XXXIII.—*A New Alkaloid from Corydalis cava.*

By JAMES J. DOBBIE, M.A., D.Sc., and ALEXANDER LAUDER, University College of North Wales, Bangor.

IN a paper which recently appeared in the *Berichte* (25, 2411), Messrs. Freund and Josephy describe several alkaloids which they obtained from the roots of *Corydalis cava*. One of these is identical with the corydaline described by us (Trans., 1892, 61, 244 and 605), and Freund and Josephy confirm our formula for this alkaloid. Part of the crude material with which they worked was obtained from Schuchardt of Görlitz, and they mention at the close of their paper that this material contains a small quantity of an alkaloid soluble in alkali, and melting at 205—207°, so that it is distinct from the other bases described by them. Before the appearance of this paper we had already partially examined an alkaloid obtained from the same source, and apparently identical with the base referred to by Freund and Josephy. We therefore communicated with them, and they courteously agreed to leave the investigation of this substance in our hands.

When Schuchardt's crude corydaline is treated with hot water, it yields a green solution with a magnificent blue fluorescence, from which tufts of small slender needles separate on cooling. When collected on a filter, the crystals form a compact film with a metallic lustre, recalling that of freshly cut potassium. The substance is readily purified by recrystallisation from alcohol, but if crystallised from water there is slight decomposition, indicated by the darkening of the solution. The alcoholic solution is colourless when freshly prepared, but quickly assumes a pale pink colour, accompanied by a slight fluorescence, which becomes more intense on standing or heating. The alkaloid is nearly insoluble in cold, but dissolves readily in hot, water. The green colour and fluorescence of the aqueous extract of corydaline are due apparently to the presence of a decomposition product. The new alkaloid crystallises from alcohol in fine, silky needles, which dissolve easily in solutions of the caustic alkalis and ammonia, slightly in benzene, but not appreciably in ether or chloroform. The alkaloid is colourless when pure, but on standing, even at the ordinary temperature, gradually becomes somewhat discoloured. On long continued heating at 100°, this change is more pronounced, the alkaloid assuming a slate-grey colour. When the altered substance is dissolved in alcohol, it gives a pink-coloured fluorescent solution, confirming our view that the fluorescence is due to a decom-

position product of the alkaloid, and not to the pure substance. The alkaloid has no definite melting point. When heated to 200° , it blackens, and slowly decomposes. The alcoholic solution of the pure substance is slightly dextrorotatory.

The following are the results of the analysis of the alkaloid, purified by repeated recrystallisation from alcohol, and dried at 100° .

0.1931	gave	0.4893 CO_2	and	0.1260 H_2O .	C = 69.11; H = 7.25.
0.2866	„	0.7271 CO_2	„	0.1852 H_2O .	C = 69.12; H = 7.18.
0.2761	„	0.6988 CO_2	„	0.1909 H_2O .	C = 69.03; H = 7.68.
0.2712	„	0.0810 Pt.			N = 4.30.
0.2846	„	0.0824 Pt.			N = 4.18.

The mean of these numbers gave C = 69.09; H = 7.37; N = 4.24.

From this we deduce the formula $\text{C}_{19}\text{H}_{25}\text{NO}_4$, which requires C = 68.88; H = 7.55; N = 4.23 per cent.

We propose for this alkaloid the name *corytuberine*; from *Corydalis tuberosa*, a synonym for *Corydalis cava* (Dec.).

Corytuberine dissolves readily in acids, forming salts, some of which crystallise with ease.

Corytuberine Hydrochloride.—This salt is prepared by dissolving corytuberine in hydrochloric acid, and evaporating until crystals begin to separate. The hydrochloride crystallises without water of crystallisation in small, well-developed, colourless rhombohedra. It is stable when dry, but its solution becomes brown when heated. The specimen analysed was crystallised from water and dried over strong sulphuric acid. The chlorine was determined by direct precipitation with silver nitrate.

I. 0.3042 gave 0.1205 AgCl = 9.79 Cl.

II. 0.3171 „ 0.1256 „ = 9.78 Cl.

$\text{C}_{19}\text{H}_{25}\text{NO}_4 \cdot \text{HCl}$ requires Cl = 9.66 per cent.

Corytuberine Sulphate.—This compound is obtained by treating corytuberine hydrochloride with the calculated amount of silver sulphate. It is easily soluble in water, from which it crystallises with difficulty. It shows the same tendency to decompose as the hydrochloride, and we have not succeeded in obtaining it in well developed crystals. Analysis of this salt dried at 100° gave the following result.

0.2951 gave 0.0948 BaSO_4 = 13.50 H_2SO_4 .

$(\text{C}_{19}\text{H}_{25}\text{NO}_4)_2 \cdot \text{H}_2\text{SO}_4$ requires H_2SO_4 = 12.89 per cent.

Corytuberine Platinochloride.—The platinochloride is prepared by adding a solution of hydrogen platinochloride to a solution of corytuberine hydrochloride in water. It is a pale yellow, crystalline

stance only slightly soluble in water, and, therefore, easily purified in excess of hydrogen platinochloride by washing. Analysis of this salt dried at 100° gave the following results.

I. 0.2778 gave 0.0496 Pt = 17.85 Pt.

II. 0.1998 „ 0.0361 Pt = 18.07 Pt.

$(C_{19}H_{25}NO_4)_2, H_2PtCl_6$ requires Pt = 18.19 per cent.

Corytuberine Methiodide.—Corytuberine is only soluble to a slight extent in methyl iodide. The methiodide is prepared by digesting a solution of the alkaloid in alcohol with methyl iodide for several hours in a flask attached to a reflux condenser. On evaporating the solution, the methiodide crystallises out in small hemispherical tufts of needle-shaped crystals. This compound is colourless when pure, but it shows the same tendency to decompose as the other salts, and we were unable, for this reason and on account of the small amount of substance at our disposal, to obtain it in a pure condition. The results of our analysis therefore differ by about 1 per cent. from the calculated numbers. The salt was dried over strong sulphuric acid.

I. 0.4325 gave 0.2065 AgI = 25.79 I.

II. 0.4908 „ 0.2349 AgI = 25.85 I.

$C_{19}H_{25}NO_4, CH_3I$ requires I = 26.84 per cent.

Action of Hydrogen Iodide on Corytuberine.—Corytuberine was treated with a fuming solution of hydrogen iodide by Zeisel's method, described in our second paper on corydaline (Trans., 1892, **61**, 609). Ethyl iodide was evolved, a yellow, crystalline compound, which we were investigating, remaining in the distilling flask. The determination of the methoxy-groups in pure corytuberine, dried over sulphuric acid, gave the following results.

I. 0.2292 gave 0.3206 AgI = 18.47 CH_3O .

II. 0.2500 „ 0.3509 AgI = 18.53 CH_3O .

Calculated for two CH_3O groups, $C_{19}H_{25}NO_4$ requires 18.73 per cent.

CH_3O .

Corytuberine, therefore, contains only two of its oxygen atoms in methoxy-groups, whereas corydaline has all its four oxygen atoms present in this state of combination.

We have received from Schuchardt, of Görlitz, a small quantity of other alkaloid extracted by him from the tubers of *Corydalis cava* when working them up for corydaline. This melts or decomposes at about 180° , and differs, further, from corydaline, corytuberine, and the other alkaloids obtained from the same source, in its solubility. It crystallises from alcohol in small, acicular crystals.

Excluding this alkaloid, and another of lower melting point than

corydaline mentioned by Freund and Josephy (*Ber.*, **25**, 2412), corytuberine brings up the number of alkaloids obtained from *Corydalis cava* to four, namely:—

- I.* Corydaline, $C_{22}H_{29}NO_4$. M. P. 134·5°.
- II. Corytuberine, $C_{19}H_{25}NO_4$.
- III.† Bulbocapnin, $C_{34}H_{36}N_2O_7$. M. P. 198—199°.
- IV.† Corycavin, $C_{23}H_{23}NO_5$. M. P. 214—215°.

All the other substances hitherto described are probably mixtures of the above mentioned alkaloids.