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but he fails in accounting for the inequality of the northern and southern, for he supposes the course of the waters to tend equally from both poles towards the equator; which would render the depositions equal on both sides; which is contrary to observation.

VI. *On the Identity of the Pyromucous, Pyrotartareous, and Pyroligneous Acids; and the Necessity of not considering them any longer as distinct Acids.* By C. FOURCROY and VAUQUELIN*.

I. *On the Multiplicity of the Vegetable Acids.*

WHEN Bergman and Scheele had discovered several vegetable and animal acids before unknown, and had destroyed the pretended identity admitted in regard to those bodies, all the chemists employed themselves with great zeal in subjecting various vegetable acid substances to a new examination. The number of compounds, which till then had been reduced to two kinds, increased so much, that it was supposed it would far exceed that of the acids which had been discovered among the fossils, and that it would be impossible to set bounds to the multiplicity of these natural productions of organised bodies.

The four liquors, extracted by distillation from mucous bodies, wood, and tartar, though owing to an artificial decomposition, have been comprehended in the class of the vegetable acids, well characterised as possessing a peculiar nature: some analogies founded on their origin, their brown colour, and their burnt odour, have caused them to be referred to a special genus, under the name of the empyreumatic acids. If we collect the facts which seem to prove that they are different in nature not only from the other acids, but from each other, they will easily show that these acids have not been sufficiently examined to be well known; that chemists had only very imperfect ideas respecting their nature; and that it was for want of accurate analysis that

* From the *Annales de Chimie*, No. 104.

they were thought to be different from each other, and different in their whole nature from any other vegetable acid.

II. *Characters given to the Pyromucous Acid.*

Lemery, Boerhaave, Neumann, Cartheuser, Macquer, and Bucquet, were the first who insisted on the specific characters of that acid which has been called the pyromucous in the Methodical Nomenclature, and which had long been distinguished by the name of *spirit of boney*, of *sugar*, of *manna*, of *gum*, &c. M. Schrikel, in giving a detailed history of the analysis of sugar and of this acid in 1776, greatly enlarged and confirmed the ideas before conceived respecting the peculiar nature of the pyromucous acid, and all chemists have since adopted that opinion. It was characterised by its dark red colour when impure, and its golden yellow colour after being rectified; by its odour of caramel, its very pungent taste, its volatility, nearly similar to that of water; by its action on the skin, which it tinges red, and on the glafs of retorts, which it seems to attack. It was believed to be entirely contained in mucous matters, and to be only developed by fire; it was said to be susceptible of decomposition by heat, and of being converted into gaseous bodies. But, besides that its supposed action on glafs depended only on the adherence and penetration of the charcoal of the sugar; besides the proof, already well established, of its non-existence in saccharine and gummy matters, and of its entire production by fire, it must be allowed that, in examining what has been done in regard to saline compounds and the attractions of the pyromucous acid, no result had been obtained but vague and undetermined notions, which seemed to excite doubt and uncertainty in regard to the particular nature of this acid. The reader will be enabled to judge of the truth of this assertion by perusing, in particular, the details given under the article *Syrupy Acid* of the *Dictionnaire de Chimie Encyclopédique*, where our learned colleague Guyton has collected every thing then known respecting this empyreumatic acid: when drawing up, therefore, the article in my System of Chemical Knowledge, written and printed several months before the discovery now submitted to the Institute, I was

not able to obtain the real distinguishing characters of the pyromucous acid.

III. *Characters ascribed to the Pyrotartareous Acid.*

We are indebted to Lemery and Neumann for our first knowledge of this acid, furnished by distilled tartar, and different from the tartareous acid. They found that tartar, by distillation, gave the fourth of its weight of acid phlegm. According to the prescription of Neumann, it was to be rectified at a gentle heat; but C. Guyton was not able to perform that operation with success, and the retort was always broken by the explosion which took place. The empyreumatic odour and taste of this acid are the two most striking characters which made it be admitted by chemists as a peculiar acid. It is difficult to conceive why Venel should take this acid product of distilled tartar to be nitric acid, which he thought might be extracted alone, and in a state of purity. It is no less astonishing to hear C. Monnet maintain, in consequence of experiments made at some length, that distilled acid of tartar is muriatic acid, though he really found in it, according to his own acknowledgement, only approximative characters. The academicians of Dijon and C. Berthollet, after repeating all the experiments of Monnet, were convinced that there is no real analogy between the acid product of distilled tartar and the muriatic acid. Scheele, in proving that there is always a little real muriatic acid in the alkali of tartar, insisted on the differences between this acid and that of tartar. M. Fontana proved that the acid distilled from tartar can be entirely resolved into carbonic acid gas and carbonated hydrogen gas; so that, by bringing it nearer to all the other vegetable acids, he removed further every idea of confounding it with the mineral acids. In the last place, Guyton, in the first part of the first volume of the *Dictionnaire de Chimie Encyclopédique*, published in 1786, after detailing all the different opinions as well as the principal facts known respecting this acid, concluded that it would be necessary to consider it as a peculiar acid; a product of tartar altered by heat, distinguished from the latter by its being incapable of crystallisation, and by the soluble salt which it

forms with lime; and he called it the tartareous empyreumatic acid. These ideas, adopted in 1787 by the authors of the Methodical Nomenclature, induced them to distinguish this acid by the name of the pyrotartareous acid. Since that period, chemists have continued to consider this acid as a distinct species, and no one has subjected it to a new examination.

IV. Characters given to the Pyroligneous Acid.

Boerhaave first made known, under the name of *acid spirit of wood*, the product distilled from woody bodies; and he even compared it to a kind of vinegar. M. Goetling has given a particular history of it in Crell's Chemical Journal for the year 1779. Guyton made it known afterwards, under the name of the ligneous acid, in the first part of the *Dictionnaire Encyclopédique*, published in 1786. He collected all the information then acquired respecting this acid, according to the experiments made by the Academy of Dijon. Every kind of wood examined has hitherto furnished by distillation the same acid; the difference in regard to colour, flavour, acrid odour, and particularly that of saline compounds, formed by the liquid distilled from wood, have made it to be distinguished from every other acid: in the Methodical Nomenclature it has been called the pyroligneous acid, and in my System of Chemistry I classed it with the pyromucous and pyrotartareous acids, as forming with them a kind of acids composed of species analogous to each other in the ratio of their identic origin, and of some comparative properties manifestly depending on their empyreumatic state. The characters adopted to distinguish the pyro-ligneous acid were, its smoky smell, its reddish colour, its property of giving a lasting stain to wood, the salts which it formed with alkaline bases, and the elective attractions which it obeyed. In giving a systematic explanation of the properties of this acid, as well as in regard to those of the pyromucous and pyrotartareous acid, the want of more accurate knowledge was always felt; characters sufficiently striking and well defined, proper to distinguish these three acids from each other, could not be found; and even after they had been classed together into a distinct genus, on account of their empyreu-

matic nature, which gave them a striking resemblance, when chemists wished to explain what were the peculiarities of each species, they were obliged to acknowledge that the examination of these productions of fire had not been carried to a sufficient length, and that their properties had not been so thoroughly studied as to enable them to assign characters sufficiently striking, and to give a correct history of them.

V. First View of the Acetous Nature of the Empyreumatic Acids.

Such was the uncertain state of the science in regard to the three acids extracted from vegetable matters by fire, when a circumstance, presented, as it were, accidentally, gave us an opportunity of discovering a new fact respecting their nature. In the course of those researches in which C. Vauquelin and myself have been so long engaged respecting the chemical analysis of vegetable substances, and of the experiments which we made on the solid or ligneous parts of plants, we were employed some months in the examination of cork. This epidermal covering of a species of oak had appeared to me, for several years, to be of a nature so very distinct from other vegetable tissues as to deserve a particular research: several experiments on the epidermis of other trees had inclined me to think that in their characters they approached near to cork, - and I thought it my duty to present it as one of the immediate materials of plants under the name of *suber*. Being desirous of carrying my first essays still further, and of giving more extent to these first ideas, we began to employ ourselves this summer on a more exact analysis of cork. Having subjected a pretty large quantity of it, 0.6 lb. (three hectogrammes), to distillation with a naked fire, we obtained from it a fourth of its weight of a very light and volatile oil, and almost the same quantity of a reddish empyreumatic liquid, which exhibited all the apparent characters of the pyroligneous acid. But this acid liquor, when examined with more care, rectified and combined with alkalies, and disengaged from its bases by weak sulphuric acid, soon exhibited properties of real acetous acid, and, after having separated it by slow distillation from the portion of coloured oil
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which it held in solution, it evidently appeared to be that acid.

When this fact was once ascertained, it was not difficult for us to presume that the pyroligneous acid, from whatever wood extracted, could only be acetous acid: we had even reason to suspect that the two other empyreumatic acids were of the same nature; but as a conjecture, however well founded, has no real value in physics, we called in the aid of experiment to enable us to discover the truth, or to reject our opinion as an error.

VI. *New Examination of the Pyromucous, Pyrotartareous, and Pyroligneous Acids.*

1. Having distilled, with great caution, sixteen parts of pure sugar, which furnished us with ten parts and a half of water charged with reddish pyromucous acid, a little more than four parts and a half of light charcoal, and half a part of gas, we combined this acid liquor with lime; the liquor was then evaporated to dryness, and afterwards treated in a retort with weak sulphuric acid. We thus obtained a pretty thick, clear, or very little coloured liquid, having a very sensible acetous smell, and which, when combined with potash, gave a very evident acetite of potash. This salt, indeed, had a dirty gray colour; but, by filtering a warm solution of it through pounded charcoal; it lost the oil which coloured it, and became quite clear.

The acid product, obtained from the first calcareous salt by the sulphuric acid, was already much less coloured than the pyromucous acid; it now retained only very faintly the smell of caramel (pan fugar), which characterises the acetous acid.

When disengaged a second time from alkaline salt by the sulphuric acid, it was still purer, had nothing of its first origin, and now exhaled only a pure acetous odour. We had reason, therefore, to conclude, from these experiments, that the pyromucous acid was nothing else than acetous acid united to an empyreumatic oil arising from the decomposition of the sugar by fire.

The same result took place with acid liquors extracted
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from gums, honey, manna, starch, paper, and several other vegetable substances which are known to yield pyromucous acid by distillation.

2. White and purified tartar gave by the retort nearly a half less of acid liquor, than sugar furnished of pyromucous acid. This tartareous acid product, obtained by a well regulated heat, was almost transparent, and had not the reddish-brown colour of the empyreumatic acids extracted by means of a strong heat. It however had an acrid empyreumatic odour, a heavy and highly coloured oil floated over it, and, notwithstanding its pungent nature, it would have been difficult to ascertain it to be acetous acid by this single experiment: but it did not long deceive us. Having saturated it with potash immediately, on account of its little colour and impurity, we distilled it, after being evaporated to dryness, with diluted sulphuric acid, and it furnished acetous acid, easy to be distinguished as such, without any mixture of empyreuma.

We found that by distilling pyrotartareous acid, even not rectified and in a red state, from off pounded charcoal, previously well lixiviated and carefully dried, it lost by this simple operation its empyreumatic nature: we are even persuaded that mere filtration of this acid warm, through charcoal, several times repeated, would be sufficient to separate from it the oil, and to bring it to the state of acetous acid almost pure.

No doubt, therefore, can remain, that the pyrotartareous acid is acetous acid rendered impure by a portion of empyreumatic oil produced by the decomposition of the tartareous acid by caloric.

3. The pyro-ligneous acid obtained from shavings of beech wood, distilled with care, formed with lime a brown salt not crystallisable. This salt, when treated with very weak sulphuric acid, gave acetous acid, known by its smell, the deliquescent acetite it formed with potash, or the crystallisable acetite obtained from it with soda.

Another portion of the same primitive pyroligneous acid, when immediately united to potash, and filtered in its solution through powdered charcoal, gave an acetite of potash almost colourless, from which weak sulphuric acid disengaged,
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by distillation, very pure acetous acid, almost without empyreumatic odour or fumes.

It must here be observed that the pyroligneous acid, that of the three acids obtained by fire which has the most striking empyreumatic odour and character, is also one of the three most difficult to be purified, and to be carried to the state of very pure vinegar. It does not, therefore, assume the nature of the last, as the tartareous acid does, by filtration alone, nor even by two successive distillations from off powdered charcoal. By employing even the aid of ebullition and strong agitation with charcoal, it cannot be deprived of its oil, while both of these processes succeed with certainty and ease in purifying the pyromucous acid, which, indeed, gives up with most ease its oil; and even in purifying the pyrotartareous acid, though it be a little more difficult to separate its oil than that of the pyromucous acid.

But though it is more refractory in opposing purification, and that kind of analysis of which I here speak, it is no less proved, that the pyroligneous acid, like the two preceding, is only acetous acid impregnated with empyreumatic oil, produced from wood altered by heat.

VII. Artificial Conversion of the pure Acetous Acid into the Pyromucous, Pyrotartareous, and Pyroligneous Acids.

The preceding experiments might be sufficient to make us acquainted with the identic and real acetous nature of the three empyreumatic acids, which have been hitherto considered as forming three distinct acids, and belonging to a genus well characterised. But to these experiments a supplement was still wanting; it was necessary to inquire whether it was not possible to imitate these acids with that of vinegar, by adding what seemed to be added to it in each of these acids produced by fire.

It was before fully proved that each of these products of distillation differed from the other two by an empyreumatic oil united to it by the effect of its distillation alone. It was very easy, therefore, to try to distil vinegar from off oils distilled from a mucilage, tartar, and wood. This trial was attended with all the success that could be expected. Acid
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of vinegar, heated in a retort with each of these three oils, furnished a coloured and odorous product exactly of the same nature as primitive pyromucous, pyrotartareous, and pyroligneous acids: the odour and smell of these acids were very perceptible; only these factitious empyreumatic acids were a little stronger and sourer than those arising from distillation, but nothing more was necessary to carry them to the same state of weakness than to add to them a little water.

By repeated trial we obtained a manner of forming with the acid of vinegar the three empyreumatic acids much speedier, and in a more simple manner, than by distillation. We found that it was sufficient to throw some drops of the empyreumatic oil of mucilages, of tartar, or of wood, into the acetous acid, to suffer them to remain some time together, or to shake them strongly, to imitate these acids made by fire. The oil almost immediately unites with the acid, dissolves in it, gives it a red or brown colour, and communicates to it, at the same time, the acrid odour and bitter pungent taste known in the pyromucous, pyrotartareous, and pyroligneous acids.

The acetous acid is then a real solvent of empyreumatic oils, and in that case it assumes the characters of the acid liquors or odorous spirits, as they were formerly called, which issue from vegetable matters treated by fire. To separate these oils dissolved in the acetous acid, and to bring back the latter to its purity and to its primitive simplicity, the same means must be employed as for freeing the acetous acid from the empyreumatic acids united to it when obtained by distillation, *viz.* filtration, agitation, ebullition with charcoal, union with lime and alkalies, and the disengagement of these combinations by weak sulphuric acid.

It is to this solubility of oils in the acetous acid, that the odour which this acid so easily acquires and retains seems to be owing: it is to it that we must ascribe the distinction of a great number of empyreumatic acids, which several chemists have been induced to make, and which they could not avoid doing, while continuing to consider, in the acid products of distilled vegetable matters, the odour, colour, and flavour, as characters proper, if not for positively ascertaining,
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at least for conjecturing them to be acids different from each other; and especially by comparing these characters in acid products furnished by kinds of wood very different in their properties, and consequently in their products.

VIII. *Reflections on the Frequency and the Nature of the different Processes which furnish Acetous Acid.*

After having proved that mucilages, saccharine bodies, fæculæ, as well as wood and tartareous compounds, give by distillation real acetous acid, concealed in the products of each of these bodies by a portion of oil, having a peculiar odour, smell, and colour, and that, consequently, we ought to deduct from the number of the vegetable acids these three empyreumatic acids, we thought it might be useful to science to give some observations here on the production of the acetous acid. The knowledge which the chemical art possesses at present respecting this production, though much more extensive than formerly, has never yet been collected into any work; it may, however, be of great importance in vegetable analysis: such is the motive which induced us to present a short view of it, without, however, entering into all the details which the subject might require in a systematic work.

The formation of the acetous acid, which has always been believed to be necessarily produced by a fermentation peculiar to vinous liquors, is so frequent in the processes of art and the operations of nature, that it is indispensably necessary to make it a general phenomenon, and to study this phenomenon under the name of *acetification*, as proper to throw light on the chemical properties of organised bodies. We may consider it either in regard to substances, susceptible of acetification, or in regard to circumstances which favour transformation into acetous acid.

Under the first point of view, besides vinous liquors, which were first found, and long thought to be, the only ones capable of acetification, we have found a multitude of bodies susceptible of experiencing this change. There is scarcely any vegetable extract in which acetites are not found: sap, if it has been kept only a few hours, contains some of it;

even different kinds of mould itself are charged with it, as may be easily proved by distilling them with a little diluted sulphuric acid: tan, when heated, emits an odour of vinegar, and furnishes some of it by the same treatment: water in which pulse, cabbages, carrots, turnips, potatoes, cucumbers, the pods of French beans, &c. have been steeped and grown sour, is exceedingly acetous: the water from the starch manufactories is the same: the juices of acid fruits, those of apples, pears, gooseberries, strawberries, raspberries, cherries, oranges, and lemons, when exposed some hours to the warm air, assume, along with a strong and pungent odour, a taste differently and more strongly acid than that which they had naturally; besides perceiving in them acetous acid, you will obtain it pure and insulated by subjecting these juices to distillation. It is well known from the experiments of Scheele, that milk in becoming sour gives acetous acid; we have found that bouilli and animal jelly form this acid also: in a word, we have said in other memoirs that the urine of the mammifera, and that of man in particular, had the property of becoming acetous, and gave a great quantity of very strong acid by distillation.

Thus the number of the substances susceptible of acetification is very considerable: extractive matter, mucilage, saccharine bodies, fæcula, and starch; even ligneous bodies, tan, the greater part of the primitive vegetable acids, the gelatin of animals, the caseous matter, and even *urée*, that body peculiar to urine, and which characterises it by its remarkable properties, all these products of vegetable and animal organisation and life are equally susceptible of acetification.

It is true, that the circumstances under which we have presented their conversion into acetous acid, seem all to belong to a fermentation, and that it might be thought that they follow a formation more or less striking or fugitive of vinous matter, but it remains for us to show that these matters may be acetified by phenomena or causes different from fermentation; and this fact is already proved by the acid productions of the distillation, which form the principal subject of this memoir. It is here seen that the action of fire really acetifies gums, mucilages, tartrites, wood. A know-
ledge

ledge of the chemical phenomena exhibited by vegetable substances in regard to their acidification in general, enables us to observe and distinguish four circumstances which promote their acetification or conversion into acetous acid.

The first is, the decomposing action of the fire in distillation. Without here entering into more extensive details on this subject, which, when we consider the object of this memoir, are less necessary, we shall content ourselves with observing, that this action of caloric, by disuniting the constituent principles of vegetable matters, combines a part of them in such a manner as to give birth to acetous acid; and that this conversion is accompanied with the formation of water, the formation and disengagement of gaseous carbonic acid, and the precipitation of carbon in the state of charcoal.

The second mode of acetification of vegetable compounds is that arising from the action of powerful acids, and particularly of the sulphuric, the nitric, and the oxygenated muriatic on these compounds. This kind of production takes place in gums, sugar, extracts, and gelatin, when treated by acids; the greater part of the other vegetable acids, and even alcohol itself, often experience such a change by the decomposing influence of the acids above mentioned. While this kind of acetification takes place, there are formed also water and carbonic acid; sometimes carbon likewise is deposited. We must here add, that this acetification is the last term of vegetable acidification in general, since in treating acetous acid by the same decomposing action of the mineral acids, you destroy its acetous nature, and make it pass to the state of water and carbonic acid, as is the case in every vegetable decomposition carried to its *maximum*.

The third mode of acetification is the oldest known of the whole, and the only one formerly admitted: it is the acetous fermentation that converts all the different kinds of wine into vinegar: in this there is neither a precipitation of carbon, nor disengagement of carbonic acid. It is well known that it takes place in consequence of an absorption of the oxygen of the atmosphere, and that it supposes the preexistence of vinous liquors.

In the last place, we consider as the fourth and last mode

of acetification, a kind of peculiar fermentation, which does not require the presence of wine, which takes place in matters foreign to the nature of vinous liquors, and which has some relation to putrid decomposition. It is that observed in animal liquors abandoned to themselves, and particularly in urine.

Each of these modes of acetification, though equally giving birth to acetous acid, and supposing the same composition from which that acid arises, since it is the same in every case when it has been purified, admits, however, a difference in the products which accompany it. Each of the acetous acids arising from it, presents indeed a specific character proper for making it known and for indicating the source which has given birth to it.

Thus, 1st, The acetous acid obtained by fire is empyreumatic; it holds in solution an acrid oil, which gives it a peculiar odour, colour, and flavour.

2d, Factitious acetous acid, produced by the action of other acids, is characterised by the presence of the malic, or of the oxalic acid, formed at the same time as itself, and by its weakness, depending on the proportion of the water, which is also formed with the three preceding acids.

3d, The acetous acid arising from wine contains tartar, alcohol, and a colouring matter, which give it a peculiar character. It is, as has been said, a spirituous acid.

4th, In the last place, the acetous acid produced by putrid fermentation is always united, in whole or partially, to ammonia, which, like it, arises from this septic commotion.

But whatever may be the matters or new compounds united to the acetous acid formed under any of the four circumstances abovementioned, this acid, capable of being separated with greater or less ease from each of these substances, is always the same, and always similar to that extracted from sour wine by the help of distillation.

It must therefore be now admitted that the acetous acid is not the sole and necessary product of the fermentation of wine, and that its production, exceedingly frequent, is one of the most constant phenomena of vegetable and animal analysis.