

the raised parts was carved out by any mechanical agency on a frozen or a freezing surface. That produces the forms spoken of (if we are judging rightly) on rather dry ground. I assume that the origin is not quite the same. But the second action was considered to be that of the growing plant; and that is probably the degree required to form the peat-bog forms. One may notice that, from the earliest commencement, the plants found in them seem to grow in tufts by preference, either from a defect in the ground having few spots capable of giving nutriment or from a defect in the plants, there being few that take firm root. When once the beginning is formed, the growth is easily accounted for in the same manner.

I conclude that the results seen on the fields in Iceland are not identical in kind, and are only somewhat similar in appearance.

---

XXVIII. *On Anthraflavic Acid, a Yellow Colouring-matter accompanying Artificial Alizarine.* By EDWARD SCHUNCK, Ph.D., F.R.S., F.C.S.

---

Read March 7th, 1871.

---

THE artificial formation of alizarine is a process of very great interest to the scientific chemist as affording the first instance of the production of a natural colouring-matter by artificial means, and also to the technologist, since it is chiefly to alizarine that madder owes its valuable dyeing properties. The process itself, as described by its discoverers (Graebe and Liebermann), seems exceedingly simple. It consists essentially in the conversion of the hydrocarbon anthracene,  $C_{14}H_{10}$ , into alizarine,  $C_{14}H_8O_4$ . Nevertheless the product obtained on a large



scale (for the use of dyers and printers) by their process is very far from being pure alizarine—so much so, indeed, that some chemists are inclined to doubt its perfect identity with the natural substance. Its solution in caustic alkali, for instance, has not the fine violet colour of a solution of pure alizarine, but is more or less purple or even red. There can be no doubt, however, that the differences observed between the natural and artificial products are mainly due to impurities accompanying the latter. A few simple experiments are sufficient, indeed, to prove that artificial alizarine, as ordinarily prepared, is always accompanied by other substances, some of which are coloured while others are colourless or nearly so. My object on the present occasion is to describe one of these substances, and to point out the relation in which it stands to alizarine.

My attention was first directed to this subject in consequence of some experiments which I made to obtain alizarine from anthracene according to the directions of Graebe and Liebermann. I was surprised to find that, in spite of all the precautions taken, I always obtained besides alizarine a notable quantity of another body, also crystalline, but differing essentially from the former by its dissolving in alkalies with a yellow colour. About the same time Mr. Perkin, who, as is well known, is engaged in the manufacture of alizarine on a large scale, sent me for examination a specimen of the residue obtained by him in evaporating the mother-liquors of alizarine. This residue, which was a crystalline reddish-brown mass soluble in alkalies with a cherry-red colour, I found to contain, in addition to alizarine, a quantity of a substance apparently identical with that which I had previously obtained directly from anthracene. I afterwards found the same body, though in much smaller quantities, in commercial alizarine, both in that manufactured by the



Messrs. Perkin and in a sample from a continental firm. I therefore requested Mr. Perkin to supply me with a quantity of commercial alizarine sufficient to enable me to prepare a pure specimen of this body—a request to which he very kindly acceded.

The product supplied to me, which was a yellow, almost amorphous powder, was in the first place treated with dilute caustic soda, in which it dissolved for the most part, yielding a dark purple solution. A small quantity of pale yellow powder, consisting of impure anthraquinone, was left undissolved. An excess of acid, added to the filtered liquor, produced a bulky brownish-yellow precipitate, which was filtered off and dissolved in boiling alcohol. The alcohol, on cooling, deposited a quantity of almost pure alizarine in small mica-like scales. The mother-liquor was freed from alizarine by adding acetate of lead, which gave a bulky purple precipitate. The filtered liquid, which had a dark yellow colour, was evaporated, when it left a yellowish-brown residue, consisting for the most part of the yellow colouring-matter or acid. In order to separate the latter from the impurities accompanying it, the residue was treated first with water and then with cold alcohol, the latter of which removed a quantity of a brown resinous substance. It was then dissolved in dilute caustic soda; and the solution having been raised to the boiling-point, chloride of barium was added. The filtered liquor deposited, on cooling, a mass of small shining crystals of the barium salt of the acid. These were purified by recrystallization from boiling water and then treated with hydrochloric acid. The lemon-yellow flocks left by the acid were filtered off, washed, and dissolved in boiling alcohol. This, on cooling, deposited yellow silky needles, consisting of an acid which I have named *anthraflavic acid*, in order to indicate its source and its most obvious external property.



The chief properties of this acid are these:—When crystallized from alcohol and dried, it has the appearance of a dark lemon-yellow silky mass, which, under the microscope, is seen to consist of slender four-sided prisms. Heated on platinum foil, it gives off copious yellow fumes, and then burns with a luminous flame, without leaving any residue. When cautiously heated between large watch-glasses, it may be almost entirely volatilized, yielding a vapour which condenses in the form of a yellow sublimate. This sublimate consists of small lustrous crystalline plates, some of which, when examined under the microscope, are found to have very regular forms. The acid is only slightly soluble in boiling water, and almost insoluble in cold. It is more soluble in alcohol and ether, but insoluble in boiling benzol and sulphide of carbon. It dissolves readily in concentrated sulphuric acid even in the cold, forming a yellow solution, from which it is precipitated, by water, in yellow flocks. It is not much affected by dilute nitric acid even on boiling. In fuming nitric acid it dissolves very readily even in the cold, yielding a deep-yellow solution, which, on standing for some hours, becomes lighter in colour without evolving any gas. On now adding water, a quantity of light-yellow shining crystals is deposited, having the general properties of a so-called nitro-acid.

The salts of anthraflavic acid are compounds of well-defined character, some of them being regularly crystallized. When an alcoholic solution of the acid is mixed with an alcoholic solution of potash, it assumes a dark yellow colour, and, on standing, deposits long orange-coloured needles exhibiting considerable lustre. The sodium compound, prepared in the same manner, crystallizes in needles and resembles the potassium salt, but is lighter in colour. The ammonium salt may be obtained in dark-yellow lustrous crystals by dissolving the acid in boiling absolute alcohol and adding a slight excess of



ammonia. These crystals, however, after a short exposure to the air, lose the whole of their ammonia, leaving a yellow residue of uncombined acid. This inability to retain ammonia, even at the ordinary temperature, is a proof of the feeble nature of the acid. The potassium and sodium salts are also rather unstable compounds; for if it be attempted to recrystallize either of them from boiling water, a portion of the acid separates, the solubility of the base in water being sufficient to overcome its affinity for the acid. Anthraflavate of barium may be obtained by dissolving the acid in boiling baryta-water, or by adding chloride of barium to a solution of the substance in caustic alkali. The salt may be dissolved in boiling water without decomposition, and is deposited from the solution, on cooling, in small shining crystalline plates of a brownish-red colour, which, when examined under the microscope, are found to be very regular in form. The strontium salt is very similar, being soluble in boiling water, and crystallizing in long needles. The calcium salt, however, is insoluble in water, and is precipitated, in orange-coloured flocks, on the addition of chloride of calcium to a solution of the acid in ammonia. On adding sulphate of magnesium to an ammoniacal solution of the acid, no precipitate is produced; but, on standing some time, the magnesium salt is deposited in dark yellow crystalline plates and needles, arranged in star-shaped clusters, and possessed of much lustre. The aluminium compound, prepared in a similar manner, appears as a yellow deposit, consisting of microscopic crystals. The ammoniacal solution gives with acetate of lead a voluminous orange-coloured precipitate, with acetate of copper a light brown, and with nitrate of silver a reddish-brown precipitate.

All the compounds of the acid which are soluble in water yield yellow solutions. It is chiefly the presence of this acid in crude alizarine which affects the colour of the



alkaline solution, changing the violet, due to alizarine itself, into purple, or, when present in larger quantity, into red. From the same cause an alkaline solution of crude alizarine does not show the absorption-bands in the spectrum so distinctly as one of pure alizarine. Alkaline as well as alcoholic solutions of anthraflavic acid absorb the blue end of the spectrum very powerfully (though no bands are visible) even with very dilute solutions. A solution of the acid in concentrated sulphuric acid, however, if not too dark, shows a broad but well-defined absorption-band on the border of the blue and green of the spectrum, accompanied by a total darkening of the violet end.

If pure anthraflavic acid be dissolved in an excess of caustic potash-lye, and the solution be boiled down to dryness, a yellow residue is left, which, after being carefully heated almost to fusion, dissolves in water with a red colour. This solution contains alizarine, as it shows the absorption-bands in the spectrum peculiar to the latter—though not very clearly, on account of undecomposed anthraflavic acid still present. Pure alizarine may, however, be obtained from it by adding an excess of acid, filtering off the flocculent precipitate, dissolving the latter in alcohol and adding to the solution acetate of lead, when a purple precipitate falls, which contains the whole of the alizarine, the excess of anthraflavic acid remaining in solution. The lead precipitate, suitably treated, yields pure alizarine. It appears therefore that by the action of caustic potash anthraflavic acid is converted into alizarine. It should at the same time be stated that the conversion is never complete, probably because the action, if carried far enough to convert the whole of the acid, leads to the decomposition of the alizarine already formed.

Though anthraflavic acid gives, with bases, compounds of an intensely yellow colour, it seems to possess no dyeing properties. The freshly precipitated acid, suspended in



water, communicates not the least tinge of colour to alumina and iron mordants on calico, however long the liquid may be boiled. The effect produced in dyeing by artificial alizarine would appear therefore to be in no way due to the presence of the acid.

The analysis of the acid yielded the following results:—

I. 0.3014 grm. of the substance, dried at 100° C., gave 0.7808 grm. carbonic acid and 0.1062 water.

II. 0.3194 grm. gave 0.8288 grm. carbonic acid and 0.1140 water.

III. 0.3226 grm. gave 0.8372 grm. carbonic acid and 0.1138 water.

These numbers lead to the following composition:—

	Calculation.		Experiment.		
			I.	II.	III.
C <sub>15</sub> .....	180	70.86	70.65	70.76	70.77
H <sub>10</sub> .....	10	3.93	3.91	3.96	3.91
O <sub>4</sub> .....	64	25.21	25.44	25.28	25.32
	254	100.00	100.00	100.00	100.00

The barium salt, prepared in the manner above described, was dried at first *in vacuo*, then at 100°, and finally at 120° C., before being analyzed.

I. 0.4980 grm. of the dry salt gave 0.8026 grm. carbonic acid and 0.1080 water.

0.4442 grm. gave 0.2528 grm. sulphate of barium.

II. 0.4844 grm. gave 0.7892 grm. carbonic acid and 0.1052 water.

0.4904 grm. gave 0.2790 grm. sulphate of barium.

The composition of the salt is therefore as follows:—

	Calculation.		Experiment.	
			I.	II.
C <sub>15</sub> .....	180	44.22	43.95	44.43
H <sub>10</sub> .....	10	2.45	2.40	2.41
Ba .....	137	33.66	33.46	33.45
O <sub>5</sub> .....	80	19.67	20.19	19.71
	407	100.00	100.00	100.00



The formulæ of the acid and its barium salt are therefore respectively  $C_{15}H_{10}O_4$  and  $C_{15}H_8BaO_4 + aq.$  It is probable that the latter, when freshly crystallized, contains some water of crystallization which is expelled at  $100^\circ$ , in addition to that which is retained at  $120^\circ C.$ ; but I made no attempt to determine the amount.

The silver salt also retains water with great pertinacity, even when heated to a temperature of  $140^\circ C.$  The salt was obtained as a reddish-brown precipitate by adding nitrate of silver to a solution of the acid in liquid ammonia.

Its analysis led to the following results:—

I.  $0.4792$  grm., dried at  $100^\circ C.$ , gave  $0.6628$  grm. carbonic acid and  $0.0742$  water.

$0.4836$  grm. gave  $0.2882$  grm. chloride of silver.

II.  $0.3976$  grm., dried at  $100^\circ C.$ , gave  $0.1782$  grm. silver.

III.  $0.4952$  grm. silver salt of another preparation, dried at  $140^\circ C.$ , gave  $0.6810$  grm. carbonic acid and  $0.0764$  water.

$0.4924$  grm. gave  $0.2240$  grm. silver.

IV.  $0.5484$  grm., dried at  $140^\circ C.$ , gave  $0.7616$  grm. carbonic acid and  $0.0810$  water.

$0.4714$  grm. gave  $0.2132$  grm. silver.

In 100 parts:—

	I.	II.	III.	IV.
C .....	37.72	.....	37.50	37.87
H .....	1.72	.....	1.71	1.64
Ag .....	44.85	44.81	45.49	45.22
O .....	15.71	.....	15.30	15.27
	<hr/> 100.00		<hr/> 100.00	<hr/> 100.00

These numbers correspond with the formula  $2C_{15}H_8Ag_2O_4 + aq.$  which requires in 100 parts:—

C .....	37.73
H .....	1.88
Ag .....	45.28
O .....	15.11
	<hr/> 100.00



If the formula  $C_{15}H_{10}O_4$  for anthraflavic acid were correct, it would stand in a very simple relation to that of alizarine, and the conversion of the acid into alizarine by the action of caustic alkalies would not be difficult to understand. If, however, the crude material which I employed was prepared from pure anthraquinone, as I am informed it was, it is not easy to see how a substance with 15 ats. C could have been obtained from it, and it may therefore be questioned whether the acid examined was perfectly pure. An experiment which I made for the purpose of removing doubt on this point, rather tends to increase it. Having heated a quantity of the acid with fifty times its weight of zinc powder, in the manner described by Graebe and Liebermann, I obtained a quantity of a brownish crystalline sublimate, amounting to about 10 per cent. of the substance employed, and consisting apparently of anthracene. It still retained, after being purified as far as possible, the yellowish tinge which, according to the chemists just named, adheres so pertinaciously to anthracene; but it did not differ in other respects from the pure substance. It melted at the same temperature as anthracene, and began to sublime before fusing; it dissolved in boiling alcohol, but more readily in benzol, and was deposited from these solutions in lustrous crystals of a very regular form; and it gave, like anthracene, with picric acid a compound crystallizing in long red needles. If, by heating with metallic zinc, anthraflavic acid, like alizarine, yields anthracene, we may infer, in accordance with the principle laid down by Graebe and Liebermann, that it also contains 14 ats. C. It is evident, therefore, that further experiments are required in order to ascertain exactly the composition and formula of the acid.

---





Schunck, Edward. 1876. "On Anthraflavic Acid, a yellow Colouring-matter accompanying Artificial Alizarine." *Memoirs of the Literary and Philosophical Society of Manchester* 5, 227–235.

**View This Item Online:** <https://www.biodiversitylibrary.org/item/109366>

**Permalink:** <https://www.biodiversitylibrary.org/partpdf/305307>

**Holding Institution**

Smithsonian Libraries and Archives

**Sponsored by**

Biodiversity Heritage Library

**Copyright & Reuse**

Copyright Status: Public domain. The BHL considers that this work is no longer under copyright protection.

This document was created from content at the **Biodiversity Heritage Library**, the world's largest open access digital library for biodiversity literature and archives. Visit BHL at <https://www.biodiversitylibrary.org>.