VI.—On an Alkaloid from Cinchona Bark hitherto Undescribed.

By DAVID HOWARD.

In experimenting upon impure crystallisations of quinine salts obtained from the mother-liquors of the manufacture of sulphate of quinine, I have occasionally been perplexed by an unusual loss in recrystallising, which the mechanically adhering mother-liquor did not seem to account for.

A more careful examination of some of these substances, shows that the cause, in some cases at least, is the presence of an alkaloid hitherto undescribed, the extreme solubility of the salts of which, both distinguishes it at once from the cinchona alkaloids already known, and renders it very difficult to separate from the uncrystallisable quinoïdine.

The most convenient method of obtaining it, is to purify the alkaloids contained in the mother-liquor from the recrystallisation of such impure products as I have mentioned, by solution in ether, and after evaporation of the ether to dissolve with oxalic acid in as small a quantity of water as possible, and allow it to crystallise.

The oxalate thus obtained may be purified by recrystallisation from water, with addition of animal charcoal, but I have never been able to free it entirely from a yellow colour.

The most satisfactory salt for analysis is the platino-chloride, which is prepared in the usual manner; it is almost insoluble in water or in cold hydrochloric acid, but soluble with difficulty in hot strong acid; it forms a crystalline powder by precipitation, and well defined crystals by solution in acid.

The analysis shows that it is isomeric with the platino-chloride of quinine, but anhydrous, instead of containing one atom of water of crystallisation, given off at 120° , as does the salt of quinine.

The ultimate analysis for which, as well as for the other combustions which I shall have to mention, I am indebted to the skill of Mr. Huxley and Mr. Gray, of the Royal College of Chemistry, gives the following results:—

	C.	H.	Pt.
Experiment I.....	32.67	3.67	26.63
„ II	32.67	3.82	26.62

Gerhardt's formula for the anhydrous platino-chloride of quinine, $C_{20}H_{24}N_2O_2$, $2HCl$, $PtCl_4$ requires

C 32.60 H 3.53 Pt 26.76.

The salt taken for analysis was precipitated from a hot acid solution, and was a distinctly crystalline powder.

The composition is the same whether it be precipitated cold in a
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neutral solution, or crystallised from a strong acid solution, as the following results will show :—

Platino-chloride precipitated cold, Pt 26.50
do crystallised 26.62

The oxalate, as I have before mentioned, though it is the most easily crystallised of the salts of this alkaloid, is unfortunately very difficult to purify entirely, and changes so readily under the influence of air, light, or heat, that I have been unable to obtain it colourless. When a dilute aqueous solution is concentrated by evaporation in a water-bath, the change of colour shows that decomposition has to a certain extent taken place, and on the addition of water, a brown resinoid matter separates from the solution. To find out if this was caused by impurities or was a property of the salt itself, I decomposed the platino-chloride of known purity by several processes, but in each case the resulting oxalate had the same colour and the same tendency to decompose. Even when prepared from perfectly colourless solutions of the alkaloid in ether, I have still found the oxalate of a greenish-yellow hue, even before the application of heat; in fact, I am not sure that this colour may not be inherent in the salt itself.

It is extremely soluble in water, the wet crystals melting at 100°, but much less so in cold water; insoluble in ether, but very soluble in alcohol, and to a less degree in amyl alcohol, from hot concentrated solutions in either of which menstrua, it crystallises freely on cooling. The water of crystallisation is partially given off in vacuo, and entirely at 100° after previous drying; if the salt is at once heated to 100° without previous exsiccation, it is apt to fuse.

The combustion proved exceedingly difficult; the usual process with cupric oxide was found inadmissible, the oxalate assuming a dark brown colour as soon as it touched the oxide. The only practicable method is burning in oxygen gas, and even in this mode of analysis, the low temperature at which the substance partially decomposes, makes it difficult to accomplish successfully. It will be seen that the results, though agreeing very closely among themselves, differ considerably from the probable formula, showing plainly the difficulty of obtaining a pure product.

The hydration and the oxalic acid point to the formula $2(C_{20}H_{24}N_2O_2), C_2H_2O_4 + 9aq.$, the numbers obtained being :—

	C.	H.	$C_2H_2O_4$.	H_2O at 100.	H_2O in vacuo.
Theory ..	56.00	7.55	10.00	18.00	
Exp. I ..	57.57	8.64	10.07	17.98	14.23
„ II ..	57.42	8.74	9.98	17.98	14.09
„ III .	57.74	9.14	10.08	17.89	14.02
„ IV .	57.85	8.79	10.23	17.72	13.82
„ V ..	—	—	10.19	17.98	—

The water lost by drying in vacuo agrees very closely with 7 atoms, viz., 14.00 per cent.

The salt thus differs from oxalate of quinine by 3 atoms of water of crystallisation, the formula of the latter being $2(C_{20}H_{24}N_2O_2) \cdot C_2H_2O_4 \cdot 6aq$.

The properties of the other salts which I have examined are as follows:—The sulphate, tartrate, citrate, hydrochlorate, phosphate, and acetate are all exceedingly soluble in water; on evaporation in vacuo they form semi-crystalline masses, impossible to obtain in a state fit for analysis.

The hydrobromate and ferrocyanide obtained by double decomposition form oily strata at the bottom of the solution, soluble in an additional quantity of water, but even on long standing they show no sign of crystallisation.

The hydriodate also forms an oily stratum in strong solutions, but on standing it becomes semi-solid by the formation of crystals; weaker solutions also deposit a small quantity of flocculent crystals, but in neither case can they be separated from the mother-liquor.

The sulphocyanide, while also forming an oil when in concentrated solutions, crystallises from a somewhat larger quantity of water in long silky needles, almost white, very soluble, and readily decomposed by heat.

The iodo-sulphate I have not as yet succeeded in forming. I much regret this, on account of the great importance of this salt in the cinchona alkaloids, and further experiments are needed, either to form it or to prove its absence.

The alkaloid itself, as obtained by precipitation from a solution of its salts by potash or soda, is a yellowish oil. I have not been able to obtain it pure in the solid state, for it will not bear heat without decomposition, and holds water too strongly to dry in vacuo. It is very soluble in alcohol, soluble to a large extent in ether, from which it separates as an oil when the ether is allowed to evaporate. It is a strong base; the salts are neutral to test-paper; a small excess of the base strongly restores the colour of reddened litmus. Ammonia precipitates its solutions but imperfectly, and, if we may judge from this it is even a stronger base than quinine.

Chlorine-water followed by ammonia, produces in solutions of its salts the green colour and precipitate of dalleiochin which distinguishes quinine and quinidine. Strong acids, even in the cold, produce a change of colour, and even when diluted with a considerable quantity of water; heat renders the action much more rapid. This coloration is strongest when nitric acid is used, an excess of which, with the aid of heat, will develop a strong yellow-green colour, even in a weak solution. In this reaction, as well as in the persistent colour of its salts, this alkaloid shows a curious resemblance to aricine.

The yellow colour renders the examination of its optical properties difficult, but, as far as has been hitherto tried, it is inactive. I have not been able to recognize fluorescence in its solutions.

Its taste is a peculiar bitter, very much less, both in intensity and permanence, than that of the other cinchona alkaloids.

I have not been able to find out whether this alkaloid is contained in all the species of cinchona, or, if not, to which it belongs, for the difficulty of the crystallisation of the impure salts makes it a matter of uncertainty to obtain it.

My uncle, Mr. J. E. Howard, when investigating the leaves of the *Cinchona Succirubra*, from India, found minute quantities of an alkaloid, soluble in ether, from which an alcoholic solution of oxalic acid precipitated it in a crystalline form; but the small quantities at his disposal prevented his examining it further than to show its analogy with quinine; his present conviction is that this substance is identical with the alkaloid I have been describing, and though the evidence is not yet sufficient to enable us to speak with certainty, it tends strongly to prove it. It seemed so desirable to settle this point, and to throw some light, if possible, on the order of formation, and possibly on the far more important and far more difficult question of the mode of formation of the alkaloids of the descending sap, that he has written to Mr. Broughton, and we hope shortly to receive a quantity of the leaves sufficient to enable us to investigate it.

VII.—On the Origin of Nitrates in Potable Waters.

By CHARLES EKIN, Bath.

I HAVE frequently been at a loss to account for the presence of considerable quantities of nitric acid in potable waters, where contamination by sewage or manured land was out of the question. To give but one instance, there is a hill near Bath, capped by the Great Oolite, which has not a single house upon it, no drainage near it, and on whose scanty herbage browse only a few sheep, and yet the springs rising at the junction of the Oolite with the Fuller's earth contain as much as 65 grains of nitric acid per gallon. Here, then, after making all due allowance for the combined nitrogen contained in rain water, which, according to the observations of Lawes, Gilbert, and Way, amounts to 24 parts nitrogen in 1,000,000, there still remains the large proportion of eight to one to be accounted for. And this proportion will be still further increased if we consider that much of the nitric acid and ammonia