

XII. *On an artificial Substance which possesses the principal characteristic Properties of Tannin.* By Charles Hatchett, Esq. F. R. S.

Read April 25, 1805.

§ I.

THE discovery of the principle on which the effects of tanning essentially depend, may be partly attributed to Mr. DEYEUX, who obtained a substance from galls which he considered as a species of resin,\* but which was afterwards proved by Mr. SEGUIN to be that which renders the skins of animals insoluble in water, and imputrescible, and thus to be the principle by which they are converted into leather.†

The chief characteristic property of this substance was ascertained by Mr. SEGUIN to be that of precipitating gelatine or glue from water in a state of insolubility, and as it was evidently different from any vegetable substance hitherto discovered, he gave it the name of tannin.

This discovery of Mr. SEGUIN at once unveiled the theory of the art; an easy and certain method was afforded by which tannin could be detected, and its relative quantity in different substances be determined, whilst the nature and properties of this newly discovered vegetable principle could be subjected to accurate investigation.

\* *Mémoire sur la Noix de Galle*, par M. DEYEUX; *Annales de Chimie*, Tome XVII. p. 23.

† Ibid. Tome XX. p. 15.

The former has derived elucidation from the experiments of Mr. BIGGIN,\* and much has been contributed in every respect by Mr. PROUST,† but the subject has received the greatest extension and some of the most valuable additions from the ingenious labours of Mr. DAVY, particularly the discovery of the important fact, that catechu or terra japonica consists principally of tannin.‡

The united results of the experiments made by these and other eminent chemists, appear therefore to have fully established, that tannin is a peculiar substance or principle which is naturally formed, and exists in a great number of vegetable bodies, such as oak-bark, galls, sumach, catechu, &c. &c. commonly accompanied by extract, gallic acid, and mucilage.

But no one has hitherto supposed that it could be produced by art, unless a fact noticed by Mr. CHENEVIX may be considered as some indication of it.

Mr. CHENEVIX observed, that a decoction of coffee-berries did not precipitate gelatine unless they had been previously roasted; so that tannin had in this case either been formed or had been developed from the other vegetable principles by the effects of heat. §

Some recent experiments have however convinced me, that a substance possessing the chief characteristic properties of tannin may be formed by very simple means, not only from vegetable, but even from mineral and animal substances.

\* Phil. Trans. 1799, p. 259.

† *Annales de Chimie*, Tome XXV. p. 225. Ibid. Tome XLI. p. 331. Ibid. XLII. p. 89.

‡ Phil. Trans. 1803, p. 233.

§ Nicholson's Journal for 1802, Vol. II. p. 114.

§ II.

In the course of my experiments on lac, and on some of the resins, I had occasion to notice the powerful effects produced on them by nitric acid, and I have since observed, that by long digestion, almost every species of resin is dissolved, and is so completely changed, that water does not cause any precipitation, and that by evaporation a deep yellow viscid substance is obtained, which is equally soluble in water and in alcohol, so that the resinous characters are obliterated.

When I afterwards had discovered a natural substance, which was composed partly of a resin similar to that of recent vegetables, and partly of asphaltum,\* I was induced to extend the experiments already mentioned to the bitumens, in the hope of obtaining some characteristic properties by which the probable original identity of these bodies with vegetable substances might be farther corroborated. In this respect I succeeded, in some measure better than I expected; but I observed a very material difference between the solutions of the resins and those of many of the bitumens, such, for instance, as asphaltum and jet. The first effect of nitric acid, during long digestion with these substances, was to form a very dark brown solution, whilst a deep yellow or orange coloured mass was separated, which by subsequent digestion in another portion of nitric acid was completely dissolved, and by evaporation was converted into a yellow viscid substance, equally soluble in water and in alcohol, so as to perfectly resemble that which by similar means had been obtained from the resins, excepting, that when burned, it emitted an odour somewhat resembling that of the fat oils.

\* Phil. Trans. 1804, p. 385.

It therefore appeared to me, that the first or dark brown solution had been formed by the action of the nitric acid on the *uncombined* carbonaceous part of the bitumens, or that by which they are rendered black, and that the deep yellow portion which was separated, was that which constituted the real or essential part of these bituminous substances. This opinion was confirmed by some experiments which I purposely made upon amber, and having every reason therefore to believe, that the dark brown solution obtained from asphaltum and jet was in fact a solution of coal, I repeated the experiments on several varieties of the pit or mineral coal, from all which, I obtained the dark brown solution in great abundance; but those coals, which contained little or no bitumen, did not yield the deep yellow substance which has been mentioned.

In each experiment I employed 100 grains of the coal, which I digested in an open matrass with one ounce of nitric acid diluted with two ounces of water. (The specific gravity of the acid was 1.40.)

After the vessel had been placed in a sand-bath, and as soon as it became warm, a considerable effervescence attended with much nitrous gas was produced; after about two days I commonly added a second and sometimes a third ounce of the acid, and continued the digestion during five or six days, or until the whole, or nearly the whole, was dissolved, excepting in those cases when the deep yellow substance was formed; for this I constantly separated.

The next experiment was made upon charcoal, which was more readily dissolved than the preceding substances, without leaving any residuum; the solution was perfect, and the colour was reddish-brown.\*

\* The solubility of charcoal in nitric acid, and some of its properties when thus

Having thus by means of nitric acid obtained solutions from asphaltum, from jet, from several of the pit-coals, and from charcoal, I evaporated them to dryness in separate vessels, taking care in the latter part of the process to evaporate very gradually, so as completely to expel the remainder of the acid without burning the residuum; this, in every case, proved to be a brown glossy substance, which exhibited a resinous fracture.

The chemical properties of these residua were as follows.

1. They were speedily dissolved by cold water and by alcohol.

2. Their flavour was highly astringent.

3. Exposed to heat, they smoked but little, swelled much, and afforded a bulky coal.

4. Their solutions in water reddened litmus-paper.

5. The same solutions copiously precipitated the metallic salts, especially muriate of tin, acetite of lead, and oxysulphate of iron. The colour of these precipitates was commonly brown, inclining to that of chocolate, excepting the tin, which was blackish-gray.

6. They precipitated gold from its solution, in the metallic state.

7. They also precipitated the earthy salts, such as the nitrates of lime, barytes, &c. &c.

8. The fixed alkalis, as well as ammonia, when first added

dissolved, have been noticed by Professor LICHTENSTEIN in CRELL's Chemical Annals, 1786; by Mr. LOWITZ; (CRELL's Chem. Journal, translated into English, Vol. II. p. 255;) and by Mr. JAMESON, in his Outline of the Mineralogy of the Shetland Islands, &c. 8vo. edit. p. 167.

to these solutions only deepened the colour, but, after some hours, rendered them turbid.

9. Glue or isinglass was immediately precipitated by these solutions from water, and the precipitates were more or less brown according to the strength of the solutions. The precipitates were also insoluble in cold and in boiling water, so that in their essential properties they proved similar to those formed by the varieties of tannin hitherto known, with the difference, that this factitious substance appeared to be exempt from gallic acid, and mucilage, which commonly accompany the varieties of tannin, and which occasion modifications in the colour and appearance of some of their precipitates.

Having thus had the satisfaction to discover that a product resembling tannin could be formed by such a simple method, not only from vegetable but also from mineral coal, I was induced to examine how far the same might be extended to animal coal, and I therefore reduced a portion of isinglass to that state in a close vessel, and having rubbed it into fine powder, I digested it with nitric acid in the manner which has been described. At first the acid did not appear to act upon it, but at length it was slowly dissolved excepting a small quantity, which however was in every respect unchanged; and here we may remark, that as animal coal is incinerated with much more difficulty than vegetable coal or charcoal, so was the same difference to be observed, when oxygen was presented to these bodies in the humid way.

The solution resembled those which have been described, excepting, that the brown colour was more intense. It was evaporated to dryness, and was then dissolved in distilled

water, after which, the solution being examined by the re-agents which had been employed in the former experiments, was found to produce similar effects, excepting some difference in the colour of the precipitates.

I next added some of the liquid to a solution of isinglass, and obtained a copious precipitate. Thus it is evident, that a tanning substance may be formed from animal as well as from vegetable and mineral coal; and it is not a little curious, that this enables us to assert as a matter of fact, although not of economy, that one portion of the skin of an animal may be employed to convert the other into leather.

In the course of these experiments, I also subjected coak to the action of nitric acid, and obtained a product which resembled that which had been afforded by pit-coal; but in this case (as might be expected) there was not any appearance of the deep yellow substance which has so often been mentioned.

These experiments therefore prove, that a tanning substance may be artificially formed by exposing carbon to the action of nitric acid; and it also appears, that this is best effected when the carbon is uncombined with any other substance excepting oxygen. The following experiments seem to corroborate this opinion.

1. A piece of Bovey coal, which had perfectly the appearance of half-charred wood, was reduced to powder, and was digested with nitric acid until the whole was dissolved.

The colour of the solution was deep yellow; and, by evaporation, a yellow viscid mass was obtained, which was dissolved in distilled water. This solution was then examined by various re-agents, and particularly by gelatine, but not any

vestige of tanning matter could be discovered, and the predominant substance appeared to be oxalic acid.

2. Another piece of Bovey coal, which had less of the characters of wood, and was more perfectly carbonized, was treated in the way which has been described; the solution was brown, and, unlike the former, afforded a considerable precipitate with gelatine.

3. A portion of the first sort of Bovey coal was exposed to a red heat in a close vessel, and was then reduced to powder and digested with nitric acid; here a remarkable difference was to be observed, for nearly the whole was thus converted into the tanning substance.

4. A coal from Sussex, extremely like the second sort of Bovey coal, also afforded the same product.

5. A piece of the Surturbrand from Iceland yielded a similar result.

6. Some deal saw-dust was digested with the nitric acid until it was completely dissolved; by evaporation a yellow viscid mass was obtained, the solution of which in water afforded results like those of the first experiment on the Bovey coal, for oxalic acid was found in it, but not any of the tanning substance.

7. Another portion of the same deal saw-dust was converted into charcoal in a close vessel; the charcoal was then treated in the manner already described, and was thereby formed into a liquid which copiously precipitated gelatine.

8. Having previously ascertained that teak wood does not contain gallic acid nor tannin, I reduced some of it into charcoal, which was afterwards readily converted into the substance above mentioned.



In these experiments, the deal and the teak wood had been reduced to the state of coal, as usual, by fire, but as this does not appear to have been the means generally employed by nature to convert organized substances into the varieties of mineral coal, I for a considerable time, previous to the discovery of the artificial tanning product, had been employed in a series of experiments on the slow carbonization of a great number of vegetable substances by the humid way.

The agent which I most commonly used to produce this effect, was sulphuric acid occasionally diluted; and although many of the processes were extremely unpleasant and tedious, yet I have not any reason to regret the time which has been thus employed. The subject however I foresee will branch out into several details, none of which as yet I can regard as sufficiently completed to merit the honour of being submitted to this learned Society; but I am in a manner almost compelled in the present case to anticipate a few of the experiments, with their results, because they are intimately connected with the subject now under consideration.

In these experiments, I have observed that concentrated sulphuric acid, when poured upon any of the resinous substances reduced to powder, dissolved them in a few minutes; at this period the solution was transparent, commonly of a yellowish-brown colour, and of the consistency of a viscid oil. But if, after this, the vessel was placed on a sand-bath, the colour of the solution became progressively darker, sulphureous gas was evolved, and at length the whole appeared like a very thick liquid of an intense black. I purposely for the present pass over many phenomena, some of which are peculiar to the different substances when thus treated, whilst others are

general, and may be referred to those attendant on etherification, for my intention here is only to notice, in a concise manner, such as immediately tend to elucidate the subject of this Paper.

When concentrated sulphuric acid is poured on the common turpentine of the shops, it almost immediately dissolves it like the solid resins ; and if a portion of this solution be poured into cold water, the turpentine is precipitated in the solid brittle state of common yellow resin. But if a second portion of the same solution, after the lapse of an hour or more, be in like manner poured into cold water, the resin thus formed is not yellow but dark brown ; and if four or five hours are suffered to elapse before a third portion is poured into water, the resin is found to be completely black. After this, supposing the digestion to be carried on during several days, or until there is no longer any production of sulphureous gas, the turpentine or resin will be found converted into a black porous coal, which, if the operation has been properly conducted, does not contain any resin, although a substance may frequently be separated by digestion in alcohol, which I shall soon have occasion to notice.

When common resin was thus treated, I obtained about 43 *per cent.* of the coal, which, after being exposed to a red heat in a loosely covered platina crucible, still amounted to 30 *per cent.* and by the slowness of its combustion and other circumstances which need not here be related, approached very nearly to the characters of some of the mineral coals.\*

\* The difference of the quantity of carbon, which may be obtained in the state of coal from resinous substances by the humid and by the dry way, is very considerable ; we may take common resin as an example, for when 100 grains were exposed to simple

The effects produced by sulphuric acid upon turpentine and resin are manifestly caused by the union of the two constituent principles of the latter (namely, hydrogen and carbon) with part of the oxygen of the former, so that sulphureous acid, water, and coal are produced. I therefore availed myself of this process, by which coal could be progressively formed whilst the original substance was gradually decomposed, to make the following experiment.

A quantity of common turpentine was treated with sulphuric acid in the way which has been described, and different portions of the solution being poured at different periods into water whilst the remainder was digested during several days, I thus obtained from the same original substance, yellow resin, brown resin, black resin, and coal. I then digested a portion of each of these, as well as some of the turpentine, in separate vessels with nitric acid until they were completely dissolved, and afterwards reduced them to dryness. The different residua varied in colour from yellow to dark brown, corresponding to the substances which had been employed. These were then dissolved in distilled water, and were examined by solution of isinglass and other reagents.

1. The solution of the residuum of turpentine was pale straw colour, and did not precipitate gelatine.
2. That of yellow resin resembled the former in every respect.
3. That of the brown resin was of a deeper yellow, but in other particulars resembled the above.
4. That of the black resin on the contrary yielded a considerable portion of the tanning substance,—and

distillation in a small glass retort placed over an open charcoal fire, the residuum of coal only amounted to  $\frac{3}{4}$  of a grain.

5. That of the coal afforded it in great abundance.

Hence it appears, that these different modifications of turpentine yielded the tanning substance only in proportion to the quantity of their original carbon, which, by oxidizement, had been progressively converted into coal.\*

Other substances, when reduced into coal in the humid way, were in like manner formed into the tanning substance by nitric acid. In fact I found this to be the constant result, and amongst the many substances which were examined, I shall mention various kinds of wood, copal, amber, and wax, all of which, when reduced to coal by sulphuric acid, yielded similar products, by subsequent treatment with nitric acid.

But this substance may likewise be artificially produced without the help of nitric acid, although in a less proportion, as well as with some slight variations in its characteristic properties; for, as I have already observed, when any of the resins or gum resins (such as common resin, elemi, asa foetida, &c.) have been long digested with sulphuric acid so as to assume the appearance and general characters of coal, if afterwards they are digested with alcohol, a portion is dissolved, and a dark brown solution is formed which by evaporation yields a mass soluble in water as well as in alcohol, and which precipitates gelatine, acetite of lead, and muriate of tin, but produces only a very slight effect on oxysulphate of iron. This substance, therefore, which may thus be separated by alcohol from the coal formed from resinous bodies by sulphuric acid, evidently contains some of the tanning matter, which has been produced during the carbonization of those substances.

\* Some late experiments have however convinced me that carbon need not be absolutely converted into coal in order to produce the artificial tanning substance; but this will be more fully explained in a subsequent Paper.

A natural process very similar to this, I much suspect takes place in some cases where peat is formed ; I say in some cases, because the production of tanning matter does not seem to be absolutely a necessary consequence attendant on the formation of peat ; for in many places where the latter abounds, the former cannot be detected, whilst in others, it is very abundant, and acts powerfully on animal bodies which have accidentally been exposed to its effects.

There are many facts of this kind upon record, such as the account of the bodies of the man and woman preserved in the moors near the woodlands in Derbyshire, and also of the woman found in the morass at Axholm, in Lincolnshire.\* Now I am much inclined to believe, that the tanning substance which so much abounds in these and some other peat moors, did not originally exist in the vegetable substances from which the peat has been produced, but that it has been and continues to be progressively formed (under certain favourable circumstances) during the gradual carbonization and conversion of the vegetable matter into peat.

### § III.

In most of the former papers which I have had the honour to lay before the Royal Society, I have for greater perspicuity generally concluded with a recapitulation of the contents, but in the present case, this appears to be superfluous, as the whole may be concentrated into one simple fact, namely, that a substance very analogous to tannin, which has hitherto been considered as one of the proximate principles of vegetables, may at any time be produced, by exposing carbonaceous substances,

\* Phil. Trans. Vol. XXXVIII. p. 413. Ibid. Vol. XLIV. p. 571.

whether vegetable, animal, or mineral, to the action of nitric acid.

Since the preceding experiments were made, I have farther proved the efficacy of this substance by actual practice, and have converted skin into leather by means of materials which, to professional men, must appear extraordinary, such as, deal saw-dust, asphaltum, common turpentine, pit-coal, wax candle, and a piece of the same sort of skin.

Allowing, therefore, that the production of this substance must for the present be principally regarded only as a curious chemical fact not altogether unimportant, yet as the principle on which it is founded appears to be developed, we may hope, that a more economical process will be discovered, so that every tanner may be enabled to prepare his leather even from the refuse of his present materials.

The organized bodies and their products have only of late years much attracted the attention of chemists, many of whom, even at this time, (although the modes of chemical examination have been so much improved,) seem disgusted and deterred by the Proteus-like changes which take place whenever these substances are subjected to experiment.

But these variable and endless alterations of their properties seem rather calculated to operate as incitements to investigation; for by the accumulation of facts resulting from the changes produced in these bodies by disuniting and by recombining their elementary principles, not only will chemistry as a science become farther illumined and extended, but it will, as it has hitherto done, render great and essential services to the arts and manufactures.