CHEMICAL CONSTITUENTS OF CORYDALIS STEWARTII FEDDE

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Three alkaloids provisionally named and formulated as (a) Corycidine, $C_{11}H_{11}O_4N$, m.p. 290-92° (dec.), (b) Corydinine, $C_{17}H_{17}O_4N$, m.p. 199-200° and (c) Corydicine, $C_{19}H_{17}O_5N$, m.p. 181-82° have been isolated from *Corydalis stewartii* Fedde. Besides, a saturated alcohol $C_{30}H_{62}O$, m.p. 76-77° has also been obtained from the fatty portion.

Corydalis stewartii Fedde,[1] locally called mamiri, is a small annual herb belonging to the family "Fumariaceae". It is found growing by shady road-sides and in forests at Murree and the Gallies during the monsoon. It also occurs, in fair quantities, in Kaghan valley, Azad Kashmir, Dir and Swat States. The juice of the plant is used by local people in the treatment of eye diseases. The plant was taken up for investigation as no work on it has so far been reported in literature. As a result of the present work, it has been possible to isolate three alkaloids provisionally named as (a) Corycidine, (b) Corydinine, and (c) Corydicine which, on the basis of elemental analysis and molecular weight determinations have been assigned the formulae:

(a) Corycidine, $C_{11}H_{11}O_4N$, m.p. 290-92° (dec.).

(b) Corydinine, $C_{17}H_{17}O_4N$, m.p. 199-200° and

(c) Corydicine, $C_{19}H_{17}O_5N$, m.p. 181-82°.

All the three alkaloids were found to contain methylene dioxy [2] group and the tertiary nitrogen.[3] The purity of the bases was established by the technique of T.L.C. The results of the combustion analysis correspond very closely with the molecular formula assigned to corycidine. Molecular weight determination by titration with perchloric acid in non-aqueous medium gave the value of 405, which is double the calculated figure. Further work to decide whether the formula of corycidine exists as such or as $(C_{11}H_{11}O_4N)_2$ is in hand.

The petroleum ether-soluble fraction yielded a colourless crystalline alcohol provisionally named as Corydanol, m.p. 76-77°, formulated as $C_{30}H_{62}O$ on the basis of combustion analysis and molecular weight determination. It did not decolorise potassium permanganate or bromine, gave negative Leibermann-Burchard test, indicating its non-steroidal character and lack of unsaturation. The acetyl derivative melted at 37-38°.

Further studies on the characterisation of these constituents are in progress.

Experimental

The plants were collected in the month of July from Dunga Galli and immediately after collection were cut into 1-2 cm. bits and repeatedly percolated with 95 percent ethyl alcohol until the extract gave a negative test for alkaloids. The combined extracts were first concentrated in a cyclone evaporator and then under reduced pressure to a thick syrupy consistency. The residue was macerated with dilute acetic acid (10 percent) until free from alkaloids. The acid-soluble fraction was basified with dilute ammonia (10 percent) and extracted with ethyl acetate. The residue obtained on removal of the solvent under reduced pressure, was extracted with chloroform and the chloroform-insoluble residue was dissolved in alcohol, treated with activated charcoal, filtered and concentrated. On keeping, colourless shining plates of corycidine were obtained m.p. 280-85° (dec.). (yield 0.04 percent). This fraction, on repeated crystallisation from hot methyl alcohol, finally melted at 290-92° (dec.).

It was also observed that, on treatment of the original ethyl acetate extract with activated charcoal, corycidine was selectively absorbed and could be separated by treatment with hot methanol.

The chloroform-soluble fraction after washing and drying over anhydrous sodium sulphate was concentrated and an equal volume of methyl alcohol added when corydinine crystallised out as colourless thick rectangular plates m.p. 190-95° (yield 0.096 percent). On further crystallisation from the same solvent, it finally melted at 199-200°. The mother liquor, on further concentration and keeping, yielded fresh crop of crystals. Fractional crystallisation from methyl alcohol and chloro-

Melting points were taken in J.W. Tower's electrical melting point apparatus. Micro analysis was done by A. Bernhardt 433, Mulheim (Ruhr), West Germany. Infra-red was taken on Beckmann IR-5 Spectrophotometer.

form (1:1) finally gave colourless thick rectangular plates of corydicine m.p. 181-82° (yield 0.03 percent).

Corycidine.—It is soluble in hot methyl or ethyl alcohol and ethyl acetate, insoluble in acetone, chloroform, benzene, ether and petroleum ether. The nitrogen was found to be tertiary in nature, the test for methylene dioxy group was also positive. Its Infra-red Spectra (Fig. 1) shows peaks at 719, 850, 900, 1030, 1060, 1265, 1360, 1430, 2700, and 2800 cm.$^{-1}$ Nujol Mull.

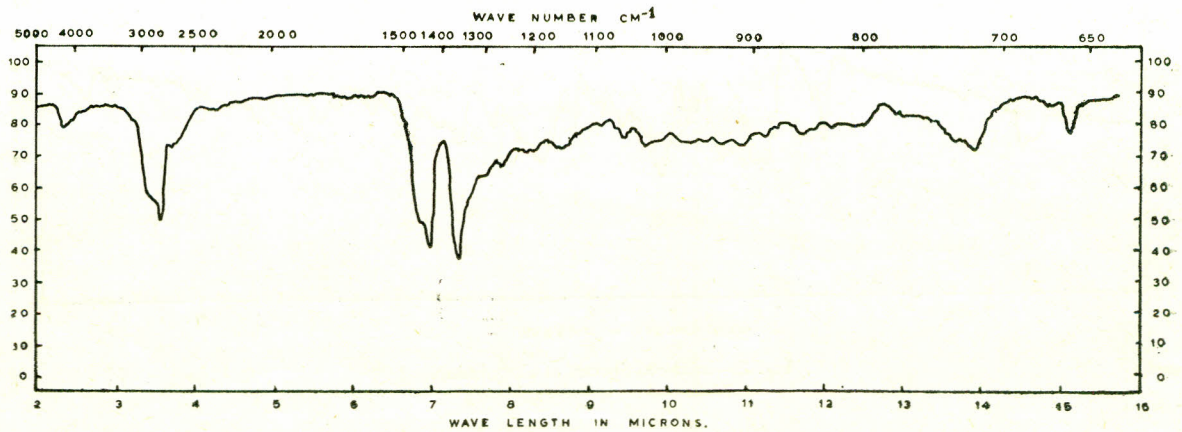

Fig. 1.—Infra-red Spectra of Corycidine.

Found: C, 59.95; H,5 .15; N, 6.41. Calc. for: $C_{11}H_{11}O_4N$; C, 59.72; H, 5.01; N, 6.33. Rf at 15°, 0.00 (ethyl acetate, T.L.C.—May & Baker alumina).

Corydicine Hydroiodide.—It was prepared by adding solid potassium iodide to the acetic acid solution of the base. The turbid solution on standing for some time gave semi-crystalline deposit, which crystallised from methyl alcohol in shining needles m.p. 265-70° (dec.).

Corydicine Picrate.—It was prepared by adding aqueous picric acid to the acetic acid solution of the base. The crystalline precipitate, on crystallisation from methyl alcohol, melted at 158-60° (dec.).

Corydicine Gold Chloride and Corydicine Chloroplatinate.—These were prepared by mixing ice-cold aqueous solution of the base hydrochloride with ice-cold aqueous solutions of gold and platinic chloride respectively. The gold chloride was obtained as a bright golden yellow amorphous powder. It melted at 148-50° (dec.) while the chloroplatinate, a slightly darker amorphous powder, melted at 233-35° (dec.).

Corydinine.—It is easily soluble in acetone, chloroform, ethyl acetate, benzene, difficultly soluble in hot ethyl and methyl alcohol and insoluble in ether or petroleum ether. It gave positive test for the presence of methylene dioxy and a tertiary nitrogen. Its Infra-red Spectra (Fig. 2) shows peaks at 663, 710, 755, 763, 800, 815, 847, 885, 895, 905, 912, 935, 973, 1035, 1080, 1110, 1130, 1160, 1230, 1280, 1305, 1360, 1410, 1425, 1495, 1605, 1650 and 2800 cm-.^{1}. Nujol Mull.

$[\alpha]_D^{15}$ -32, (in chloroform, C=1.65).

Found: C, 68.23; H, 5.47 and N, 4.59. Calc. for: $C_{17}H_{17}O_4N$; C, 68.20; H, 5.72 and N, 4.68. Mol. wt. 299, by Rast Method 325. Rf at 15°, 0.49 (ethyl acetate, T.L.C.—May & Baker alumina).

Corydinine Hydrochloride.—Alcoholic hydrochloric acid was added to a suspension of the base in the same solvent, the clear solution thus obtained, on standing and scratching the sides of the flask deposited crystalline needles. It was filtered and recrystallised from dilute alcohol melted at 258-60° (dec.).

Corydinine Chloroplatinate.—It was obtained in the usual manner as a yellow powder m.p. 229-30° (dec.).

Corydinine Picrate.—It was obtained by adding aqueous picric acid to the base hydrochloride in

water as a bright yellow crystalline powder. This was crystallised from hot ethyl alcohol and the fine needles obtained melted at 255-56° (dec.).

Corydicine.—It is easily soluble in acetone, chloroform, ethyl acetate and benzene, difficulty soluble in hot ethyl and methyl alcohol and insoluble in ether or petroleum ether. It also gave positive tests for the presence of methylene dioxy and tertiary nitrogen. The Infra-red Spectra of this alkaloid (Fig. 3) shows peaks at 663, 763, 785, 800, 815, 885, 925, 970, 1035, 1080, 1110, 1130, 1163, 1233, 1280, 1310, 1360, 1438, 1493, 1600 1650, *1750, 2325* and 2800 cm.$^{-1}$ Nujol Mull.

Found: C, 67.20; H, 5.22; N, 4.20. Calc. for: $C_{19}H_{17}O_5N$; C, 67.25; H, 5.05; N, 4.13. Mol. wt. is 339, by Rast Method 347. Rf at 15° is 0.46 (ethyl acetate, T.L.C. -May & Baker alumina).

Corydicine Hydrochloride.—It was obtained by adding alcoholic hydrochloric acid to a suspension of the base in the same solvent. The clear solution, on standing and scratching the sides, deposited crystalline needles. It was filtered and recrystallised from dilute alcohol and melted at 244-45° (dec.). (Found: C, 61.45; H, 5.29; N, 4.07; Cl, 9.68. Calc. for: $C_{19}H_{18}O_5NCl$; C, 60.70; H, 5.00; N, 3.62 and Cl, 9.12.)

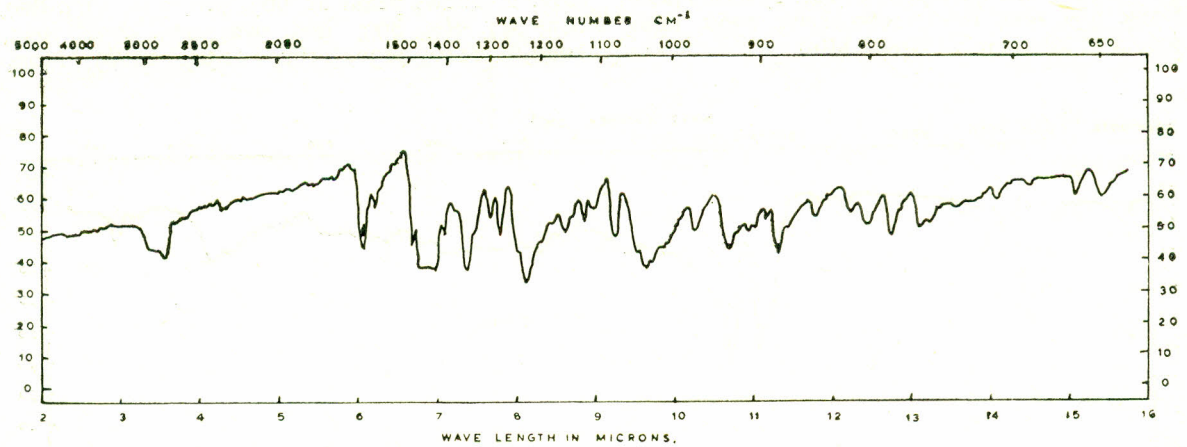

Fig. 2.—Infra-red Spectra of Corydinine,

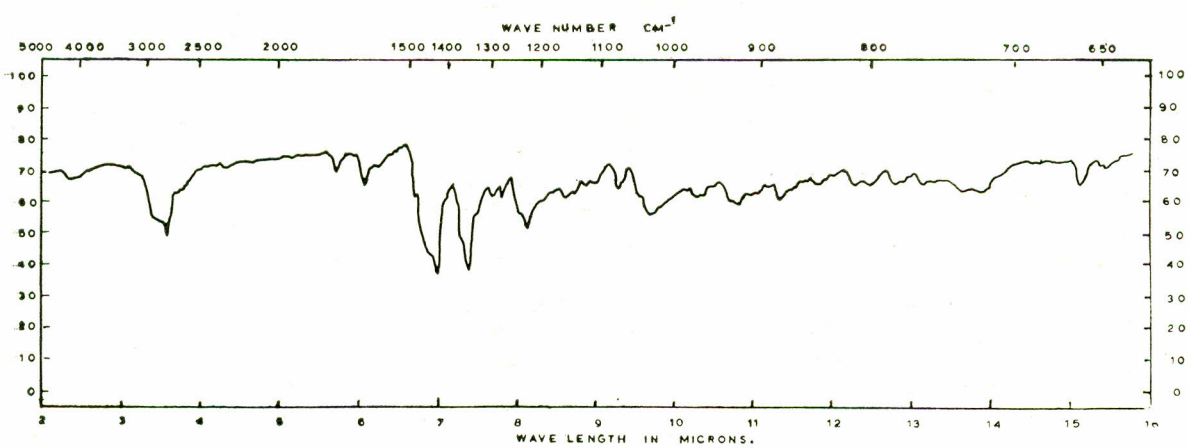

Fig. 3.—Infra-red Spectra of Corydicine.

Corydicine Picrate.—It was prepared in the usual manner and the powdered residue obtained was crystallised from dilute alcohol when rod-like needles were obtained, m.p. 268-70° (dec.).

Corydicine Chloroplatinate.—It was obtained in the usual manner as a bright yellow powder, melting at 212-15° (dec.).

Corydanol.—The dark greenish semi-solid residue left after extraction with acetic acid was taken up in petroleum ether, treated with activated charcoal and filtered. The light greenish solution was passed through a column packed with alumina (May & Baker—Chromatography). Fractions of (50 ml.) were collected. On removal of the solvent, the fractions 1-5 gave solid residue while fractions 6-8 contained mainly oil. The solid residue, obtained from fractions 1-5, was dissolved in methyl alcohol and acetone mixture (5:1) and allowed to stand when colourless plates of corydanol, $C_{30}H_{62}O$ m.p. 74-75° were obtained. On recrystallisation they finally melted at 76-77°.

(Analysis: C, 82.15; H, 14.23. Calc. for: $C_{30}H_{62}O$; C, 82.11; H, 14.24. Mol. wt. 438, by Rast Method 428.)

It is easily soluble in acetone, chloroform, ethyl acetate, benzene, ether and petroleum ether but difficultly soluble in hot ethyl and methyl alcohol. It did not decolourise potassium permanganate, gave negative Liebermann-Burchard test, indicating the absence of unsaturation and steroidal character.

Corydanol Acetate.—It was prepared in the usual manner. The sticky mass obtained was repeatedly crystallised from methanol and the fine lustrous scaly crystals were obtained. They melted at 38-39°.

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