

IX. *An Account of some Experiments and Observations on the constituent Parts of certain astringent Vegetables; and on their Operation in Tanning.* By Humphry Davy, Esq. Professor of Chemistry in the Royal Institution. Communicated by the Right Hon. Sir Joseph Banks, Bart. K. B. P. R. S.

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THE discovery made by M. SEGUIN, of a peculiar vegetable matter which is essential to the tanning of skin, and which is possessed of the property of precipitating gelatine from its solutions, has added considerably to our knowledge of the constituent parts of astringent vegetables.

Mr. PROUST has investigated many of the properties of this substance; but, though his labours, and those of other chemists, have led to various interesting observations, yet they are far from having exhausted the subject. The affinities of tannin have been hitherto very little examined; and the manner in which its action upon animal matters is modified by combination with other substances, has been scarcely at all studied.

At the desire of the Managers of the Royal Institution, I began, in September, 1801, a series of experiments on the substances employed in the process of tanning, and on the chemical agencies concerned in it. These experiments have occupied, ever since, a considerable portion of my leisure hours; and I now presume to lay before the Royal Society an account of their general results. My chief design was, to attempt to elucidate the

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practical part of the art; but, in pursuing it, I was necessarily led to general chemical inquiries concerning the analysis of the different vegetable substances containing tannin, and their peculiar properties.

#### I. OBSERVATIONS ON THE ANALYSIS OF ASTRINGENT VEGETABLE INFUSIONS.

The substances that have been supposed to exist most generally in astringent infusions are, tannin, gallic acid, and extractive matter.

The presence of tannin in an infusion, is denoted by the precipitate it forms with the solution of glue, or of isinglass. And, when this principle is wholly separated, if the remaining liquor gives a dark colour with the oxygenated salts of iron, and an immediate precipitate with the solutions of alum and of muriate of tin, it is believed to contain gallic acid, and extractive matter.

The experiments of MM. FOURCROY, VAUQUELIN, and SEGUIN, have shown that many astringent solutions undergo a change by exposure to the atmosphere; an insoluble matter being precipitated from them. A precipitation is likewise occasioned in them by the action of heat; and these circumstances render it extremely difficult to ascertain, with any degree of precision, the quantities of their constituent parts, as they exist in the primitive combination.

After trying several experiments on different methods of ascertaining the quantity of tannin in astringent infusions, I was induced to employ the common process of precipitation by gelatine, as being the most accurate.

This process, however, requires many precautions. The tanning principle in different vegetables, as will be seen hereafter, demands for its saturation different proportions of gelatine; and

the quantity of the precipitate obtained by filtration, is not always exactly proportional to the quantities of tannin and gelatine in solutions, but is influenced by the degree of their concentration. Thus, I found that 10 grains of dry isinglass, dissolved in two ounces of distilled water, gave, with solution of galls in excess, a precipitate weighing, when dry, 17 grains; whilst the same quantity, dissolved in six ounces of water, produced, all other circumstances being similar, not quite 15 grains. With more diluted solutions, the loss was still greater; and analogous effects took place, when equal portions of the same solution of isinglass were acted on by equal portions of the same infusion of galls diluted in different degrees with water; the least quantity of precipitate being always produced by the least concentrated liquor. In all cases, when the weak solutions were used, it was observed, that the residual fluid, though passed two or three times through the filtre, still remained more or less turbid and opaque; so that it is most likely that the deficiency arose from the continued suspension of some of the minutely divided solid matter in the liquid mass.

The solutions of gelatine, for the purposes of analysis, should be employed only when quite fresh, and in as high a state of saturation as is compatible with their perfect fluidity. I have observed, that in cases when they approach towards the state of jelly, their power of acting upon tannin is materially altered, and they produce only a very slight precipitation. As the degree of fluidity of solutions of gelatine is influenced by their temperature, I have found it expedient, in all comparative experiments, to bring them and the astringent infusions on which they are designed to act, as nearly as possible to a common degree of heat. My standard temperature has been between 60

and 70° FAHRENHEIT; and the solutions of gelatine that I have used, were made by dissolving 120 grains of isinglass in 20 ounces of water.

In ascertaining the proportions of tannin in astringent infusions, great care must be taken to prevent the presence of any excess of gelatine; for, when this excess exists, I have found that a small portion of the solid compound formed is redissolved, and the results of the experiment otherwise affected. It is not difficult to discover the precise point of saturation, if the solution of isinglass be added only in small quantities at a time, and if portions of the clear liquor be passed through a filtre at different periods of the process. The properties of these portions will indicate the quantities of the solution of gelatine required for the completion of the experiment.

That the composition of any precipitate containing tannin and gelatine may be known with a tolerable degree of precision, it is necessary that the isinglass employed in the solution, and the new compound formed, be brought as nearly as possible to the same degree of dryness. For this purpose, I have generally exposed them, for an equal time, upon the lower plate of a sand-bath, which was seldom heated to more than 150°. This method I have found much better than that of drying at the temperatures of the atmosphere, as the different states of the air, with regard to moisture, materially influence the results.

Mr. HATCHETT has noticed, in his excellent Paper on Zoophytes, &c.\* that isinglass is almost wholly composed of gelatine. I have found, that 100 grains of good and dry isinglass contain rather more than 98 grains of matter soluble in water. So that, when the quantity of isinglass, in any solution employed for

\* Phil. Trans. for 1800, page 327.

acting upon an astringent infusion, is compared with the quantity of the precipitate obtained, the difference between them will indicate the proportion of tannin, as it exists in the combination.

After the tannin has been separated from an astringent infusion, for the purpose of ascertaining its other component parts, I have been accustomed to evaporate the residual liquor very slowly, at a temperature below 200°.\* In this process, if it contains extractive matter, that substance is in part rendered insoluble, so as to fall to the bottom of the vessel. When the fluid is reduced to a thick consistence, I pour alcohol upon it. If any gallic acid or soluble extractive matter be present, they will be dissolved, after a little agitation, in the alcohol; whilst the mucilage, if any exist, will remain unaltered, and may be separated from the insoluble extract, by lixiviation with water.

I have made many experiments, with the hope of discovering a method by which the respective quantities of gallic acid and extractive matter, when they exist in solution in the alcohol, may be ascertained; but without obtaining success in the results. It is impossible to render the whole of any quantity of extractive matter insoluble by exposure to heat and air, without at the same time decomposing a portion of the gallic acid. That acid cannot be sublimed, without being in part destroyed; and, at the temperature of its sublimation, extractive matter is wholly converted into new products.

Ether dissolves gallic acid; but it has comparatively little

\* M. DEYBUX has shewn, (*Annales de Chimie*, Tome XVII. page 36,) that in the process of evaporating solutions of galls, no gallic acid is carried over by the water, at a temperature below that of ebullition. Many astringent infusions, however, lose a portion of their aromatic principle, even in cases when they are not made to boil; but this substance, though evident to the smell, in the water that comes over, cannot be detected by chemical reagents.

action upon extractive matter. I have been able, in examining solutions of galls, to separate a portion of gallic acid by means of ether. But, when the extractive matter is in large quantities, this method does not succeed, as, in consequence of that affinity which is connected with mass,\* the greatest part of the acid continues to adhere to the extract.

Alumine has a strong attraction for extractive matter; but comparatively a weak one for gallic acid.† When carbonate of alumine is boiled for some time with a solution containing extractive matter, the extractive matter is wholly taken up by the earth, with which it forms an insoluble compound; but, into this compound, some of the gallic acid appears likewise to enter; and the portion remaining dissolved in the solution is always combined with alumine.

I have not, in any instance, been able to separate gallic acid and extractive matter perfectly from each other; but I have generally endeavoured to form some judgment concerning their relative proportions, by means of the action of the salts of alumine, and the oxygenated salts of iron. Muriate of alumine precipitates much of the extractive matter from solutions, without acting materially upon gallic acid; and, after this precipitation, some idea may be formed concerning the quantity of the gallic acid, by the colour it gives with the oxygenated sulphate of iron. In this process, however, great care must be taken not to add the solution of the sulphate of iron in excess; for, in this case, the black precipitate formed with the gallic acid will be redissolved, and a clear olive-coloured fluid only will be obtained.

\* See BERTHOLLET, *Récherches sur les Lois de l'Affinité*. *Mém. de l'Institut National*. Tome III. p. 5.

† See FIEDLER, *Journal de Chimie*, par J. B. VAN-MONS, Tome I. pag. 85.

The saline matters in astringent infusions, adhere so strongly to the vegetable principles, that it is impossible to ascertain their nature with any degree of accuracy, by means of common reagents. By incineration of the products obtained from the evaporation of astringent infusions, I have usually procured carbonate of lime and carbonate of potash.

In the different analyses, as will be seen from the results given in the following sections, I have attended chiefly to the proportions of the tanning principle, and of the principles precipitable by the salts of iron, as being most connected with practical applications.

With regard to the knowledge of the nature of the different substances, as they exist in the primitive astringent infusion, we can gain, by our artificial methods of examination, only very imperfect approximations. In acting upon them by reagents, we probably, in many cases, alter their nature; and very few of them only can be obtained in an uncombined state. The comparison, however, of the products of different experiments with each other, is always connected with some useful conclusions; and the accumulation of facts with regard to the subject, must finally tend to elucidate this obscure but most interesting part of chemistry.

## II. EXPERIMENTS ON THE INFUSIONS OF GALLS.

I have been very much assisted in my inquiries concerning the properties of the infusions of galls, by the able Memoir of M. DEYEUX, on galls.\*

The strongest infusion of galls that I could obtain, at 56°

\* *Annales de Chimie*, Tome XVII. pag. 1.

FAHRENHEIT, by repeatedly pouring distilled water upon the best Aleppo galls broken into small pieces, and suffering it to remain in contact with them till the saturation was complete, was of the specific gravity 1.068. Four hundred grains of it produced, by evaporation at a temperature below 200°, fifty-three grains of solid matter; which, as well as I could estimate, by the methods of analysis that have been just described, consisted of about  $\frac{2}{10}$  of tannin, or matter precipitable by gelatine, and  $\frac{1}{10}$  of gallic acid, united to a minute portion of extractive matter.

100 grains of the solid matter obtained from the infusion, left, after incineration, nearly  $4\frac{3}{4}$  grains of ashes; which were chiefly calcareous matter, mixed with a small portion of fixed alkali. The infusion strongly reddened paper tinged with litmus. It was semitransparent, and of a yellowish-brown colour. Its taste was highly astringent.

When sulphuric acid was poured into the infusion, a dense whitish precipitate was produced; and this effect was constant, whatever quantity of the acid was used. The residual liquor, when passed through the filtre, was found of a shade of colour deeper than before. It precipitated gelatine, and gave a dark colour with the oxygenated sulphate of iron.

The solid matter remaining on the filtre, slightly reddened vegetable blues; and, when dissolved in warm water, copiously precipitated the solutions of isinglass. M. PROUST,\* who first paid attention to its properties, supposes that it is a compound of the acid with tannin: but I suspect that it also contains gallic acid, and probably a small portion of extractive matter.

\* The fact of the precipitation of solution of galls by acids, was noticed by M. DIZE'. See *Annales de Chimie*, Tome XXXV. p. 37.



This last substance, as is well known, is thrown down from its solutions by sulphuric acid; and I found, in distilling the precipitate from galls by sulphuric acid, at a heat above  $212^{\circ}$ , that a fluid came over, of a light yellow colour, which was rendered black by oxygenated sulphate of iron; but which was not altered by gelatine.

Muriatic acid produced, in the infusion, effects analogous to those produced by sulphuric acid; and two compounds of the acid and the vegetable substances were formed: the one united to excess of acid, which remained in solution; the other containing a considerable quantity of tannin, which was precipitated in the solid form.

When concentrated nitric acid was made to act upon the infusion, it was rendered turbid; but the solid matter formed was immediately dissolved with effervescence, and the liquor then became clear, and of an orange colour. On examining it, it was found that both the tannin and the gallic acid were destroyed; for it gave no precipitate, either with gelatine or the salts of iron, even after the residual nitric acid was saturated by an alkali. By evaporation of a portion of the fluid, a soft substance was obtained, of a yellowish-brown colour, and of a slightly sourish taste. It was soluble in water, and precipitated the nitro-muriate of tin, and the nitrate of alumine; so that its properties approached to those of extractive matter; and it probably contained oxalic acid, as it rendered turbid a solution of muriate of lime.

When a very weak solution of nitric acid was mixed with the infusion, a permanent precipitate was formed; and the residual liquor, examined by the solution of gelatine, was found to contain tannin.

A solution of pure potash was poured into a portion of the

infusion. At first, a faint turbid appearance was perceived; but, by agitation, the fluid became clear, and its colour changed from yellow brown to brown red; and this last tint was most vivid on the surface, where the solution was exposed to the atmosphere. The solution of isinglass did not act upon the infusion modified by the alkali, till an acid was added in excess, when a copious precipitation was occasioned.

The compound of potash and solution of galls, when evaporated, appeared in the form of an olive-coloured mass, which had a faint alkaline taste, and which slowly deliquesced when exposed to the air.

Soda acted upon the infusion in the same manner as potash; and a fluid was formed, of a red-brown colour, which gave no precipitate to gelatine.

Solution of ammonia produced the same colour as potash and soda, and formed so perfect an union with the tannin of the infusion, that it was not acted upon by gelatine. When the compound liquor was exposed to the heat of boiling water, a part of the ammonia flew off, and another part reacted upon the infusion, so as to effect a material change in its properties. A considerable quantity of insoluble matter was formed; and the remaining liquor contained little tannin and gallic acid, but a considerable portion of a substance that precipitated muriate of tin, and the salts of alumine.

When the experiment on the ebullition of the compound of the infusion and ammonia was made in close vessels, the liquor that came over was strongly impregnated with ammonia; its colour was light yellow, and, when saturated with an acid, it was very little altered by the salts of iron. The residual fluid, after the process had been continued for some time, as in the

other case, precipitated gelatine slightly, but the salts of alumine copiously; and it gave a tinge of red to litmus paper.

When solution of lime, of strontia, or of barytes, was poured in excess into a portion of the infusion, a copious olive-coloured precipitate was formed, and the solution became almost clear, and of a reddish tint. In this case, the tannin, the gallic acid, and the extractive matter, seemed to be almost wholly carried down in the precipitates; as the residual fluids, when saturated by an acid, gave no precipitate to gelatine, and only a very slight tint of purple to oxygenated sulphate of iron.

When the solutions of the alkaline earths were used only in small quantities, the infusion being in excess, a smaller quantity of precipitate was formed, and the residual liquor was of an olive-green colour; the tint being darkest in the experiment with the barytes, and lightest in that with the lime. This fluid, when examined, was found to hold in solution a compound of gallic acid and alkaline earth. It became turbid when acted on by a little sulphuric acid; and, after being filtrated, gave a black colour with the solutions of iron, but was not acted upon by gelatine.

When a large proportion of lime was heated for some time with the infusion, it combined with all its constituent principles, and gave, by washing, a fluid which had the taste of lime-water, and which held in solution only a very small quantity of vegetable matter. Its colour was pale yellow; and, when saturated with muriatic acid, it did not precipitate gelatine, and gave only a slight purple tinge to the solutions of the salts of iron. The lime in combination with the solid matter of the infusion, was of a fawn colour. It became green at its surface, where it was exposed to the air; and, when washed with large quantities of water,

it continued to give, even to the last portions, a pale yellow tinge.

Magnesia was boiled in one portion of the infusion for a few hours; and mixed in excess with another portion, which was suffered to remain cold. In both cases, a deep green fluid was obtained, which precipitated the salts of iron, but not the solutions of gelatine; and the magnesia had acquired a grayish-green tint. Water poured upon it became green, and acquired the properties of the fluid at first obtained. After long washing, the colour of the magnesia changed to dirty yellow; and the last portions of water made to act upon it were pale yellow, and altered very little the solutions of iron.

When the magnesia was dissolved in muriatic acid, a brownish and turbid fluid was obtained, which precipitated gelatine and the oxygenated salts of iron. So that there is every reason to believe, that the earth, in acting on the astringent infusion, had formed two combinations; one containing chiefly gallic acid, which was easily soluble in water; the other containing chiefly tannin, which was very difficultly soluble.

Alumine boiled with the infusion became yellowish-gray, and gave a clear white fluid, which produced only a tinge of light purple in the solutions of iron. When the earth\* was employed in very small quantity, however, it formed an insoluble compound only with the tannin and the extract; and the residual liquor was found to contain a gallate of alumine with excess of acid.

The oxides of tin and of zinc, obtained by nitric acid, were boiled with separate portions of the infusion for two hours. In both cases, a clear fluid, which appeared to be pure water, was

\* Mr. FIEDLER, I believe, first observed the action of alumine upon tannin. VAN-MONS'S Journal, Vol. I. page 86.

obtained; and the oxides gained a tint of dull yellow. A part of each of them was dissolved in muriatic acid. The solution obtained was yellow: it copiously precipitated gelatine; and gave a dense black with the salts of iron. Mr. PROUST,\* who first observed the action of oxide of tin upon astringent infusions, supposes that portions of tannin and gallic acid are decomposed in the process, or converted, by the oxygen of the oxide, into new substances. These experiments do not, however, appear to confirm the supposition.

M. DEYEUX observed, that a copious precipitation was occasioned in infusion of galls, by solutions of the alkalis combined with carbonic acid. Mr. PROUST has supposed that the solid matter formed is pure tannin, separated from its solution by the stronger affinity of the alkali for water; and he recommends the process, as a method of obtaining tannin.

In examining the precipitate obtained by carbonate of potash fully combined with carbonic acid, and used to saturation, I have not been able to recognise in it the properties which are usually ascribed to tannin: it is not possessed of the astringent taste; and it is but slightly soluble in cold water, or in alcohol. Its solution acts very little upon gelatine, till it is saturated with an acid; and it is not possessed of the property of tanning skin.

In various cases, in which the greatest care was taken to use no excess, either of the astringent infusion or of the alkaline solution, I have found the solid matter obtained possessed of analogous properties; and it has always given, by incineration, a considerable portion of carbonate of potash, and a small quantity of carbonate of lime.

The fluid remaining after the separation of the precipitate,

\* *Annales de Chimie*, Tome XLII. p. 69.

was of a dark-brown colour, and became green at the surface, when it was exposed to the air. It gave no precipitate to solution of gelatine; and afforded only an olive-coloured precipitate with the salts of iron.

When muriatic acid was poured into the clear fluid, a violent effervescence was produced; the fluid became turbid; a precipitate was deposited; and the residual liquor acted upon gelatine and the salts of iron, in a manner similar to the primitive infusion.

M. DEYEUX, in distilling the precipitate from infusion of galls by carbonate of potash, obtained crystals of gallic acid. In following his process, I had similar results; and a fluid came over, which reddened litmus-paper, and precipitated the salts of iron black, but did not act upon gelatine.

When the precipitate by carbonate of potash was acted upon by warm water, applied in large quantities, a considerable portion of it was dissolved; but a part remained, which could not in any way be made to enter into solution; and its properties were very different from those of the entire precipitate. It was not at all affected by alcohol: it was acted on by muriatic acid, and partially dissolved; and the solution precipitated gelatine and the salts of iron. It afforded, by incineration, a considerable portion of lime, but no alkali.

In comparing these facts, it would seem, that the precipitate from infusion of galls, consists partly of tannin and gallic acid united to a small quantity of alkali, and partly of these vegetable matters combined with calcareous earth; and it will appear probable, when the facts hereafter detailed are examined, that both the potash and the lime are contained in these compounds in a state of union with carbonic acid.

The solutions of carbonate of soda and of carbonate of

ammonia, both precipitated the infusion of galls in a manner similar to the carbonate of potash; and each of the precipitates, when acted on by boiling water, left a small quantity of insoluble matter, which seemed to consist chiefly of tannin and carbonate of lime.

The entire precipitate by carbonate of soda produced, when incinerated, carbonate of soda and carbonate of lime. The precipitate by carbonate of ammonia, when exposed to a heat sufficient to boil water, in a retort having a receiver attached to it, gave out carbonate of ammonia, (which was condensed in small crystals in the neck of the retort,) and a yellowish fluid, which had the strong smell and taste of this volatile salt. After the process of distillation, the solid matter remaining was found of a dark brown colour; a part of it readily dissolved in cold water, and the solution acted on gelatine.

The residual fluid of the portions of the infusion which had been acted on by the carbonates of soda and of ammonia, as in the instance of the carbonate of potash, gave no precipitate with gelatine, till they were saturated with an acid; so that, in all these cases, the changes are strictly analogous.

The infusion of galls, as appears from the analysis, contains in its primitive state calcareous matter. By the action of the mild alkalis, this substance is precipitated in union with a portion of the vegetable matter, in the form of an insoluble compound. The alkalis themselves, at the same time, enter into actual combination with the remaining tannin and gallic acid; and a part of the compound formed is precipitated, whilst another part remains in solution.

When the artificial carbonates of lime, magnesia, and barytes, were separately boiled with portions of the infusion of galls for

some hours, they combined with the tannin contained in it, so as to form with it insoluble compounds; and, in each case, a deep green fluid was obtained, which gave no precipitate to gelatine, even when an acid was added, but which produced a deep black colour in the solutions of the salts of iron.

Sulphate of lime, when finely divided, whether natural or artificial, after having been long heated with a small quantity of the infusion, was found to have combined with the tannin of it, and to have gained a faint tinge of light brown. The liquid became of a blue-green colour, and acted upon the salts of iron, but not upon gelatine; and there is every reason to suppose, that it held in solution a triple compound, of gallic acid, sulphuric acid, and lime.

We owe to Mr. PROUST, the discovery that different solutions of the neutral salts precipitate the infusion of galls; and he supposes, that the precipitation is owing to their combining with a portion of the water which held the vegetable matter in solution. In examining the solid matters thrown down from the infusion, by sulphate of alumine, nitrate of potash, acetite of potash, muriate of soda, and muriate of barytes, I found them soluble, to a certain extent, in water, and possessed of the power of acting upon gelatine. From the products given by their incineration, and by their distillation, I am however inclined to believe that they contain, besides tannin, a portion of gallic acid and extractive matter, and a quantity of the salt employed in the primitive solution.

It is well known, that many of the metallic solutions occasion dense precipitates in the infusion of galls; and it has been generally supposed, that these precipitates are composed of tannin and extractive matter, or of those two substances and gallic acid, united



to the metallic oxide ; but, from the observation of different processes of this kind, in which the salts of iron and of tin were employed, I am inclined to believe, that they contain also a portion of the acid of the saline compound.

When the muriate of tin was made to act upon a portion of the infusion, till no more precipitation could be produced in it, the fluid that passed through the filtre still acted upon gelatine, and seemed to contain no excess of acid ; for it gave a precipitate to carbonate of potash, without producing effervescence. The solid compound, when decomposed by sulphuretted hydrogen, after the manner recommended by Mr. PROUST, was found strongly to redden litmus-paper, and it copiously precipitated nitrate of silver ; whereas, the primitive infusion only rendered it slightly turbid ; so that there is every reason to believe, that the precipitate contained muriatic acid.

By passing the black and turbid fluid, procured by the action of solution of oxygenated sulphate of iron in excess upon a portion of the infusion, through finely-divided pure flint, contained in four folds of filtrating paper, I obtained a light olive-green fluid, in which there was no excess of sulphuric acid, and which I am inclined to suppose was a solution of the compound of gallic acid and sulphate of iron, with superabundance of metallic salt. I have already mentioned that gallic acid, when in very small proportion, does not precipitate the oxygenated salts of iron ; and Mr. PROUST, in his ingenious Paper upon the Difference of the Salts of Iron, has supposed that, in the formation of ink, a portion of the oxide of iron in union with gallic acid is dissolved by the sulphuric acid of the sulphate. This comes near to the opinion that they form a triple compound : and, in reasoning upon the general phenomena, it seems fair to

conclude, that, in the case of the precipitation of tannin by the salts of tin and of iron, compounds are formed, of tannin and the salts; and that, of these compounds, such as contain tin are slightly soluble in water, whilst those that contain iron are almost wholly insoluble.

In examining the action of animal substances upon the infusion of galls, with the view of ascertaining the composition of the compounds of gelatine, and of skin, with tannin, I found that a saturated solution of gelatine, which contained the soluble matter of 50 grains of dry isinglass, produced from the infusion a precipitate that weighed nearly 91 grains; and, in another instance, a solution containing 30 grains of isinglass, gave about 56 grains; so that, taking the mean of the two experiments, and allowing for the small quantity of insoluble matter in isinglass, we may conclude, that 100 grains of the compound of gelatine and tannin, formed by precipitation from saturated solutions, contain about 54 grains of gelatine, and 46 of tannin.

A piece of dry calf-skin, perfectly free from extraneous matter, that weighed 180 grains, after being prepared for tanning by long immersion in water, was tanned in a portion of the infusion, being exposed to it for three weeks. When dry, the leather weighed 295 grains: so that, considering this experiment as accurate, leather quickly tanned by means of an infusion of galls, consists of about 61 grains of skin, and 39 of vegetable matter, in 100 grains.

After depriving a portion of the infusion of all its tanning matter, by repeatedly exposing it to the action of pieces of skin, I found that it gave a much slighter colour to oxygenated sulphate of iron, than an equal portion of a similar infusion which had been immediately precipitated by solution of isinglass;

but I am inclined to attribute this effect, not to any absorption of gallic acid by the skin, but rather to the decomposition of it by the long continued action of the atmosphere; for much insoluble matter had been precipitated, during the process of tanning, and the residuum contained a small portion of acetous acid.

In ascertaining the quantity of tannin in galls, I found that 500 grains of good Aleppo galls gave, by lixiviation with pure water till their soluble parts were taken up, and subsequent slow evaporation, 185 grains of solid matter. And this matter, examined by analysis, appeared to consist,

Of tannin	-	-	-	-	130 grains.
Of mucilage, and matter rendered insoluble by evaporation	-	-	-	-	12
Of gallic acid, with a little extractive matter	-	-	-	-	31
Remainder, calcareous earth and saline matter	-	-	-	-	12

The fluid obtained by the last lixiviation of galls, as M. DEYEUX observed, is pale green; and I am inclined to believe, that it is chiefly a weak solution of gallate of lime. The ashes of galls, deprived of soluble matter, furnish a very considerable quantity of calcareous earth. And the property which M. DEYEUX discovered in the liquor of the last lixiviations, of becoming red by the action of acids, and of regaining the green colour by means of alkalis, I have observed, more or less, in all the soluble compounds containing gallic acid and the alkaline earths.

### III. EXPERIMENTS AND OBSERVATIONS ON CATECHU OR TERRA JAPONICA.

The extract called catechu is said to be obtained from the wood of a species of the *Mimosa*,\* which is found abundantly in India, by decoction and subsequent evaporation.

There are two kinds of this extract; one is sent from Bombay, the other from Bengal; and they differ from each other more in their external appearance than in their chemical composition. The extract from Bombay is of an uniform texture, and of a red-brown tint, its specific gravity being generally about 1.39. The extract from Bengal is more friable, and less consistent; its colour is like that of chocolate externally, but, when broken, its fracture presents streaks of chocolate and of red-brown. Its specific gravity is about 1.28. Their tastes are precisely similar, being astringent, but leaving in the mouth a sensation of sweetness. They do not deliquesce, or apparently change, by exposure to the air.

The discovery of the tanning powers of catechu, is owing to the President of the Royal Society, who, concluding from its sensible properties that it contained tannin, furnished me, in December, 1801, with a quantity for chemical examination.

In my first experiments, I found that the solutions of catechu copiously precipitated gelatine, and speedily tanned skin; and, in consequence, I began a particular investigation of their properties.

The strongest infusions and decoctions of the two different kinds of catechu, do not sensibly differ in their nature, or in their composition. Their colour is deep red-brown, and they

\* See KERR. *Medical Observations*, Vol. V. page 155.

communicate this tinge to paper; they slightly redden litmus-paper; their taste is highly astringent, and they have no perceptible smell.

The strongest infusions that I could obtain from the two kinds of catechu, at  $48^{\circ}$  FAHRENHEIT, were of the same specific gravity, 1.057. But, by long decoction, I procured solutions of 1.102, which gave, by evaporation, more than  $\frac{1}{6}$  of their weight of solid matter.

Five hundred grains of the strongest infusion of catechu from Bombay, furnished only 41 grains of solid matter; which, from analysis, appeared to consist of 34 grains of tannin, or matter precipitable by gelatine, and 7 grains that were chiefly a peculiar extractive matter, the properties of which will be hereafter described. The quantity of solid matter given by the strongest infusion of the Bengal catechu, was the same, and there was no sensible difference in its composition. Portions of these solid matters, when incinerated, left a residuum which seemed to be calcareous; but it was too small in quantity to be accurately examined, and it could not have amounted to more than  $\frac{1}{200}$  of their original weights.

The strongest infusions of catechu acted upon the acids and pure alkalis in a manner analogous to the infusion of galls. With the concentrated sulphuric and muriatic acids, they gave dense light fawn coloured precipitates. With strong nitrous acid they effervesced; and lost their power of precipitating the solutions of isinglass, and the salts of iron. The pure alkalis entered into union with their tannin, so as to prevent it from being acted upon by gelatine.

When the solutions of lime, of strontia, or of barytes, were

poured into the infusions, copious precipitates, of a shade of light brown, were formed; and the residual fluid assumed a paler tint of red, and was found to have lost its power of precipitating gelatine.

After lime had been boiled for some time with a portion of the infusion, it assumed a dull red colour. The liquor that passed from it through the filtre had only a faint tint of red, did not act upon gelatine, and seemed to contain only a very small portion of vegetable matter. Pure magnesia, when heated with the infusion, acted upon it in an analogous manner; the magnesia became light red, and the residual fluid had only a very slight tinge of that colour. With carbonate of magnesia, the infusion became deeper in colour, and lost its power of precipitating gelatine; though it still gave, with oxygenated sulphate of iron, a light olive precipitate.

The carbonates of potash, of soda, and of ammonia, in their concentrated solutions, produced only a slight degree of turbidness in the infusion of catechu: they communicated to them a darker colour, and deprived them of the power of acting upon gelatine; though this power was restored by the addition of an acid.

After the mixture of the solution of carbonate of potash and the infusions had been exposed to the atmosphere for some hours, a brown crust was found to have formed upon its surface, and a slight precipitation had taken place.

The salts of alumine precipitated the infusions, but less copiously than they precipitate the infusion of galls. A similar effect was produced by nitrate of potash, sulphate of magnesia, prussiate of potash, and many other neutral salts.

The nitrate, or acetite, of lead, in concentrated solution, when poured into the infusion, produced in it a dense light brown precipitate, which gave to the fluid a gelatinous appearance. After this effect, there was no free acid found in it; and both the tannin and the extractive matter seemed to have been carried down, in union with a portion of the metallic salt.

The solution of muriate of tin, acted upon the infusion of catechu in a manner similar to that in which it acts upon the infusion of galls.

The least oxygenated sulphate of iron produced no change in the infusion. With the most oxygenated sulphate it gave a dense black precipitate, which, when diffused upon paper, appeared rather more inclined to olive than the precipitate from galls.

The infusions were precipitated by the solution of albumen.

The precipitates by gelatine had all a pale tint of red-brown, which became deeper when they were exposed to the air. The compound of gelatine and the tannin of the strongest infusions of catechu appeared, by estimation of the quantity of isinglass in the solutions used for their precipitation, to consist of about 41 parts of tannin, and 59 of gelatine.

Of two pieces of calf-skin which weighed, when dry, 132 grains each, and which had been prepared for tanning, one was immersed in a large quantity of the infusion of catechu from Bengal, and the other in an equal portion of the infusion of that from Bombay. In less than a month they were found converted into leather. When freed from moisture, by long exposure in the sunshine, they were weighed. The first piece had gained about 34 grains; and the second piece  $35\frac{1}{2}$  grains. The leather was of a much deeper colour than that tanned with galls,

and on the upper surface was red-brown. It was not acted on by hot or cold water; and its apparent strength was the same as that of similar leather tanned in the usual manner.

In examining the remainder of the infusions of catechu, in which skin had been converted into leather, I found in them much less extractive matter than I had reason to expect, from the comparative analysis of equal portions of the unaltered infusions made by solutions of gelatine. At first, I was inclined to suppose that the deficiency arose from the action of the atmosphere upon the extractive matter, by which a part of it was rendered insoluble. But, on considering that there had been very little precipitation in the process, I was led to adopt the supposition, that it had entered into union with the skin, at the same time with the tannin; and this supposition was confirmed by new experiments.

Both kinds of catechu are almost wholly soluble in large quantities of water; and, to form a complete solution, about 18 ounces of water, at 52°, are required to 100 grains of extract. The residuum seldom amounts to  $\frac{1}{4}$  of the original weight of the catechu; and, in most cases, it is found to consist chiefly of calcareous and aluminous earths, and of fine sand, which, by accident or design, had probably been mixed with the primitive infusion at the time of its evaporation.

A considerable portion of both kinds of catechu is soluble in alcohol; but, after the action of alcohol upon it, a substance remains, of a gelatinous appearance and a light brown colour, which is soluble in water, and is analogous in its properties to gum or mucilage.

The peculiar extractive matter in the catechu, is much less



soluble in water than the tanning principle; and, when a small quantity of water is used to a large quantity of catechu, the quantity of tannin taken up, as appears from the nature of the strongest infusion, is very much greater than that of the extractive matter.

The extractive matter is much more soluble in warm water than in cold water; and, when saturated solutions of catechu are made in boiling water, a considerable quantity of extractive matter, in its pure state, falls down, as the liquor becomes cool.

The peculiar extractive matter of the catechu may be likewise obtained, by repeatedly lixiviating the catechu, when in fine powder, till the fluids obtained cease to precipitate gelatine; the residual solid will then be found to be the substance in question.

The pure extractive matter, whether procured from the Bombay or Bengal catechu, is pale, with a faint tinge of red-brown. It has no perceptible smell; its taste is slightly astringent; but it leaves in the mouth, for some time, a sensation of sweetness, stronger than that given by the catechu itself.

Its solution in water is at first yellow-brown; but it gains a tint of red by exposure to the air. Its solution in alcohol does not materially change colour in the atmosphere; and it is of an uniform dull brown.

The extractive matter, whether solid or in solution, was not found to produce any change of colour upon vegetable blues.

It became of a brighter colour by the action of the alkalis; but it was not precipitated from its solution in water by these bodies, nor by the alkaline earths.

The aqueous solution of it, when mixed with solutions of nitrate of alumine and of muriate of tin, became slightly turbid.

To nitrate of lead, it gave a dense light brown precipitate.

It was not perceptibly acted upon by solution of gelatine; but, when solution of sulphate of alumine was added to the mixture of the two fluids, a considerable quantity of solid matter, of a light brown colour, was immediately deposited.

To the solution of oxygenated sulphate of iron, it communicated a fine grass-green tint; and a green precipitate was deposited, which became black by exposure to the air.

It was not precipitated by the mineral acids.

Linen, by being boiled in the strongest solution of the extractive matter, acquired a light red-brown tint. The liquor became almost colourless; and, after this, produced very little change in the solution of oxygenated sulphate of iron.

Raw skin, prepared for tanning by being immersed in the strong solution, soon acquired the same kind of tint as the linen. It united itself to a part of the extractive matter; but it was not rendered by it insoluble in boiling water.

The solid extractive matter, when exposed to heat, softened, and became darker in its colour, but did not enter into fusion. At a temperature below that of ignition, it was decomposed. The volatile products of its decomposition were, carbonic acid, hydrocarbonate, and water holding in solution acetous acid and a little unaltered extractive matter. There remained a light and very porous charcoal.

In considering the manner in which the catechu is prepared, it would be reasonable to conclude, that different specimens of that substance must differ in some measure in their composition,

even in their pure states; and, for the purposes of commerce, they are often adulterated to a considerable extent, with sand and earthy matter.\*

In attempting to estimate the composition of the purest catechu, I selected pieces from different specimens, with which I was supplied by the President, and reduced them together into powder; mixing, however, only those pieces which were from catechu of the same kind.

Two hundred grains of the powder procured in this way, from the catechu of Bombay, afforded by analysis,

	Grains.
Tannin - - - - -	109
Peculiar extractive matter - - - - -	68
Mucilage - - - - -	13
Residual matter; chiefly sand and calcareous earth	10

The powder of the Bengal catechu gave, by similar methods of analysis, in 200 grains,

	Grains.
Tannin - - - - -	97
Peculiar extractive matter - - - - -	73
Mucilage - - - - -	16
Residual matter; sand, with a small quantity of calcareous and aluminous earths - - - - -	14

In examining those parts of the catechu from Bengal which were differently coloured, I found the largest proportion of tannin in the darkest part of the substance; and most extractive matter in the lightest part. It is probable that the inequality of composition in this catechu, is owing to its being evaporated

\* One specimen that I examined, of the terra japonica of commerce, furnished, by incineration,  $\frac{2}{3}$  of sand and earthy matter; and another specimen, nearly  $\frac{1}{2}$ .

and formed without much agitation; in consequence of which, the constituent parts of it that are least soluble, being first precipitated, appear in some measure distinct from the more soluble parts, which assume the solid form at a later period of the process.

From the observations of Mr. KERR,\* it would appear, that the pale catechu is that most sought after in India; and it is evidently that which contains most extractive matter. The extractive matter seems to be the substance that gives to the catechu the peculiar sweetness of taste which follows the impression of astringency; and it is probably this sweetness of taste which renders it so agreeable to the Hindoos, for the purpose of chewing with the betle-nut.

#### IV. EXPERIMENTS AND OBSERVATIONS ON THE ASTRINGENT INFUSIONS OF BARKS, AND OTHER VEGETABLE PRODUCTIONS.

The barks that I examined were furnished me by my friend SAMUEL PURKIS, Esq. of Brentford; they had been collected in the proper season, and preserved with care.

In making the infusions, I employed the barks in coarse powder; and, to expedite the solution, a heat of from 100 to 120° FAHRENHEIT was applied.

The strongest infusions of the barks of the oak, of the Leicester willow, and of the Spanish chesnut, were nearly of the same specific gravity, 1.05. Their tastes were alike, and strongly astringent; they all reddened litmus-paper; the infusion of the Spanish chesnut bark producing the highest tint; and that of the Leicester willow bark the feeblest tint.

Two hundred grains of each of the infusions were submitted

\* Medical Observations, Vol. V. page 155.

to evaporation; and, in this process, the infusion of the oak bark furnished 17 grains of solid matter; that of the Leicester willow about  $16\frac{1}{2}$  grains; and that of the Spanish chesnut nearly an equal quantity.

The tannin given by these solid matters was, in that from the oak bark infusion, 14 grains; in that from the willow bark infusion  $14\frac{1}{2}$  grains; and in that from the Spanish chesnut bark infusion 13 grains.

The residual substances of the infusions of the Spanish chesnut bark, and of the oak bark, slightly reddened litmus-paper, and precipitated the solutions of tin of a fawn colour, and those of iron black. The residual matter of the infusion of the willow bark, did not perceptibly change the colour of litmus; but it precipitated the salts of iron of an olive colour, and rendered turbid the solution of nitrate of alumine.

The solid matters produced by the evaporation of the infusions, gave, by incineration, only a very small quantity of ashes, which could not have been more than  $\frac{1}{150}$  of their original weights. These ashes chiefly consisted of calcareous earth and alkali; and the quantity was greatest from the infusion of chesnut bark.

The infusions were acted on by the acids, and the pure alkalis, in a manner very similar to the infusion of galls. With the solutions of carbonated alkalis, they gave dense fawn-coloured precipitates. They were copiously precipitated by the solutions of lime, of strontia, and of barytes; and, by lime-water in excess, the infusions of oak and of chesnut bark seemed to be deprived of the whole of the vegetable matter they held in solution.

By being boiled for some time with alumine, lime, and magnesia, they became almost colourless, and lost their power of

acting upon gelatine and the salts of iron. After being heated with carbonate of lime and carbonate of magnesia, they were found deeper coloured than before; and, though they had lost their power of acting on gelatine, they still gave dense olive-coloured precipitates with the salts of iron.

In all these cases, the earths gained tints of brown, more or less intense.

When the compound of the astringent principles of the infusion of oak bark with lime, procured by means of lime-water, was acted on by sulphuric acid, a solution was obtained, which precipitated gelatine, and contained a portion of the vegetable principles, and a certain quantity of sulphate of lime; a solid fawn-coloured matter was likewise formed, which appeared to be sulphate of lime, united to a little tannin and extractive matter.\*

The solutions were copiously precipitated by solution of albumen.

The precipitates they gave with gelatine were similar in their appearance; their colour, at first, was a light tinge of brown, but they became very dark by exposure to the air. Their composition was very nearly similar; and, judging from the experiments on the quantity of gelatine employed in forming them, the compound of tannin and gelatine from the strongest infusion of oak bark, seems to consist, in the 100 parts, of 59 parts of

\* M. MERAT GUILLOT proposes a method of procuring pure tannin, (*Annales de Chimie*, Tome XLI. p. 325.) which consists in precipitating a solution of tan by lime-water, and decomposing it by nitric or muriatic acid. The solution of the solid matter obtained in this way in alcohol, he considers as a solution of pure tannin; but, from the experiments abovementioned, it appears, that it must contain, besides tannin, some of the extractive matter of the bark; and it *may* likewise contain saline matter.

gelatine and 41 of tannin; that from the infusion of Leicester willow bark, of 57 parts of gelatine and 43 of tannin; and that from the infusion of Spanish chesnut bark, of 61 parts of gelatine and 39 of tannin.

Two pieces of calf-skin, which weighed when dry 120 grains each, were tanned; one in the strongest infusion of Leicester willow bark, and the other in the strongest infusion of oak bark. The process was completed, in both instances, in less than a fortnight; when the weight of the leather formed by the tannin of the Leicester willow bark was found equal to 161 grains; and that of the leather formed by the infusion of oak bark was equal to 164 grains.

When pieces of skin were suffered to remain in small quantities of the infusions of the oak bark, and of the Leicester willow bark, till they were exhausted of their tanning principle, it was found, that though the residual liquors gave olive-coloured precipitates with the solutions of sulphate of iron, yet they were scarcely rendered turbid by solutions of muriate of tin; and there is every reason to suppose, that a portion of their extractive matter had been taken up with the tannin by the skin.

I attempted, in different modes, to obtain uncombined gallic acid from the solid matter produced by the evaporation of the barks, but without success. When portions of this solid matter were exposed to the degree of heat that is required for the production of gallic acid from Aleppo galls, no crystals were formed; and the fluid that came over gave only a brown colour to the solution of salts of iron, and was found to contain much acetous acid and empyreumatic oil.

When pure water was made to act, in successive portions, upon oak bark in coarse powder, till all its soluble parts were

taken up, the quantities of liquor last obtained, though they did not act much upon solution of gelatine, or perceptibly redden litmus-paper, produced a dense black with the solution of sulphate of iron: by evaporation, they furnished a brown matter, of which a part was rendered insoluble in water by the action of the atmosphere; and the part soluble in water was not in any degree taken up by sulphuric ether; so that, if it contained gallic acid, it was in a state of intimate union with extractive matter.

Two pieces of calf-skin, which weighed when dry 94 grains each, were slowly tanned; one by being exposed to a weak infusion of the Leicester willow bark, and the other by being acted upon by a weak infusion of oak bark. The process was completed in about three months; and it was found, that one piece of skin had gained in weight 14 grains, and the other piece about  $16\frac{1}{2}$  grains. This increase is proportionally much less than that which took place in the experiment on the process of quick tanning. The colour of the pieces of leather was deeper than that of the pieces which had been quickly tanned; and, to judge from the properties of the residual liquors, more of the extractive matters of the barks had been combined with them.

The experiments of Mr. BIGGIN\* have shown, that similar barks, when taken from trees at different seasons, differ as to the quantities of tannin they contain: and I have observed, that the proportions of the astringent principles in barks, vary considerably according as their age and size are different; besides, these proportions are often influenced by accidental circumstances, so that it is extremely difficult to ascertain their distinct relations to each other.

In every astringent bark, the interior white bark (that is, the

\* Phil. Trans. for 1799, p. 299.



part next to the alburnum) contains the largest quantity of tannin. The proportion of extractive matter is generally greatest in the middle or coloured part: but the epidermis seldom furnishes either tannin or extractive matter.

The white cortical layers are comparatively most abundant in young trees; and hence their barks contain, in the same weight, a larger proportion of tannin than the barks of old trees. In barks of the same kind, but of different ages, which have been cut at the same season, the similar parts contain always very nearly the same quantities of astringent principles; and the interior layers afford about equal portions of tannin.

An ounce of the white cortical layers of old oak bark, furnished, by lixiviation and subsequent evaporation, 108 grains of solid matter; and, of this, 72 grains were tannin. An equal quantity of the white cortical layers of young oak produced 111 grains of solid matter, of which 77 were precipitated by gelatine.

An ounce of the interior part of the bark of the Spanish chesnut, gave 89 grains of solid matter, containing 63 grains of tannin.

The same quantity of the same part of the bark of the Leicester willow, produced 117 grains, of which 79 were tannin.

An ounce of the coloured or external cortical layers from the oak, produced 43 grains of solid matter, of which 19 were tannin.

From the Spanish chesnut, 41 grains, of which 14 were tannin.

And, from the Leicester willow, 34 grains, of which 16 were tannin.

In attempting to ascertain the relative quantities of tannin in the different *entire* barks, I selected those specimens which appeared similar with regard to the proportions of the external

and internal layers, and which were about the average thickness of the barks commonly used in tanning, namely,  $\frac{1}{2}$  an inch.

Of these barks, the oak produced, in the quantity of an ounce, 61 grains of matter dissolved by water, of which 29 grains were tannin.

The Spanish chesnut 53 grains, of which 21 were tannin.

And the Leicester willow 71 grains, of which 33 were tannin.

The proportions of these quantities, in respect to the tanning principle, are not very different from those estimated in Mr. BIGGIN's table.\*

The residual substances obtained in the different experiments, differed considerably in their properties; but certain portions of them were, in all instances, rendered insoluble during the process of evaporation. The residuum of the chesnut bark, as in the instance of the strongest infusion, possessed slightly acid properties; but more than  $\frac{3}{4}$  of its weight consisted of extractive matter. All the residuums in solution, as in the other cases, were precipitated by muriate of tin; and, after this precipitation, the clear fluids acted much more feebly than before on the salts of iron; so that there is great reason for believing, that the power of astringent infusions to precipitate the salts of iron black, or dark coloured, depends partly upon the agency of the extractive matters they contain, as well as upon that of the tanning principle and gallic acid.

In pursuing the experiments upon the different astringent infusions, I examined the infusions of the bark of the elm and of the common willow. These infusions were acted on by reagents, in a manner exactly similar to the infusions of the other barks: they were precipitated by the acids, by solutions of the

\* Phil. Trans. for 1799, p. 263.

alkaline earths, and of the carbonated alkalis; and they formed, with the caustic alkalis, fluids not precipitable by gelatine.

An ounce of the bark of the elm, furnished 13 grains of tannin.

The same quantity of the bark of the common willow, gave 11 grains.

The residual matter of the bark of the elm, contained a considerable portion of mucilage; and that of the bark of the willow, a small quantity of bitter principle.

The strongest infusions of the sumachs from Sicily and Malaga, agree with the infusions of barks, in most of their properties; but they differ from all the other astringent infusions that have been mentioned, in one respect; they give dense precipitates with the caustic alkalis. Mr. PROUST has shown, that sumach contains abundance of sulphate of lime; and it is probably to this substance that the peculiar effect is owing.

From an ounce of Sicilian sumach, I obtained 165 grains of matter soluble in water, and, of this matter, 78 grains were tannin.

An ounce of Malaga sumach, produced 156 grains of soluble matter, of which 79 appeared to be tannin.

The infusion of Myrobalans\* from the East Indies, differed from the other astringent infusions chiefly by this circumstance, that it effervesced with the carbonated alkalis; and it gave with them a dense precipitate, that was almost immediately redissolved. After the tannin had been precipitated from it by gelatine, it strongly reddened litmus-paper, and gave a bright black with the solutions of iron. I expected to be able to procure

\* The Myrobalans used in these experiments are the fruit of the Terminalia Chebula. RETZ. *Obs. Botan.* Fasc. V. p. 31.

gallic acid, by distillation, from the Myrobalans; but in this I was mistaken; they furnished only a pale yellow fluid, which gave merely a slight olive tinge to solution of sulphate of iron.

Skin was speedily tanned in the infusion of the Myrobalans; and the appearance of the leather was similar to the appearance of that from galls.

The strongest infusions of the teas are very similar, in their agencies upon chemical tests, to the infusions of catechu.

An ounce of Souchong tea, produced 48 grains of tannin.

The same quantity of green tea, gave 41 grains.

Dr. MATON has observed, that very little tannin is found in cinchona, or in the other barks supposed to be possessed of febrifuge properties. My experiments tend to confirm the observation. None of the infusions of the strongly bitter vegetable substances that I have examined, give any precipitate to gelatine. And the infusions of quassia, of gentian, of hops, and of chamomile, are scarcely affected by muriate of tin; so that they likewise contain very little extractive matter.

In all substances possessed of the astringent taste, there is great reason to suspect the presence of tannin; it even exists in substances which contain sugar and vegetable acids. I have found it in abundance in the juice of sloes; and my friend Mr. POOLE, of Stowey, has detected it in port wine.

#### V. GENERAL OBSERVATIONS.

Mr. PROUST has supposed, in his Paper upon Tannin and its Species,\* that there exist different species of the tanning principle, possessed of different properties, and different powers

\* *Annales de Chimie*, Tome XLI. p. 332.

of acting upon reagents, but all precipitable by gelatine. This opinion is sufficiently conformable to the facts generally known concerning the nature of the substances which are produced in organised matter; but it cannot be considered as proved, till the tannin in different vegetables has been examined in its pure or insulated state. In all the vegetable infusions which have been subjected to experiment, it exists in a state of union with other principles; and its properties must necessarily be modified by the peculiar circumstances of its combination.

From the experiments that have been detailed it appears, that the *specific* agencies of tannin in all the different astringent infusions are the same. In every instance, it is capable of entering into union with the acids, alkalis, and earths; and of forming insoluble compounds with gelatine, and with skin. The infusions of the barks affect the greater number of reagents in a manner similar to the infusion of galls; and, that this last fluid is rendered green by the carbonated alkalis, evidently depends upon the large proportion of gallic acid it contains. The infusion of sumach owes its characteristic property, of being precipitated by the caustic alkalis, to the presence of sulphate of lime; and, that the solutions of catechu do not copiously precipitate the carbonated alkalis, appears to depend upon their containing tannin in a peculiar state of union with extractive matter, and uncombined with gallic acid or earthy salts.

In making some experiments upon the affinities of the tanning principle, I found that all the earths were capable of attracting it from the alkalis: and, so great is their tendency to combine with it, that, by means of them, the compound of tannin and gelatine may be decomposed without much difficulty; for, after pure magnesia had been boiled for a few hours with

this substance diffused through water, it became of a red-brown colour, and the fluid obtained by filtration produced a distinct precipitate with solution of galls. The acids have less affinity for tannin than for gelatine; and, in cases where compounds of the acids and tannin are acted on by solution of gelatine, an equilibrium of affinity is established, in consequence of which, by far the greatest quantity of tannin is carried down in the insoluble combination. The different neutral salts have, comparatively, feeble powers of attraction for the tanning principle; but, that the precipitation they occasion in astringent solutions, is not simply owing to the circumstance of their uniting to a portion of the water which held the vegetable substances in solution, is evident from many facts, besides those which have been already stated. The solutions of alum, and of some other salts which are less soluble in water than tannin, produce, in many astringent infusions, precipitates as copious as the more soluble saline matters; and sulphate of lime, and other earthy neutral compounds, which are, comparatively speaking, insoluble in water, speedily deprive them of their tanning principle.

From the different facts that have been stated, it is evident that tannin may exist in a state of combination in different substances, in which its presence cannot be made evident by means of solution of gelatine; and, in this case, to detect its existence, it is necessary to have recourse to the action of the diluted acids.

In considering the relations of the different facts that have been detailed, to the processes of tanning and of leather-making, it will appear sufficiently evident, that when skin is tanned in astringent infusions that contain, as well as tannin, extractive matters, portions of these matters enter, with the tannin, into

chemical combination with the skin. In no case is there any reason to believe that gallic acid is absorbed in this process; and M. SEGUIN'S ingenious theory of the agency of this substance, in producing the deoxygenation of skin, seems supported by no proofs. Even in the formation of glue from skin, there is no evidence which ought to induce us to suppose that it loses a portion of oxygen; and the effect appears to be owing merely to the separation of the gelatine, from the small quantity of albumen with which it was combined in the organised form, by the solvent powers of water.

The different qualities of leather made with the same kind of skin, seem to depend very much upon the different quantities of extractive matter it contains. The leather obtained by means of infusion of galls, is generally found harder, and more liable to crack, than the leather obtained from the infusions of barks; and, in all cases, it contains a much larger proportion of tannin, and a smaller proportion of extractive matter.

When skin is very slowly tanned in weak solutions of the barks, or of catechu, it combines with a considerable proportion of extractive matter; and, in these cases, though the increase of weight of the skin is comparatively small, yet it is rendered perfectly insoluble in water; and is found soft, and at the same time strong.

The saturated astringent infusions of barks contain much less extractive matter, in proportion to their tannin, than the weak infusions; and, when skin is quickly tanned in them, common experience shows that it produces leather less durable than the leather slowly formed.

Besides, in the case of quick tanning by means of infusions of barks, a quantity of vegetable extractive matter is lost to the

manufacturer, which might have been made to enter into the composition of his leather. These observations show, that there is some foundation for the vulgar opinion of workmen, concerning what is technically called the *feeding* of leather in the slow method of tanning; and, though the processes of the art may in some cases be protracted for an unnecessary length of time, yet, in general, they appear to have arrived, in consequence of repeated practical experiments, at a degree of perfection which cannot be very far extended by means of any elucidations of theory that have as yet been made known.

On the first view it appears singular that, in those cases of tanning where extractive matter forms a certain portion of the leather, the increase of weight is less than when the skin is combined with pure tannin; but the fact is easily accounted for, when we consider that the attraction of skin for tannin must be probably weakened by its union with extractive matter; and, whether we suppose that the tannin and extractive matter enter together into combination with the matter of skin, or unite with separate portions of it, still, in either case, the primary attraction of tannin for skin must be, to a certain extent, diminished.

In examining astringent vegetables in relation to their powers of tanning skin, it is necessary to take into account, not only the quantity they contain of the *substance* precipitable by gelatine, but likewise the quantity, and the nature, of the extractive matter; and, in cases of comparison, it is essential to employ infusions of the same degree of concentration.

It is evident, from the experiments detailed in the IIIId section, that of all the astringent substances which have been as yet examined, catechu is that which contains the largest proportion of tannin; and, in supposing, according to the common



estimation, that from four to five pounds of common oak bark are required to produce one pound of leather, it appears, from the various synthetical experiments, that about half a pound of catechu would answer the same purpose.\*

Also, allowing for the difference in the composition of the different kinds of leather, it appears, from the general detail of facts, that one pound of catechu, for the common uses of the tanner, would be nearly equal in value to  $2\frac{1}{4}$  pounds of galls, to  $7\frac{1}{2}$  pounds of the bark of the Leicester willow, to 11 pounds of the bark of the Spanish chesnut, to 18 pounds of the bark of the elm, to 21 pounds of the bark of the common willow, and to 3 pounds of sumach.

Various menstruums have been proposed for the purpose of expediting and improving the process of tanning, and, amongst them, lime-water and the solutions of pearl-ash: but, as these two substances form compounds with tannin which are not decomposable by gelatine, it follows that their effects must be highly pernicious; and there is very little reason to suppose, that any bodies will be found which, at the same time that they increase the solubility of tannin in water, will not likewise diminish its attraction for skin.

\* This estimation agrees very well with the experiments lately made by Mr. PURKIS, upon the tanning powers of Bombay catechu in the processes of manufacture, and which he has permitted me to mention. Mr. PURKIS found, by the results of different accurate experiments, that one pound of catechu was equivalent to seven or eight of oak bark.