





# OBSERVATIONS

ON THE

# COMBINATION

OF

ACIDS, BITTERS, AND ASTRINGENTS:

BEING A

REFUTATION OF SOME OF THE PRINCIPLES,  
CONTAINED IN DR. PERCIVAL'S  
ESSAY, ON BITTERS AND  
ASTRINGENTS.

By JAMES WOODHOUSE, M. D.

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*Let's canvass him in his broad cardinal's hat.*

SHAKESPEARE.

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OBSERVATIONS

ON THE

COMPOSITION

OF

ACID METALS AND METALLOIDS

BY

WILLIAM H. MILLER, M.D.

CONTAINED IN THE

TRANSACTIONS OF THE

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OF THE UNITED STATES

IN THE YEAR

1846

NEW YORK

1846



P R E F A C E

TO THE  
MEMBERS

OF THE  
*Philadelphia Medical Society,*

THIS  
DISSERTATION

IS RESPECTFULLY INSCRIBED,  
BY THEIR HUMBLE SERVANT,  
THE AUTHOR.



# P R E F A C E.

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OF all the essays with which Dr. Percival has favoured the world, no one appears to have met a more candid or indulgent reception, than his famous *Essay on Bitters and Astringents*.

THIS work, first published in the year 1769, has not only undergone four editions, but, as we are informed by the doctor, large portions of it have been translated into foreign cyclopedias, and into different systems of the *materia medica*.

Two late writers Drs. Skeete and Irwin, in their ingenious dissertations on the Peruvian bark, have attempted to controvert some of the principles, contained in Dr. Percival's essay.

THE former of those gentlemen, has not touched upon that part, which is the subject of the following pages; the latter, having made one or two experiments, was led to doubt the opinion of Dr. Percival,



although he acknowledges, the doctor's experiments do not prove an union of acids, bitters and astringents, and that his own do not fully prove the contrary.

BOTH were deceived in the same manner, from using a fallacious test of astringency, and from being ignorant of that change which takes place upon adding an astringent vegetable, to a solution of green vitriol.

A MORE notorious instance of self deception perhaps never occurred, than in an experiment related by Dr. Skeete; having triturated magnesia with some bark and water, and added the mixture to a solution of sal martis, he found the black color produced more intense, than that struck by a simple solution of the bark.

DECIPIMUR specie reſti; from this and other circumstances, he supposed the astringency of the bark increased, and thought the fact might be of some importance in the tanning of leather, whereas, had he digested the magnesia on the bark for twenty-four hours, or triturated it with a solution of galls, he would have found the astringent principle completely destroyed.

IN a note to the last edition of Dr. Percival's works, we are informed he still adheres to his

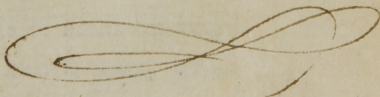
former opinions, but as neither health nor time, will permit him to engage in the controversy, he leaves it to be decided by others.

THE errors of a great man, it is said, are contagious; the truth of this is evinced, from the principles contained in Dr. Percival's essay being generally adopted; bitters have been exhibited under the fallacious idea of neutralising acidity, the doctor has been quoted, and implicit credit given to his experiments.

THE author of the following trifle, has but one object, the establishment of truth; as he has made free with the opinions of his predecessors, he wishes his own may be diligently scrutinised, for he is as ~~×~~ equally liable to be deceived, as others of his medical brethren.

As and equally signify the same thing. I imagine he had better have used more in the room of these two words.

W. Connors







# OBSERVATIONS

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**D**R. PERCIVAL has divided his essay on astringents and bitters into four sections; in the eighth experiment of the first section, having infused a quantity of powdered Peruvian bark in vinegar and water, and added some of the infusion to a chalybeate solution, he found at first no change of color take place, though in a few minutes a slight black tinge appeared.

THE result of this experiment, induced him to make further trials of the effects of acids on vegetable astringents, and having added some white wine vinegar to an infusion of chamomile flowers,

and a triturated infusion of the bark, and added these infusions to a solution of *sal martis*, he found no change of color produced. Afterwards having made ink, with an infusion of galls, and a solution of *sal martis*, he discharged the black color by the acid of vitriol, and then restored the original blackness with the spirit of hartshorne.

FROM these experiments he supposed an affinity between acids, bitters and astringents, and this suggested to him an idea, that they might possibly neutralise each other, and form what the chymists call a *tertium quid*. This point he attempted to ascertain, by adding vinegar to infusions of the bark, Aleppo galls and gentian, and concluded from his experiments, that acids, bitters and astringents neutralise each other.

HAVING given this summary of the experiments of Dr. Percival, I shall

1. TAKE notice of the best method of discovering an astringent quality in vegetables.
2. SHEW that change which takes place, upon adding a vegetable astringent to a solution of green vitriol.
3. POINT out the manner in which the doctor was deceived, and



4. RELATE several decisive experiments, in which mineral and vegetable acids, were added to bitters and astringents.

1. THE property of striking a black color with a solution of green vitriol, has long been regarded as an indubitable test of astringency, but as this is owing to the gallic acid uniting with the iron of the green vitriol, as many vegetables contain this acid, which are not astringent, as the black color produced is not in proportion to the astringency, as it *does not happen* when the astringency is *not destroyed* by the acids, and it *takes place* when the astringent principle is *completely destroyed* by magnesia or the alkalies, it follows that the property by which vegetables strike a black color, with a solution of green vitriol, cannot be considered as a proof of their astringency.

IN the fifth volume of the London Medical Essays, and in Irwin on the bark, two sketches of machines may be seen for determining the astringent power of different substances, but as these machines are unnecessary refinements, and astringent vegetables readily impart a sense of constriction to the mouth and fauces, the taste appears to be the most easy and least fallacious test that can be used.



2. UPON adding a vegetable astringent to a solution of *sal martis*, a black color is produced.

THERE have been many different explanations of this fact; the opinion to which Dr. Percival seems to have adhered, is that the astringent principle was united to the iron of the green vitriol.

IN an inaugural dissertation on the chemical and medical properties of the Perfimmon tree, and the analysis of astringent vegetables, I proved the astringent principle to be composed of the gallic acid united to that precipitate, which is thrown down by alkalies from vegetable astringents, which possesses all the properties of the earth of alum.

IN the making of ink then, a double elective attraction takes place, the gallic acid unites with the iron of the green vitriol, while the vitriolic acid unites with the *radical*, or base of the astringent principle.

\* *The double elective attraction only takes place when the astringent principle undecomposed is added to a solution of sal martis; ink may be made either by adding the gallic acid to the green vitriol, or to the calx of iron precipitated from sal martis by the vegetable alkali, or by adding the astringent principle to the calx*

3. DR. PERCIVAL was deceived, first, from using a fallacious test of astringency, secondly, from being under the influence of a preconceived opinion, and thirdly from being ignorant of that change which takes place, upon adding a vegetable astringent to a solution of *sal martis*. As he thought he had proved, that acids neutralise astringents, so when he added the vitriolic acid, to a decoction of galls and a solution of *sal martis*, he supposed the acid neutralised the astringent principle, whereas, it only dissolved the ferruginous particles; that this is actually the case may be proved by adding the pure gallic acid, which is *not astringent*, to a solution of green vitriol, and then discharging the black color, by dissolving the precipitate, with the vitriolic or marine acid.

*of iron; in the same manner, if Glauber's salt is added to a solution of muriated barytes, a double elective attraction takes place, the vitriolic acid unites to the ponderous earth, which for some time remains suspended in the fluid, and the decomposition happens, if the vitriolic acid alone is used, or any salt containing the vitriolic acid, hence Professor Bergman has made the muriated barytes a test for the discovery of the vitriolic acid, as others have made the gallic acid, a test for the discovery of iron.*



4. I SHALL relate a few experiments, in which mineral and vegetable acids, were added to bitters and astringents, and take notice of the result.

#### EXPERIMENT I.

DIFFERENT portions of the vitriolic, nitrous, and marine acids, vinegar and lime juice, were separately added to solutions of gentian, chamomile flowers and columbo root; the bitter principle always predominated to the taste, a piece of paper stained blue, was in every instance turned to a red color.

#### EXPERIMENT II.

DIFFERENT portions of the vitriolic, nitrous, marine acids, vinegar and lime juice, were separately added to solutions of galls, Spanish oak and Peruvian bark; in no one instance was the astringent principle neutralized; the solution of galls was more pleasant to the taste, the astringency of the oak bark appeared to be increased; upon adding the vegetable alkali to it, a more copious precipitation took place, than from the watery solution alone.



## EXPERIMENT III.

ALUM added to a solution of galls and Spanish oak bark, caused a precipitate, partly soluble in the vitriolic acid.

THIS experiment was suggested, by reading an essay intituled " Considerations on different materials as objects of the art of dying ;" by Mr. HENRY, published in the third volume of the Manchester memoirs, wherein he asserts a complete decomposition of alum takes place when added to a solution of galls, which is by no means the case, as the alum may be obtained by chryftallization after the addition.

THE insoluble precipitate is the resin of the galls, which may be thrown down, by using a solution of columbo root, instead of alum, but which will not take place with chamomile flowers or gentian, or by adding the alum to a solution of Peruvian bark.

THE frequent opportunities Dr. Percival had of observing the effects, arising from a combination of green vitriol and astringents, naturally led him to examine into the principles of ink, and from a number of fallacious experiments, he was led to

differ materially from Dr. Lewis, who has paid particular attention to this subject.

HAVING immersed a piece of polished iron, into a cold infusion of the Peruvian bark, made with distilled water, he found the liquor in three hours just perceptibly tinged black; while the same piece of iron wiped clean, and immersed in another infusion of the cortex, made with common spring water, in a less time gave a deep purple color to the liquor.

THE spring water employed, he tells us, contained a considerable portion of selenitic salt, and hence, by dissolving the iron immersed in it, formed a perfect *sal martis*, from which he inferred an acid is essentially necessary in the formation of ink, and having afterwards prosecuted the subject, concluded “whatever deprives green vitriol of its acid, whether it be heat, the addition of an alkali, or repeated *affusions of water*, destroys its power of striking a black color, with vegetable astringents.”

THE experiments detailed by the Doctor, by no means justify this conclusion; he did not attempt to make ink, with a *calx of iron*, precipitated from green vitriol by an *alkali*, and it clearly appears he



made use of the *earth*, which never fails to be mixed with green vitriol, in the decomposition of the *pyrites* instead of a *calx of iron*, and which separates from it by solution in water, in the form of a yellow ochre, or he never would have thought of depriving green vitriol of its acid, by “*repeated affusions of water.*”

To put this matter beyond a doubt :

#### EXPERIMENT IV.

A QUANTITY of the calx <sup>of</sup> iron, thrown down from green vitriol by the vegetable alkali, being several times washed, until the water was insipid to the taste, and produced no further precipitation upon the addition of an alkali, when added to a solution of galls, produced an ink, equal to that made with common green vitriol.

HAVING thus taken a summary of part, and the most important part, of the essay on bitters and astringents, pointed out the taste as the least fallacious test of astringency, shewn the manner in which Dr. *Percival* was deceived, and confuted him in several particulars, we may conclude.



1. *ACIDS* and bitters do not neutralise each other.

2. *ACIDS* by a superior affinity to the base of the astringent principle, by detaching the gallic acid, decompose, but do not neutralise astringents, forming *salts* or *saline gums* of different degrees of astringency, according to the acids employed.\*

*THE* astringency of the oak bark was increased by the vitriolic acid, because it contains a large proportion of earth unfaturated by the gallic acid, hence the copious precipitation, upon the addition of the alkali, after adding the vitriolic acid.

By spontaneous evaporation in the open air, an acid salt is produced, and during the crystallization, *micaceous spangles*, resembling drops of tar thrown into water, appear swimming on the surface of the fluid.

*THE* bark of an oak tree may be considered as a coat of pure argillaceous earth ; to prove this, let

\* *THE* distilled acid of sugar, the acids of citrons, sorrel and phosphorus, and the acid of tartar, which appears to be a modification of the gallic acid, form gums with the earth of alum.

Vid. Keir's chemical dictionary.

a small quantity of the ashes which falls upon a log of wood, after the combustion of the bark be collected, and they will be found insipid to the taste, upon adding weak vitriolic acid once or twice, and washing the mixture in water, the *phlogistic* matter will be destroyed, and the pure white earth may be obtained, mixed with a small proportion of filex. Alum in this case will not be formed, as the solution will not take place in the cold. \*

THE *argillacious* earth which is found in common ashes, comes principally from the bark, the vegetable alkali, from the body of the wood, though no doubt in the latter case, argill and filex may be obtained, but in no proportion to the vast quantities contained in the bark.

\* *Vitriolic acid readily dissolves the earth of alum when moist, and newly obtained, but does not act with equal rapidity when it is dry. This solution in the quantity of many ounces affords crystals of alum, mixed with small scales, similar to those of mica. Mr. Baume adds, that if this experiment be made in the small way, the scaly substance only is obtained, and scarcely any alum.*

Vide Fourcroy's Chemistry, article Alum.

3. THE vitriolic acid, according to the opinion of Dr. Lewis, and contrary to the opinion of Dr. Percival, is not necessary in the formation of ink.

F I N I S.





