



XXV. Additional experiments and remarks on an artificial substance which possesses the principal characteristic properties of tannin

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To cite this article: Charles Hatchett Esq. F.R.S. (1806) XXV. Additional experiments and remarks on an artificial substance which possesses the principal characteristic properties of tannin , Philosophical Magazine Series 1, 24:94, 155-162, DOI: [10.1080/14786440608563351](https://doi.org/10.1080/14786440608563351)

To link to this article: <http://dx.doi.org/10.1080/14786440608563351>



Published online: 18 May 2009.



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experiment, in which a pyrometer-piece was placed within the barrel, and another in the muffle; they agreed in indicating 23°. The inner tube, which was of Reaumur's porcelain, contained eighty grains of pounded chalk. The carbonate was found, after the experiment, to have lost $3\frac{1}{4}$ grains. A thin rim, less than the 20th of an inch in thickness, of whitish matter, appeared on the outside of the mass. In other respects the carbonate was in a very perfect state; it was of a yellowish colour, and had a decided semi-transparency and saline fracture. But what renders this result of the greatest value is, that on breaking the mass a space of more than the tenth of an inch square was found to be completely crystallized, having acquired the rhomboidal fracture of calcareous spar. It was white and opake, and presented to the view three sets of parallel plates which are seen under three different angles. This substance, owing to partial calcination and subsequent absorption of moisture, had lost all appearance of its remarkable properties in some weeks after its production; but this appearance has since been restored by a fresh fracture, and the specimen is now well preserved by being hermetically inclosed.

[To be continued.]

XXV. *Additional Experiments and Remarks on an artificial Substance which possesses the principal characteristic Properties of Tannin.* By CHARLES HATCHETT, Esq.
F. R. S.

[Concluded from p. 68.]

§ VII.

FROM the experiments which have been related, it appears, that three varieties of the artificial tanning substance may be formed, viz.

1st, That which is produced by the action of nitric acid upon any carbonaceous substance, whether vegetable, animal, or mineral.

2dly, That which is formed by distilling nitric acid from
common

common resin, indigo, dragon's blood, and various other substances : and,

3dly, That which is yielded to alcohol by common resin, elemi, asa fœtida, camphor, &c., after these bodies have been for some time previously digested with sulphuric acid.

Upon these three products I shall now make a few remarks, which I have hitherto postponed, in order that the account of the experiments might not be interrupted.

The first variety is that which is the most easily formed ; and from some experiments which were purposely made, I find that 100 grains of dry vegetable charcoal afford 120 of the tanning substance ; but, as it is extremely difficult completely to expel moisture, or even the whole of the nitric acid which has been employed*, an allowance of about three or four grains ought to be made ; so that after this deduction we may conclude, that 100 grains of vegetable charcoal yield 116 or 117 of the dry tanning substance.

The proportions of the constituent parts of this substance I have not as yet ascertained ; but, from the manner by which it is produced, carbon is evidently the base of it, and is the predominating essential ingredient.

From § III. experiment F. it also appears, that the other component parts are oxygen, hydrogen, and nitrogen ; for, when the artificial tanning substance was distilled, ammonia and carbonic acid were obtained, exclusive of a very small portion of a yellow liquor, which stained the upper part of the retort, and which, from its tenacity and insolubility in water and alcohol, appeared to be of an oily nature.

As I had taken every precaution respecting the charcoal which had been employed, I was at first induced to consider the above facts as almost positively demonstrative of the presence of hydrogen in charcoal ; but upon further reflection, and upon weighing some of the circumstances which attend the formation of the artificial tanning substance, I still feel on this point very considerable doubt ; for I have constantly

* The most effectual method of expelling the nitric acid is, to reduce the tanning substance to powder, and repeatedly evaporate different portions of distilled water from it in a glass or porcelain basin,

observed,

observed, that diluted nitric acid acts upon charcoa more effectually in the formation of the tanning substance than when it is employed in a concentrated state; and it appears therefore very probable that hydrogen may have been afforded by a portion of water decomposed during the process. For, admitting that the new compound (formed by the action of nitric acid upon charcoal) may possess a certain degree of affinity for hydrogen, this, being exerted simultaneously with the affinity for oxygen possessed by nitrous gas, may (especially when the last is in a nascent state) effect a decomposition of a portion of water, the hydrogen of which would therefore enter into the composition of the tanning substance, whilst the oxygen would supply the place of part of that which had been taken from the nitric acid.

Many of the properties of the tanning substance prepared from coal by nitric acid are very remarkable, particularly those which have been noticed in § III. experiments F and G; for surely it is not a little singular, that this substance when burned should emit an odour so very similar to animal matter, notwithstanding that the tanning substance had been prepared from pure vegetable charcoal. And again, in experiment G, the portion which had not been precipitated by solution of isinglass was, when dried, found to possess a strong vegetable odour very analogous to oak bark, although charcoal is inodorous, and isinglass very nearly so.

But, after all, the most extraordinary properties of this substance are certainly those which so nearly approach it to the vegetable principle called *tannin*; for it perfectly resembles this principle by its solubility in water and in alcohol, by its action upon gelatine and upon skin, by the effects which it produces upon metallic solutions, upon those of the earths, and of the alkalis.

The sulphuric and muriatic acids also affect the solutions of it as they do those of tannin; and the only marked difference which as yet has been found in the characters of the artificial substance and of tannin is, that the former is produced, whilst the varieties of the latter are more or less destroyed by nitric acid. This, for the present at least, must draw a line of separation between them; but we must not forget,

forget, that even the varieties of tannin* do not accord in the degree of destructibility.

The second variety of the tanning substance is obtained from a great number of vegetable bodies; such as indigo, dragon's blood, common resin, &c. &c., by digesting and distilling them with nitric acid. It is not, therefore, quite so readily prepared as that which was first described, and its relative quantity, when compared with that of the substance employed to produce it, is less.

As resin and some of the other bodies do not afford it until they have been repeatedly treated with nitric acid, and as during each operation nitrous gas is produced, whilst the strength of the acid which comes over is diminished, it seems

* I shall here venture to state some ideas which have occurred to me on the probable cause and mode of the formation of tannin.

Mr. Biggin has proved, that similar barks, when taken from trees at different seasons, differ as to the quantities of tannin contained in them.—(Phil. Trans. 1799, p. 259.)

Mr. Davy also observes, "that the proportions of the astringent principles in barks vary considerably according as their age and size are different."

"That in every astringent bark the interior white bark (which is the 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."

Moreover Mr. Davy remarks, "that 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."—(Phil. Trans. 1803, p. 264.)

We find, therefore,

1st, That the proportion of tannin in the same trees is different at different seasons.

2dly, That tannin is principally contained in the white cortical layers, or interior white bark, which is next to the alburnum or new wood: and,

3dly, That these white cortical layers are comparatively most abundant in young trees, and that their barks consequently contain in the same weight more tannin than the barks of old trees.

I shall not make any remarks on the first of these facts, as it accords with other similar effects, which are the natural consequences of the processes and periods of vegetation; but the second and third appear to be important; for they prove that tannin is principally formed, or at least deposited, in the interior white bark, which is next to the alburnum or new wood; so that in the very same part where the successive portions of new wood are to be elaborated and deposited, we find the principal portion of tannin.

It should seem, therefore, that there is an intimate connection between the formation

seems almost evident that this tanning substance is formed in consequence of part of the oxygen of the nitric acid becoming combined with the hydrogen of the original body, so as to form water; and the carbon, being thus in some measure denuded, is rendered capable of being gradually acted upon by the nitric acid in a manner nearly similar to that which takes place when it has been previously converted into coal.

The colour of the precipitates which this tanning substance yields with gelatine is constantly pale or deep yellow, whilst that of the precipitates formed by the first variety is always brown; I am therefore induced to believe that the different colours of the precipitates produced by the varieties of tannin depend on the state of their carbon.

When resin and the other bodies were treated as above formation of new wood and the formation of tannin in such vegetables as afford the latter; and this idea is corroborated when the chemical nature of these substances is considered.

From experiments made on the ligneous substance of vegetables, or the woody fibre, it appears to be composed of carbon, oxygen, hydrogen, and nitrogen; but of these its principal and essential ingredient is carbon.

In like manner carbon is unquestionably the basis and principal ingredient of tannin. Considering, therefore, that both of these substances consist principally of carbon; that tannin is secreted in that part of barks where the formation and deposition of new wood take place; and that the quantity of tannin is the most considerable in young trees, and seems therefore to keep pace with their more vigorous growth, and consequent rapid formation of wood; it appears very probable that those vegetables which contain tannin have the faculty of absorbing more carbon and of the other principles than are immediately required in the formation of the different proximate vegetable substances, especially the woody fibre: that this excess, by chemical combination, becomes tannin, which is secreted in the white interior bark: that in this state it is a principle peculiarly fitted to concur by assimilation to form new wood: that it is therefore subsequently decomposed at the proper period, and is employed in the formation of the new wood: that there is not a continual accumulation of tannin in the vegetables which afford it, as it is successively formed in and with the white cortical layers, and is successively decomposed by concurring to form new wood: and, lastly, that as the vegetable approaches more nearly to the full maturity of its growth, when wood is less rapidly and less plentifully formed, so in like manner less tannin is secreted; for, the fabric being nearly completed, fewer materials are required.

Such I am inclined to suspect, from the facts which have been adduced, to be the cause and mode by which tannin is formed in oaks and other vegetables; but I make this statement only as a probable conjecture, which may be refuted or confirmed by future observations.

described

described with nitric acid, the quantity obtained of the tanning substance was much less than when an equal quantity of coal was employed, or even when these bodies had been previously converted into coal in the humid way by sulphuric acid.

The cause of this seems to be, that a number of other products are simultaneously formed, all of which require more or less of carbon as a constituent ingredient, so that, in consequence of the affinities which prevail under the existing circumstances, some bodies by treatment with nitric acid afford but little, and others none, of the tanning substance.

The greatest proportion of this substance was yielded by indigo, common resin, and stick lac.

The quantity obtained from *asa foetida* and gum ammoniac was less.

Benzoin, balsam of Tolu, balsam of Peru, and dragon's blood, were inferior to the former in this respect; so that the development, or rather production of benzoic acid*, appeared

* The expression "production of benzoic acid" may appear objectionable, and I shall therefore take this opportunity so observe, that I much suspect the present established opinion respecting the balsams and benzoic acid to be erroneous: for the balsams are defined as bodies composed of resin and benzoic acid; consequently the latter, when obtained in a separate state, is considered as an original ingredient or educt.

I am, however, inclined to a contrary opinion; for I consider the balsams as peculiar substances, which, although nearly approaching to the nature of resins, are nevertheless different in respect to the original combination of their elementary principles; which combination, however, is with much facility modified by various causes, and especially by a certain increase of temperature, so that a new arrangement of the elementary principles takes place, part being formed into resin, and part into benzoic acid.

Many facts appear more or less to support this opinion; for whether benzoic acid is obtained by simple sublimation, or by merely digesting benzoin in boiling water, according to Geoffroy's method, or by the addition of lime, as recommended by Scheele, or by employing alkalis in a similar manner, nothing positive can be inferred from any of these operations to prove that benzoic acid is obtained as an educt, but rather the contrary, when we reflect on the affinities which are most likely to prevail under the circumstances of the different processes, and on the variable proportions of the benzoic acid; and although benzoic acid has been discovered in the urine of infants, in that of many adults, and constantly in that of graminivorous quadrupeds,
such

peared partly to counteract the formation of the tanning substance; but oxalic acid, when formed in any considerable quantity, seemed absolutely to prevent the formation of this substance; for whilst abundance of the former was obtained from gum arabic, tragacanth, manna, and guaiacum, not any of the latter could be produced.

Common liquorice appears at first to be an exception; but from the smallness of the quantity, and the colour of the precipitate which it produced with solution of isinglass, I am almost convinced that the tanning substance was formed by the action of the nitric acid on a portion of uncombined carbon, which, being in a state approaching to coal, is probably the cause of the blackness of the common liquorice.

As the formation of the tanning substance has been my

such as the camel, the horse, and the cow, (*Système des Connoissances Chimiques*, par Fourcroy, 4to edit. tom. iv. p. 158;) yet all this certainly appears to be in favour of its being a chemical product.

I have observed, when benzoin, balsam of Tolu, and balsam of Peru, were dissolved in sulphuric acid, that a great quantity of beautifully crystallized white benzoic acid was sublimed during digestion; and as it is produced in so very pure a state by this single and simple operation, I would recommend a trial of the process to those who prepare benzoic acid for commerce; but I am not certain whether this mode may prove more æconomical than those which at present are employed.

When dragon's blood, however, was treated in the same manner with sulphuric acid, I could not obtain a particle of benzoic acid; nor did I succeed much better when I had recourse to lime, according to Scheele's process; for, although a considerable quantity of the substance was thus rendered soluble in water, yet by the addition of muriatic acid I obtained only a slight appearance of benzoic acid, accompanied by a copious precipitate of red resin, notwithstanding that the solution had acquired a powerful and peculiar balsamic odour.

But in a former part of this paper I have stated, that when dragon's blood was dissolved in nitric acid, and afterwards evaporated to dryness, it yielded about 6 per cent. of benzoic acid. Now, if this had been originally present in dragon's blood in the state of benzoic acid, some stronger evidence of it might reasonably have been expected in each process; but this not being the case, I am inclined to consider it as produced, and not educed, by the action of the nitric acid on the original principles of the dragon's blood; and I am also persuaded that similar but more general effects take place when benzoin or any of the balsams are subjected to the different processes by which benzoic acid is obtained; so that to me this last seems to be as much a chemical product as the oxalic, the acetous, and other of the vegetable acids.

The succinic acid also appears to be a product and not an original ingredient of amber.

principal object, I have not thought it necessary to enter at present into too minute a detail of other particulars, and have therefore only thus cursorily noticed some of the principal effects produced by nitric acid on the resins, balsams, &c. Those, however, who are conversant with chemistry, will undoubtedly perceive that these effects deserve to be accurately investigated; and that the resins, balsams, gum resins, and gums, should be regularly examined by every possible method, not merely on account of the individual substances which may become the subjects of experiment, but because there is reason to expect that from such an investigation, medicine, with the arts and manufactures, may derive many advantages, whilst the mysterious processes and effects of vegetation may very probably receive considerable elucidation.

Concerning the third variety of the tanning substance, which is produced by the action of sulphuric acid on the resins, gum resins, &c., I shall here add but little to that which I have already stated in the latter part of the second section of my first paper, and in the account which I have lately given of an experiment on camphor.

This variety appears to be uniformly produced during a certain period of the process, but by a long continuance of the digestion I have reason to believe that it is destroyed.

Substances, such as the gums, which afford much oxalic acid by treatment with other acids, do not apparently yield any of this tanning substance.

The energy of its action on gelatine and skin is certainly inferior to that of the first variety, into which however, as we have seen, it may easily be converted by nitric acid.

From the mode of its formation there does not appear to be any positive evidence that it contains nitrogen like the first and second varieties, and perhaps the absence of nitrogen may be the cause of its less powerful action; this I have not as yet ascertained, but it is my intention more particularly to notice in a future paper the general properties of this substance.