forming super-sorbate of lead, while the disengaged malic acid dissolved as much as it could of the remaining undecomposed malate, forming super-malate of lead. The brown colour was produced by disengaged malic acid. The super-malate, as it cooled, deposited its malate in the state of powder, and the super-sorbate soon after deposited sorbate of lead in the state of crystals; and the original mass was found to contain gritty particles of sub-sorbate.

In the same manner, when a precipitate, obtained by acetate of lead from the juice of the Sorbus berries, is washed with boiling water, scarcely any malate of lead is deposited; and if the fluid contain much free sorbic acid, the iridescent pellicle, which is a characteristic of malate of lead, does not appear.

I shall now proceed to the combinations of this acid, so as to distinguish it from malic acid: and first the salts which it forms with lead should be briefly recapitulated.

The sub-sorbate is insoluble in water; if in a mass, it is dense and hard; if in powder, it is gritty.

The neutral sorbate, if obtained by precipitation, is a white powder, but if obtained from solution in its own acid, it is in beautiful silvery crystals. Neither of these salts is soluble in 5000 times its weight of water. The sorbate when heated to redness, undergoes a somewhat brilliant combustion.

The super-sorbate never assumes the solid form; its taste is sweet. Thus the sorbic acid forms three combinations with lead: malic forms but two, the neutral malate, which is an uncrystallizable soft powder, and the super-malate. Not less distinguishable are the two acids by their combinations with the alkalies.

Sorbate of potash, when there is an excess of acid, forms permanent crystals soluble in water, but insoluble in alcohol.

Sorbate of soda, when there is an excess of acid, forms permanent crystals, which agree in characters with the former.

Sorbate of ammonia, when there is an excess of acid, also forms permanent crystals of similar characters with the preceding.

These three salts will not crystallize unless there be a tolerable excess of acid; they are to be considered as super-salts. That of soda even requires the aid of cold to render it solid. The malates of potash, soda, and ammonia are known to be uncrystallizable and deliquescent.

In the combinations of these acids with earths, there are also striking differences. Scheele found, that when he added carbonate of lime to malic acid, a great quantity was dissolved, but the solution gave with litmus, indications of an abundant acid which it was impossible to neutralise with farther additions of chalk.* I obtained the same result with malic acid from the Sempervivum; I even found that the solution might be boiled to dryness, on a fresh portion of carbonate of lime,

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* Scheele, Chem. Annal. 1785. 2. 292.

yet when lixiviated, the filtered solution would still redden litmus, and the salt finally afforded was readily soluble. These results often obtained, prove that it is not possible to form neutral malate from carbonate of lime.

But with sorbic acid the case was quite different. When it was diluted, and agitated for a little while with carbonate of lime, the solution, before it could be filtered, deposited the principal part of the sorbate in the form of a discrete, gritty powder. The liquor when filtered produced no redness in tincture of litmus, and every thing proved that the fluid by mere agitation over the carbonate, had been completely neutralised.

The same results which SCHEELE obtained from lime were afforded by carbonate of barytes: but with sorbic acid I produced a liquor which showed no signs of acidity. The best test for ascertaining this fact, seemed to be infusion of brazil wood altered by distilled vinegar; and with this it even appeared, that the solution contained an excess of base.

Thus it appears, that malic acid never forms with carbonate of lime, any other than *acidulous salts;* and, as SCHEELE observes, these solutions in *some days* deposit the neutral salt in *crystals.* But with these carbonates, the sorbic acid forms *neutral salts,* which, *as soon as formed,* precipitate.

SCHEELE ascertained, that malate of magnesia is a deliquescent salt,* and in my trials I could not obtain it in a crystalline form. When evaporated, it became thick, and dried into a semitransparent substance, which softened with the smallest quantity of water, and formed matter of a syrupy consistence. The same earth, heated in sorbic acid, afforded a

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* CRELL's Chem. Annal. 1785. 2. 297.

liquor which, after filtration, deposited permanent crystals in abundance: they required for solution no less than 28 parts of water at 60.*

The malate of alumina was found by Scheele to be a salt very difficult of solution. I wished to discover the properties of the sorbate. I therefore boiled some very pure alumina that had been just prepared, and was therefore still soft, with sorbic acid: the boiling was continued for almost an hour, and after filtration, I discovered with no small surprise, that the alumina had not been acted upon. The acid was tried by every means, and nothing but the most minute vestiges of the earth could be obtained. Thus there is no sorbate of alumina.

I consider that from this property the sorbic acid may become a valuable instrument of analysis. The process for separating alumina from other earths, has been complicated and uncertain: may it not be rendered simple by the use of this acid, employed in excess?

Thus, I think there can be no doubt, that the sorbic acid is an acid *sui generis*, and probably intermediate between malic and oxalic. With regard to the other acids, with which the sorbic coexists in fruits, it is to be observed, that it is never found in mature fruits that contain any other than the malic; that the latter is never found alone in any mature fruit, but always accompanied by the sorbic, and that these two acids, when together, exclude all others. To this, however, there is an apparent exception, namely, the berry of the Sambucus Nigra, which (probably from the immense quantity of mucilage and

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* It deserves remark, that in Scheele's experiments, there could have been no sorbic acid present, as might have been expected, had he prepared his acid from apples: he obtained it from gooseberries, and thereby avoided this source of fallacy.

colouring matter present) afforded me no sorbic acid. The fruits that contain the sorbic and malic acids together are apples, plums, berries of the sorbus, barberries, and sloes. Of these, the berries of the sorbus contain the greatest quantity of sorbic acid, unripe apples less, ripe apples and sloes still less, barberries very little, and plums least of all. The green berries of the sorbus, (perhaps,) those of the sambucus, and the plant sempervivum tectorum, contain no other than the malic; and agreeing with the foregoing statements, raspberries and gooseberries, as they contain citric and malic acids, contain no sorbic whatever.

Observations on the malic acid.

In 1785, during an examination of different fruits and berries, SCHEELE discovered that gooseberries, beside lemon acid, contained one of a peculiar nature: this he afterwards found to exist in apples, without, as he thought, a sensible admixture of any other. On this account he gave it the name of apple acid, or malic acid.

He also ascertained, that by the action of nitrous acid on sugar, a substance is produced, which shows no traces of nitric acid, yet unites and forms a soluble salt with lime, "it therefore is not the oxalic acid." By some other experiments he found that an acid is produced "which does not differ in the least from the properties of the apple acid, and is accordingly the same."

This acid he detected in a great variety of vegetable juices. Since that period, VAUQUELIN has extended the catalogue, but of all other plants, it is most abundantly contained in the Sempervivum Tectorum.

SCHEELE's process for obtaining malic acid is as follows.

"Saturate the juice of apples, whether ripe or unripe, with carbonate of potash; add solution of acetate of lead until it cease to produce a precipitation. To the edulcorated precipitate, add as much dilute vitriolic acid, as is necessary to give the mixture a perfectly acid taste, without any sweetness."*

There are several objections to this process, all of which seem to have considerable weight. In the preceding pages I have shown, that the juice of apples, whether ripe or unripe, always contains two acids of very different properties. By the above process these acids are not separated; they are in fact found in what is supposed to be the resulting pure malic acid, and it is impossible, without the most complicated processes, to obtain this substance in the insulated form.

The precipitation of the lead by means of sulphuric acid, appears to be objectionable. I have often attempted to adjust the proportion of the latter substance, so as to throw down all the lead, without leaving any free sulphuric acid, but I uniformly failed: and it is evident, that, if not impossible, it is exceedingly difficult and troublesome.

Scheele also attempted to obtain malic acid from malate of lime, by means of sulphuric acid, but found "the mode rather difficult, as the acid would not let the calx fall completely." Vauquelin observed the same thing.

The last process proposed by Scheele, is to distil equal parts of weak nitric acid and sugar, until the mixture become brown, which is a sign that all the nitrous acid has been abstracted: the oxalic acid formed, is to be separated by lime water, and the remaining acid to be saturated with carbonate of lime.

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* Crell's Chemische Annal. 1785. Vol. II. 295.

The solution is to be filtered, the filtered liquor to be mixed with alcohol, and the coagulum thus obtained, is to be edulcorated with new portions of alcohol. The coagulum is then to be dissolved in water, and mixed with a solution of acetate of lead: a precipitate falls, which is to be treated with sulphuric acid, in the manner already directed.

No one who has not gone through this process, can fully conceive the difficulty and expense of it: and I have found that the acid obtained is variable in its nature. In one case I obtained an acid, which, when mixed with solution of acetate of lead, did not at first produce any effect, but at length slowly deposited a precipitate. The heating of another portion of the acid with carbonate of lime, produced a separation of a black powder, which possessed the properties of charcoal. There were also many other peculiarities; and the combined effect of all was to convince me, that great differences exist between the acid obtained in this manner, and that obtained by other processes.

The experiments of VAUQUELIN satisfied him that the acid which is combined with lime in the Sempervivum Tectorum, is the true malic: and all my trials convince me, that it does not contain even the least quantity of the sorbic. Since then, by the means generally employed, we do not obtain malic acid, the only alternative is to adopt the hitherto neglected process of VAUQUELIN; and it will be found that his process affords the acid with greater ease, and in much greater purity, than any other. The method of detaching the acid from the malate of lead by sulphuric acid is, as we have seen, difficult; and the criterion of the taste is liable to this fallacy, that as the sourness increases, the sweetness decreases. There will on this account, be a period when the latter will disguise the former, and yet the lead will be still present. I would therefore suggest the substitution of sulphuretted hydrogen in place of sulphuric acid.

If it were required to obtain malic acid exceedingly pure, and still more divested of vegetable matter, the following process may be adopted.

The juice of Sempervivum Tectorum is to be evaporated to two-thirds, and, after standing some hours, it is to be filtered, and mixed with an equal quantity of alcohol. The coagulum is to be separated by the filter, edulcorated with fresh portions of alcohol, and dried in the air, lest any adhering alcohol should impede its subsequent solution. The mass is then to be dissolved in water, mixed with solution of acetate of lead, and the precipitate collected on a filter. After being well edulcorated from any superfluous acetate of lead, the precipitate is to be boiled for 15 minutes with a little less of dilute sulphuric acid than is sufficient to saturate the oxide of lead: and for this part of the process, the criterion of sweetness will very well answer the purpose. The whole is to be set aside for some days, and, during this period, a small quantity of sulphate of lead which the malic acid held dissolved, will be deposited. The liquor is now to be filtered, and in order to separate the last portions of lead, a stream of sulphuretted hydrogen is to be transmitted through it: the black precipitate is to be filtered off, and the liquor should be boiled in a vessel freely exposed, until paper moistened with acetate of lead is no longer blackened by the discharged vapour. This acid is the purest that can be obtained; it retains a slight odour of the gas, but even this is destroyed by exposure to the air for a few days.

VAUQUELIN observes, that malic acid thus obtained is nearly colourless: his was therefore diluted. I have found that it becomes perfectly brown by concentration: and I have decomposed and recomposed malate of lead several times, using each time the same specimen of malic acid, yet so obstinately did the colouring matter adhere, that it was always found in the resulting acid. Thus, as far as we know, this acid cannot be procured free from colour; and the nearest approximation is that obtained by VAUQUELIN's process.

Suggestions concerning the state in which acids may previously have existed in vegetables.

I have sometimes indulged in the supposition, that the vegetable acids are not primarily formed by the immediate union of their elements, but that they may have previously existed in a definite combination, called the bitter principle. It is possible that this principle may be a compound basis, which by uniting to oxygen, or by undergoing more complicated processes, might change its nature so far as to become an acid. The whole is a mere conjecture, and perhaps deserving of little consideration; the facts, however, which suggested it may be noticed.

The sweetness of any vegetable juice, has been generally attributed to a sweet principle called sugar. In the same manner it has been lately supposed, that bitterness depends on a bitter principle, which, although variously disguised, is always identical. Dr. THOMSON has shown, that when water is digested over Quassia, and afterwards evaporated to dryness, a transparent substance is obtained, which differs in its properties from all other vegetable principles: this he considers as the bitter principle, and, I believe, with very great justice. I found that the liquor obtained by digestion, although slightly coloured, was transparent even to the end of the evaporation. The resulting mass was nearly transparent, and minute in quantity, considering the proportion of Quassia employed; and such was its bitterness, that a particle placed on the tongue, which could not have exceeded $\frac{1}{50}$th of a grain, diffused an intense bitterness over the whole mouth and fauces.

This matter was heated with nitric acid; it dissolved with effervescence, and the bitterness was no longer sensible. The remaining substance formed a precipitate in acetate of lead, which possessed all the properties of malate of lead: and it appeared that no other than the malic acid was produced. With this experiment the following agrees in a remarkable manner.

Five ounces of white sugar, and an equal weight of very strong nitric acid were mixed in a retort. Without the application of external heat the action commenced, and soon became violent. When cold, the residual matter was found to be thick and tenacious; its taste was sour, and extremely bitter. The malic acid being abstracted from a portion of this by means of lime, it was found that the bitterness, now no longer disguised by acidity, had become intense. The other portion, which had not been saturated with lime, by being treated with more nitric acid, lost all its bitterness, and oxalic acid was formed. In this experiment it appears, that by some action of nitrous acid on sugar, a bitter substance and malic acid were produced together; that by the farther action of nitrous acid, the bitter substance disappeared, and acid appeared in its stead.

The foregoing conjectures correspond also with the fact, that by the action of certain substances on each other, the bitter principle is evolved at the same time with those acids which I suppose to have been produced from that compound basis: and the appearance of both at the same time may be accounted for by admitting that the conversion was not complete. Thus, if alcohol be distilled with nitrous acid, a liquor is produced which has a sweet taste. If this liquor be re-distilled with another portion of acid, a bitter liquor comes over. And if this bitter liquor be distilled a third time with a fresh portion of nitrous acid, crystals of oxalic acid make their appearance in the residuum. This series of changes bears a striking resemblance to that produced by the action of nitrous acid on sugar.

HAUSSMAN observed, that when nitric acid is digested with indigo, a very bitter substance results, to which WELTHER gave the name of Amer: in this process, oxalic acid is also formed.

The vegetable acids are even formed by the action of nitrous acid on animal substances; in the instance of muscle we obtain the abovementioned Amer with oxalic acid. In bile the bitter principle is already formed; when acted on by nitrous acid, oxalic acid is produced.

On examination we shall not be at a loss to find operations analogous to some of the preceding, taking place naturally in the vegetable kingdom. The Pyrus Malus or common crab apple, while young, is very bitter, and has little sourness: as the fruit advances towards maturity, the taste becomes proportionately sour, and the bitterness diminishes. The young berries of the Sorbus Aucuparia also are bitter, contain but one acid, and even that in small quantity: when the berry is ripe, it contains two acids, the combined quantity of both is considerable, but the bitterness has in a great degree given place to a coarse astringency.

It is not improbable, that the bitterness produced in all the foregoing cases, should be owing to the formation of the same bitter principle: and its constant conjunction with a vegetable acid, seems to show that there is some very intimate connexion between them, at present unknown.

The preceding observations are offered as mere conjecture; and I am fully sensible of what little consideration should be attached to them: they are not however entirely devoid of probability. An hypothesis is below the dignity of a system which is founded on the indestructible basis of experiment: and even though it be supported by the coincidence of admitted facts, by direct analogies, and by the correspondence of received opinions, it should nevertheless be the beginning and not the end of knowledge.