

XV.—On the Decomposition-products of Quinine.

By W. RAMSAY, Ph.D., Tutorial Assistant of Chemistry, Glasgow University; and J. J. DOBBIE, M.A., Clark Scholar in Nat. Sc., Glasgow University.

First Paper (Oxidation with Permanganate).

CLOEZ and Guignet (*Compt. rend.*, xlvii, 710), by oxidising quinine with permanganate of potash, obtained nitrate and carbonate of potassium and a *peculiar acid*.

With the view of examining this acid and the other products of decomposition of quinine, we repeated their experiment.

The oxidation, and subsequent separation of the acid were conducted in the following manner:—5 grams of quinine were treated with 50 grams of permanganate, at the ordinary temperature, a gentle heat only being applied to start the action. When reduction of the permanganate was complete, the alkaline liquid was filtered from the manganese dioxide and neutralised with nitric acid. On adding nitrate of lead to the hot neutral solution, a curdy white precipitate of the lead salt of the unknown acid was obtained. This salt was decomposed with a current of sulphuretted hydrogen, the liberated acid filtered from the lead sulphide, and evaporated to dryness. On taking up the residue with alcohol, the alcoholic solution deposited on standing a red powdery substance. The free acid, filtered from the red powder, was thrown down with silver nitrate, and the silver salt treated in the same way as the lead salt with sulphuretted hydrogen. The filtrate from the silver sulphide, on being slowly evaporated over sulphuric acid, gave delicate needle-like crystals of the free acid. A small portion of the acid thus liberated, on being heated, gave off the smell characteristic of the decomposition by heat of *dicarbopyridenic acid*, and afforded strong evidence in favour of the identity of the acid produced from quinine with that which Professor Dewar obtained by oxidising picoline with potassium permanganate.

The acid from quinine has been obtained in two different forms—viz., in plates and in short prisms. As yet we have not succeeded in getting the long hair-like needles, in which dicarbopyridenic acid crystallises when free from water.

On heating for several hours at 100°C., 0.3373 gram of the acid lost 0.0324 gram = 9.6 per cent.

$C_7H_5NO_4 \cdot H_2O$ contains 9.83 per cent. H_2O .

Combustion of 0.1334 gram acid gave 0.338 gram H_2O , and 0.218 gram CO_2 = 3.16 per cent. H, and 44.56 per cent. C.

Dicarbopyridenic acid contains H, 3.00 per cent.; C, 50.39 per cent. The carbon of the acid obtained from quinine is thus between 5 and 6 per cent. lower than that of dicarbopyridenic acid; but as the quantity burned was very small and apparently not quite pure, the approximation of the results obtained by experiment to the calculated percentage of C and H in dicarbopyridenic acid may, taken together with the facts to be mentioned, render the identity of the acids at least highly probable. A qualitative examination of the acid showed that it contained nitrogen.

Owing to the difficulty of getting entirely rid of the red powder already mentioned—a trace of which always comes down with the salts—it was found impossible to make an exact determination of the melting point. The purest specimen obtained blackened below 200° , and melted apparently at $251\text{--}252^{\circ}$. The melting point of dicarbopyridenic acid is 237.5° ; but this can be observed only when very pure specimens are used. With ferrous sulphate the acid gave the red colour characteristic of dicarbopyridenic acid.

The silver salt of the acid comes down in boiling solution as a white curdy precipitate. 0.1425 gram of the salt gave 0.0801 gram Ag = 56.21 per cent. The neutral silver salt of dicarbopyridenic acid contains 56.69 per cent. Ag.

The silver salt, on heating, behaves like mercury sulphocyanide. The silver salt of dicarbopyridenic acid has the same peculiarity.

On titrating the acid with a standard solution of potash, 0.2948 gram acid required for neutralization 0.1692 gram K_2O = 0.1404 gram K. Calculating this amount of potassium to hydrogen, we obtain 0.00358 gram, as the weight of hydrogen replaced by potassium; therefore, 0.2948 gram less 0.00358 gram, plus 0.1404 gram = 0.43162 gram = the amount of potassium salt formed, and $\frac{100 \times 0.1404}{0.43162} = 32.50$ per cent.

The percentage amount of potassium in the neutral potassium salt is therefore 32.50.

The corresponding salt of dicarbopyridenic acid contains 32.15 per cent. K.

On titrating the acid from the products of another oxidation with soda in the same way, 0.0792 gram acid required for neutralization 0.0239 gram Na_2O = 0.0218 gram Na. Calculating this to H as before, we find 0.00095 gram. Therefore, 0.0792 gram, less 0.00095 gram, plus 0.0218 gram = weight of salt = 0.10015 gram, and $\frac{100 \times 0.0218}{0.10015} = 21.76$ per cent. Percentage of Na in salt = 21.76.

The neutral sodium salt of dicarbopyridenic acid contains 21.80 per cent. Na.

These results—the analysis of the silver and alkali salts, the analysis of the acid itself and its behaviour on burning, and with ferrous sulphate—seem to leave but little doubt as to the identity of the acid which we have obtained from quinine with that got in the same way from picoline.

Unfortunately the very high price of quinine prevented us in the first instance working with a quantity sufficient to give a yield of the acid large enough for a complete investigation. Having ascertained how the acid may be most economically separated, it was our intention to repeat our experiments on a larger scale; but as the attention of others (*Deut. Chem. Ges. Ber.*, 1877, p. 1930) has recently been directed to the same acid, we believe that it is unnecessary to apologize for the immediate publication of our results in their present imperfect form.

It has been mentioned, that on dissolving in alcohol the residue obtained by evaporation of the filtrate from the lead salt, the solution, after standing for some time, gave a red deposit. This red substance is probably a product of imperfect oxidation, and seems to be identical with Marchand's quinetin, which is obtained by oxidizing quinine with peroxide of lead and sulphuric acid. If the oxidation of quinine with potassium permanganate, instead of being conducted at the ordinary temperature, is carried on at 100° C., the quantity of red substance obtained is less, and the yield of acid greater.

M. Marchand having kindly furnished us with the details of his method of oxidation with peroxide of lead, we prepared a quantity of quinetin. On subjecting this quinetin to oxidation with permanganate, we obtained an acid apparently identical with that got by the direct oxidation of quinine.

At present we are engaged in investigating the nature of Marchand's quinetin, and in our next paper shall give the results of that investigation, together with those of experiments on the action of barium hydrate, and various oxidising agents on quinine and allied alkaloids.
