# Studies on Orchidaceae Alkaloids

## XVII.* Alkaloids from *Vandopsis longicaulis* Schltr.

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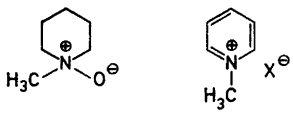
*N*-Methylpiperidine *N*-oxide (I), as the hydrobromide, and *N*-methylpyridinium ion (II), as the iodide, have been isolated from *Vandopsis longicaulis* Schltr.



I II

The alkaloids were separated by chromatography on alumina with chloroform and methanol as eluents. The structures I and II were assigned to the alkaloids on the basis of elemental analyses, IR, and NMR spectra, and were confirmed by comparison with synthetic samples. The total alkaloid content was 0.2 %, based on the weight of the fresh plants, and the ratio between I and II was 2:3, as revealed by the NMR spectrum of the natural mixture. To our knowledge, I or II have not previously been isolated from plant material, but II has been found in some lower animals.[2-8]

*Experimental.* Evaporations were done under reduced pressure. Melting points are uncorrected. The NMR spectra were measured on a Varian A-60 A spectrometer and the IR spectra on a Perkin Elmer 221 instrument. The elemental analyses were carried out at the laboratories of Dr. A. Bernhardt, West Germany.

*Isolation and separation of the alkaloids.* The fresh plant material ** (17 kg) was minced twice in methanol (25 l). After filtration, the plant extract was concentrated to 0.7 l, acidified and washed with chloroform (3×700 ml+4×300 ml). The aqueous solution was then made weakly alkaline and extracted with chloroform. The chloroform layer did not show positive Dragendorff reaction. After neutralization (pH 6.5), the aqueous layer was filtered and concentrated to 150 ml. A 9 ml aliquot was passed through a column of Dowex 1-X4 (3×30 cm, $Cl^{\ominus}$) using water as eluent. The concentrated eluate was dissolved in ethanol and filtered through a column of neutral alumina (3×20 cm) using 99 % ethanol as eluent. The Dragendorff-positive fraction of the eluate was concentrated and chromatographed on neutral alumina (3×17 cm). Chloroform (3.5 l) eluted a compound (III) which, after recrystallization from methylene chloride-carbon tetrachloride melted at 131–134°. (Found: Cl 13.0. Calc. for $(C_6H_{13}NO)_2 \cdot HCl$: Cl 13.3). Subsequent elution with methanol afforded II (X=Cl).

*Characterization of the alkaloids.* To a methanolic solution of III a stoichiometric amount of 40 % hydrobromic acid was added and the solution filtered through an ion exchange column (Dowex 1-X4, $Br^{\ominus}$). The water was evaporated and the residue crystallized from acetone, giving the *hydrobromide* as needles, m.p. 175–190° (decomp.) (Found: C 36.7; H 7.54; Br 40.4; N 7.21; O 8.28. Calc. for $C_6H_{14}BrNO$: C 36.7; H 7.20; Br 40.8; N 7.14; O 8.16). IR: $\sigma_{max}$ (KBr) 2750 (s, broad), 1519 (m), 962 (m), 937 (m), 921 $cm^{-1}$ (m). This product was indistinguishable from synthetic *N*-methylpiperidine *N*-oxide hydrobromide (IR, m.p.).

The corresponding *hydrochloride*, m.p. 180–200° (decomp.), $pk_a$ 5.26, was produced by exchange on a Dowex 1-X4 ($Cl^{\ominus}$) column. The salt was recrystallized from chloroform. After drying under vacuum at 40° the product analysed as $(C_6H_{13}NO)_2 \cdot HCl$ (Found: C 53.9; H 10.1; Cl 13.2; N 10.7. Calc. for $C_{12}H_{27}ClN_2O_2$: C 54.0; H 10.2; Cl 13.3; N 10.5).

The chromatographic fraction containing II as the chloride was filtered through an ion exchange column (Dowex 1-X4, $I^{\ominus}$). The solvent (methanol) was evaporated and the residue crystallized from methylene chloride-acetonitrile, yielding II as the iodide, m.p. 114–116°. II was indistinguishable from a synthetic sample of *pyridine methiodide* (IR, NMR, m.p.).

*N-Methylpiperidine N-oxide hydrobromide.* Hydrogen peroxide (14 g, 30 %, 0.12 mole) was added under stirring to ice-cooled *N*-methylpiperidine (5 g, 0.05 mole) over a period of 30 min. The stirring was continued for 12 h and the excess peroxide destroyed with manganese dioxide. After filtration, hydrobromic acid (8.5 g, 48 %) was added and the solution concentrated to form a crystalline

* For number XVI in this series, see Ref. 1.

** Collected near Wau, Territory of New Guinea.

residue. The *hydrobromide* was recrystallized from acetone, m.p. 175–190° (decomp.). (Found: Br 40.4; N 7.22. Calc. for $C_6H_{14}BrNO$: Br 40.8; N 7.14).

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# Studies on Orchidaceae Alkaloids

## XVIII.* Isolation of Phalaenopsin La from *Kingiella taenialis* (Lindl.) Rolfe

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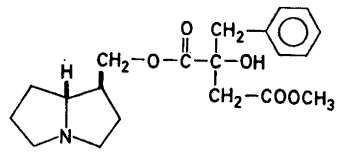
Phalaenopsin La, previously found in *Phalaenopsis mannii* Rchb.f.[2] has been isolated from *Kingiella taenialis* (Lindl.) Rolfe, a species closely related to those of the genus *Phalaenopsis*. The yield of alkaloid from the plant is 0.1 % based on the fresh weight. By using chloroform stabilized with 1 % ethanol in extractions and in chromatography on alumina, 60 % of the total alkaloid fraction is obtained



as the ethyl ester (MS, NMR). In order to establish whether the ethyl ester is a naturally occurring alkaloid or is a product of transesterification, the plant was extracted with water at pH 3. The aqueous solution was made slightly alkaline and extracted with ethanol-free chloroform. The alkaloid was dissolved in dilute hydrochloric acid, the solution filtered and made alkaline, and the base again extracted with chloroform. The base so obtained is a colourless oil which, according to its mass spectrum, consists of the pure methyl ester. It was not possible to obtain the base or the hydrochloride in crystalline form. However, the use of ethanol as solvent in the crystallization of a hydrochloride produced from the chromatographically purified alkaloid, results in a product, m.p. 155–7°, which to 75 % extent consists of the ethyl ester hydrochloride (NMR). An NMR investigation of the hydrochloride of phalaenopsin La, m.p. 131–133°, isolated from *Phalaenopsis mannii* [2] showed the presence of 40 % of ethyl ester. The easy transesterification of this alkaloid consequently demands great care in its isolation.

Methanolysis of the alkaloid from *Kingiella taenialis* produced (−)-dimethyl 2-benzylmalate $[\alpha]_D^{24}$ −8.5° (*c* 9.0, ethanol) and laburnine (*cf.* Ref. 2). The latter was transformed into its acetate, which was indistinguishable from an authentic sample of laburnine acetate [3] (retention time on GLC, SE-52, optical rotation and m.p. of the picrate).

This work has been supported by the *Swedish Natural Science Research Council.* The mass spectra were kindly measured by Dr. R. Ryhage.

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