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CHRYSANTHINE AND CHRYSANTHENE, CRYSTALLINE NEUTRAL PRINCIPLES FROM *CHRYSANTHEMUM CINERARIAEFOLIUM*, BOCC.

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The flowers of *Chrysanthemum cinerariaefolium*, Bocc. and allied species, commonly known as pyrethrum flowers are being much used for making insect powder. An alcoholic extract of the entire plant, freed from the waxes, resins and other impurities by precipitating with ether and with petroleum ether was found by Chevalier and Mercier [1923] to be toxic to cold blooded animals, less toxic to warm blooded animals, and harmless to man. Investigated chemically, Fujitani [1901] obtained from the insect powder a highly insecticidal viscous oil which he termed pyrethrone. By alkaline hydrolysis of this, he obtained an alcohol, pyrethrol and an acid, both of which are inactive. In [1924] Staudinger and Ruzicka isolated from Dalmatian insect powder 2 highly active constituents which they termed pyrethrine I and pyrethrine II, esters of a ketonic alcohol, pyrethrolone, combined with chrysanthemum carboxylic acid and chrysanthemum dicarboxylic acid respectively. In investigating the chemical constitutents of the pyrethrum flowers cultivated in China, the writers found that, there are present, besides the acitve oily liquid, 2 well crystalline neutral principles, to which the names Chrysanthine and Chrysanthene are provisionally assigned. These principles are also found present in the insect powder of foreign origin. Chrysanthine crystallized from a mixture of chloroform and alcohol in colorless rhomboid crystals, and has an empirical formula $C_{10}H_{13}O_3$, a melting point 200°C

and a specific rotation $-30°$. Chrysanthene has the empirical formula $C_{18}H_{35}O$ and is optically inactive. It crystallizes from acetone in fine needles, melting at 80°C. As shown by Dr. H. P. Chu (private communication) Chrysanthine is toxic to warm blooded animals, 52 mg per kilo body weight hypodermically killing a rabbit in 48 hours.

EXPERIMENTAL

Two kilograms of the pyrethrum flower, cultivated and gathered in the neighbourhood of Shanghai, were finely powdered and percolated with cold benzene for 3 days. The benzene extract was filtered and distilled over water bath to a syrupy residue which was taken up with a sufficient quantity of ether. The ethereal solution, when dried, concentrated and allowed to stand over-night, deposited a crystalline material consisting chiefly of the 2 neutral principle chrysanthine and chrysanthene; whilst the other oily active constitutents of the flower remained soluble in ether and could be separated by distilling off the solvent and precipitating alternatively with alcohol and petroleum ether, the alcoholic extract being found to be highly insecticidal.

Chrysanthine $C_{10}H_{13}O_3$.

When crystallized pure from a mixture of chloroform and alcohol or from acetone, it forms large colorless rhomboid crystals (see fig. 1), m.p. 200°C. It is easily soluble in chloroform or hot acetone, less so in ether or alcohol and is insoluble in water, dilute acids or alkalies. Its alcoholic solution was neutral to litmus. When its solution in chloroform was boiled for a few hours, a white amorphous compound resulted, becoming insoluble in the solvent. A one per cent solution in chloroform in 2 dm tube gave a specific rotation $-0.6°$, whence $[\alpha]_D^{20} = -30°$. Its empirical formula was found to be $C_{10}H_{13}O_3$ according to the following analysis:—

(1) 0.1168 g substance gave 0.2343 g CO_2 and 0.0766 g H_2O
C = 66.38; H = 7.34

(2) 0.1211 g substance gave 0.2953 g CO_2 and 0.0774 g H_2O
C = 66.50; H = 7.15

$C_{10}H_{13}O_3$ requires C = 66.30; H = 7.18

Tested on the rabbit hypodermically, Dr. H. P. Chu (private communication) found that it is toxic to warm blooded animals and causes

death of a rabbit in 24 hours after receiving 75 mg per kilo, and of another rabbit in 48 hours after 52 mg per kilo.

The quantity of Chrysanthine present in the flower amounted to about 0.2 per cent.

Fig. 1. Chrysanthine $C_{10}H_{13}O_3$
M. P. 200°C
S. R. −30°

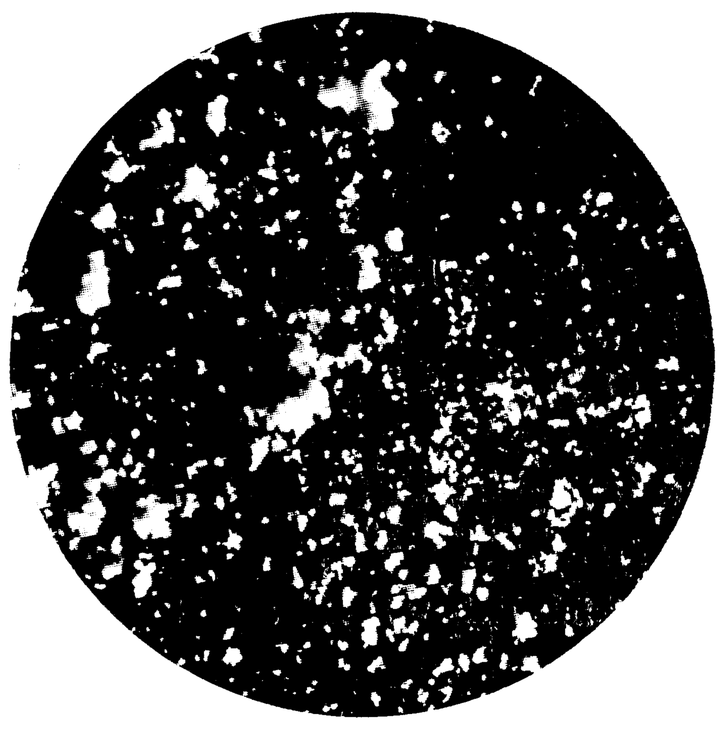

Fig. 2. Chrysanthene $C_{18}H_{35}O$
M. P. 80°C
S. R. 0°

Chrysanthene $C_{18}H_{35}O$.

It was separated from Chrysanthine by fractional crystallization from a mixture of chloroform and alcohol. When crystallized pure from acetone, it forms fine needles (see fig. 2) melting at 80°C. Its solubilities in organic solvents were found to be very much the same as those of Chrysanthine. When boiled with chloroform, it remained unchanged. Its solution in alcohol was neutral to litmus. It is optically inactive and has the empirical formula $C_{18}H_{35}O$ according to the following analysis:—

(1) 0.1004 g substance gave 0.2977 g CO_2 and 0.1189 g H_2O
C = 80.92; H = 13.25

(2) 0.1011 g substance gave 0.2996 g CO_2 and 0.1208 g H_2O
C = 80.82; H = 13.10

$C_{18}H_{35}O$ requires C = 80.82; H = 13.10

When the stems of pyrethrum were extracted with benzene in a similar way as described above, Chrysanthene was found to be present in larger quantity than in the flower.

SUMMARY

From the flower of *Chrysanthemum cinerariaefolium*, Bocc. cultivated in China, 2 crystalline neutral principles, Chrysanthine and Chrysanthene, have been isolated, besides the oily active constituents.

Chrysanthine crystallizes from a mixture of chloroform and alcohol or from hot acetone in rhomboid crystals, m.p. 200°C. It has the empirical formula $C_{10}H_{13}O_3$ and a specific rotation −30°. It is toxic to warm blooded animals.

Chrysanthene crystallizes from acetone in needles melting at 80°C. It has the empirical formula $C_{18}H_{35}O$ and is optically inactive.

LITERATURE

CHEVALIER, J. AND MERCIER, F. (1923) C. R. Acad. Sci., Paris, **176**, 1847.
FUJITANI, J. (1909) Arch. exp. Path. Pharmak., **61**, 47.
STAUDINGER, H. AND RUZICKA, L. (1924) Helv. Chim. Acta., **7**, 177.

中國除蟲菊之研究

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除蟲菊在國內銷路甚廣，市上所售之蚊香，佳者以菊花之粉爲之，其中之有效質素，由前人所發明者，多係流質物，作者今從中國產之除蟲菊花中提出二結晶物，一則對於動物有毒性，一則尚未加以試驗，二者之西文命名爲 Chrysanthine 及 Chrysanthene; Chrysanthine 之分子式爲 $C_{10}H_{13}O_3$ 溶點爲 200°C 旋轉度爲 −30° 兎之體重每公斤，注射 52 公絲時越四十八小時卽斃.

Chrysanthene 之分子式爲 $C_{18}H_{35}O$，溶點爲 80°C，旋轉度等於零，除蟲菊梗中含此物較花中爲多.