

XV.—*On Morindon.*

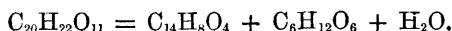
By T. E. THORPE, F.R.S., and WILLIAM J. SMITH, M.B. (Lond.).

IN a previous communication (Trans., 1887, 52), one of us, in conjunction with Mr. T. H. Greenall, sought to show that, contrary to the supposition of Rochleder and of Stenhouse, morindin, the active colouring matter of A'l, the root-bark of *Morinda citrifolia*, is not identical with ruberythric acid, although both bodies are glucosides, and possess apparently the same percentage composition. That A'l contains substantially the same dyeing principles as madder appears to have been conjectured many years ago, although Anderson, who

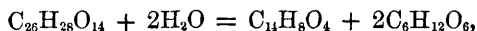
first isolated morindin, was unable to satisfy himself of the identity of these substances. Direct evidence that ruberythric acid and morindin are not the same was first adduced by Stein (*J. pr. Chem.*, **97**, 234), who showed that their barium compounds are dissimilar in colour, and that they behave differently towards caustic potash. Moreover, the products obtained on hydrolysing the two substances give different colour reactions, although Stein found that the optical behaviour of solutions of morindon—the product formed on hydrolysing morindin—agreed perfectly with the description given by Stokes, and on which Stenhouse based his assumption that morindon and alizarin were identical.

Part of the obscurity which hangs over the subject is due to the doubt which has existed as to the nature of ruberythric acid. Graebe and Liebermann have, as is well known, suggested that the formula of ruberythric acid is $C_{26}H_{28}O_{14}$, in contradistinction to that of $C_{20}H_{22}O_{11}$, as proposed by Rochleder.

According to Rochleder, the decomposition of ruberythric acid on hydrolysis is represented by the equation—



which affords 54·8 per cent. of alizarin; whereas according to Graebe and Liebermann it should be—



or ruberythric acid should afford 42·5 per cent. alizarin.

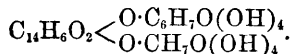
It will be noticed that a fundamental difference in the modes of representing the decomposition is that whilst Rochleder's equation requires the separation of water, that of Graebe and Liebermann, in accordance with the generally accepted mode of explaining the process of the hydrolysis of a glucoside, demands its assimilation.

For this reason, we had in the paper referred to adopted Graebe and Liebermann's equation, and we further sought to prove its validity by determining the amount of alizarin yielded by hydrolysing a known weight of some pure ruberythric acid, for which we were indebted to the kindness of Dr. Schunck. This gave 42·1 per cent. of alizarin, in close agreement with the amount demanded by Graebe and Liebermann's equation.

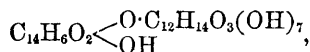
Since the publication of our paper, Liebermann and Bergami (*Ber.*, **20**, 2241) have likewise studied the mode of hydrolysis of ruberythric acid, and they have also analysed the barium salt and an octacetyl compound, with the result that there is no longer any doubt that ruberythric acid has the formula $C_{26}H_{28}O_{14}$.

Ruberythric acid may be regarded as formed by the replacement of

each of the two phenylhydroxyls in alizarin by a grape-sugar rest; thus—



Liebermann and Bergami, who have traced the existence of cane-sugar in madder, have proposed the formula—



which equally well explains all that is known respecting ruberythric acid, and more especially the fact that it is a monobasic acid.

When morindin is heated to a sufficiently high temperature, it chars, and yields a red crystalline sublimate, termed *morindon* by Anderson, its discoverer. This substance, which may more readily be obtained by the hydrolysis of morindin, is, according to Stenhouse, identical with alizarin. In the paper referred to, it was shown that morindon differed from alizarin in certain well-marked colour reactions; the crystalline forms of the two substances were dissimilar, and lastly, their percentage composition was different, that of morindon corresponding to a trihydroxymethylanthraquinone, $\text{C}_{15}\text{H}_{10}\text{O}_5$. The quantity obtained was, however, too small to enable us to do more than determine the percentage composition of the substance and to make a few qualitative reactions.

Mr. Thomas Wardle, of Leek, having placed a quantity of the roots of *M. citrifolia* at our disposal, we have attempted to obtain further evidence of the nature of morindon. The finely powdered root-bark was heated with successive quantities of dilute alcohol (50 per cent.) so long as any colouring matter was dissolved out. The solution was concentrated to half its volume by distillation, and filtered, the filtrate being afterwards subjected to hydrolysis. The precipitate, consisting of morindin and morindon mixed with a large quantity of resin, having been extracted many times, first with benzene, and then with absolute alcohol, in order to remove the morindon, was dissolved by heating with 50 per cent. alcohol. The morindon and morindin were then repeatedly crystallised, the former from benzene, and the latter from dilute alcohol. The total yield from rather less than 4 lbs. of bark was 1·9465 gram of morindin, and 0·3407 gram of morindon.

As the object of the present inquiry was to determine the nature of morindon, all the morindin was converted into morindon by dissolving it in dilute (50 per cent.) alcohol, and heating the solution in a flask attached to a reflux condenser with a small quantity of dilute hydrochloric acid. The operation was made quantitatively, and the yield of morindon determined.

0.4890 gram morindin gave 0.2368 morindon, or 48.4 per cent.
 0.9065 „ „ 0.4393 „ 48.4 „

In the former paper we gave the percentage yield of morindon from morindin as 48.5 per cent.

The morindon was then analysed, with the following results :—

- (1.) 0.1510 gram gave 0.3683 CO₂ and 0.0534 H₂O.
 (2.) 0.1510 „ 0.3682 „ 0.0547 „
 (3.) 0.0937 „ 0.2291 „ 0.0327 „

	I.	II.	III.	Calculated for C ₁₅ H ₁₀ O ₅ .
C	66.52	66.50	66.68	66.66
H	3.92	4.02	3.87	3.70
O	—	—	—	29.64
				<hr/> 100.00

These analytical numbers agree almost exactly with those given in the first paper.

In order to obtain further insight into the nature of the substance, it was next distilled for us by Dr. Japp with zinc-dust. Only about 0.6 gram was available for this purpose. The product of the distillation was dissolved in hot glacial acetic acid; on cooling, it separated out in lustrous, pale-yellow plates, but the amount was too small to warrant recrystallisation. The once crystallised plates after being dried in the steam oven, melted at 190—191°. This agrees with the melting point (190°) found for *yellow* methylanthracene from coal-tar by Japp and Schultz (*Ber.*, **10**, 1887). Pure (white) methylanthracene melts at 200°.

As the quantity was insufficient for recrystallisation, the crystals were next dissolved in hot glacial acetic acid, and oxidised by chromic acid, the product being treated with solution of sodium carbonate, and precipitated by hydrochloric acid. The gelatinous precipitate, when washed and dried, exhibited the properties of anthraquinone-carboxylic acid. Heated between watch-glasses, it sublimed in slender yellowish needles, melting at 278—280°, indistinguishable in appearance from those of anthraquinone, but soluble in ammonia. The sublimate was recrystallised from hot glacial acetic acid, which deposited it in small yellowish needles with the same melting point as before. When treated with caustic soda solution and zinc-dust, the liquid acquired a yellowish-red colour, which disappeared after exposure to the air. The addition of caustic soda occasioned a precipitate of the sodium salt. These properties agree with those of anthraquinone-carboxylic acid, as described by Liebermann (*Annalen*, **183**, 167).

An attempt was next made to see if phthalic acid could be obtained from morindon. 0.25 gram of the substance was oxidised with permanganate in alkaline solution, but oxalic acid was the only product of oxidation that could be detected. A comparative experiment, in which the same weight of alizarin was oxidised under precisely similar circumstances, yielded phthalic acid, identified by the fluoresceïn reaction.

There appears, therefore, to be no doubt that morindon is not identical with alizarin, but that it is a trihydroxymethylantraquinone. Up to the present, eight other compounds of the empirical formula $C_{15}H_{10}O_5$ seem to be known, but morindon is not identical with any one of these. It is not possible, with the amount of information which we have as yet, to determine its relations, either to the parent glucoside morindin, or to ruberythric acid.

Since morindin yields 48.4 per cent. of morindon on hydrolysis, it is easy to construct a formula for the former, which shall agree with the quantitative results of the hydrolysis, and at the same time with the empirical composition of morindin as determined by analysis. The formula so got is $C_{26}H_{28}O_{14}$, which expresses the composition of ruberythric acid. But the hydrolysis of a compound containing C_{26} into one containing C_{15} involves the splitting off of an uneven number of carbon-atoms, and this would only be possible if the glucoside contained a sugar like arabinose, that is, one containing 5 atoms of carbon, in addition to a six-carbon sugar. It is at all events certain that the amount of sugar obtained by hydrolysis and as determined by Fehling's solution, did not exceed 35 per cent., on the assumption that the reducing power was the same as that of glucose.
