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Studies on Orchidaceae Alkaloids

XIII.* A New Alkaloid, Laburnine Acetate, from *Vanda cristata* Lindl.

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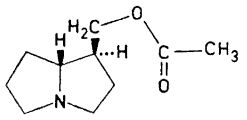
Laburnine acetate has been isolated from *Vanda cristata* Lindl. The acetates of the pyrrolizidine carbinoles constitute stable derivatives of these sensitive compounds and can be gas chromatographed without decomposition.

In the study of *Orchidaceae* alkaloids the subtribe Sarcantheae within the tribe Monopodiales contains many alkaloid rich species. The alkaloids hitherto found in *Phalaenopsis spp.* are esters of pyrrolizidine *exo* carbinols. A simple ester laburnine acetate (I) has now been isolated from *Vanda cristata*,



I

the first *Vanda sp.* investigated. So far, only one alkaloid has been detected in this species. The alkaloid was identified by comparison with synthetic laburnine acetate. Laburnine was obtained by lithium aluminium hydride cleavage of malaxin [2] and was then acetylated with ketene. For comparison the corresponding *endo* carbinol was prepared by reduction of chysin [3] and acetylated. The amino esters are considerably more stable than the free alcohols on gas chromatography. The mass spectra of all esters of pyrrolizidine 1-carbinols have the base peak *m/e* 124, which can serve as a sensitive method of identification.

* For paper XII in this series, see Ref. 1.

EXPERIMENTAL

Mass spectra were measured on an LKB 9000 spectrometer, and with a double focussing Atlas SM 1 mass spectrograph. IR spectra were recorded on a Perkin Elmer 257 instrument, and the NMR spectra on a Varian A60-A spectrometer. Elemental analyses were carried out at the laboratories of Dr. A. Bernhardt, Germany.

Isolation of the alkaloid. Fresh plants of *Vanda cristata* Lindl.* (7.5 kg) were extracted with methanol (30 l). The extract was concentrated to 1.5 l, acidified with hydrochloric acid and washed with chloroform (5 × 250 ml). The aqueous solution was made alkaline (pH 9) with sodium hydroxide and extracted with chloroform (3 × 500 ml). This chloroform solution was extracted with 2 % hydrochloric acid (2 × 500 ml), and the aqueous solution, after being made alkaline (pH 9) was again extracted with chloroform (3 × 200 ml). The chloroform solution was dried (Na_2SO_4) and filtered through a column of neutral alumina (20 × 3 cm) using chloroform as eluent. Evaporation of the eluate gave 1.5 g (0.02 %) of crude alkaloid.

The alkaloid (I) was further purified by preparative GLC: Column 20 % SE-52 on chromosorb AW DMCS, 60/80 mesh; 4 mm × 2 m; gas flow rate 35 ml/min, retention time 15 min at 168°, and was collected as a colourless viscous oil; $[\alpha]_D^{24}+13°$ (*c* 1.3, ethanol). (Found: M^+ 183.1264. Calc. for $C_{10}H_{17}NO_2$: 183.1259. $^{12}C=12.00000$). IR spectrum: ν_{CHCl_3} 1738 cm^{-1}. NMR spectrum ($CDCl_3$): τ 5.90 (d, 2H, $J=6$ cps), τ 6.6—7.7 (m, 5H) τ 7.97 (s, 3H), τ 7.8—8.7 (m, 7H); pertinent MS peaks *m/e* (rel. intensity): 183 (27), 124 (100), 83 (54), 55 (22).

Picrate of I, fine needles from ethanol, m.p. 138°. (Found: C 46.8; H 5.02; N 13.5; O 35.1. Calc. for $C_{16}H_{20}N_4O_9$: C 46.6; H 4.90; N 13.6; O 34.9).

Methiodide of I, small prisms from acetone, m.p. 104—106°, indistinguishable from the methiodide of II (m.p., IR).

Laburnine acetate (II). Malaxin [2] (243 mg) in tetrahydrofuran was reduced with lithium aluminium hydride and the excess reagent was destroyed by the addition of an equivalent amount of water. To the filtered tetrahydrofuran solution ketene was added to the point of saturation. During the addition the solution turned dark red. After evaporation of the solvent the residue was dissolved in chloroform and extracted with 1 M HCl. The aqueous solution was made alkaline and extracted with chloroform. After drying (Na_2SO_4) and evaporation of the solvent, II was obtained in an almost quantitative yield as a yellowish oil which was further purified by preparative GLC, the retention time being identical to that of I. II was indistinguishable from I by IR, NMR, MS and optical rotation.

Picrate of II, fine needles from ethanol; m.p. 138°. (Found: C 46.9; H 4.80; N 13.5; O 34.9. Calc.for $C_{16}H_{20}N_4O_9$: C 46.6; H 4.90; N 13.6; O 34.9).

Methiodide of II, small prisms from acetone, m.p. 104—106°. (Found: C 40.4; H 6.28; N 4.31; O 9.92; I 39.1. Calc. for $C_{11}H_{20}INO_2$: C 40.6; H 6.20; N 4.31; O 9.84; I 39.0).

Lindelofidine acetate (III). Chysin [3] (200 mg) was reduced with lithium aluminium hydride in ether, followed by reaction with ketene in the same way as for the preparation of II, giving an almost quantitative yield of III as a yellow oil. III was further purified by preparative GLC using the same conditions as for I and II, retention time 18 min; $[\alpha]_D^{24}$ +69° (*c* 0.6, chloroform); IR spectrum: ν_{CHCl_3} 1738 cm^{-1}; NMR spectrum ($CDCl_3$): τ 5.88 (d, 2H, $J=8$ cps), τ 6.48 (m, 1H), τ 6.8—7.9 (m, 4H), τ 7.97 (s, 3H), τ 7.9—8.9 (m, 6H); pertinent MS, peaks *m/e* (rel. intensity): 183 (28), 124 (100), 83 (59), 55 (24).

Picrate of III, needles from ethanol, m.p. 107—109°. (Found: C 46.6; H 4.76; N 13.5; O 35.2. Calc. for $C_{16}H_{20}N_4O_9$: C 46.6; H 4.90; N 13.6; O 34.9).

Methiodide of III, small prisms from acetone, m.p. 108—110°. (Found: C 40.4; H 6.32; N 4.19; O 9.86; I 39.1. Calc. for $C_{11}H_{20}INO_2$: C 40.6; H 6.20; N 4.31; O 9.84; I 39.0).

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