

XVII.—Contributions to our Knowledge of the Aconite Alkaloids. VIII. On Picraconitine.

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PICRACONITINE is the name given by Wright (*J. Chem. Soc.*, 1877, i, 143; see also Wright and Luff, *Trans.*, 1878, 332 and 336) to an amorphous alkaloid obtained in 1874 by T. B. Groves, from the roots of *Aconitum Napellus*.

The composition and properties of the substance were described by Wright (*loc. cit.*) in 1877. The free base is stated to be a varnish, which could not be crystallised, although, when dissolved in acids, crystalline salts were produced. The compound did not give rise to the tingling of the tongue and lips which is so characteristic of aconitine, but both the base and its salts were intensely bitter; hence the name proposed for the alkaloid. It was found not to be toxic in small doses. The formula $C_{31}H_{45}NO_{10}$, deduced from analyses of the base and its salts, differs from that of aconitine in containing 2 atoms less of carbon and oxygen and 2 atoms more of hydrogen; Wright's formula for aconitine being $C_{33}H_{45}NO_{12}$. The hydrochloride of the base was represented by the formula $C_{31}H_{45}NO_{10}, HCl, 1\frac{1}{2}H_2O$, and the yellow, sparingly soluble, amorphous aurichloride by the formula $C_{31}H_{45}NO_{10}, HCl, AuCl_3$. The actual analytical figures agreed fairly well with those calculated from these formulæ. When heated with strong aqueous alkalis, picraconitine was hydrolysed, yielding benzoic acid and a base closely resembling aconine; the latter was named *picraconine*, the hydrolysis being represented by the equation $C_{31}H_{45}NO_{10} + H_2O = C_7H_6O_2 + C_{24}H_{41}NO_9$. Neither picraconine nor any of its salts could be crystallised. Whilst the base resembled aconine in its chief properties, it was observed to be rather more soluble in ether and to differ from it in composition; the analyses of the base and of its mercurio-iodide agreeing fairly with the formula $C_{24}H_{41}NO_9$, which contains H_2 more and C_2O_2 less than the formula for aconine.

Some mystery has always surrounded this alkaloid on account of its having only once been obtained from the roots of *A. Napellus*. Groves, who had many times previously extracted the total alkaloids from the roots of this plant, had not before obtained any such substance, and, moreover, neither he nor Wright were able to obtain it from undoubtedly genuine specimens of *A. Napellus*. Later observers, also, have failed to find picraconitine, and the suggestion has been

made that, in all probability, it was derived from the roots of some other species of aconite than *A. Napellus*, which were present in the collection on which Groves originally operated.

After reading Wright's description of the properties of picraconitine, it occurred to us as probable that it might be isaconitine, which we have shown to occur in *A. Napellus*, and to be producible from aconitine, contaminated with a small proportion of other base. All the properties attributed by Wright to this alkaloid are consistent with this view as to its nature, the presence of impurity giving rise to the analytical numbers which this observer recorded, and also to the slight difference he noticed between aconine and picraconine. Moreover, the great difficulty that there is in completely purifying isaconitine rendered it extremely likely that if this alkaloid had been isolated it would not have received sufficient purification to make clear its real nature and composition.

It was obviously not at all easy for us to verify this hypothesis as to the composition of picraconitine. Dr. Alder Wright, who has rendered considerable assistance to our enquiry by putting authentic specimens of his products at our disposal, was unable to help us on this occasion, as all the picraconitine he possessed was used up in making the analyses referred to above. We next applied to Mr. T. B. Groves, who very kindly searched his collection of aconite products, and most fortunately discovered among them small quantities of picraconitine salts, which he was good enough to send us for the purposes of examination. One specimen, weighing less than half a gram, was labelled "Picraconitine muriate"; the other, of which there was a similar quantity, was labelled "Picraconitine nitrate." The *picraconitine hydrochloride* was a whitish powder, having a very bitter taste, and producing scarcely any tingling sensation on the tongue and lips; it melted somewhat indefinitely near 212° , and on decomposing a portion of it with ammonia a base was obtained soluble in ether, and presenting the appearance of a varnish which refused to crystallise. The salt was recrystallised from hot water in the manner described in a previous paper in connection with the purification of isaconitine hydrochloride; as, however, the crystals still melted at rather a lower temperature than the pure isaconitine salt, they were again recrystallised from a mixture of alcohol and ether, from which they separated quite characteristically. The crystals now melted at the same temperature as isaconitine hydrochloride, with which they corresponded in every respect.

The specimen of *picraconitine nitrate* was slightly yellowish, and melted near 170° . On recrystallisation from water, it separated as a white, crystalline powder, which melted indefinitely, with decomposition, near 212° . The addition of ammonia to an aqueous

solution of the salt precipitated the base in white flocks, which dissolved in ether and remained as an uncrystallisable varnish on evaporating the solvent. The base thus obtained was converted into hydrochloride, and, like isaconitine hydrochloride, the salt separated from a hot solution during evaporation; in order to completely purify the salt, it was several times recrystallised from a mixture of alcohol and ether, when it appeared as rosettes of silky needles, which finally melted at the same temperature as pure isaconitine hydrochloride, 217° .

There was thus little room for doubt that we were dealing with a salt of the alkaloid we have previously described under the name of isaconitine. As a small quantity of material remained, it was decided, in order to make the proof conclusive, to prepare the very characteristic aurichlor-derivative of isaconitine, $C_{33}H_{44}(AuCl_2)NO_{12}$. The addition of a solution of auric chloride to a solution of the hydrochloride produced a pale yellow, amorphous precipitate, which was dissolved in warm absolute alcohol and the solution allowed to stand. No crystalline aurichloride separated. Ether was now added to the solution and the mixture kept for a day in a stoppered bottle; small, colourless crystals gradually separated, and these melted at the same temperature as pure aurichlorisaconitine, namely, at 204° .

These observations prove that "picraconitine" is only impure isaconitine, and that, therefore, this name can no longer be employed to designate an alkaloidal constituent of *Aconitum Napellus*.

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