XXVI. Memoir on the chemical nature of ants, and the simultaneous existence of two vegetable acids in these insects

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ters of reference are the same in both, where they can be applied.

The bar A, of which the side BC is of iron, and the other DE of zinc, is about one inch broad, a quarter of an inch thick, and eight inches in length. It is firmly fixed, at the lower extremity I, to a board *a, b, c, d*, made of mahogany.

On the application of heat, this bar, by the superior expansion of the zinc, is inclined at the top towards B. In the upper end of the bar there is a pin (seen at A, fig. 2.) which goes into the fork-like opening L of the index LM (fig. 1.), and carries the short end of this index along with it; consequently the long end is carried along the scale from 0° to 100°.

When the instrument is exposed to a lower temperature, the movement is exactly the reverse of what I have been describing.

Beneath the index LM are two others on the same axis G, one of which can be carried towards the right, and the other towards the left, by means of a pin which goes through the first-mentioned index at H. By this means, the greatest and lowest degree of temperature that occurs from the time the thermometer is set or adjusted till it be again consulted, is accurately marked.

In adjusting the thermometer for observation, all that is necessary is to bring the two small indexes immediately below the broad one. As the last-mentioned one is moved backwards or forwards by variations of temperature, it carries one or other of the small ones along with it, by means of the pin H, leaving one of them at the highest and the other at the lowest degree that may have occurred from the last time of adjustment.

The face of the upper part of the instrument is covered with a glass door, the hinges of which are at N and O.

The greatest range of any thermometers of this kind which I have yet made, is from 10° below to 100° above 0°. This instrument proves very accurate in its indications.

XXVI. *Memoir on the Chemical Nature of Ants, and the simultaneous Existence of two Vegetable Acids in these Insects.* By A. F. FOURCROY*.

1st. SO much has been already said in regard to ants and their acid, that it appears nothing more remains to be added

* From *Annales du Museum National*, No. 5.

on the subject. Since the time that Samuel Fisher first described this acid in 1670, and taught a method of obtaining it by distillation, till citizen Deyeux confirmed by exact experiments the identity of the acid of ants with the acetous acid, (an identity first announced in 1749 by Margraff, then in 1777 by Arédivillon and Oëhrn, and afterwards by Bergman,) all that chemists have done on this subject seems merely to be, that some of them have maintained the supposed analogy; while others have wished that this analogy should be only apparent, and that the formic acid should be considered as a peculiar acid *sui generis*. I do not speak here of the opinion of Thouvenel, who pretended that the acid of ants was the phosphoric acid, because this opinion was supported by no positive fact: I thought it might be still useful to resume the analysis of ants; and the reader will find that, having been employed in this research with C. Vauquelin, it presented to us some facts which had escaped our predecessors.

2d. Having cleaned the ants which were collected in the wood of Boulogne, and of that kind called by Linnæus *formica rufa*, they were bruised in a marble mortar. During this operation a vapour was disengaged of an odour so sharp and pungent that it hurt the eyes, and could be compared to nothing but the acetic acid or radical vinegar.

3d. The ants thus bruised were put to macerate in alcohol for several days, and in a temperature of about 68 or 70 degrees the alcohol assumed a yellow colour.

4th. The alcoholic infusion of ants subjected to distillation furnished an inflammable liquor slightly acid. During the distillation there was formed in the liquor a brownish deposit which was collected on a filter.

5th. The acid liquor which remained after distillation, when filtered and separated from the deposit, was saturated with lime. It then became brown, thick, and acquired a nauseous and pungent flavour. By blowing through a tube into the thick liquor there was formed a multitude of bubbles, which exhibited the same prismatic colours as soap bubbles.

6th. This combination of the acid of ants with lime, when subjected to the test of different re-agents, exhibited the following phenomena:

a. Mixed with concentrated sulphuric acid it exhaled the odour of vinegar.

b. With nitrate of lead it gave an abundant white precipitate.

c. With nitrate of silver a yellowish precipitate.

d. With muriate of barytes there was nothing sensible.

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e. Ammo-

e. Ammonia produced no change in it.

f. Alcohol formed a rosy and ductile precipitate.

7th. A part of the thick liquor being mixed with half a part of concentrated sulphuric acid and two parts and a half of water, there was immediately formed a very thick magma. This mixture was subjected to distillation, and the product was divided into three parts. They were all clear and colourless: they had an empyreumatic odour, and a very strong acid taste.

The residuum of this distillation had acquired a very dark brown colour, and a disagreeable burnt taste, though it had not been carried to dryness.

The first product tried with acetite of lead gave no signs of the presence of the sulphuric acid: the second and third gave the same result; which proves that they contained no sulphuric acid.

This acid distilled and combined with potash furnished real acetite of potash which attracted the moisture of the air; exhaled, by the addition of concentrated sulphuric acid, a strong vapour like that of radical vinegar; and in a solution of nitrate of mercury formed a flaky precipitate like common acetite of potash.

The greater part then of the acid of ants is acetic acid, as C. Deyeux has already proved by a careful analysis and experiments*.

8th, The calcareous combination of the acid of ants, obtained by infusing them in alcohol, exhibited to us a very remarkable character. In a solution of acetite of lead it formed a very abundant deposit, which was redissolved by

* Bergman had found in it some resemblance to the acid of vinegar; the following is what he says on this subject:—*Hoc acidum indole aceto proximè accedit, in variis tamen differunt. Prius cum magnesia, ferro et zinco crystallisabiles præbet sales, posterius nonnisi deliquescentes. Magnesia formicata in primis notatu digna est.* In another part of his works, *A Dissertation on Magnesia*, Bergman speaks also of the formic acid, and describes the properties of the salt which it forms with magnesia as follows:—*Acidum formicarum magnesiâ saturatum aquam deferens fundum petit, abundante autem acido solvendum et evaporatione crystallos deponens, quæ saporis fere expertes ægerime aquâ solvuntur, in igne non funduntur; sed tamen, parum decrepitant, subito nigrescunt, tandemque in pulverem faciscunt album, in acidis effervescentem quum acidum formicarum sub destructione magnesiâ præbeat æream. Crystallorum figura est hemisphærica, plano secante forsum verso, paulum concavo, polito, striisque, oculo armato vix discernendis, è centro radiante: hinc luculenter aceto dignoscitur acidum formicarum, cui alioquin indole proximè accedit, illi tamen, æquè ac acidis vitrioli nitrique phlogificatis, magnesiâ eripiens hujus salis dimidium pondus est ex magnesiâ. Una ejusdem pars tredecim requirit aquæ, ut solvatur in calore quindecim graduum; spiritus vini eundem non suscipit.*

the acetous acid, and even by that which was obtained in the solution above described, No. 7.

As this experiment shows that the acid taken from the ants by alcohol, and combined with lime, contained something else than acetous acid, since this calcareous salt precipitated acetite of lead; and as this different matter was not volatile, since the product of the distillation with sulphuric acid did not produce the same effect, we tried to find it again in the residuum of the distillation: but this residuum contained so much sulphuric acid that it was impossible for us to succeed; we therefore had recourse to the following experiment.

9th. A part of the combination of the formic acid with lime was mixed with a solution of nitrate of lead, and there was immediately formed a very abundant precipitate of a yellowish colour, which when put upon burning coals, after having been well washed and dried, became immediately black, exhaled an animal and ammoniacal odour, while the lead was reduced to a metallic state.

Sulphuric acid diluted with about six parts of water was poured over this precipitate reduced to fine powder. At the moment of mixture the powder remained at the surface of the liquor as if it had been a fat substance, and it did not become mixed with sulphuric acid till after long agitation.

When the mixture was well made the volume of the precipitate was diminished: it became heavier and whiter. The liquor then had a slight acid and saccharine flavour, which was destroyed by the addition of the sulphuric acid, and was soon succeeded by a nauseous flavour. It precipitated slightly muriate of barytes, which indicates some traces of sulphuric acid. It precipitated lime water only very weakly; but at the end of some hours there were formed a great many crystals at the surface of the liquor, and on the sides of the glass containing the mixture.

It precipitated in abundance nitrate of mercury, and those of silver and lead.

Combined with barytes it gave a reddish solution of a saline and pungent flavour. This combination reduced to a small volume did not crystallize; a slight pellicle only was formed at its surface. Potash did not separate the barytes from this combination, but the alkaline carbonate produced a precipitation. The oxalic acid formed in it a very abundant deposit, but the tartarous and citric acids produced in it no change.

10th. The facts here detailed indicate to us that the matter combined with lime along with the acetous acid was of the nature of the malic acid; but to be more certain we examined it comparatively with the latter, combining both of

them with the same substances. Without here entering into a tiresome account of these comparative experiments, we shall content ourselves with saying that these two compounds exhibited phænomena absolutely similar.

Ants contain then, and consequently form, malic acid, like vegetables. It is no doubt the presence of this acid which had misled the chemists who preceded us in this labour. While they acknowledged in the acid of ants a great analogy with vinegar, they however found differences which induced them to consider it as a particular acid; and these differences arose from the presence of the malic acid in the acetous acid of ants.

Distillation of the Product of Ants treated with Alcohol.

11th. The ants, exhausted by alcohol, furnished a limpid and slightly alkaline water, a reddish brown oil, thick and exceedingly foetid. The first liquor, diluted with water, and filtered to separate the oil, produced a slight effervescence with acids.

As it emitted at the same time an odour of vinegar, easily distinguished amidst the foetidity by which it was accompanied, a certain quantity of it mixed with sulphuric acid was distilled, and we obtained a colourless acid product of an empyreumatic odour, which contained a small quantity of acetous acid. Was this acetous acid completely formed in the ants exhausted by alcohol, or was it formed by the action of the fire?

The product of the distillation of the exhausted ants contained then a foetid empyreumatic oil, carbonate of ammonia, and acetite of ammonia, all dissolved in a large mass of water.

Examination of the Matter which separated from the Alcohol during the Distillation mentioned in No. 4.

12th. The reader will remember that the alcoholic infusion subjected to distillation suffered to be deposited a brown substance which had been separated from it by the filter. This substance was of so dark a red colour that when seen in a large mass it appeared to be black: when dried it was brittle, its fracture was smooth and brilliant like that of resin, it had no sensible flavour, it was not soluble in water; and this may serve to explain its precipitation in proportion as the alcohol evaporated. Though insoluble in water, when macerated a long time in that fluid it communicated to it a slight fawn colour, owing, in all probability, to a small quantity of extractive matter interposed between its parts.

Alcohol

Alcohol slightly heated over this substance dissolved the greater part of it. It assumed a pretty dark red colour: there however remained a brownish matter, which did not combine with that liquid whatever quantity of it was added. This alcoholic solution became milky by the addition of water, and at the end of some days there was separated a resin-like deposit soft and ropy, of a reddish colour and a very disagreeable nauseous taste, slightly soluble in water, since it communicated to it a little of the colour and of the nauseous taste. This deposit is a fat matter of a peculiar nature.

The brownish matter not dissolved by alcohol, already mentioned, appeared to us to be albumen, which the moisture, and perhaps the acid contained in the ants, contributed to render soluble in alcohol. This albumen was coagulated by the heat, and precipitated with the fat matter in proportion as the alcohol was volatilized. When placed on burning coals it decrepitated, became corneous, swelled, and puffed up, emitting white foetid ammoniacal fumes: it left on the support a large and light charcoal. It was in no manner soluble in water; it contained a little hydrogenated carbon, which gave it a brownish colour.

13th. A portion of the ants exhausted by the action of alcohol was subjected to distillation in an open fire. There remained a charcoal, which, like all those of animal substances, burnt with difficulty, and left, after long combustion, white ashes, which contained nothing but phosphate of lime.

This was proved by treating it with nitric acid, which dissolved the greater part of it without effervescence, and by adding to the solution ammonia, which formed in it a white gelatinous deposit which exhibited all the properties of phosphate of lime.

The portion of ashes which did not dissolve in the acid was filix; but as the incineration had taken place in an earth crucible, this substance arose, in all probability, from that vessel. However, to ascertain whether this earth had been really furnished by the crucible, some of this charcoal was burnt in small portions in a crucible of platina until we obtained a quantity of ashes sufficient to be subjected to examination, and the following result was obtained:—150 parts of charcoal of ants were reduced in an ignited platina crucible, at the end of several hours, to 22 parts of ashes; 14 parts of these ashes were dissolved by nitric acid; the eight parts not dissolved were sand mixed at first with the ants.

It results from this experiment that the osseous skeleton of ants is formed, like that of warm-blooded animals, of phosphate of lime. It is not improbable that the long and strong calcination

calcination to which it was necessary to subject their charcoal in order to incinerate it, decomposed this salt, and carried it to the state of lime: to confirm this conjecture would have required more of the charcoal than we were able to procure.

14th. It results from this analysis that ants are formed of a large quantity of carbon united to a small quantity of hydrogen, and no doubt also to a little oxygen. This compound is mixed with phosphate of lime, which constitutes the solid part or the skeleton of the insect. Ants, besides the preceding compound, contain a pretty large quantity of resin, soluble in alcohol, which seems to exist in them completely formed, since the application of this re-agent is sufficient to extract and obtain it separately. It is probable that they conceal also some parts of animal albumen and gelatine; but as these animals were subjected to distillation immediately after their treatment by alcohol, it was impossible to obtain the two materials separately.

What ought to be most interesting to chemists among the results obtained by the analysis of ants, is the presence of the acetous and malic acids in these insects. These acids, as appears, exist in them in a very large quantity and in a very considerable state of concentration, since in bruising them in a mortar there is disengaged, as already observed, an acetic acid vapour so sharp and penetrating that it is impossible to endure it even at the distance of three feet. It appears also that acetous acid continually exudes and distills, as we may say, from these animals; for they leave traces of it on the bodies which they traverse. All chemists know, that if moistened turnsole paper be put into an ant-hill, or even if it be suspended at some distance, it soon acquires a red colour. It is known also, that if a certain number of ants be collected in a small quantity of milk it becomes curdled; and that if sugar attacked by ants, and on which they have remained some time, be put into milk, it curdles in the same manner. The acidity of ants is proved besides by the strong impression they make on the mouth when chewed: this impression is almost as strong as that produced by radical vinegar. There is reason to presume that it is this acid in a concentrated state, which by insinuating itself into the places bit by ants renders them so painful, and causes the parts wounded by these insects to swell.

One is astonished on the first view at the quantity of acid which these insects continually furnish, and in particular that they can live in the midst of so sharp a liquid; but it is probable that this acid is separated from the other humours by peculiar vessels which have no communication with the essen-

tial

tial organs of life, and which open only on the outside of their bodies. Anatomy only can unveil to us this remarkable apparatus of secretion.

15th, In regard to the malic acid which in ants accompanies the acetic acid. We shall terminate this memoir by a general remark on the existence of this acid in organic compounds.

Few vegetable acids are so generally and so abundantly diffused throughout nature as the malic acid; and, though it has not been long known in comparison of many others, it has been discovered in a multitude of substances, and its properties have been carefully studied.

It has been found in fruits with seeds, with stones, and in a great number of berries.

It exists in a multitude of plants in the state of malate of lime. The joubarbes, crassula, and cotyledons, mesembryanthemum, sedum, and even aloes, contain more or less considerable quantities of it, according to the analysis made by C. Vauquelin, and inserted in the *Annales de Chimie*.

It is found in abundance in the liquor which is separated by the hairs of chicken pease (*cicer arietinum*), where it is accompanied with a small quantity of oxalic acid and by some atoms of acetic acid.

It is formed by the action of the nitric and oxygenated muriatic acids on all vegetable substances, and in particular on sugar, gums, starch, honey, &c.: it always precedes the formation of the oxalic acid by these re-agents: vegetable and even animal substances are constantly changed into malic acid before they are converted into oxalic acid, by the acids above indicated.

It is thus that blood, urée, the uric acid, and jelly, when treated with either of the acids above mentioned, are first changed into malic acid, and afterwards into oxalic acid if the action of the acid be continued in a powerful manner; but it is always united with ammonia when it arises from animal matters, because there is formed at the same time a certain quantity of that alkali.

It is not vegetables only that continually give birth to the malic acid: animals are equally susceptible of producing it: it is in the class of insects in particular that this property is manifested.

It appears that the malic acid is in some measure the first stage of acidification in the processes of nature and of art. It precedes in a special manner the formation of the oxalic and acetic acids, because it contains a greater quantity of the radicals, or of carbon and hydrogen, and consequently less

less oxygen than they do. It is that of all the vegetable or animal acids which retains in the fullest manner the nature of the animal or vegetable substance from which it has been formed; it is that which is decomposed with the greatest ease by the action of the fire. Preceding all the vegetable acids, by ulterior and successive elaborations it produces the tartareous, citric, oxalic, and acetous acids: it is by losing a part of its radicals, which are converted into water and carbonic acid by atmospheric oxygen, that it passes itself to the state of these other acids; and though none of the latter but the acetous acid has yet been found in animals, there is reason to believe that all the rest will be found.

The malic acid is then formed by living plants: it often exists in them in its full purity: sometimes it is found in them united to lime, and no doubt to potash, according to the nature of the circumstances which accompany its formation. It is also formed during the life of certain animals, particularly in ants, and certainly in many other insects: in a word, it is produced by the action of the nitric and the oxygenated muriatic acids on animal and vegetable compounds.

Nature then, every time it can dispose of the necessary principles, tends to form malic acid; and there is no reason to doubt, that if plants were examined when very young, at which time they are all acid, the malic acid would always be found present in them. These successive changes afterwards give birth to the other acids already mentioned, and which may be found by further analyses in animals, as it has been found in vegetables.

XXVII. *On the Property which the Acetic Acid possesses of dissolving Camphor and various essential Oils.*

SIR, *To Mr. Tillock.*

I AM sensible that an apology is necessary for obtruding on you and on your readers a subject which may appear, on first view, to have little claim to general attention. If the rights and privileges of an individual were alone involved on this occasion, I should not have requested a place in your *Magazine* for the following statement. But it is a surely matter of general concern, that the appropriation of inventions and improvements should be dealt, with strict justice, to their authors: for the prospect of this distribution of "honour where it is due" is one of the most animating principles of action; and the extinction of this motive would certainly fol-