

CCV. *On Cochineal (Coccus Cacti). First Memoir.*
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THE beautiful theoretical results which have been lately obtained by a closer examination of indigo blue and its products of decomposition, made it desirable to undertake similar investigations with other colouring matters. I made choice of the colouring principle of cochineal (*Coccus Cacti*), hoping that a detailed research might not only prove of interest in a scientific point of view, but also throw some light on its practical applications, and the more so, as the recent investigations of Preisser had seemed to point out a very close

analogy in the chemical properties of a variety of colouring matters with indigo blue.

Before entering into the detail of my experiments, I think it desirable to give a brief outline of the results obtained by the chemists who have hitherto worked on this subject.

Dr. Jean Frédéric John, in a quarto volume translated from the German and entitled *Tableaux Chimiques du Règne Animal*, appears to have published the first analysis of cochineal: he does not describe his method, but merely states that it contains the following per-centage:—

Colouring principle (semi-solid, soluble in water and alcohol)	50·00
Gelatine	10·50
Waxy fat	10·00
Modified mucus	14·00
Membrane	14·00
Alkaline phosphates and chlorides, phos- phate of lime, phosphate of iron, and phosphate of ammonia	1·50
	100·00

Pellétier* and Caventou, in a very long memoir read before the Institut de France in 1818, have gone very elaborately into the examination of cochineal and obtained many interesting results. In analysing this substance they employed the following process:—They removed the fatty bodies by boiling æther, in which they found the colouring matter but slightly soluble; these fatty substances, recovered by distilling off the æther, were considered to consist of stearine, oleine, and an aromatic acid, from which latter substance it was difficult to remove the adhering colouring matter.

The cochineal, exhausted with æther, was treated with alcohol of 40° Beaumé, which dissolved the colouring matter, together with a small quantity of fatty and nitrogenous substances.

On cooling, and by spontaneous evaporation, they obtained a granular red residue of a semi-crystalline appearance, and which they considered to be the colouring matter contaminated still with nitrogenous matter (*matière animalisée*) and some fatty bodies, the greater part of which remained undissolved in strong cold alcohol; by repeating the operation once or twice they considered that the substance was obtained almost in a state of purity. To remove the last traces of foreign matter it was dissolved in strong alcohol, and

* *Annales de Chimie et de Physique*, sér. 2, tome viii. p. 250. *Journal de Pharmacie*, sér. 2, tome iv. p. 193.

an equal volume of æther added, which precipitated the colouring matter and retained the fat, which was still adhering to it. The colouring matter thus purified they named carmine (*carminium*), and described as being very soluble in water, from which it did not crystallize, more or less soluble in alcohol, according to its strength, and quite insoluble in æther and the fixed and volatile oils. Acids did not precipitate it from its aqueous solution if free from animal matter. They found hydrochloric and sulphuric acid to decompose it; the latter with elimination of carbon. By the action of nitric acid they obtained an acid in prismatic crystals resembling oxalic acid, but differing in some of its properties.

On heating the "carmine" it intumescd and gave off carburated hydrogen, a considerable quantity of oily substances, a little acid water, but no trace of ammonia. Chlorine and iodine decomposed it; the alkalies in the commencement produced merely a change in colour, turning it violet, but by the assistance of time or heat they effected a complete alteration. They found an aqueous solution of "carmine" to exhibit the following comportment with reagents.

Of the alkaline earths, lime only produced a precipitate; hydrate of alumina showed a marked affinity, absorbing the whole of the colouring matter from an aqueous as well as an alcoholic solution; the presence of alum prevented this reaction: iron, copper, and silver salts were without reactions; terchloride of gold destroyed the colour; neutral salts of lead merely changed it to violet, except the neutral acetate, which precipitated it, the free acetic acid retaining a little of the compound in solution; the colouring matter could be recovered by decomposing the lead compound with hydrosulphuric acid. The nitrate of mercury gave a purple, and the pernitrate a scarlet-red precipitate; the bichloride no precipitate; chloride of tin gave a violet precipitate; the bichloride changed the colour to scarlet without causing a precipitate. Albumen and gelatine had no marked action, but if precipitated by reagents the colouring matter was carried down.

In a later communication (1832), Pelletier* gave the composition of the colouring matter as prepared by himself and Caventou. In a previous qualitative examination they had failed to exhibit the presence of nitrogen which M. Pelletier now detected. The substance was dried *in vacuo* at a gentle heat to remove every trace of alcohol and æther, and burnt with oxide of copper it yielded—

* *Annales de Chimie et de Physique*, sér. 2, tome li. p. 194.

Carbon	49·33
Hydrogen	6·66
Nitrogen	3·56
Oxygen	40·45
	<hr/>
	100·00

M. Pelletier stated, however, that he did not greatly rely on the correctness of this analysis.

After alcohol had dissolved out all the colouring matter removable by it, they extracted the last traces, by repeatedly washing the residue with boiling water, and along with it a little fatty and some nitrogenous matter; the residue was a brownish transparent mass. The later decoctions, containing no red colouring matter, left likewise on evaporation a brownish transparent mass, which they considered identical with the organic residue of the insect. This animal matter had, according to them, some analogy with gelatine, but differed in many of its properties, as it did also from albumen and fibrine, they therefore considered it as peculiar to the cochineal insect; the alkalies and ammonia dissolved it readily; chlorine precipitated it; all acids and acid salts precipitated it, as also acetate of lead, salts of tin and copper, and nitrate of silver; and they considered the latter reagent as a good test of the purity of the colouring matter, as it did not precipitate the latter if free from nitrogenous substances. If the colouring matter were contaminated with nitrogenous substances, all the salts which precipitated the latter carried down likewise some of the colouring matter.

An examination of the ashes showed the presence of phosphate of lime, carbonate of lime, chloride of potassium, and phosphate of potash, to the extent of 0·7 per cent.

In the second part of the memoir they went into the theory of the technical applications of the colouring matter: this having no reference to the present subject, I do not think it necessary to reproduce it here.

M. Lassaigue, in 1819*, examined *Kermes* (*Coccus ilicis*), an insect common in the South of Europe, and employed as a red dye before the discovery of America, and obtained by following the methods of Pelletier and Caventou, substances agreeing in their properties with the analogous ones found in cochineal.

M. F. Preisser†, in an elaborate paper on the origin and nature of colouring matters, has again drawn the attention of chemists to the subject. This gentleman, from a study of a variety of colouring substances, comes to the conclusion that all resemble indigo in its behaviour with reducing agents.

* *Journal de Pharmacie*, sér. 2, tome v. p. 435.

† *Ibid.* p. 191.

He affirms that he obtained by the action of hydrosulphuric acid on the lead compounds of a great number of organic colouring matters, substances bearing the same relation to the original colouring matters as white indigo does to blue indigo. In order to obtain the colourless modification of the colouring matter of cochineal, he adds what he terms "hydrate of oxide of lead" to an aqueous decoction of cochineal, the fats being previously removed by æther. The colouring matter is entirely removed by the so-called oxide of lead, which is nothing but a basic nitrate of lead, $2(3\text{PbO}, \text{NO}_3) + 3\text{HO}$. The lead compound suspended in water (hot?) was decomposed by a stream of hydrosulphuric acid; the nearly colourless filtrate deposited on cooling needles of a pale yellow colour, which became perfectly white by washing with æther and pressing between bibulous paper; these crystals, which, according to his statement, are soluble in water and alcohol, but less so in æther, assume in contact with the atmosphere the purple-red of the colouring matter of cochineal. He moreover asserts that his colourless modification gives a white lead salt on adding acetate of lead to its aqueous solution, and that this assumes a purple colour in contact with the air.

He proposes to give the name carmine, hitherto applied to the red colouring matter, to the white crystals, and to designate the red substance by the name "Carméine."

The statements of Preisser, generalizing most beautifully under one head the chemical character of all colouring matters, making indigo as it were the prototype of them all, could but induce other chemists to work out more in detail the relations cursorily pointed out in the memoir of this chemist. Unfortunately a careful repetition of these experiments has not confirmed the basis on which his theory reposes.

M. A. E. Arppe repeated Preisser's experiments on the colouring matter of cochineal*. He found that by proceeding in the manner described by Preisser that he could only obtain a red solution, which on evaporation was converted into white crystals of oxalic acid by the nitric acid derived from the basic lead salt.

Arppe now prepared a pure oxide of lead by precipitating acetate of lead with potash. He found that this would not take down the colouring matter in the cold, but by boiling it is carried down as a blue lake, which he decomposed by hydrosulphuric acid; the supernatant liquor was nearly colourless, the colouring matter he found adhered with great obstinacy to the sulphide of lead, from which water, alcohol and ammonia failed to separate it; but sulphide of ammo-

* Liebig's *Annalen*, vol. lv. p. 101.

nium and acids rendered it perceptible. He likewise tried to obtain the colouring matter in a state of purity by precipitating with hydrated oxide of lead an aqueous decoction of cochineal (previously purified from nitrogenous substances by nitrate of silver). On treating the precipitate by hydrosulphuric acid, he obtained a red liquor of *strongly acid reaction*, the acid of which was not derived from the lead salt: on evaporation it left a dark red mass, emitting the smell of burnt sugar. Wishing to separate the acid, which he thought contaminated the colouring matter, he prepared a strong aqueous decoction of cochineal, and after separating the nitrogenous matter by means of nitrate of silver, filtering, and then saturating by ammonia, and afterwards adding the hydrated oxide of lead, he found that the supernatant ammoniacal liquor, which was nearly colourless, yielded by evaporation an acid liquid; and on decomposing the lead lake with hydrosulphuric acid, he obtained a liquid slightly coloured (the colouring matter adhering to the sulphide of lead), which was likewise acid. From this he concluded that the colouring matter had not up to that period been obtained in a state of purity.

Microscopic Examination of Living Cochineal.

By the kindness of Sir James Clark, who furnished me with specimens of the living insect, I have been enabled to examine the physical characters of the colouring matter as it exists in the organism of this little insect before it is subjected to the process of drying for commerce. On examination by the microscope, the white dust which covers the insect and the adjacent parts of the cactus leaves, on which it feeds, has all the characters of an excrement; it has a curled cylindrical form, is of very uniform diameter and of a white colour. On removing the powder with a little æther and piercing the side of the little creature, a quantity of a purplish red fluid exudes, which contains the colouring matter in minute granules assembled round a colourless and larger nucleus, and these groups float in a colourless fluid. It is evident from this, that, whatever may be the function of the colouring matter, it has a distinct and marked form, and does not pervade as a mere tint the fluid portion of the insect.

Separation of the Colouring Matter.

It became evident from a few preliminary experiments that the investigation would be greatly facilitated by the employment of a large quantity of material; and as in the course of the inquiry different methods were adopted for the prepara-

tion of the colouring matter, capital letters will be used to designate the various preparations.

A. About 3 lbs. of ground cochineal (technically known as shelly black) was introduced into 15 gallons of boiling distilled water, and the mixture maintained at that temperature for twenty minutes; the decoction, strained through a sieve, was allowed to subside for a quarter of an hour and then decanted off; whilst still hot the transparent liquid was mixed with basic nitrate of lead, added with caution to avoid excess; a fine purple lake was thus obtained, the supernatant liquor retaining only a pale buff tinge. After decantation of the supernatant liquor, the lake was thrown on a cloth filter and washed with distilled water until the filtrate gave but a slight opalescence with chloride of mercury, which was found to be a test for the presence of nitrogenous matter. The lead lake was then suspended in distilled water and treated with a copious stream of hydrosulphuric acid, when a precipitate of sulphide of lead and a deep red supernatant liquid was obtained; on stirring the liquid this colour almost disappeared, the colouring matter being evidently absorbed by the sulphide, agreeing perfectly with Arppe's observation. A fresh stream of gas reproduced the colour, which was again absorbed on stirring; after continuous treatment with hydrosulphuric acid, the lead lake being completely decomposed, the filtered liquid was evaporated in a water-bath to a syrupy consistence, and the evaporation finished as far as possible at a temperature of 38°C . The semi-solid substance thus obtained was of a deep purple colour, had a strongly acid reaction, and evolved the smell of burnt sugar, as noticed by Arppe. The weight of this substance, which I call crude carminic acid, was $3\frac{1}{2}$ ozs., and 1 oz. more was obtained from the residue by similar treatment.

B. On repeating the same process the whole product was lost. An excess of the basic nitrate having been employed, the nitric acid set free by the hydrosulphuric acid caused a violent decomposition, with evolution of nitrous fumes, as soon as the carminic acid arrived at a pasty consistence; this agrees also with Arppe's experience.

C. In this operation a decoction of cochineal, made in the described manner, was precipitated with a solution of acetate of lead acidulated with acetic acid (six parts by weight of crystallized acetate, and one part of strong acetic acid). The resulting lead lake, being very bulky, was washed by decantation with boiling distilled water, collected on a filter, dried in a current of warm air, and finely powdered; 17 ozs. of *crude carminate of lead* were thus obtained.

D. Half a pound of cochineal was boiled with five pints of alcohol, spec. grav. .830. The filtered tincture deposited on cooling a granular precipitate, consisting chiefly of fatty matter retaining a portion of colouring matter; on concentrating the tincture by distillation a further quantity was deposited, which was filtered off; the filtrate was evaporated to dryness *in vacuo*, when after eight weeks a gummy residue was obtained. This mass dissolved with great difficulty in a large quantity of absolute alcohol, a red flocculent substance consisting chiefly of nitrogenous matter remaining undissolved. The alcoholic solution filtered off from this deposit, concentrated by distillation and finally evaporated *in vacuo* over sulphuric acid, dried to a tenacious semi-solid mass, covered with a colourless oily fluid, and containing crystalline particles of a solid fat. After removal of the fats by means of æther, this mass was digested in water at 38° C., which partly dissolved it with a fine red colour, leaving a brown mass of resinous aspect behind, more of which deposited on the cooling of the coloured liquid; the decoction was now evaporated to the consistence of a syrup, and finally dried *in vacuo* over sulphuric acid.

These are all the processes employed to *extract* the colouring matter from the cochineal; I may here remark, before entering on the details of its further purification, that I obtained other substances on evaporating the mother-liquors from which the colouring matter had been separated by lead salts, which will be hereafter described.

Purification of the Carminic Acid.—In my first attempts to purify the colouring matter I proceeded in the following way:—An aqueous solution of the crude carminic acid (A) was precipitated with acetate of lead, the precipitate of carminate of lead well-washed and decomposed by hydrosulphuric acid; the red supernatant liquid was first concentrated on the water-bath and finally dried *in vacuo*; a highly hygroscopic purple residue was thus obtained.

I could not, by whatever means I adopted, effect the decolorization of the colouring principle. In several attempts I heated the solution for some hours to 100° C., keeping up a continuous current of hydrosulphuric acid, and in other experiments a stream was made to pass for several days through the disengaged colouring matter, but without the slightest change in its aspect. From these experiments, made with the greatest care and at several periods, I am led to the same conclusion as Arppe, that Preisser must have been mistaken in his results, and I regret that I cannot throw any light on the probable cause of his error.

Several combustions of the carminic acid thus purified were made, the resulting numbers however became useless by the subsequent observation that this acid was by no means pure. A sufficient quantity being incinerated left a residue of acid reaction, which was suspected to contain phosphoric acid. Carminic acid burning only with great difficulty, it was reconverted into carminate of lead, the oxide of lead dissolved out of the residue obtained after fuming by acetic acid, which left a white residue of metaphosphate of lead, together with a little lead. The white residue was soluble in dilute nitric acid, and exhibited, when treated before the blowpipe, the characters of metaphosphate of lead; other tests likewise confirmed the presence of phosphoric acid. It will hereafter be seen that the process of extracting the colouring matter by alcohol (D) does not exclude the phosphoric acid, which in all probability existed in the colouring matter analysed by Pelletier. It is further evident that the presence of phosphoric acid explains most satisfactorily the facts observed by Arppe.

a. In order to separate the phosphoric acid, another portion of crude carminic acid (A) was precipitated with acetate of lead. Three-fourths of the carminate of lead produced were decomposed by hydrosulphuric acid and evaporated to dryness in the way already mentioned. The dry mass being dissolved in cold absolute alcohol, and filtered from a slight flocculent brownish residue, was heated to ebullition in a water-bath and mixed with the remaining fourth of the carminate of lead, which had been previously reduced to a fine powder; the ebullition was continued for a few hours. In this method the free phosphoric acid combined with the lead, liberating an equivalent proportion of carminic acid, which was taken up by the alcohol. The alcoholic solution was filtered whilst hot, concentrated by distillation, and then evaporated *in vacuo* in the presence of sulphuric acid; it dried into a granular mass of a deep purple-brown colour, detaching itself spontaneously from the sides of the vessel, and on examination by the microscope was found to be a beautiful transparent crimson substance, exhibiting only slight, if any, signs of crystalline structure; by pulverization it became of a fine scarlet colour; it left a mere trace of ash, and was found to be perfectly free from phosphoric acid. It was highly hygrometric*.

* In consequence of this it was found convenient to dry the carminic acid intended for analysis in little stoppered tubes in the air-pump, as the stopper could be rapidly inserted after desiccation, and access of air effectually prevented.

Burnt with chromate of lead,—

I. ·4647 grm. gave ·9096 grm. carbonic acid and ·2175 grm. water.

II. ·4630 grm. gave ·9105 grm. carbonic acid and ·2140 grm. water.

For the latter analysis I am indebted to my friend Mr. Nicholson.

b. A second preparation of carminic acid was made by operating on the crude carminate of lead (C) and treating the resulting crude carminic acid in the manner just described for the preparation *a.* It left on incineration 0·2 per cent. of ash (·1609 grm. giving ·0003 grm. ash), which was neglected in the following analyses:—

III. ·3710 grm. gave ·7316 grm. carbonic acid and ·1710 grm. water.

IV. ·3685 grm. gave ·7235 grm. carbonic acid and ·1722 grm. water.

c. To effect the purification of the carminic acid (D) obtained by digesting cochineal in alcohol, it was dissolved in water and precipitated by acetate of lead; the filtrate was found to contain nitrogenous matter, and the carminate of lead to be contaminated with phosphate of lead; it was therefore treated in the manner already detailed.

V. ·3925 grm. of this substance gave ·7658 grm. carbonic acid and ·1780 grm. water.

d. A fourth preparation of carminic acid was obtained by substituting phosphoric acid for hydrosulphuric in the decomposition of the crude carminate of lead (C), and evaporating the carminic acid to dryness in contact with a fresh portion of carminate of lead; this did not however separate entirely the phosphoric acid, it was therefore redissolved in boiling absolute alcohol, and maintained some time at that temperature with more carminate of lead. On analysis—

VI. ·3805 grm. gave ·7530 grm. carbonic acid and ·1848 grm. water.

Pelletier having obtained in his analysis of “carmine” (carminic acid) as much as 3·56 per cent. of nitrogen, all the before-cited preparations of carminic acid were carefully examined qualitatively for nitrogen by heating with soda-lime, and without exception gave indications of its presence; in most cases but a mere trace was found, but I thought it necessary notwithstanding to make a few quantitative determinations, especially as M. Berzelius* had pointed out the improbability of it being an essential constituent.

* *Traité de Chim.* t. iii. p. 308. Brussels, edit. 1839.

The last preparation (*d*) appearing to contain more than any of the others, it was chosen and burnt with soda-lime.

It was indispensable in experiments of this nature to test the purity of the soda-lime as regarded the absence of ammonia. A tube having 9 inches of its length filled with soda-lime was heated to redness, just as in a nitrogen determination; the hydrochloric acid, being treated with bichloride of platinum in the usual manner, gave 7.5 milligrammes of ammonio-chloride of platinum; and a repetition of the experiment gave a similar result. This allowance has been made on all the nitrogen determinations by soda-lime.

.5938 grm. carminic acid (*d*) gave .0717 grm. ammonio-chloride of platinum = 0.76 per cent. of nitrogen.

This quantity of nitrogen could not be supposed to belong to the composition of the colouring matter, but was evidently due to some foreign substance, and not improbably to ammonia. In order to purify the carminic acid still more, the same specimen (*d*) was dissolved in a small quantity of boiling absolute alcohol and the filtered solution mixed with three times its bulk of anhydrous æther; a splendid scarlet precipitate was immediately produced, which absorbed water rapidly from the atmosphere, and agglutinated into a dark purple mass; when dried it weighed 0.3 grm. (*e*). The filtrate, which was of a pale orange-red colour, left on evaporation 0.5 grm of carminic acid (*f*).

.2635 grm. (*e*) burnt with soda-lime gave .0637 grm. ammonio-chloride of platinum = 1.52 per cent of nitrogen.

.4732 grm. (*f*) gave .0150 grm. ammonio-chloride of platinum = 0.2 per cent. of nitrogen.

We have therefore (*e*) 0.3 grm. found to contain by analysis 1.5 per cent. nitrogen, and (*f*) 0.5 grm. 0.2 per cent.,

$$\frac{(3 \times 1.5) + (5 \times 0.2)}{8} = .69 \text{ average per cent., which agrees}$$

closely with .76, found previous to treatment with æther.

g. Another preparation of carminic acid was obtained by precipitating crude carminic acid with acidulated acetate of copper, which salt was found to carry down the carminic acid, and to leave in solution by far the greater portion of the phosphoric acid. The carminate of copper, which occupied a long time in washing, was collected and decomposed by hydrosulphuric acid. The filtrate was evaporated to dryness, dissolved in boiling absolute alcohol, filtered, concentrated by distillation, and again evaporated to dryness *in vacuo*. It still contained a trace of phosphoric acid. On evaporating the mother-liquor and filtering, from an impure carminate of copper which deposited as the acetic acid was driven off, and

again concentrating to dryness, a brown mass was obtained, which on incineration left a greenish-white very hygrometric ash, in which phosphoric acid, soda and copper were found. Burnt with chromate of lead—

VII. $\cdot 4020$ grm. carminic acid (*g*) gave $\cdot 7842$ grm. carbonic acid and $\cdot 1662$ grm. water.

This acid however still retained some impurities : on incineration it left $0\cdot 4$ per cent. of ash ($\cdot 5489$ grm. giving $\cdot 0022$ grm. ash), and examined for nitrogen it gave the following numbers:—

$\cdot 4731$ grm. burnt with soda-lime gave $\cdot 0150$ grm. ammoniochloride of platinum = $0\cdot 2$ per cent. of nitrogen.

h. In order to separate these impurities the greater portion was dissolved in boiling absolute alcohol, and filtered from a slight residue ; the remainder, about an eighth, was converted into carminate of lead and digested with the boiling alcoholic solution for some hours ; the alcoholic tincture filtered off whilst hot and mixed with about six times its volume of anhydrous æther ; this threw down a bulky precipitate of a fine red colour, which was separated by filtration and the filtrate concentrated in a retort, and finally evaporated to dryness *in vacuo* (*h*).

i. The precipitate retained on the filter was dried *in vacuo*, then dissolved in as small a quantity of alcohol as possible, and again mixed with a large quantity of æther ; this determined a precipitate which was no longer of a fine red but of a brown colour, and on re-solution and similar treatment it diminished in quantity and became darker in colour, leaving the colouring matter in solution. From the filtrates a quantity of carminic acid (*i*) was obtained on evaporating to dryness *in vacuo*. It therefore appears that the æther precipitates a nitrogenous body which carries down with it variable quantities of carminic acid, according as a larger or smaller relative proportion is present. The carminic acid (*h*) was found to be free from phosphoric acid as well as nitrogen.

$\cdot 3003$ grm. burnt with soda-lime gave $\cdot 0015$ grm. ammoniochloride of platinum = $0\cdot 03$ per cent. of nitrogen.

From this analysis I venture to assert that the colouring principle of cochineal contains no nitrogen, thus fully confirming the anticipation of Berzelius. We can now understand from the preparation of the specimen of carminic acid (*e*), that the method employed by Pelletier for the preparation of the substance he analysed was calculated to accumulate all the nitrogenous matter contained originally in his alcoholic decoction ; a fact which fully explains the large amount of nitrogen he obtained in his analysis.

An analysis of the carminic (*h*) acid by chromate of lead gave from—

VIII. ·3167 grm. ·6203 grm. carbonic acid and ·1402 water.

The following table exhibits the per-centage results deduced from the foregoing analyses: the specimens were all dried over sulphuric acid *in vacuo*, with the exception of analysis VII., in which the carminic acid was dried at 100° C.

	I.	II.	III.	IV.	V.	VI.	VII.	VIII.	Mean.
Carbon ...	53·38	53·63	53·78	53·55	53·21	53·97	53·20	53·42	53·51
Hydrogen	5·20	5·14	5·12	5·19	5·04	5·39	4·59	4·92	5·07

By the analysis of a copper salt of carminic acid hereafter to be mentioned, it became probable that carminic acid might still retain, when only dried *in vacuo*, a portion of the solvents employed; a presumption which was supported by the analysis VII., in which the substance analysed had been dried at 100° C., and which gave a smaller per-centage of hydrogen. A portion of carminic acid (*i*), being first dried *in vacuo*, and then heated to a temperature of 121° C., was found to yield a small quantity of acetic acid, and was not altered in its properties, which were not in fact changed even at a temperature of 136° C.

In the following analyses the carminic acid, previously dried *in vacuo** and then at a temperature of 120° C., gave, on burning with chromate of lead, the following results:—

IX. ·3347 grm. (*h*) gave ·6648 grm. carbonic acid and ·1381 grm. water.

X. ·3583 grm. (*i*) gave ·7108 grm. carbonic acid and ·1504 grm. water.

These analyses give the following per-centage quantities:—

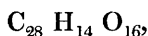
	IX.	X.
Carbon . . .	54·17	54·10
Hydrogen . .	4·58	4·66

The analysis IX. being of the same preparation as had served for analysis VIII., it is fair to presume that all the other specimens of carminic acid would have given the same per-centage quantities as the specimen (*h*) if dried at 120° C., as this particular specimen, dried *in vacuo*, yielded numbers in close accordance with the mean of the other analyses.

These numbers converted into the most simple expression lead to the following formula, C₁₄ H₇ O₈; but an analysis of a copper salt renders it probable that this formula has to be

* The carminic acid fuses if exposed to a temperature of 120° C. without having been previously dried.

doubled; and that the composition of carminic acid is expressed by the formula,



as may be seen from the following table containing the comparison of the theoretical per-centages with the mean of analyses IX. and X.

		Theory.	Experiment.
C_{28}	. 168	54·19	54·13
H_{14}	. 14	4·52	4·62
O_{16}	. 128	41·29	41·25
	<u>310</u>	<u>100·00</u>	<u>100·00</u>

From the foregoing experiments, it seems that the best method of obtaining pure carminic acid is to precipitate the aqueous decoction by acetate of lead; to decompose the washed carminate of lead by hydrosulphuric acid, and to throw down the carminic acid once more by acetate of lead, previously mixed with acetic acid; to decompose the carminate of lead by hydrosulphuric acid; to evaporate to dryness and redissolve the carminic acid in absolute alcohol; then to digest the alcoholic tincture with carminate of lead; and lastly, to precipitate the trace of nitrogenous matter by æther, the pure carminic acid is obtained from the filtrate.

As thus prepared, carminic acid has the following properties. It is a purple brown friable mass, transparent when viewed by the microscope, and pulverizing to a fine red powder; soluble in water and alcohol in all proportions, very slightly soluble in æther, which does not however precipitate it from its alcoholic solution if free from nitrogenous matter. It is soluble without decomposition in concentrated hydrochloric and sulphuric acids. It is decomposed by chlorine, iodine and bromine, which change its colour to yellow, and the latter on warming or by standing gives a yellow precipitate soluble in alcohol. Nitric acid decomposes it even if highly diluted: I shall have occasion to refer to this decomposition presently. It bears a temperature of 136° C. without decomposition; on gradually increasing the temperature a quantity of an acid liquor is produced, and at a red heat it intumescs and gives off a small quantity of red fumes, which condense: it gives no trace of oily matter.

The aqueous solution has a feeble acid reaction; it does not absorb oxygen. A volume of this gas contained in a tube with carminic acid over mercury did not change by absorption after exposure for several months. The fixed alkalies and ammonia give no precipitate in the aqueous solution, merely changing its colour to purple; in the alcoholic tincture they

produce purple precipitates; all the alkaline earths produce purple precipitates; sulphate of alumina gives no precipitate, but on addition of a drop of ammonia the carminic acid is immediately taken down as a beautiful crimson lake; acetates of lead, copper, zinc and silver give purple precipitates; the latter is immediately decomposed, and silver deposited; the nitrates of lead, mercury and silver reddish precipitates; protochloride and bichloride of tin no precipitates, but change the colour to a deep crimson.

The acid character of carminic acid being so very little pronounced, I met with considerable difficulties in determining its atomic weight; it is only with great reserve that I bring forward the formula before cited. Several attempts were made to produce soda, baryta, lead and copper compounds, but it was only with the copper salt that I obtained results agreeing in different preparations.

It seems that carminic acid attaches itself to salts, for it was found that the precipitants could be removed from the precipitates only with the greatest difficulty. I omit several soda, baryta and lead determinations which have not led to any satisfactory result, and confine myself to the statement of the result of the analysis of the copper compound. It was obtained by acidulating an aqueous solution of pure carminic acid with acetic acid, and then precipitating by the cautious addition of acetate of copper, so as to leave an excess of carminic acid in the liquid. The precipitate was well-washed by decantation (by which a great loss was sustained) and dried. It formed into masses of a bronze colour, very hard and difficult to powder. Two specimens were prepared at different times (*a* and *b*).

I. .2800 grm. (*a*) dried at 100° C. left, after ignition and treatment with nitric acid and re-ignition, .0330 grm. oxide of copper.

II. .3782 grm. (*b*) dried at 100° C. gave .0426 grm. oxide of copper.

III. .4702 grm. (*b*) dried at 100° C. gave on burning with chromate of lead .8210 grm. carbonic acid and .1743 grm. water.

These numbers lead to the following per-centage results:—

	I.	II.	III.
Carbon	47.62
Hydrogen	4.12
Oxide of copper	11.78	11.27	

agreeing closely with the formula, $C_{28}H_{14}O_{16}$, CuO , as will be seen from a comparison of the theoretical and experimental numbers.

		Calculated.	Found.
Carbon . . . 28	168	48·05	47·62
Hydrogen . . . 14	14	4·01	4·12
Oxygen . . . 16	128	36·61	36·74
Oxide of copper 1	39·6	11·33	11·52
	<u>349·6</u>	<u>100·00</u>	<u>100·00</u>

Action of Nitric Acid on Carminic Acid.

Nitrococcusic Acid.—When acting with nitric acid on “carmine” (carminic acid), MM. Pelletier and Caventou obtained white acid crystals resembling oxalic acid, but differing from this acid in several of its properties. M. Arppe found that the acid produced was oxalic acid. In my experiments I obtained the following results:—One pound and a half of crude carminic acid was gradually introduced into ten pounds of nitric acid, spec. grav. 1·4, and digested at a moderate heat; a violent evolution of nitrous fumes succeeded each addition of the carminic acid; after the whole quantity had been introduced and the action had somewhat subsided, the mixture was transferred into a smaller vessel and the action continued at the boiling-point for about two hours; by this time the greater part of the nitric acid had evaporated, and on withdrawing the vessel from the fire and allowing the mixture to cool, a crystalline cake was obtained, which on examination was found to consist partly of a new acid and partly of oxalic acid. To separate the oxalic acid, it was dissolved in a large quantity of boiling water and treated with nitrate of lead as long as any precipitate formed; this was collected and decomposed by boiling with dilute sulphuric acid; the filtrate from the sulphate of lead yielded a large quantity of prismatic crystals of oxalic acid, which were obtained perfectly white and pure after two or three crystallizations with the aid of a little animal charcoal.

The yellow liquid filtered from the oxalate of lead was concentrated and separated from a fresh portion of oxalate which deposited on concentration, the evaporation was then continued until a large quantity of crystals formed; the solution on cooling deposited a very bulky mass of yellow rhombic prisms, which were drained and dried, and re-dissolved in a sufficient quantity of boiling water, which on cooling deposited the acid (for which I propose the name of nitrococcusic acid) in beautiful crystals free from any lead salt; it was recrystallized twice more, by which means it was obtained perfectly pure.

Several preparations were made, sometimes using pure car-

minic acid, at other times carminate of lead, with similar results.

The analyses of four different preparations dried at 100° C. gave, on burning with chromate of lead (unless otherwise stated), the following numbers:—

I. .3152 grm. (*a*) gave .3892 grm. carbonic acid and .0561 grm. water.

II. .2500 grm. (*a*) gave .3080 grm. carbonic acid and .0445 grm. water.

(For this analysis I am indebted to Mr. Nicholson.)

III. .3068 grm. (*a*) gave .3820 grm. carbonic acid and .0502 grm. water.

IV. .4498 grm. (*b*) gave .5626 grm. carbonic acid and .0757 grm. water.

V. .4461 grm. (*c*) gave .5515 grm. carbonic acid and .0777 grm. water.

VI. .4503 grm. (*d*) gave, on being burnt with oxide of copper, .5585 grm. carbonic acid and .0757 grm. water.

VII. .4796 grm. (*c*) gave, on being burnt with oxide of copper, and a layer of copper twelve inches long used so as to completely decompose the binocide of nitrogen, .5882 grm. carbonic acid and .0815 grm. water.

The foregoing analyses lead to the following per-centage quantities:—

	I.	II.	III.	IV.	V.	VI.	VII.
Carbon .	33·67	33·60	33·95	34·11	33·72	33·82	33·44
Hydrogen	1·98	1·98	1·82	1·87	1·93	1·87	1·89

In the following experiments the nitrogen of the nitrococcus acid was ascertained by burning with oxide of copper in an atmosphere of carbonic acid.

VIII. .6808 grm. (*b*) dried at 100° C. gave 84 cub. cent. of moist nitrogen at 6·5 C. and 0·7585 m. barometer corrected.

IX. .7162 grm. (*c*) dried at 100° C. gave 91·5 cub. cent. of moist nitrogen at 17°·5 C. and 0·7641 m., barometer corrected.

These numbers correspond to the following per-centage quantities:—

	VIII.	IX.	Mean.
Nitrogen . .	15·03	14·92	14·97

X. In this experiment the nitrogen was determined according to Bunsen's* method, which consists in burning the substance mixed with oxide of copper in the presence of copper turnings in a hard glass tube. The tube being freed from air by a stream of hydrogen, is then exhausted, sealed hermetically, and placed in an iron mould filled with plaster of Paris; it is then heated to redness and allowed to cool. After the com-

* Liebig's *Annalen*, vol. xxxvii. p. 27.

bustion, the gas is transferred into a graduated jar over mercury and its volume noted; the carbonic acid being absorbed by a potash ball, the volume is again read off. This analysis gave the following numbers:—

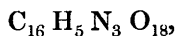
	Vol.	Temp.	Diff. of level.	Barom.
Carbonic acid + nitrogen (moist)	123	20°·7 C.	0 ^m ·0640	0 ^m ·7543
Nitrogen	22·2	20°·0	0 ^m ·1650	0 ^m ·7529

The height of the column of mercury in the eudiometer above the level in the trough and the barometric column are corrected for temperature.

Carbonic acid + nitrogen corrected to 0° C. and barom.	1 ^m = 76·84
Nitrogen	0° 1 ^m = 12·16
Carbonic acid	0° 1 ^m = 64·68

$\frac{64·68}{12·16} = 5·32$, which is the ratio of carbon equivalents to one nitrogen equivalent.

The preceding analyses of nitrococcus acid agree with the following formula, confirmed by the analyses of several of its compounds,



as will be seen on referring to the table.

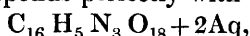
	Theory.		Experiment.
			Mean.
Carbon . 16	96	33·45	33·75
Hydrogen 5	5	1·74	1·91
Nitrogen . 3	42	14·63	14·97
Oxygen . 18	144	50·18	49·37
	287	100·00	100·00

By analysis VII., in which the precaution was taken of using a very long layer of copper turnings, there was obtained, carbon 33·44, hydrogen 1·89; these numbers agree as closely as possible with the theoretical quantities, as does likewise the nitrogen determination (X.) by Bunsen's method; in this experiment the ratio of carbon equivalents to nitrogen equivalents was found to be as 5·32 to 1, or as 16 eqvts. of carbon to 3·007 eqvts. of nitrogen; taking analysis VII. as the basis of calculation, it gives 14·67 per cent. of nitrogen, the theoretical number being 14·63.

The acid, as it separates from its aqueous solution, contains water of crystallization, which it loses at 100° C.; four experiments gave the following results:—

·4800 grm. lost	·0289 grm.	= 6·02 per cent.
·6613	·0395	= 5·97
·6586	·0385	= 5·84
·4804	·0289	= 6·01
	Mean	= 5·96

This mean corresponds perfectly with the formula



as may be seen by a comparison of the theoretical and experimental numbers.

	Theory.		Experiment. Mean.
1 equiv. dry acid . . .	287	94·10	94·04
2 ... water	18	5·90	5·96
1 ... crystallized nitrococcus acid . . }	305	100·00	100·00

Properties of Nitrococcus Acid.—It is of a yellow colour, crystallizing in rhombic plates, and presenting very different aspects, according to the circumstances under which it is crystallized. Its solution stains the skin yellow, it is soluble in cold, but considerably more so in hot water; soluble in alcohol, and very soluble in æther. All its salts dissolve readily in water, and most of them in alcohol; it deflagrates violently on being heated; it dissolves iron and zinc, becoming dark-coloured. It is decomposed by sulphide of ammonium with separation of sulphur and the formation of the ammonia salt of a new acid, which I have not yet examined.

Compounds of Nitrococcus Acid.

Nitrococcusate of Potash.—I have prepared this salt by two different methods.

a. A solution of nitrococcus acid in boiling water was accurately saturated with carbonate of potash; by evaporation to a small bulk and cooling, the salt was obtained in small yellow crystals; it was purified by draining and recrystallizing.

b. An ætherial solution of the acid was precipitated by the cautious addition of an alcoholic solution of potash; the pale yellow precipitate washed with æther and dried, then dissolved in as small a quantity of cold water as possible, and the solution poured into about five times its bulk of absolute alcohol; after standing some time the salt crystallized in well-formed crystals; it was washed with æther and dried. The ætherial washings being added to the mother-liquor, a further portion was obtained and washed with æther. The latter process is less troublesome than the process *a.*

I. ·5469 grm. (*a*) dried at 100° C. were dissolved in a small quantity of boiling water and decomposed by sulphuric acid; dried in a water-bath, the nitrococcus acid, removed by æther and the residue ignited, gave ·2606 grm. sulphate of potash.

II. ·4383 grm. (*b*) dried at 132° C. gave ·2103 grm. sulphate of potash.

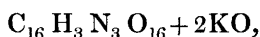
III. ·6251 grm. (*b*) dried at 100° C. and burnt with chro-

mate of lead, gave .6064 grm. carbonic acid and .0662 grm. water.

These numbers give the following per-centage quantities:—

	I.	II.	III.
Carbon	26.46
Hydrogen	1.18
Potash . . .	25.74	25.92	

corresponding with the formula



as may be seen by comparing the theoretical and experimental numbers.

	Theory.		Experiment.
			Mean.
Carbon . 16	96	26.45	26.46
Hydrogen . 3	3	.83	1.18
Nitrogen . 3	42	11.57	
Oxygen . 16	128	35.26	
Potash . 2	94	25.89	25.83
	363	100.00	

I was not successful in preparing a nitrococcusate of potash with one equivalent of fixed base; the method I adopted was saturating a given weight of acid with carbonate of potash, and then adding the same amount of acid to the bibasic potash salt; on washing with æther the greater part of the excess of acid was removed, leaving the bibasic salt behind.

Nitrococcusate of Ammonia.—This salt was prepared by passing an excess of dry ammoniacal gas through an ætherial solution of the acid dried in the atmosphere; the solution became turbid, and by standing for a short time deposited the salt in clusters of needles adhering firmly to the sides of the vessel; these were removed, washed with æther, and dried on bibulous paper. It is volatile, and sublimes on being heated, most probably with decomposition.

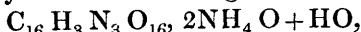
I. .6011 grm. of the salt dried *in vacuo* was dissolved in a small quantity of boiling water and decomposed by strong hydrochloric acid, which immediately separated the acid in crystals; the mixture was dried in a water-bath, and the nitrococcusic acid removed by æther, a little bichloride of platinum and alcohol being added to the ætherial washings to precipitate a trace of chloride of ammonium. The residue, precipitated as ammonio-chloride of platinum, gave .8208 grm. of the double chloride.

II. .6126 grm. dried *in vacuo* and burnt with oxide of copper, the mixture being made in the combustion-tube, gave .6525 grm. carbonic acid and .2191 grm. water.

These numbers correspond with the following per-centage quantities:—

	I.	II.
Carbon	29·05
Hydrogen	3·97
Oxide of ammonium . .	15·91	

agreeing closely with the following formula,



as may be seen by a comparison of the theoretical and experimental numbers.

	Theory.		Experiment.
Carbon . 16	96	29·09	29·05
Hydrogen 12	12	3·64	3·97
Nitrogen . 5	70	21·21	
Oxygen . 19	152	46·06	
	<u>330</u>	<u>100·00</u>	

Or

	Theory.		Experiment.
Acid 1	269		
Water 1	9		
Oxide of ammonium 2	52	15·76	15·91
	<u>330</u>		

Nitrococcusate of Baryta was prepared by adding an excess of a solution of baryta to an aqueous solution of nitrococcus acid, a stream of carbonic acid gas being passed through the solution to separate the excess of baryta. The solution was warmed, filtered and evaporated in a water-bath, and again filtered from a small quantity of carbonate of baryta. The evaporation being continued until a pellicle formed on the surface, the solution on cooling deposited this salt in minute yellow crystals. It is insoluble in alcohol, which precipitates it in the form of a jelly from the aqueous solution.

I. ·6750 grm. of substance dried at 100° C. and decomposed by sulphuric acid, gave ·3602 grm. of sulphate of baryta.

II. ·6439 grm. of nitrococcusate of baryta dried at 100° C. and burnt with chromate of lead, gave ·5185 grm. of carbonic acid and ·0800 grm. of water.

These numbers correspond to the following per-centage quantities:—

	I.	II.
Carbon	21·96
Hydrogen	1·38
Baryta	35·06	

agreeing with the formula $C_{16}H_3N_3O_{16} + 2BaO + 2HO$, as may be seen from the following table:—

	Theory.		Experiment.
Carbon . 16	96·00	21·80	21·96
Hydrogen 5	5·00	1·14	1·38
Nitrogen . 3	42·00	9·54	
Oxygen . 18	144·00	32·71	
Baryta . . 2	153·28	34·81	35·06
	<u>440·28</u>	<u>100·00</u>	

Nitrococcusate of Silver.—I attempted to make this salt by boiling oxide of silver with an aqueous solution of nitrococcusic acid, but there was an evident decomposition of the acid, a large quantity of carbonic acid being evolved; after warming the filtered liquor a brown deposit was formed. On filtering off this brown deposit a silver salt was obtained by evaporation, which yielded on analysis—

Carbon	23·64
Hydrogen	1·26
Oxide of silver . .	38·10

per-centage numbers not reconcilable with those of nitrococcusate of silver.

On decomposing a hot solution of this salt with hydrochloric acid a new acid was obtained, perfectly distinct from nitrococcusic acid; it crystallized in long needles; very insoluble in water, but soluble in æther and alcohol. I refrain from giving any further account of this acid until the study is completed.

In order to avoid decomposition the nitrococcusate of silver was prepared without the aid of heat, by dissolving carbonate of silver in a cold aqueous solution of nitrococcusic acid and evaporating the filtered solution *in vacuo* over sulphuric acid. The salt crystallized in long bulky needle-like crystals of a yellow colour; when dried at 100° C. the powdered salt becomes deep orange.

It is soluble in alcohol and water, and is highly explosive when heated; in small quantities it may be decomposed by a progressive heat without any violent action; but on attempting to decompose a quantity amounting to ·45 grm. in a porcelain crucible, heated in an air-bath, the salt exploded with great violence, shattering the copper air-bath and driving fragments of the crucible through the copper; the temperature was noted just before the explosion, the thermometer standing at 200° C.; the silver was therefore determined as chloride.

I. .4698 grm. of substance (*a*) dried at 100° C. and decomposed by nitric acid and the silver precipitated by the addition of hydrochloric acid, gave .2675 grm. chloride of silver.

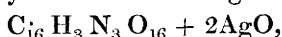
II. .5085 grm. of substance (*b*) dried at 100° C. gave .2892 grm. chloride of silver.

III. .8184 grm. of substance (*a*) dried at 100° C. and burnt with oxide of copper, gave .5700 grm. carbonic acid and .0554 grm. water.

Corresponding to the following per-centage quantities :—

	I.	II.	III.
Carbon	18.99
Hydrogen	0.75
Oxide of silver	46.03	45.97	

and agreeing closely with the following formula,



as may be seen by the following table :—

	Theory.		Experiment.
			Mean.
Carbon 16	96	19.162	18.99
Hydrogen . . . 3	3	.599	.75
Nitrogen . . . 3	42	8.383	
Oxygen 16	128	25.549	
Oxide of silver . 2	232	46.307	46.00
	501	100.000	

Nitrococcusate of Copper.—This was made by dissolving carbonate of copper in nitrococcusic acid and deposited on evaporation in pale apple-green needles. I made no analysis of this salt.

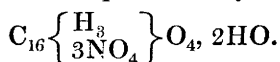
The following is a synoptical table of the analyses of nitrococcusic acid and its compounds :—

Hydrate of nitrococcusic acid .	$C_{16}H_3N_3O_{16} + 2HO.$	
Hydrate of nitrococcusic acid } as crystallized from water }	+ 2HO + 2Aq.
Nitrococcusate of potash	+ 2KO.
Nitrococcusate of ammonia	+ 2NH ₄ O + Aq.
Nitrococcusate of baryta	+ 2BaO + 2Aq.
Nitrococcusate of silver	+ 2AgO.

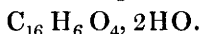
The properties of nitrococcusic acid and its salts exhibit a great analogy with those of a number of acids obtained by the action of nitric acid on organic bodies, more especially nitropicric and styphnic acids, from which it differs by the greater solubility of its salts.

If we assume with many chemists the nitrogen of these

acids to exist in the form of hyponitric acid, the formula of nitrococcusic acid will be represented by



This acid would consequently derive from a non-nitrogenous acid, having the composition expressed by the formula



When I first began this investigation I imagined that a similar relation might exist between nitrococcusic acid and carminic acid; the analysis of these acids, however, as well as the simultaneous production of a large quantity of oxalic acid in its oxidation, showed that this view was erroneous, and that nitrococcusic acid was derived from carminic acid in a more complex manner. Some attempts were made to produce the non-nitrogenous acid, the coccusic acid, but unsuccessfully.

The experiments of MM. Cahours and Laurent on the oxidation of the oils of anise and of tarragon (*Oleum dracunculii*) have made us acquainted with anisic acid, the composition of which is $C_{16} H_8 O_6$. The formula agrees with the composition of the hypothetical hydrated coccusic acid.

Anisic acid, however, as well as nitranisic acid, being monobasic, it was not probable that the further introduction of the elements of hyponitric acid would convert it into a bibasic one; nevertheless it was my intention to have studied the further action of nitric acid on the acids mentioned, in order to obtain if possible trinitroanisic acid, and to compare this substance with the acid obtained from carminic acid, when an account of some new experiments of M. Cahours came under my notice, of the action of a mixture of concentrated sulphuric and nitric acids on anisic acid, by which he has succeeded in preparing trinitroanisic acid. The experiments of M. Cahours have not yet been published in detail, and from his short account it was not possible to decide on the identity or non-identity of nitrococcusic and trinitroanisic acids. A small specimen of anisic acid at my disposal was treated in the manner described by him; after acting for some time water threw down an acid, from the insolubility of which I conclude that these acids are only isomeric.

Investigation of the Mother-liquor from which the Carminic Acid had been separated.

On evaporating the mother-liquors of carminic acid and separating the lead held in solution by means of hydrosul-

phuric acid, they all gave the following results: on acquiring a syrupy consistence, a white chalky-like matter subsided; this was separated by filtration, and proved to be a new crystalline body. The liquor filtered off from this substance deposited a small quantity more on further concentration, and could only be dried to a soft tenacious mass, partly soluble in alcohol, the rest being soluble in water. From three pounds of cochineal five ounces of this soft matter were obtained, showing that the precipitation by a lead salt had effected the separation of carminic acid from a large quantity of foreign matters. This gelatinous matter appears to be of a complex character, but I have not yet examined it fully.

To purify the chalky-like matter, it was well-washed with cold water and crystallized twice by solution in boiling water and evaporation; it was then dissolved by boiling it in a just sufficient quantity of water; animal charcoal was now added, and the ebullition continued for a few minutes; the solution filtered whilst hot deposited on cooling a mass of silky crystalline tufts, completely filling the liquid, and when collected and dried they aggregated into paper-like masses of a silky aspect. I obtained in three experiments 4 parts of the new body from 1000 of cochineal.

I. .4918 grm. of substance, preparation (*a*), dried *in vacuo* and burnt with oxide of copper, gave 1.0705 grm. carbonic acid and 0.2838 grm. water.

II. .5680 grm. of substance (*b*) gave 1.2416 grm. carbonic acid and .3160 grm. water.

III. .4700 grm. of substance (*b*) gave 1.0210 grm. carbonic acid and .2660 grm. water.

For the latter analysis I am indebted to the kindness of Mr. Nicholson.

A qualitative examination having pointed out the presence of nitrogen, it was determined by Varrentrapp and Will's method.

IV. .5046 grm. of substance (*a*) dried *in vacuo* and burnt with soda-lime, gave .6131 grm. ammonio-chloride of platinum.

V. .5076 grm. of substance (*b*) gave .6239 grm. ammonio-chloride of platinum.

From these numbers the following per-centages are calculated:—

	I.	II.	III.	IV.	V.
Carbon .	59.36	59.62	59.25		
Hydrogen	6.41	6.18	6.29		
Nitrogen	7.62	7.71

These per-centages, translated into the most simple expression, lead to the formula, $C_{81}H_{11}NO_6$ as may be seen from the following table:—

	Theory.		Experiment.
			Mean.
Carbon . . . 18	108	59.668	59.41
Hydrogen . . 11	11	6.077	6.29
Nitrogen . . 1	14	7.735	7.66
Oxygen . . . 6	48	26.520	
	181	100.000	

Careful and repeated examinations for sulphur proved the absence of this element as a component of the new white substance. I have been unable to produce a compound to control the proposed formula, though several methods were adopted; amongst others, I attempted to form a lead compound by adding acetate of lead to an ammoniacal solution of the substance; I obtained merely a bulky precipitate, consisting of little else than oxide of lead.

This substance is sparingly soluble in cold water, much more so in boiling water; insoluble in alcohol and æther; soluble in hydrochloric acid, which appears to be driven off by evaporation, leaving the substance in large crystals. In a large quantity of nitric acid it dissolves with a slight evolution of gas; the solution evaporated spontaneously furnishes long crystals, which are in all probability a new acid; if dissolved in a small quantity of nitric acid, the mixture becomes spontaneously heated, violent action takes place, and the product is lost; frequently the substance becomes blackened into charred masses. It is soluble in ammonia, from which it is again recovered by the evaporation of the ammonia. It is soluble in the fixed alkalis, and is precipitated from these solutions by saturating with an acid.

In a short paper, entitled "Valerianic Acid and a new body from Casein," Baron Liebig* describes a new substance obtained by fusing casein with hydrate of potash until an evolution of hydrogen takes place along with ammonia. On saturating with acetic acid the aqueous solution of the fused mass an aggregate of fine needles was produced, which were purified by repeated solution in carbonate of potash and re-precipitation by acetic acid. A preliminary analysis led to the formula $C_{16}H_9NO_5$, differing from the result I obtained in the analysis of the white substance from cochineal by two carbon, two hydrogen, and one oxygen. The properties of the two bodies being however so analogous, it is extremely probable that they are identical, a presumption I am sup-

* Liebig's *Annalen*, vol. lvii. p. 127.

ported in by a comparison of a specimen kindly furnished me by Dr. Hofmann *; further investigations will clear up this point: in the meantime I refrain from proposing a name, as Liebig † has lately proposed the name Tyrosine for the substance prepared from casein. As the latter body arises evidently from a process of oxidation, and as I had obtained the first crop of crystals from a liquid from which the colouring matter had been precipitated by the basic nitrate of lead, I thought that this body might owe its formation to the action of the nitric acid liberated by the sulphuretted hydrogen; but this supposition proved to be erroneous, for in later experiments in which acetate of lead had been used, the same body, and in exactly the same quantity, was obtained. From this we may assume that this substance is contained ready-formed in the cochineal insect.

My engagements for the present preventing me from continuing these researches, I must defer for a future period their completion, but hope to be enabled to communicate to the Society a second paper. In conclusion I may be allowed to express my thanks to my friend Dr. Hofmann for his valuable instruction in the methods of organic research, and his kind advice during the progress of this investigation.
