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NEW ALKALOIDS FROM HONG KONG PLANTS

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Abstract—From Hong Kong plants the following have been isolated: *Acronychia pedunculata*, bauerenol and potassium oxalate: *Elaeagnus loureiri;* two bases named *Elaeagnus Alkaloids E*1 and *E*2: *Eustigma oblongifolia; Eustigma Alkaloid O*1: *Gnetum indicum; Gnetum Alkaloid G*1: *Hypserpa nitida;* friedelin, and a quaternary base mixture: *Maesa perlarius; Maesa Alkaloid M*1: *Michelia figo;* magnolamine: *Pavetta hongkongensis;* γ-sitosterol, Quercus alcohol A1, and a carbonyl compound.

A SEARCH for alkaloids has been made in eight Hong Kong plants on which qualitative tests of the sort described by Arthur *et al.*[1,2] suggested their presence. Six of the plants yielded alkaloids including five new bases which have been characterized.

Acronychia pedunculata (Rutaceae) gave very weak qualitative tests; no bases were isolated but the rare triterpenoid bauerenol first obtained from *Acronychia baueri*[3] was found. *Elaeagnus loureiri* (Elaeagnaceae) yielded two bases different from those already recorded[4] from other *Elaeagnus* species. *Eustigma oblongifolia* (Hamamelidaceae) contains several basic fractions, from one of which Eustigma Alkaloid O1 has been isolated and characterized. The genus has not previously been reported as containing alkaloids. *Gnetum indicum* (Gnetaceae) has yielded a base obtained both as the hydrochloride and as the sulphate. No alkaloids have previously been reported in this genus. *Hypserpa nitida* (Menispermaceae), a genus which likewise does not seem to have been reported as alkaloidal, contains a quaternary base fraction; friedelin was also isolated. *Maesa perlarius* (Myrsinaceae) yielded Maesa Alkaloid M1, $C_{26}H_{54}O_2N_4$, which has been characterized as the picrate, the trihydrochloride and the (tri-)toluene-*p*-sulphonate. This alkaloid is the first reported from *Maesa* species. *Michelia figo* (Magnoliaceae) yielded the alkaloid magnolamine which has previously been reported in *M. fuscata.*[5] Although *Pavetta hongkongensis* (Rubiaceae) gave positive alkaloid tests no bases were isolated. However, γ-sitosterol, Quercus Alcohol A1,[6] and a low m.p. carbonyl compound were obtained.

EXPERIMENTAL

Analyses were by the Microanalytical Laboratories of the Universities of Melbourne and Singapore; Alumina used was B.D.H. preparative grade; light petrol had b.p. 60–80°. Rotations were measured in chloroform solution at room temperature; i.r. spectra were determined on a P–E model 137 Infracord spectrophotometer.

[1] H. R. ARTHUR and H. T. CHEUNG, *J. Pharmac. Pharmacol.*, **12**, 567 (1960).
[2] H. R. ARTHUR and R. P. K. CHAN, *Trop. Sci.*, **4**, 147 (1962).
[3] F. N. LAHEY and M. V. LEEDING, *Proc. Chem. Soc.*, 73, 42 (1958).
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[5] H. G. BOIT, *Ergebnisse der Alkaloid-Chemie bis* 1960, p. 235, Akademie-Verlag, Berlin (1961).
[6] H. R. ARTHUR, K. F. CHENG, M. P. LAU and K. J. LIE, *Phytochem.* **4**, 969 (1965).

Acronychia pedunculata

Stem bark (400 g) was extracted with petrol and then with methanol. The methanol extract was evaporated to dryness and the brown residue was triturated with methanol. Colourless crystals (2·35 g) of potassium oxalate separated. [Found: M, 165·0 (silver salt). Calc. for $(COOK)_2$ M, 166·2]. The i.r. spectrum was identical with that of authentic potassium oxalate.

The methanol filtrate deposited a yellowish solid, m.p. 160–190° which after recrystallization from methanol, methanol–chloroform, methanol–acetone, and finally ethyl acetate yielded bauerenol (30 mg), m.p. 193–194·5°, $[\alpha]_D - 26°$ (lit. $[\alpha]_D - 30°$) identical in i.r. spectrum and undepressed in m.p. in admixture with an authentic specimen.

Elaeagnus loureiri

Dried leaves (5 kg) were extracted with cold ethanol. The extract was evaporated to dryness *in vacuo* and the residue distributed between 5% aqueous ammonia and chloroform. The black residue obtained from the chloroform layer was triturated repeatedly with 2N HCl and the combined acid extracts were basified with aqueous ammonia and then extracted with chloroform from which on evaporation a syrupy mixture (10 g) was obtained. This mixture was dissolved in benzene (200 ml) and applied to a column of alumina (150 g). Elution with benzene gave a yellowish oil followed by crystals (0·03 g) which on recrystallization from light petroleum yielded *Elaegnus Alkaloid E*1, m.p. 117–120°. Infra red spectrum: ν_{max} cm^{-1}; 3250, 1725 (s), 1580 (w), 1500 (w), 1184 (s), 1124 (w), 960 (m), 925 (w).

Further elution of the column with chloroform yielded a crystalline product which on recrystallization from light petrol, separated as needles (0·03 g) of *Elaeagnus Alkaloid E*2, m.p. 124–126·5°. Infra red spectrum: ν_{max} cm^{-1}; 3590 (m), 3450 (m), 1675 (s), 1580 (s), 1500 (w), 1190 (s), 1130 (w), 1123 (w), 878 (w).

Eustigma oblongifolia

Dried leaves (12 kg) were extracted with ethanol at room temperature. The extract was examined as stated by Hui *et al.*[7] The viscous yellow residue B (6 g) was dissolved in chloroform–benzene (1:4) and the solution applied to a column of alumina (100 g). Elution with chloroform–benzene (1:1) gave a solid which on crystallization from petroleum–acetone mixture gave crystals of *Eustigma Alkaloid O*1 (1·1 g), m.p. 169°, (Found: C, 53·5; H, 6·1; N, 6·5%; M, 242. Calc. for $C_{10}H_{13}O_5N$: C, 52·9; H, 5·8; N, 6·2%; M, 227).

*Eustigma Alkaloid O*1 (150 mg) was dissolved in 2 N HCl. After evaporation at room temperature, long colourless needles separated. These were collected, washed with 2 N HCl, then dried in the desiccator over KOH. The *hydrochloride* (90 mg) had m.p. 200–204° (Found: C, 42·9; H, 5·9; N, 5·9; Cl, 13·9. Calc. for $C_{10}H_{14}O_5NCl$. H_2O: C, 42·6; H, 5·7; N, 5·0; Cl, 12·6%).

Chromatography of, and attempts to crystallize, residues (A) and (C)[7] so far have failed to yield pure bases.

Gnetum indicum

Dried chopped leaves (425 g) were extracted first with benzene, then acetone, and finally ethanol. The benzene and acetone extracts yielded waxes and carotenoids.

The alcohol extract yielded a blackish solid on evaporation. This was extracted with

[7] W. H. HUI, S. N. LOO and H. R. ARTHUR, *J. Chem. Soc.* **9**, 2285 (1965).

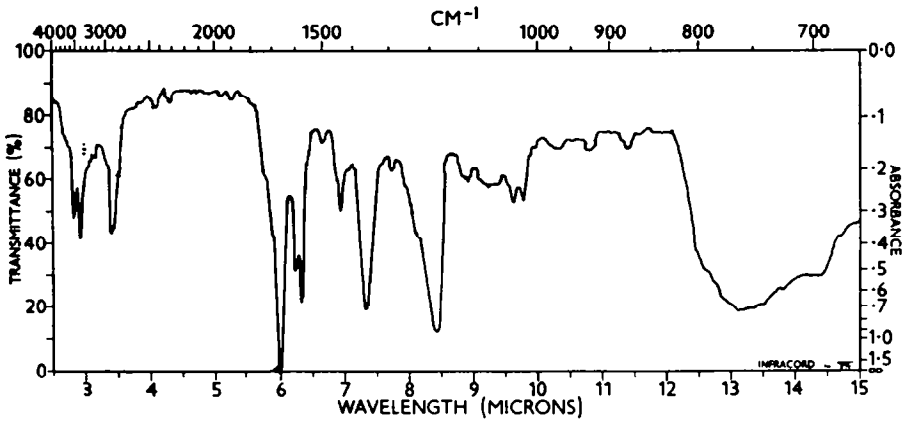

FIG. 2. ELAEAGNUS ALKALOID E2

Elution with chloroform–benzene (1:9) gave a solid which on recrystallization from ethanol yielded needles of γ-sitosterol (0·5 g) m.p. 136–138·5° identical in i.r. spectrum with an authentic sample.

Elution with methanol–chloroform (1:20) yielded a solid which on recrystallization from ethanol gave crystals (0·05 g) m.p. 73–76° which was shown by i.r. spectra to contain a carbonyl group.

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