Using electron diffraction, Allpress [6] has found that in $Nb_{53}O_{132}$, ordered regions, built up of sheets of $Nb_{25}O_{62}$ alternating with sheets of H-Nb_2O_5, are interrupted by disordered regions. The disorder in the Weissenberg photographs might be due to this lack of order in the crystal structure. Because of this disorder, space groups could not be predicted from the reciprocal lattices. Allpress [6] found $Nb_{53}O_{132}$ to be C-centered, and the same symmetry is assumed to be valid even for $Nb_{47}O_{116}$, $Nb_{59}O_{147}F$, and $Nb_{65}O_{161}F$.

The general formula $Nb_{3n+1}(O,F)_{8n-2}$ could be expressed as $Nb_{3n+2}(O,F)_{8n-4}$, with doubled n values for each member. This formula also includes the intergrowth phases, the members of this series hitherto characterised being: $Nb_{11}O_{27}$ ($Nb_{44}O_{108}$, $n=14$), $Nb_{47}O_{116}$ ($n=15$), $Nb_{25}O_{62}$ ($Nb_{50}O_{124}$, $n=16$), $Nb_{53}O_{132}$ ($n=17$), H-Nb_2O_5 ($Nb_{56}O_{140}$, $n=18$), $Nb_{59}O_{147}F$ ($n=19$), $Nb_{31}O_{77}F$ ($Nb_{62}O_{154}F_2$, $n=20$), $Nb_{65}O_{161}F_3$ ($n=21$) and $Nb_{17}O_{42}F$ ($Nb_{68}O_{168}F_4$, $n=22$).

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Studies on Orchidaceae Alkaloids

XXIV.* A Pyrrolizidine Alkaloid from *Phalaenopsis cornu-cervi* Rchb. f.

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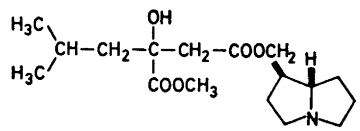
A new alkaloid, cornucervine ($C_{17}H_{29}NO_5$, I) has been isolated from *Phalaenopsis cornu-cervi* Rchb. f. Acid methanolysis of I gave an amino alcohol identified as trachelanthamidine, (−)-*exo*-1-hydroxymethylpyrrolizidine ($C_8H_{15}NO$), and an optically active compound ($C_{10}H_{18}O_5$) indistinguishable (GLC, MS, NMR) from a synthetic sample of racemic dimethyl 2-isobutylmalate.

The latter compound was synthesised by condensation of methyl isobutyl ketone with diethyl carbonate to ethyl 5-methyl-3-oxo-hexanoate, and thereafter preparation of the cyanohydrine followed by acid methanolysis.

The intense peak M − 59 (59 = $COOCH_3$) and the absence of a peak M − 73 [2] (73 = CH_2COOCH_3) in the mass spectrum of I demonstrates the nature of the methyl ester grouping in cornucervine, which accordingly has structure I. The absolute configuration of the isobutylmalate residue has not yet been determined.



I

Experimental. IR, MS, and NMR spectrometry and preparative gas chromatography were performed as previously described.[2] Optical rotations were measured on a Perkin-Elmer 141 polarimeter, and analytical GLC was carried out on a 3 % SE-52 on Chromosorb AW DMCS column (0.2 × 180 cm) using a Perkin-Elmer 900 chromatograph. The high resolution mass spectra were measured on an Atlas SM 1 instrument.

* For No. XXIII in this series, see Ref. 1.

Isolation and characterisation of the alkaloid. The plant material (1.9 kg, obtained from the Bangkrabue Nursery, Bangkok) was minced in methanol (6 l). After filtration and concentration, dilute hydrochloric acid was added and the resulting solution washed with carbon tetrachloride. The aqueous layer was made alkaline and extracted with carbon tetrachloride. The alkaloid was then extracted from the carbon tetrachloride layer with 0.5 % hydrochloric acid, the acid aqueous solution being treated with active carbon (Darco G-60), filtered, made alkaline (pH 9-10) and extracted with carbon tetrachloride. After drying (Na_2SO_4) and evaporation of the solvent, chromatographically pure (GLC, TLC) cornucervine (2.4 g) was obtained as an oil, $[\alpha]_D^{22}$ −4.3° (*c* 1.6, ethanol). MS *m/e* (rel. intensity): M^+ = 327(12), 313(9), 270(11), 268(30), 183(13), 135(40), 124(100), 83(49). (Found: 327.2038 and 268.1904. Calc. for $C_{17}H_{29}NO_5$ and $C_{15}H_{26}NO_3$ (M−$COOCH_3$): 327.2046 and 268.1918, respectively. ^{12}C = 12.00000.) IR: σ_{max} ($CHCl_3$) 3515, 1741 cm^{-1}. NMR ($CDCl_3$): τ 4.81 (s, 1H), τ 5.90 (d, 2H, *J* = 6 Hz), τ 6.29 (s, 3H), τ 6.3−8.9 (m, 17 H), τ 9.09 (t, 6H).

The acid methanolysis of I and the isolation of the products were carried out as previously described,[2] except that the acid was neutralised with barium carbonate, and the amino alcohol was extracted with chloroform-ethanol (3:2). *The neutral methanolysis product* showed $[\alpha]_{578}^{24}$ −0.64°, $[\alpha]_{436}^{24}$ +0.16°, $[\alpha]_{365}^{24}$ +3.9° (*c* 1.9, ethanol). MS: M^+ = 218 lacking, 159(100), 127(12), 101(9), 85(49), 57(23). NMR ($CDCl_3$): τ 6.31 (s, 3H), τ 6.43 (s, 3H), τ 6.63 (s, 1H), τ 7.29 and τ 7.50 (AB spectrum, 2H, *J* = 16 Hz), τ 8.0−9.0 (*m*, 3H), τ 9.16 (t, 6H). (Found: C 55.3; H 8.07; O 36.8. Calc. for $C_{10}H_{18}O_5$: C 55.0; H 8.31; O 36.7.) The *amino alcohol* was reacted in acetone solution with ketene, and the resulting acetate purified by preparative GLC.[3] $[\alpha]_D^{22}$ −14° (*c* 1.2, ethanol). Its retention time and MS were indistinguishable from those of (+)-*exo*-1-hydroxymethylpyrrolizidine (laburnine) acetate,[3] $[\alpha]_D^{24}$ +13°.

Ethyl 5-methyl-3-oxo-hexanoate (II) was prepared from methyl isobutyl ketone (0.6 mol), diethyl carbonate (1.2 mol) and sodium hydride (1.2 mol) in ether by a method analogous to that used for ethyl 3-oxo-6-octenoate.[4] Distillation at 99−101°/14 mm gave II in 85 % yield. (Found: C 62.5; H 9.48; O 28.0. Calc. for $C_9H_{16}O_3$: C 62.8; H 9.37; O 27.9.) IR: σ_{max} 1749, 1721 cm^{-1}. An alternative synthesis[5] of II, using one mole equivalent of sodium ethoxide in ethanol as base, gave a less pure product in a lower yield.

The cyanohydrine of II (III) was synthesised from II, sodium cyanide, and sodium pyrosulphite, according to the general procedure of Green and Hickinbottom.[6] The cyanohydrine was extracted from the reaction mixture with four portions of chloroform. After drying (Na_2SO_4) and concentration, distillation at 108−109°/4 mm in the presence of a small amount of 85 % orthophosphoric acid[7] gave a 33 % yield of III. NMR ($CDCl_3$): τ 5.11 (s, 1H), τ 5.71 (q, 2H), τ 7.17 and τ 7.28 (AB spectrum, 2H, *J* = 17 Hz). τ 7.6−8.2 (m, 1H), τ 8.30 (d, 2H, *J* = 6 Hz), τ 8.68 (t, 3H), τ 8.94 (d, 6H, *J* = 6 Hz).

Methanolysis of III. In a slightly modified procedure of Colonge *et al.*,[7] a cooled (dry ice-acetone) mixture of III (5.0 g, 0.025 mol) and methanol (2.7 g, 0.084 mol) was saturated with dry hydrogen chloride (3.5 h), kept at ice-bath temperature (2.5 h) and then worked up as previously described.[7] The resulting product was then further transesterified by treatment (reflux 6 days) with methanol (50 ml) and concentrated sulphuric acid (2 ml). Part of the methanol was evaporated and the residue partitioned between water and chloroform. Distillation at 131−132°/15 mm gave dimethyl 2-isobutylmalate (3.0 g, 56 %). (Found: C 55.0; H 8.54; O 36.4. Calc. for $C_{10}H_{18}O_5$: C 55.0; H 8.31; O 36.7.)

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