

acting in a different direction withdraws the oxygen and allows the potassium to unite with the compound radical ferrocyanogen; thus $\text{Fe}_2 \text{Cy}_6 3\text{K} + \text{KO} + \text{PbO} = \text{Fe}_2 \text{Cy}_6 4\text{K} + \text{PbO}_2$, the decomposition being of the same kind when an organic matter is substituted for the oxide capable of further oxidation. Soda and ammonia may be substituted for potash in the above decomposition, producing the oxidation or discharging the indigo. This is curious in the case of ammonia, for it cannot be explained by any other than by the ammonium theory, and shows the complete analogy between the oxide of ammonium and the oxide of the simple metallic radicals, potassium and sodium. It is interesting also to observe that the last member in the formula $\text{Fe}_2 \text{Cy}_6 4\text{R}$, may be substituted by any alkaline base. Thus, that it may either be $\text{Fe}_2 \text{Cy}_6 3\text{K K}$, or $\text{Fe}_2 \text{Cy}_6 3\text{K Na}$, or $\text{Fe}_2 \text{Cy}_6 3\text{K NH}_4$. This circumstance points to important theoretical considerations in the atomic constitution of the prussiates, which would be foreign to the present paper, the principal object of which is to furnish a means of discharging indigo, and thus supply a process much wanted in the art of calico-printing, and which I have followed for many years with success.

XXVI. On the Preparation of Hippuric Acid.

By WILLIAM GREGORY, M.D.*

SINCE the discovery of hippuric acid by Liebig, that body has at all times attracted much attention. Its composition and the products of its decomposition, among which were benzoic acid and benzamide, rendered it interesting, and various ingenious views were entertained of its constitution. Its detection in human urine by Liebig gave it additional importance.

The beautiful discovery of Dessaignes, that hippuric acid, when heated with strong acids, is resolved into benzoic acid and glycocoll, has greatly increased the interest already attached to hippuric acid, which now affords the best means of obtaining glycocoll, and has enabled Horsford, in his elaborate researches on that substance, to fix its formula in a very satisfactory manner.

If to hydrated hippuric acid	$\text{C}_{18} \text{N} \text{H}_9 \text{O}_6$
we add 1 equiv. water	$\text{H} \text{O}$
and from the sum	$\text{C}_{18} \text{N} \text{H}_{10} \text{O}_7$
subtract 1 equiv. glycocoll	$\text{C}_4 \text{N} \text{H}_4 \text{O}_3$
there remain	$\text{C}_{14} \text{H}_6 \text{O}_4$

which is hydrated benzoic acid.

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There cannot, I think, be any longer a doubt that $C_4N H_4 O_3$ is the true formula of glycocoll, and Horsford has, in establishing this point, at the same time confirmed and explained in the most satisfactory manner the observation of Dessaignes.

The researches of Horsford, however, have also demonstrated that glycocoll is in itself one of the most interesting compounds known to chemists, and it is evident that the further study of this most singular body will lead to very valuable results.

I have already stated that glycocoll is best obtained from hippuric acid, but as soon as I began to prepare for this purpose a considerable quantity of hippuric acid, I found, as all who have done so must have found, that the operation as prescribed in books is not only tedious and troublesome, but uncertain.

The usual process consists in evaporating the urine of the horse or cow at a moderate temperature to about one-eighth of its bulk, and adding hydrochloric acid, when on standing a few hours, crystals of impure hippuric acid are deposited. But it is well-known that if the temperature should rise too high, although still to a point short of boiling, the hippuric acid will partially or totally disappear, and benzoic acid will be found in its place. Now when we bear in mind that the urine contains but little hippuric acid, it is evident that to obtain this acid in quantity we must operate with a very large bulk of urine, and those who have done so well know how tedious the evaporation is, since if we attempt to hasten it by raising the temperature, we run the risk of losing the whole; and this indeed frequently happens.

The impure, highly-coloured acid first obtained has been purified by different chemists in a great variety of ways. Some have used chloride of lime; but this method is not easily managed, and often converts the whole into benzoic acid.

The last and by far the best method of purification is that of Schwarz, who boils the impure acid with an excess of milk of lime, and strains the alkaline liquid from the undissolved lime. It passes rapidly and clear through calico, and the lime retains the colouring matter, so that the addition of acid to the filtered liquid causes the deposition of crystals of hippuric acid nearly white. Schwarz recommends the addition of chloride of calcium to the filtered or unfiltered liquid, and the precipitation of the lime as carbonate by carbonate of potash or soda, when the precipitated carbonate of lime carries with it the last traces of colouring matter. I have not found this necessary, as a repetition of the process with the milk of lime never fails to yield colourless crystals.

As it was clear that the hippuric acid was not in the slightest degree decomposed by boiling with excess of lime, although so easily metamorphosed by acids, I thought that by applying the same principle to the urine directly, I might be enabled *to boil it down*, and thus shorten the process, and at the same time prevent the decomposition of the hippuric acid, since it would appear that hippurate of lime is not affected by boiling, nor by excess of lime.

Accordingly, I took some urine of the horse, mixed it with excess of milk of lime and boiled for a few minutes. I then strained the solution, which was very materially decolorized, and boiled the clear liquid as rapidly as possible down to the requisite bulk. On adding hydrochloric acid I obtained a copious deposit of crystals, which when pressed had a slight red colour. I then treated them by Schwarz's method and obtained an abundant crop of almost colourless crystals, which consisted entirely of the needles of hippuric acid, without a visible trace of benzoic acid, the crystallization of which is easily recognized. A second treatment with milk of lime, which was hardly needed, and probably would have been quite unnecessary had a greater excess of lime been used in the previous one, yielded snow-white crystals of the utmost beauty and purity.

The improvement which I have thus introduced in the preparation of hippuric acid may seem trifling, and is indeed only the application of Schwarz's method to the urine, instead of to the crude acid; but any one who tries to prepare some ounces, not to say pounds, of hippuric acid, will soon find that the difference is practically important. By my method it is possible to extract in one day the hippuric acid from as much urine as would require a week to operate upon on the usual plan, so that the quantity of hippuric acid which we can thus obtain is only limited, as it were, by the quantity of urine to be procured. The tedious evaporation at low temperatures is got rid of, and we are sure of obtaining the whole hippuric acid originally present; whereas, on the former plan, however carefully the evaporation is conducted, and it requires constant superintendence, it almost always happens that some of the hippuric acid is decomposed; while a very slight accidental rise of temperature may destroy the whole of it, as I have often seen.

On the whole, I am satisfied that all who wish to study hippuric acid and glycocoll will find on trial that what was formerly a disagreeable and troublesome operation is now a very easy and short one; and that they may now easily obtain these remarkable compounds in any desired quantity.