

## LVIII.—CONTRIBUTIONS FROM THE DYE-HOUSE OF THE YORKSHIRE COLLEGE.

*On some New Compounds of Hæmateïn and Brasileïn.*

By J. J. HUMMEL and A. G. PERKIN.

WHILE engaged in the preparation of specimens of the colouring principles of logwood, we devised a very simple method for obtaining hæmateïn in the crystalline state in tolerable quantity, which induced us to investigate some of the reactions of this colouring matter.

In order to prepare pure crystalline hæmateïn, commercial logwood extract is dissolved in a small quantity of hot water, and, after cooling, ammonia is added in slight excess to the syrupy solution. The solution of the ammonia-compound of hæmatoxylin thus formed is then exposed to the air for two or three days with occasional stirring, in order to convert it into the corresponding compound of hæmateïn; or this change is effected more rapidly by the aspiration of air through the solution for several hours. A dark purplish precipitate of the ammonia-compound of hæmateïn is gradually deposited. This is collected on a filter and well pressed.

About 40 grams of this precipitate are now dissolved in a litre of hot water, and from 30—160 c.c. of strong acetic acid (sp. gr. 1·04) added. After heating the mixture for some time on the steam-bath (in order to dissolve as much as possible of the amorphous hæmateïn precipitate which has been formed), it is cooled completely and filtered. The amorphous hæmateïn residue on the filter may be treated with hot dilute acetic acid in a similar manner three or four times, and the combined filtrates evaporated over the steam-bath. As the solution becomes concentrated, minute glittering crystals of hæmateïn appear.\* In order to separate these from the accompanying impurities, the

\* Crystals are also readily obtained when the filtrate from the hæmateïn-ammonia compound is precipitated with excess of acetic acid, the solution filtered and evaporated.

liquid is allowed to cool and mixed with a little acetic acid, which retains these foreign matters in solution, but leaves the hæmatein crystals for the most part undissolved. The latter are collected on a filter, washed three or four times with acetic acid, then with water, and dried.

Thus prepared, hæmatein has the form of exceedingly minute crystals, having a splendid pale yellowish-green metallic lustre.

When viewed under the microscope, they appear by transmitted light as very thin reddish-brown rhombic plates, forming occasionally stellate groups. Rubbed with a glass rod, they yield a reddish-brown powder. Hæmatein is very sparingly soluble in water, alcohol, ether, and acetic acid. Alkalis dissolve it readily; ammonia dissolves it with a rich brown-violet colour; while its strong alkaline soda solution has a rich purplish-blue colour. On exposure to the air, the colour of these alkaline solutions gradually becomes red, and finally brown, the colouring matter being apparently destroyed.

It is worthy of notice that when a very dilute solution of sodium hydrate is added to hæmatein, the latter dissolves with a bright red colour, and only when excess of sodium hydrate is added does the colour become purplish-blue.

Analyses of crystalline hæmatein gave the following numbers :—

0.1270 gram	gave	0.3002 gram of	CO <sub>2</sub>	and	0.0478 gram of	OH <sub>2</sub> .
0.1210	„	0.2838	„	CO <sub>2</sub>	and	0.0466 „ OH <sub>2</sub> .
0.1128	„	0.2635	„	CO <sub>2</sub>	and	0.0419 „ OH <sub>2</sub> .

These numbers give percentages agreeing with the formula C<sub>16</sub>H<sub>12</sub>O<sub>6</sub>.

	Theory.	I.	II.	III.
Carbon.....	64.00	64.47	63.94	63.71
Hydrogen ..	4.00	4.18	4.28	4.12

The hæmatein crystals as obtained in the above manner are anhydrous, and evidently identical with those described by Halberstadt and Reis (*Ber.*, **14**, 611), who obtained them by extracting aged Campeachy logwood with ether, but were unable to obtain them from commercial logwood extracts.

#### *Action of Sulphuric Acid on Hæmatein.*

According to Baeyer (*Ber.*, **4**, 457—555), hæmatein is probably a member of the group of bodies termed phthaleins, and possibly stands in a close relationship to gallein.

Since this latter body, when heated for some time with concentrated sulphuric acid to 200°, yields a new green colouring matter termed *coerulein*, it seemed possible that by treating hæmatein in the same

way, a similar product might be formed; but experiment proves that under these conditions the hæmatein is more or less completely destroyed, and yields no new colouring matter. Hæmatein, however, dissolves readily in cold concentrated sulphuric acid, with evolution of heat, producing a dark reddish-brown solution which, when left at rest for some time, becomes filled with lustrous yellow prismatic crystals. When this solution is poured into cold water, it gives a reddish-brown precipitate which resembles ferric oxide, and seems hitherto to have been mistaken for unchanged amorphous hæmatein (see *Gmelin's Org. Chem.*, **10**, 293). After washing free from acid, however, it is found to dissolve in sodium hydrate solution with a reddish-purple colour, whereas hæmatein, as already stated, gives a purplish-blue solution. It also dyes mordanted calico in shades quite different from those yielded by hæmatein, viz., with alumina mordants, if weak, it gives a dull red; if strong, red, inclining to chocolate; and with weak iron, a slate. It is evident, therefore, that a new body is produced.

By adding hot glacial acetic acid very gradually, and with constant stirring, to the sulphuric acid solution of hæmatein until it is diluted to the extent of two or three times its bulk, there is gradually thrown down an orange-coloured crystalline precipitate. It is collected on a filter, washed with glacial acetic acid until free from sulphuric acid, and dried. The product thus obtained forms an orange-coloured crystalline powder which, under the microscope, is seen to consist of minute transparent prisms.

On analysis it gave the following numbers:—

0·1120 gram of substance gave 0·2073 gram CO<sub>2</sub> and 0·0331 gram OH<sub>2</sub>.

0·1153 gram of substance gave 0·2120 gram CO<sub>2</sub> and 0·0341 gram OH<sub>2</sub>.

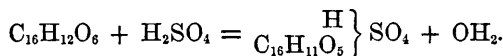
0·2325 gram of substance gave 0·1477 gram of BaSO<sub>4</sub>.

These numbers give percentages agreeing with the formula

$$\text{C}_{16}\text{H}_{11}\text{O}_5 \left\{ \begin{matrix} \text{H} \\ \text{SO}_4 \end{matrix} \right.$$

	Theory.	I.	II.	III.
Carbon.....	50·53	50·47	50·12	—
Hydrogen ..	3·16	3·28	3·29	—
Sulphur ....	8·42	—	—	8·72

The formation of this body, which we propose to call *acid iso-hæmatein sulphate*, may be represented thus:—



It is insoluble, or nearly so, in alcohol, ether, and benzene, but in strong acetic acid it dissolves to a small extent, forming a yellow solution. It is little soluble in cold ammonia solution, but on heating it dissolves with a dirty claret colour. Its sodium hydrate solution has a reddish-purple colour. Both solutions become brown on exposure to air, very much more rapidly indeed than the corresponding solutions of hæmatein.

When acid isohæmatein sulphate is washed with alcohol, its colour becomes redder, and the filtrate is found to contain a considerable quantity of sulphuric acid. With water it becomes darker than with alcohol, but the same separation of sulphuric acid takes place.

In order to examine this reaction the following preparations were made:—

(1.) A portion of acid isohæmatein sulphate was treated with alcohol, then with water, again with alcohol, and then ether, and dried.

(2.) A second quantity of this substance was treated with water, washed until no more sulphuric acid passed through, and dried.

(3.) A third quantity was placed in contact with ordinary alcohol (about 80 per cent.) and left to stand for some days.

In the course of a few hours the yellow product became covered with dark-coloured patches which were found to consist of crystals, and after two or three days the whole product was found to be converted into these crystals, which, by reflected light, have a beautiful metallic lustre, and, when seen by transmitted light, appear as plates having a dark orange-red colour. This colour is heightened by polarised light. Analyses of these preparations gave the following numbers:—

*Preparation I.*—0·1109 gram of substance gave 0·2382 gram CO<sub>2</sub> and 0·0339 gram OH<sub>2</sub>.

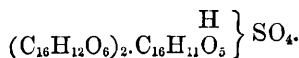
0·1092 gram of substance gave 0·2357 gram CO<sub>2</sub> and 0·0333 gram OH<sub>2</sub>.

*Preparation II.*—0·1137 gram of substance gave 0·2469 gram of CO<sub>2</sub> and 0·0325 gram of OH<sub>2</sub>.

*Preparation III.*—0·1059 gram of substance gave 0·2282 gram CO<sub>2</sub> and 0·0358 gram OH<sub>2</sub>.

0·1009 gram of substance gave 0·2167 gram CO<sub>2</sub> and 0·0340 gram OH<sub>2</sub>.

These numbers agree moderately well with the formula—



Theory.	Prep. I.		Prep. II.	Prep. III.	
	I.	II.		I.	II.
Carbon. . . .	58·77	58·55	59·22	58·63	58·57
Hydrogen . .	3·67	3·38	3·17	3·75	3·74

From the ready manner in which acid isohæmatein sulphate gives up part of its sulphur as sulphuric acid, it is evident that it is not an ordinary sulphonc acid, but has more the character of an acid sulphuric ether. The remarkable fact, however, is that with water it gives up only two-thirds of its sulphur, yielding the above peculiar body.

On boiling it with magnesium carbonate a large quantity of magnesium sulphate is formed together with a crystalline magnesium derivative, which when freshly prepared is seen to have a metallic lustre. This compound, however, is still found to contain a small quantity of sulphur. After removal of the magnesia by an acid, the product dyes mordants similarly to the original sulphuric product, but the colours are much duller.

It is proposed to examine this product further.

#### *Action of Hydrochloric Acid on Hæmatein.*

When hæmatein is heated in sealed tubes with hydrochloric acid (sp. gr. 1·195) for some time to 100°, the rich crimson colour of the solution gradually changes to a dirty yellow, and the mixture is found to contain minute crystals. As soon as the reaction is considered terminated, which is after several hours' heating, the tubes are opened and the contents evaporated to dryness in a dish over the steam-bath.

The product, which consists of a dark, almost black crystalline powder, showing an olive-green metallic lustre when viewed under the microscope, may be purified by heating it with water, slightly acidulated with hydrochloric acid, in which it easily dissolves, and filtering. On adding hydrochloric acid to the rich orange-coloured filtrate, an orange precipitate is obtained, and if the whole be now boiled so as to redissolve the product, there is deposited on cooling a red powder, which appears under the microscope to consist of minute transparent orange-red needles.

This substance was found to contain chlorine.

On analysis the following numbers were obtained :—

0·1239 gram of substance gave 0·2729 gram of CO<sub>2</sub>, and 0·0402 gram OH<sub>2</sub>.

0·1277 gram of substance gave 0·2808 gram of CO<sub>2</sub>, and 0·0411 gram OH<sub>2</sub>.

0·2169 gram of substance gave 0·0878 gram of AgCl.

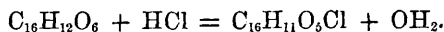
0·2053 gram of substance gave 0·0856 gram of AgCl.

These numbers give percentages agreeing with the formula



	Theory.	I.	II.	III.	IV.
Carbon . . . .	60·28	60·07	59·96	—	—
Hydrogen ..	3·45	3·60	3·57	—	—
Chlorine . . . .	11·15	—	—	10·59	10·82

The formation of this body may be expressed thus:—



This was found to take place almost quantitatively, as will be seen from the following experiment:—

0·2904 gram of hæmatein, heated with concentrated hydrochloric acid, increased in weight 5·74 per cent. Theory requires 6·13.

We propose to call this substance *Isohæmatein Chlorhydrin*. It dissolves easily in water, forming an orange-coloured solution, which is rather strongly acid, owing to the separation of hydrochloric acid, and if repeatedly evaporated and redissolved, loses most of its chlorine. It is less soluble in alcohol than in water. With alcoholic potash it gives a reddish-violet solution, which soon changes and becomes slaty, and afterwards of a blackish-brown colour, the intensity quickly diminishing.

With concentrated sulphuric acid it evolves hydrochloric acid gas, and is converted into acid isohæmatein sulphate. It dyes mordants in a similar manner to the sulphuric compound, but much more freely, and the shades are rather brighter in tone.

#### *Action of Hydrobromic Acid on Hæmatein.*

When hæmatein is heated in sealed tubes with strong hydrobromic acid, the *corresponding isohæmatein monobromhydrin* is produced.

The product consists of a dark mass of microscopic needles.

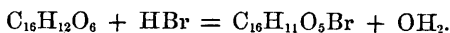
On analysis it gave the following result:—

0·2572 gram of substance gave 0·1274 gram of AgBr.

The percentage from this agrees closely with that required by the formula  $\text{C}_{16}\text{H}_{11}\text{O}_5\text{Br}$ .

	Theory.	I.
Bromine . . . . .	22·03	21·60

The reaction may be expressed thus:—



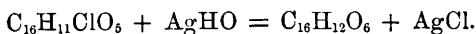
*Isohæmatein bromhydrin* dissolves in alkalis, with a violet colour,

and altogether in its general properties resembles the chlorine compound.

### *Isohæmateïn.*

If to an aqueous solution of *isohæmateïn chlorhydrin* or *bromhydrin* enough argentic hydrate be added to remove the chlorine, the dark orange solution becomes somewhat less bright, and darker in colour. This solution when concentrated on the water-bath and then evaporated to dryness over sulphuric acid, leaves *isohæmateïn* as an amorphous mass with a green metallic lustre.

This product has not yet been obtained perfectly pure and quite free from chlorine, but on analysis it gives numbers indicating that it has the same composition as hæmateïn. The formation of this body may be expressed thus :—



It is, however, an isomeride of that body, and differs from it considerably in its properties, as the following comparison will show :—

	Hæmateïn.	Isohæmateïn.
Solution of caustic alkali . . . . .	Blue-violet colour.	Red-violet colour.
„ sodium carbonate ..	Reddish-purple colour.	Purple.
Ammonia . . . . .	Bright red-purple.	Dull red-purple.
Ammonium sulphide . . . . .	Nearly decolorised, but quickly becoming purple when placed on bibulous paper, and exposed to the air.	A red-purple precipitate.
Solution of lead acetate . . . . .	Blue violet precipitate.	Red-purple precipitate.

*Isohæmateïn* dyes mordants much in the same way though not so freely as *isohæmateïn chlorhydrin*, and not at all like hæmateïn. It is also more soluble in water than that colouring matter.

### *Brazileïn.*

Crystalline *brazileïn* is obtained from commercial Brazilwood extracts by a method exactly similar to that employed for the production of crystalline hæmateïn, only that it is necessary, after treating the extract with ammonia, to expose the solution to the air for a greater length of time, the oxidation in this case taking place more slowly. Obtained in this manner *brazileïn* has the form of very minute dark crystals, having a grey metallic lustre, and forming when rubbed a brown-red powder. Under the microscope they appear as thin reddish-brown rhombic plates, sometimes grouped together in the

form of rosettes, but for the most part they are detached and lens-shaped, with the points of the lens cut off obliquely.

It is very slightly soluble in cold water, but more so in hot, the solution having a pale yellowish-pink colour, with a distinct greenish-orange fluorescence; alkalis dissolve it, forming rich carmine-red solutions, which, although much more stable than the corresponding compounds of hæmatein, gradually become brown when exposed to the air. There is but little difference in the colour of the ammonia and sodium hydrate solutions of brazileïn.

Dried at 130° it gave on analysis the following numbers:—

0·1071 gram of substance gave 0·2644 gram CO<sub>2</sub>, and 0·0408 gram OH<sub>2</sub>.

0·1024 gram of substance gave 0·2531 gram CO<sub>2</sub>, and 0·0390 gram OH<sub>2</sub>.

These numbers give percentages agreeing with the formula



	Theory.	I.	II.
Carbon .....	67·60	67·30	67·46
Hydrogen.....	4·22	4·22	4·23

But dried at 100° these crystals were found to contain one molecule of water, which is given off at from 130° to 140°.

0·1137 gram at 100° became 0·1071 gram at 130°.

0·1090 „ 100° „ 0·1054 at 130°.

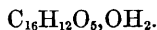
Theory.	I.	II.
5·96	5·97	6·05

Analysis of samples dried at 100° gave the following numbers:—

0·1193 gram of substance gave 0·2790 gram CO<sub>2</sub>, and 0·0485 gram OH<sub>2</sub>.

0·1386 gram of substance gave 0·3231 gram CO<sub>2</sub>.

These numbers give percentages agreeing with the formula



	Theory.	I.	II.
Carbon .....	63·57	63·78	63·57
Hydrogen.....	4·63	4·51	—

#### *Action of Sulphuric Acid on Brazileïn.*

Brazileïn gradually dissolves in cold concentrated sulphuric acid, forming a dark orange-coloured solution, which when dilute has a



very marked olive-green fluorescence. On long standing the solution becomes filled with lustrous yellow rhombic needles.

If the solution be poured into water, a bright orange-coloured amorphous precipitate is thrown down, which represents a new body. By adding to the sulphuric acid solution hot glacial acetic acid in small quantities at a time, and with constant stirring, the new product is gradually thrown down in the form of minute crystals. These are thrown on a filter, thoroughly washed with glacial acetic acid, and dried.

Thus obtained it consists of an orange-coloured crystalline mass, seen under the microscope to consist of transparent flat needles.

On analysis the following numbers were obtained :—

0.1191 gram of substance gave 0.2297 gram  $\text{CO}_2$ , and 0.0364 gram  $\text{OH}_2$ .

0.1055 gram of substance gave 0.2037 gram  $\text{CO}_2$ , and 0.0325 gram  $\text{OH}_2$ .

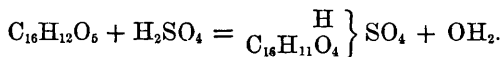
0.1102 gram of substance gave 0.2111 gram  $\text{CO}_2$ , and 0.0334 gram  $\text{OH}_2$ .

These numbers give percentages agreeing with the formula

$$\text{C}_{16}\text{H}_{11}\text{O}_4 \left. \vphantom{\text{C}_{16}\text{H}_{11}\text{O}_4}^{\text{H}} \right\} \text{SO}_4.$$

	Theory.	I.	II.	III.
Carbon .....	52.74	52.59	52.68	52.24
Hydrogen .....	3.29	3.39	3.42	3.36

The formation of this body may be expressed thus :—



This *acid isobrazileïn sulphate* as we propose to name it, is only slightly soluble in boiling glacial acetic acid, but very soluble in alkalis. Its ammonia solution has a rich carmine colour, almost identical with that of the corresponding solution of *brazileïn*. Its soda solution is somewhat bluer in tint. Both solutions rapidly become brown when exposed to the air very much more rapidly than the alkaline solutions of *brazileïn*.

On treatment with alcohol, these crystals become bright scarlet in colour, and on filtering, the filtrate is found to contain sulphuric acid in considerable quantity.

Under the microscope the product now appears as brilliant red needles. It is slightly soluble in water, alcohol, and acetic acid.

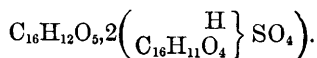
On analysis this body gave the following numbers :—

0.1158 gram of substance gave 0.2426 gram of  $\text{CO}_2$ , and 0.0400 gram of  $\text{OH}_2$ .

0.0712 gram of substance gave 0.1478 gram of  $\text{CO}_2$ , and 0.0239 gram of  $\text{OH}_2$ .

0.1433 gram of substance gave 0.2970 gram of  $\text{CO}_2$  and 0.0452 gram of  $\text{OH}_2$ .

These results give numbers corresponding with the formula



	Theory.	I.	II.	III.
Carbon .....	56.90	57.13	56.61	56.50
Hydrogen .....	3.55	3.83	3.73	3.50

The sulphuric derivatives of brazileïn dye mordants differently from brazileïn itself, and yield colours somewhat like those of garancin.

*Action of Hydrochloric Acid on Brazileïn.*

Brazileïn digested in sealed tubes with concentrated hydrochloric acid at  $100^\circ$  behaves in a very similar manner to hæmateïn. The reaction, however, takes place much more slowly. The solution, which at first has a bright scarlet colour, gradually changes to a dirty yellow, and crystals separate out.

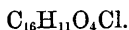
As soon as the reaction has terminated, which is generally after eight or ten hours' heating, the whole is evaporated to dryness over the steam-bath. The product consists of a very dark brown crystalline mass, having a violet lustre. Under the microscope it exhibits the form of small prisms having the colour of potassium bichromate by transmitted light.

On analysis it gave the following numbers:—

0.1436 gram of substance gave 0.3335 gram of  $\text{CO}_2$  and 0.0473 gram of  $\text{OH}_2$ .

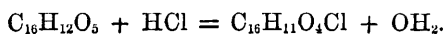
0.1179 gram of substance gave 0.2725 gram of  $\text{CO}_2$  and 0.0387 gram of  $\text{OH}_2$ .

These numbers give percentages agreeing with the formula



	Theory.	I.	II.
Carbon .....	63.13	63.28	63.03
Hydrogen.....	3.66	3.65	3.64

The formation of this substance may be expressed thus:—



*Isobrazileïn chlorhydrin*, as we have named this body, dissolves readily in water, forming an orange-coloured solution, which is acid to litmus-paper and contains free hydrochloric acid. Its alkaline solutions have a slight greenish fluorescence.

*Action of Hydrobromic Acid on Brazileïn.*

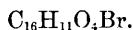
On adding fuming hydrobromic acid in excess to brazileïn, it dissolves to a small extent, and at the same time changes the undissolved portion to a beautiful carmine. On heating the mixture in a sealed tube to 100° this substance mostly dissolves, forming a red solution, which gradually changes into an orange-yellow coloured liquid. After heating for five or six hours, the undissolved portions of the product are seen to consist of crystals. On cooling, most of the product separates out as crystals, which, when seen under the microscope, appear as flat oblique prisms, their colour by transmitted light being like that of potassium bichromate, but darker.

On analysis, the following numbers were obtained:—

0.1576 gram of substance gave 0.3190 gram of CO<sub>2</sub> and 0.0460 gram of OH<sub>2</sub>.

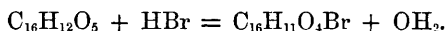
0.1613 gram of substance gave 0.3260 gram of CO<sub>2</sub> and 0.0498 gram of OH<sub>2</sub>.

These numbers give percentages agreeing with the formula



	Theory.	I.	II.
Carbon . . . . .	55.33	55.2	54.9
Hydrogen . . . . .	3.17	3.23	3.40

The formation of this body, which we have named *Isobrazileïn bromhydrin*, may be expressed thus:—



When ground logwood is boiled for some time with dilute sulphuric or hydrochloric acid and then well washed, it dyes mordants in a similar manner to the hæmatein derivatives. This is probably owing to the formation of an analogous hæmatoxylin derivative which oxidises during the process of dyeing. Brazilwood also behaves in a similar matter when treated with acids.

Other acids besides those mentioned, namely, oxalic, tartaric, &c., yield evidently analogous compounds. Nitric acid, too, appears to give a similar compound, but it is difficult to control the reaction.

Heated to 120° with phthalic anhydride for some time, hæmatein yields also a new colouring matter.

Further experiments on the action of these various substances on hæmatein are in progress.

The tinctorial power of the new compounds is much greater than that of the original hæmatein and brazilein, and a very noteworthy point is that the colours are much faster, withstanding the action of a boiling soap-solution, and a weak solution of bleaching powder tolerably well, especially those derived from the brazilein.

During the dyeing process, the whites are considerably soiled, and this, in most cases, is probably due to the liberation of the acids from the compounds when in contact with water, the liberated acid causing the mordant to dissolve and then attach itself to the unmordanted portions of the cloth.

The new hæmatein compounds give on cotton mordanted with alumina a dull red inclining to chocolate, with strong iron a black, with weak iron a slate, and with mixed alumina and iron mordant a full chocolate.

The sulphuric derivatives of hæmatein, however, produce shades with alumina mordants somewhat redder than the other products. Soaping renders all the colours produced by these compounds rather bluer in tone.

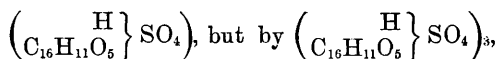
The brazilein derivatives with the same mordants give shades resembling those of the hæmatein compounds. They possess, however, a much more lively red tint, and in fact remind one of the corresponding garancine shades.

The foregoing results show how very similarly hæmatein and brazilein behave towards reagents, and confirm the views of Liebermann respecting their relationship (*Ber.*, 9, 1883). The ease with which they exchange one, and only one, hydroxyl for chlorine or bromine when treated with the corresponding haloïd acids, and the readiness with which the resulting products give up these elements again when treated with water or bases, is remarkable, and points out that this hydroxyl is not phenolic but most probably alcoholic.

The fact that these bodies, when giving up their chlorine or bromine on treatment with silver oxide or other bases, do not regenerate hæmatein or brazilein, but yield substances isomeric with them, shows either that some change takes place in the molecule itself, or else that it becomes polymerised. The fact that the products are more soluble in water than either hæmatein or brazilein is, perhaps, rather against this latter view, but in the case of the sulphuric derivatives polymerisation is believed to take place. As already stated, these substances appear to be somewhat analogous to the acid sulphuric ethers, and in fact they are decomposed by water, with separation of sulphuric acid, even more readily than these bodies; but this decomposition is only

partial, and results in the formation of products which cannot be represented as derived from less than 3 mols. of the original colouring matter.

It is therefore inferred that acid isohæmateïn sulphate should be represented, not by the formula



and the analogous brazileïn compound as  $\left( \text{C}_{16}\text{H}_{11}\text{O}_4 \right\} \text{SO}_4)_3$ . These products are moreover difficultly soluble in most fluids, which also points to the same fact.

Although it has been up to the present found impossible to produce from hæmateïn a body similar to the coeruleïn obtained from galleïn, it does not prove that hæmateïn does not belong to the class of phthaleïns. On the contrary, our experiments appear rather to confirm this view of Baeyer, as among the phthaleïns there are several which are already known to form somewhat peculiar compounds with sulphuric and hydrochloric acids, *e.g.*, fluoresceïn and phthaleïn-orcin (*Ber.*, **7**, 1213–1214), quinol-phthaleïn (*Ber.*, **11**, 715), and homofluoresceïn (*Ber.*, **13**, 547).

The formation, instability, and composition of these compounds apparently show that they are analogous to the acid-compounds of hæmateïn and brazileïn described in this paper.

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