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THE ALKALOIDS OF THE CHINESE *CORYDALIS AMBIGUA*, CHAM. ET SCH. (YEN-HU-SO) PART V. CORYDALIS L AND CORYDALIS M

With a note on Corydalis K

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In four previous communications on Chinese Corydalis [Chou, 1928, 1929a, b, 1933] the writer reported the isolation of eleven alkaloids termed Corydalis A, B, C, D, E, F, G, H, I, J. and K. Corydalis A, C and G are identical with Corydaline, Protopine and Corybulbine respectively and Corydalis F is most probably L-Corypalmine isolated for the first time. The present communication describes the isolation of 2 more new alkaloids, Corydalis L and Corydalis M from the non-phenolic fraction "2". Corydalis L crystallizes from chloroform in rhomboid crystals melting at 236°C and has a molecular formula $C_{19}H_{21}O_4N$ and a specific rotation −325°. Corydalis M crystallizes from a mixture of chloroform and alcohol also in rhomboid crystals, having a melting point of 161°C and a molecular formula of $C_{21}H_{24}O_5N$ and is optically inactive. They form well crystallized hydrochlorides easily soluble in water. Corydalis K, as reported in the last communication [Chou, 1933], has a melting point of 225°C, a specific rotation of −250° and a physiological action very similar to that of bulbocapnine, producing inactivity and a cataleptic state in albino mice and dogs. Its molecular formula has now been found to be $C_{21}H_{25}O_4N$. The physiological properties of Corydalis L and Corydalis M will be reported later by Dr. K. K. Chen.

EXPERIMENTAL

The syrupy alkaloidal residue of the fraction "2", freed as completely as possible from other non-phenolic alkaloids as reported pre-

viously, was taken up with dilute hydrochloric acid and filtered. The acid solution, after being washed several times with ether, was made alkaline with sodium carbonate and the liberated base extracted with chloroform. The chloroform solution, when dried and distilled, left behind a basic residue consisting chiefly of Corydalis C, Corydalis L and Corydalis M. The separation of these 3 alkaloids was effected by fractional crystallization from a mixture of chloroform and alcohol, Corydalis L and Corydalis M being less soluble in chloroform than Corydalis C.

Corydalis L, $C_{19}H_{21}O_4N$.

When crystallized pure from chloroform, it forms colorless rhomboid crystals (see fig. 1), m.p. 236°C. It is only slightly soluble in most organic solvents except chloroform in which it is easily soluble on warming. It is non-phenolic and becomes coloured when exposed to air or on keeping. A 0.4 per cent solution in chloroform gave in 2 dm tube a specific rotation of $-2.6°$, whence $[\alpha]_D^{20} = -325°$. It has a molecular formula of $C_{19}H_{21}O_4N$ according to the following analysis:—

(1) 0.1074 g substance gave 0.2733 g CO_2 and 0.0629 g H_2O
C = 69.40; H = 6.55

(2) 0.1167 g substance gave 0.2973 g CO_2 and 0.0704 g H_2O
C = 69.48; H = 6.75

(3) 0.1084 g substance gave 0.005449 g NH_3 by Kjeldahl's method. N = 4.13

$C_{19}H_{21}O_4N$ requires C = 69.72; H = 6.42; N = 4.28

Its hydrochloride crystallized from acidulated water in colorless long needles having no definite melting point and was easily soluble in water to a neutral solution. Its solution in dilute hydrochloric acid has the tendency to become a jelly on cooling.

Corydalis M, $C_{21}H_{24}O_5N$.

It is more soluble in chloroform than Corydalis L and crystallized from a mixture of chloroform and alcohol in rhomboid crystals (see fig. 2), m.p. 161°C. Its solution in chloroform was found to be optically inactive. It has a molecular formula of $C_{21}H_{24}O_5N$ according to the following analysis:—

(1) 0.1026 g substance gave 0.2552 g CO_2 and 0.0585 g H_2O
C = 67.83; H = 6.38

(2) 0.1013 g substance gave 0.2524 g CO_2 and 0.0581 g H_2O
C = 67.95; H = 6.42

(3) 0.1027 g substance gave 0.0046 g NH_3 by Kjeldahl's method.
N = 3.68

$C_{21}H_{24}O_5N$ requires C = 68.10; H = 6.48; N = 3.78

Its hydrochloride crystallized from a mixture of chloroform and acetone in prisms, m.p, about 190°C and was easily soluble in water.

Corydalis K, $C_{21}H_{25}O_4N$.

Its melting point, specific rotation and physiological properties were already reported in the last communication [Chou, 1933]. Its molecular formula has now been found to be $C_{21}H_{25}O_4N$ according to the following analysis:—

(1) 0.1024 g substance gave 0.2654 g CO_2 and 0.0641 g H_2O
C = 70.69; H = 7.01

(2) 0.1034 g substance gave 0.004931 g NH_3 by Kjeldahl's method. N = 3.92

$C_{21}H_{25}O_4N$ requires C = 70.95; H = 7.09; N = 3.94

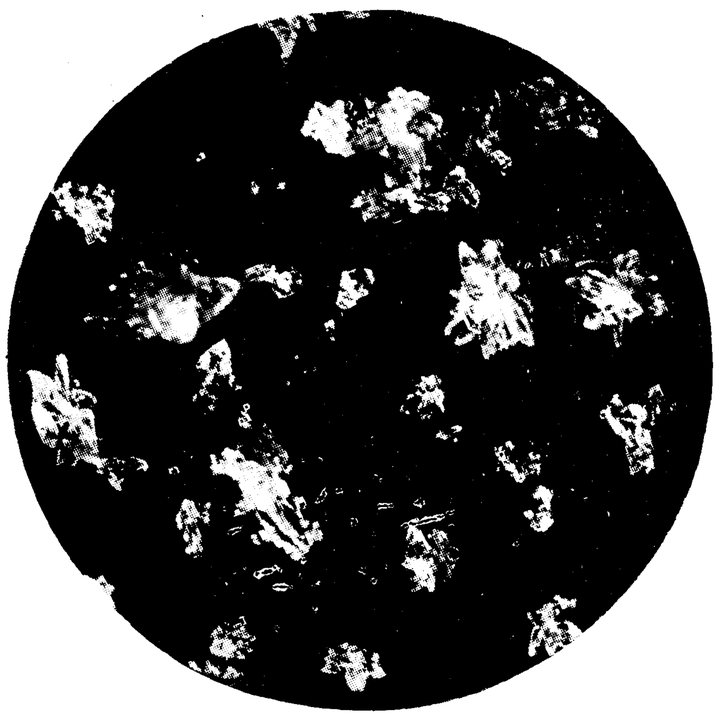

Fig. 1. Corydalis L ($C_{19}H_{21}O_4N$)
M.P. 236°C
S.R. −325°

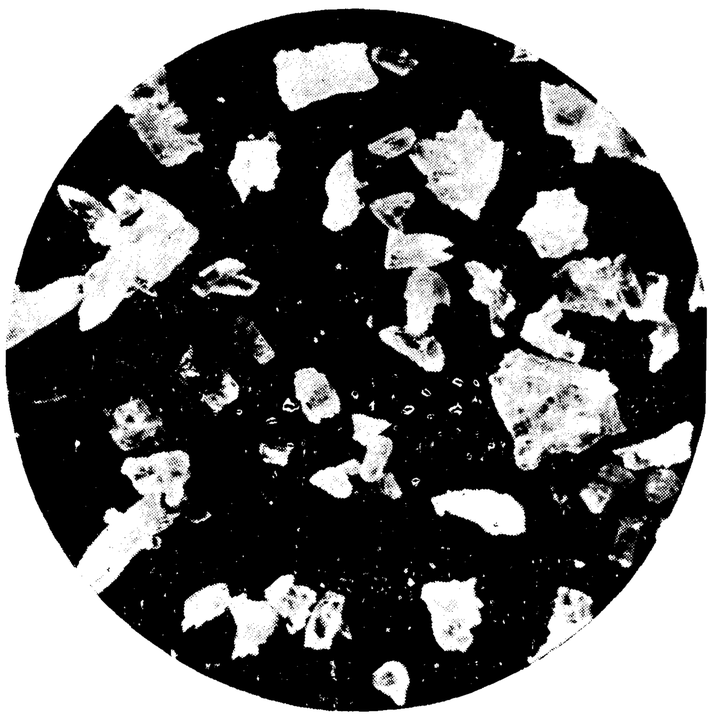

Fig. 2. Corydalis M ($C_{21}H_{24}O_5N$)
M.P. 161°C
S.R. 0°

A summary of the thirteen alkaloids already isolated from Chinese Corydalis (Yen-Hu-So) is given in table 1.

TABLE 1.

Alkaloids of Chinese corydalis

Name	Molecular formula	Melting point	Specific rotation	Identification
Corydalis A	$C_{22}H_{27}O_4N$	135°	+295°	Corydaline
Corydalis B	$C_{20}H_{23}O_4N$	148-9°	0°	———
Corydalis C	$C_{20}H_{19}O_5N$	201°	0°	Protopine
Corydalis D	$C_{19}H_{16}O_4N$ or $C_{19}H_{17}O_4N$	204°	−295°	———
Corydalis E	———	219°	———	———
Corydalis F	$C_{20}H_{23}O_4N$	237°	−250°	L-Corypalmine?
Corydalis G	$C_{21}H_{25}O_4N$	237°	+390	Corybulbine
Corydalis H (HBr salt)	———	235°	0	———
Corydalis I	———	104°	+112.5°	———
Corydalis J	$C_{30}H_{36}O_5N_2$	118°	+125°	———
Corydalis K	$C_{21}H_{25}O_4N$	225°	−250°	———
Corydalis L	$C_{19}H_{21}O_4N$	236°	−325°	———
Corydalis M	$C_{21}H_{24}O_5N$	161°	0°	———

SUMMARY

From the tubers of Chinese Corydalis (Yen-Hu-So), besides the eleven alkaloids (Corydalis A-K) already reported, two more new alkaloids, Corydalis L and Corydalis M have now been isolated.

Corydalis L crystallized in rhomboid crystals and has the molecular formula $C_{19}H_{21}O_4N$, a melting point 236°C and a specific rotation −325°. Its hydrochloride is easily soluble in water.

Corydalis M crystallized also in rhomboid crystals, m.p. 161°C, molecular formula $C_{21}H_{24}O_5N$ and is optically inactive.

Corydalis K has now been found to have the molecular formula $C_{21}H_{25}O_4N$.

LITERATURE

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中國延胡索之研究

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在中國延胡索中，作者曾提出十一種有機鹼性物質，並定名爲延胡索素甲，乙，丙，丁，戊，己，庚，辛，壬，癸及子(參觀本雜誌第二卷第二期第三卷第一期及第三期，第七卷第一期)，今又提出二新有機鹼性物，定名爲延胡索素丑 (Corydalis L)及延胡索素寅(Corydalis M).

延胡索丑之分子式爲 $C_{19}H_{21}O_4N$，熔點爲 236°，旋轉度爲 −325°.

延胡索素寅之分子式爲 $C_{21}H_{24}O_5N$，熔點爲161°，旋轉度爲 0°

今又鑑定延胡索素子之分子式爲 $C_{21}H_{25}O_4N$.