XIX.—NOTES ON THE CHRONOLOGY OF THE ISOMERIC PURPURINES AND THE ACTUAL RELATION OF THE BODIES WHICH HAVE BEEN CALLED BY THE NAMES ANTHRAPURPURINE, ISOPURPURINE AND FLAVOPURPURINE.

BY HENRY MORTON, PH.D.

There is a piece of recent chemical history which has already become somewhat involved on account of the oversight of some writers; and as the threads happen to be in my hands, I think I shall do a good office to future students by laying them out straight at the present time.

In 1870, Wm. H. Perkin published in the *Jour. of the Lond. Chemical Soc.*, a paper entitled, "On Artificial Alizarine" (volume viii, page 143), in which at the end, in a foot note, the author says: "When purifying artificial alizarine by converting it into an alumina lake, I found that upon digestion with carbonate of potash, this lake gave a red-colored solution, containing a coloring matter, dyeing mordants very similarly to alizarine, with this difference, that the reds are more scarlet, and the purples bluer, or more slaty. I have not obtained this body in a perfectly pure state as yet, but it appears to be crystalline."

The investigation thus opened by Perkin was diligently prosecuted by him, as appears from references to it in his other publications, and at the meeting of the London Chemical Society, held June 6th, 1872, he read a paper on this body, an abstract of which is published in the *Chemical News* for June 14th, and a fuller report of which appears in the *Journal of the London Chem. Soc.*, vol. xxv, p. 659, under the title "Note on a secondary coloring matter produced in the preparation of alizarine from anthracene." In these publications he gives the formula of the new body as $C_{14}H_8O_5$, and notes its relations and differences to and from the purpurine of madder. In the next volume of the proceedings, or rather *Journal of the Chem. Soc.*, viz., vol. xxvi, for 1873, p. 425, Perkin published under the title, "On anthrapurpurine," a long article on the same substance to which were attached, as illustrations, pieces of cloth dyed with it, as well as others dyed with alizarine.

This article has been translated and quoted extensively by other writers, but the others seem to have been overlooked or forgotten. Hence have arisen some of the errors which I now propose to correct.

From the above references it will be seen that Perkin first separated out and recognized this new body in 1870, and diligently following up the research, published its formula in the beginning of June, 1872, and a full and exhaustive memoir in 1873.

In the *Moniteur Scientifique*, for August, 1872, or just two years after the first publication by Perkin, and just two months after the later one, in which he gave the formula of his new substance, appeared a communication announcing the discovery of a new product extracted from artificial alizarine, by G. Auerbach, and named by him isopurpurine. No mention whatever was made in this article of Perkin's prior publication, and it was, of course, generally inferred that Auerbach, who published a pamphlet on alizarine and its derivatives, in 1878, knew of them, but regarded his isopurpurine as a new discovery of his own and not a mere confirmation of Perkin's work. Moreover, a comparison of the properties of anthrapurpurine as given by Perkin, and isopurpurine as given by Auerbach, shows that two decidedly dissimilar materials were delineated by these two writers.

In the course of time it, however, appeared that Auerbach was ignorant of Perkin's prior publications, and, believing his material to be the same as that more fully described by Perkin, in 1873, claimed priority, insisting that his product and Perkin's were identical.

Into this error he seems to have led several writers; thus Græbe and Lieberman, in their report on artificial alizarine at the Vienna Exhibition, under the heading isopurpurine, refer first to Auerbach's publication in the *Moniteur Scientifique*, of August, 1872, and then to Perkin's third publication in the *Journal of the Chem. Soc.*, of 1873, omitting all reference to, and evidently not knowing of, his earlier publications in 1870, and June of 1872.

Rosenstiehl, in a recent article, has fallen into a like error, and credits Auerbach with first obtaining this body in an impure state, and Perkin with having first extracted it pure in 1873; but, admitting that Auerbach is right in assuming that what he extracted, was only the anthrapurpurine of Perkin, it is evident that he has no claim whatever to priority, but that the substance must be credited to Perkin, and must be called by his name of anthrapurpurine.

As a matter of fact, however, the substance actually extracted by following the method described by Auerbach, in 1872, was not anthrapurpurine, but a mixture consisting mainly of a substance which was new at that time, but was afterwards isolated by Messrs. Schunck and Roemer; and, that if Auerbach had not unfortunately overlooked Perkin's prior claims, and sought to identify his isopurpurine with Perkin's anthrapurpurine, he would have been the first discoverer of flavopurpurine, in place of Schunck and Roemer.

My reasons for this opinion are the following: In the latter part of 1874, I had occasion, together with my friend, Mr. Wm. E. Geyer, B. S., to repeat both Perkin's and Auerbach's methods of treatment upon considerable quantities of artificial alizarine.

We first followed out Perkin's method, and obtained a product corresponding in all respects with his description of anthrapurpurine.

We then worked on another quantity of artificial alizarine, according to Auerbach's directions, and when we came to the last treatment, namely, solution in, and crystallization from, alcohol, we found that we evidently had to do with a mixture of two bodies, differing in a marked way as to their solubilities.

Bearing in mind that we had found Perkin's anthrapurpurine as he describes it, but little soluble in alcohol, and that Auerbach described his isopurpurine as quite soluble, we so carried on the alcohol treatment as to reserve the soluble part as isopurpurine, and reject the less soluble portion.

When we had carried this separation to a sufficient extent, we found that we had a body entirely distinct from Perkin's anthrapurpurine, but sufficiently like the description given by Auerbach of his isopurpurine, to answer for it, when due allowance was made for the uncertainties of a verbal description.

When, however, the paper of Schunck and Roemer appeared in 1876, we saw that the body we had extracted agreed still more closely with their flavopurpurine. Having obtained it, however, by the process described in 1872, by Auerbach, I continued to call it by his name, and should do so still had he not very emphatically repudiated all credit for and connection with it subsequently to his first publication and description.

I am now inclined to think that, subsequently to his first publication, Auerbach so modified his alcohol treatment (being desirous to show identity with Perkin's anthrapurpurine), as to collect the less soluble portions, and thus threw away the new discovery within his reach, in his effort to secure that which belonged to another.

In fact, a careful comparison of the description which Auerbach published in 1872, of his isopurpurine, with the known properties of anthrapurpurine, show conclusively that the body described by Auerbach could not possibly have been, even in large part, anthrapurpurine, but must have been essentially flavopurpurine, with a small amount of anthrapurpurine mixed with it.

Thus, he says, that it dissolves in ammonia with a brownish-red, and in alkaline carbonates, with a color equally red, with a very marked brownish shade. Now, pure anthrapurpurine gives purplish-red solutions with both of these solvents, while flavopurpurine gives solutions of an orange-red color, very marked. A mixture would produce the brownish shade named by Auerbach. Again, on the iron mordant, Auerbach says his isopurpurine gives a brownish-violet, which is exactly what flavopurpurine does, while pure anthrapurpurine gives a slaty-blue, as noticed by Perkin, and which is very manifest even when an impure specimen is used. So on with his other tests or properties.

The true relation of the substances which have borne the names given at the head of this article, is, then, this:

Anthrapurpurine is a single substance, first isolated by Perkin, partially in 1870, and thoroughly prior to June 6th, 1872.

Isopurpurine, as described by Auerbach, in 1872, is a mixture, in proportions varying according to the composition of the artificial alizarine, from which it is extracted, and the way in which the alcoholic treatment is conducted, of anthra- and flavopurpurine, with a trace of alizarine. This mixture was first separated and described by G. Auerbach, in the *Moniteur Scientifique*, for August, 1872.

Flavopurpurine is a single substance or chemical individual, first separated, as a matter of fact, by Mr. Geyer and myself, but not then published by us, and thus first isolated and described by Schunck and Roemer, in the Berichte d. d. chem. Gesellsch., 1876, p. 678.

The facts, as to the composition of the material obtained by treating artificial alizarine by the method described by Auerbach, are also established by the recent researches of M. A. Rosenstiehl, presented to the Chemical Society of Paris, and published in the bulletin of that body, of May 5th and 20th, 1878, where in vol. xxix, p. 408, I find as follows: "On submitting isopurpurine obtained by the method described by Mr. Auerbach, to proximate analysis, I was not slow in discovering the presence of about 15 p. c. of alizarine." Here follows a long and minute description of how this was removed by treatment with hot benzol. The material so purified was then dissolved in boiling alcohol, and allowed to deposit crystals on cooling. The author then continues:

"Comparative dyeing tests made with the part crystallizing out and with that remaining in the mother liquor, showed that the alcohol eliminated a substance coloring mordants like flavopurpurine, that is to say, of a red more orange than that of oxanthraflavone."

It should be mentioned, that in this essay its author indicates by the word oxyanthraflavone the material isolated by Perkin's method, but which, through oversight of the earlier publications, he credits to Auerbach, and names isopurpurine in consequence of this mistake. We have recently repeated, with a portion of the flavopurpurine separated by us in 1875, by repeated solutions in alcohol, all the tests given by Schunck and Roemer, including the examination of its absorption spectrum, and these tests show it to have been perfectly pure flavopurpurine.

The swatches of dyed test cloth accompanying this paper, as illustrations, speak for themselves. The peculiar slaty-blue of the iron mordant noticed by Perkin, is strongly contrasted with the "brownish-violet" of the corresponding part of the swatch dyed with flavopurpurine. The characteristic differences elsewhere are also readily seen. The materials with which these swatches are dyed, are essentially pure, or as pure as it was practicable to make so large a quantity as was required within a moderate time.

STEVENS INSTITUTE OF TECHNOLOGY, HOBOKEN, N. J.

XX.—PETROLEUM AND ITS EXAMINATION.

BY A. BOURGOUGNON.

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In this communication to the American Chemical Society, I will describe the mode of examination which I have adopted in examining the different kinds of petroleum and its products. This method of analysis is the result of several years' experiments.

Before entering directly upon my subject, I think that a brief description of the general process employed in obtaining crude oil will be acceptable, and I will therefore relate some observations made during a recent trip through the oil-bearing territory.

I here take occasion to tender my thanks to Mr. J. Labouret, for his valuable information, and to A. J. Pouch, Esq., of the firm of J. A. Bostwick & Co., who has favored me with several samples very useful in my investigations.

Petroleum is found in several parts of the world, but the most abundant field of production is situated in Pennsylvania. It is also met with in several other States of the Union, but the Pennsylvania oil is justly considered the best in quality for illuminating purposes.

Contrarily to the rule governing the occurrence of most mineral substances, which are confined to well determined geological forma-