

101(23), 103(5), 117(5), 129(1), 145(3), 159(60), 161(5) and 219(3).

III,  $[\alpha]_{578}^{24} - 11.5^\circ$  (*c* 2.2, water). NMR of acetate: 5.13 (t, 1H) proton at C-1, 5.55–5.98 (m, 8H) protons at C-2, C-3, C-4, C-5 and C-6, 6.53 (s, 3H) and 6.55 (s, 3H) two OCH<sub>3</sub>, 7.81 (s, 9.11) OOCCH<sub>3</sub>. MS of acetate: 43(100), 69(7), 71(5), 87(4), 101(6), 117(55), 129(1), 143(5), 161(1), 203(8) and 263(1).

*Acid hydrolysis of I, II and III.* The mixed acetal (approximately 0.2 M) in 0.125 M sulphuric acid (2 ml) was transferred to a jacketed polarimeter tube (10 cm), maintained at the required temperature, and the optical rotation was determined at intervals. The observed changes in rotation were approximately: I,  $-0.105^\circ \rightarrow 0^\circ$ . II,  $+0.155^\circ \rightarrow 0.075^\circ$ . III,  $-0.315^\circ \rightarrow 0.040^\circ$ . Duplicate experiments gave results in good agreement with those given in Table 1.

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## Studies on Orchidaceae Alkaloids

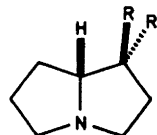
### XXXVI.\* Alkaloids from Some *Vanda* and *Vandopsis* Species

SVANTE BRANDÄNGE and INGRID GRANELLI

*Department of Organic Chemistry, University of Stockholm, Sandåsgatan 2, S-113 27 Stockholm, Sweden*

Esters of 1-hydroxymethylpyrrolizidine have previously been isolated from orchid extracts. Laburnine acetate (I) has been isolated from *Vanda cristata* Lindl.<sup>1</sup> and more complex esters from *Phalaenopsis*<sup>2</sup> and *Liparidinæ*<sup>3-6</sup> species. We now report similar studies on some other *Vanda* and closely related *Vandopsis* species.

From *Vandopsis lissochiloides* Pfitz. the alcohols laburnine (III) and lindelofidine (IV) were isolated, together with the corresponding acetates I and II,<sup>1</sup> in the *exo/endo* ratios 1/3. From *Vandopsis gigantea* Pfitz. the same alcohols and acetates were isolated in the *exo/endo* ratios 10/1. Laburnine acetate (I) has been isolated



I: R = CH<sub>2</sub>OAc, R' = H

II: R = H, R' = CH<sub>2</sub>OAc

III: R = CH<sub>2</sub>OH, R' = H

IV: R = H, R' = CH<sub>2</sub>OH

from *Vanda hindsii* Lindl., and I and III from *Vanda helvola* Bl. An extract of *Vanda luzonica* Loher contained either I or its enantiomer (GLC-MS). A small amount of hygrine was detected (GLC-MS) in an extract of *Vandopsis parishii* Schltr.

In some of the above investigations a modified reineckate procedure was used to purify and quantify small amounts of

\* For number XXXV in this series, see Ref. 6.

alkaloids. In order to regenerate an alkaloid (alk) from the reineckate precipitate,  $\text{alkH}^+ \text{Cr}(\text{NH}_3)_2(\text{SCN})_4^-$ , the latter has hitherto been treated successively with silver sulphate, hydrogen sulphide and barium hydroxide.<sup>7</sup> Instead, the reineckate has here been converted to the hydrochloride by passing a solution of it, in acetone-methanol, through an ion exchange column in chloride form. This procedure has also been used in isolations of some hydrophilic alkaloids.<sup>4-6</sup>

*Experimental.* Preparative GLC was carried out on a 20% SE-52 on Chromosorb AW DMCS column (0.8 × 290 cm, 60–80 mesh) in an Aerograph A-90-P chromatograph, and analytical GLC on a 20% SE-52 on Chromosorb AW DMCS column (0.2 × 180 cm, 80–100 mesh) using a Perkin-Elmer 900 instrument. On the latter column the retention times (155°, 35 ml/min) for compounds I–IV were 7.4, 8.4, 4.8, and 5.2 min, respectively. Optical rotations were measured on a Perkin-Elmer 141 polarimeter.

*General procedure for separation and identification of the pyrrolizidine alkaloids I–IV.* The plant extract (methanol) was concentrated, dilute hydrochloric acid was added, and the resulting solution was washed with carbon tetrachloride. The aqueous layer was made alkaline (pH 9) and the acetates I and II were extracted with carbon tetrachloride. The last traces of I and II and some III and IV were then extracted with chloroform. A final extraction with chloroform-ethanol (3:2) yielded the alcohols III and IV. The acetates were separated by repeated preparative GLC at 155°. The *exo*-acetate from *Vandopsis gigantea* showed  $[\alpha]_{\text{D}}^{24} + 12^\circ$  (c 5.1, ethanol) lit.<sup>1</sup> value for I:  $+13^\circ$ , and the *endo*-acetate  $[\alpha]_{\text{D}}^{24} + 66^\circ$  (c 0.82, ethanol), value<sup>8</sup> for II:  $+65^\circ$ . Owing to the poor recovery of the alcohols on preparative GLC these were either acetylated with ketene followed by preparative GLC, or precipitated as reineckates (see below). Acetylation of the amino alcohols from *Vandopsis gigantea* gave acetates showing  $[\alpha]_{\text{D}}^{24} + 15^\circ$  (c 3.3, ethanol) and  $[\alpha]_{\text{D}}^{24} + 64^\circ$  (c 1.26, ethanol). An increased *exo/endo* ratio and a decreased yield of acetates were obtained if prolonged reaction times were used in the reactions with ketene.

*Reineckate precipitation procedure.* Commercial ammonium reineckate was recrystallised from water, and a freshly prepared, concentrated and filtered solution in water was

added dropwise with shaking to a slightly acidic aqueous solution of the alkaloids in a weighed test tube. When the precipitation was complete (red mother liquor) the mixture was centrifuged and the mother liquor removed with a pipette, water was then added, the suspension shaken, and the new mother liquor removed. This washing procedure was repeated a few times and the precipitate was then dried in vacuum and weighed. The reineckate was dissolved in acetone and an equal amount of methanol added, and the reineckate anion was then replaced by chloride ion by passage through a column of Dowex 1-X4 ( $\text{Cl}^-$ ) with methanol (if necessary mixed with acetone) as solvent. The solvent was evaporated and the residue dissolved in ethanol. One drop of sodium hydroxide solution was then added and the solution filtered. After this treatment the reineckate (103 mg) of the alcohol from *Vanda helvola* gave an alcohol showing  $[\alpha]_{\text{D}}^{23} + 15^\circ$  (c 3.2, ethanol), lit.<sup>9</sup> value for III  $+15.45^\circ$ . The reineckate (41.4 mg) of the acetate from the same species gave an acetate (I) with  $[\alpha]_{\text{D}}^{22} + 18^\circ$  (c 1.3, ethanol).

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