which was recrystallized from ethanol (300 mg, 88 %). This compound melted at 147–148°C and on further heating new crystals were formed which melted at 184–186°C, $[\alpha]_{578}^{23}$ +69° (*c* 1.7, chloroform). (Found: C 45.66; H 3.40; N 10.39. Calc. for $C_{21}H_{18}O_{14}N_4$: C 45.83; H 3.30; N 10.18.)

Another part of the syrup (4 mg) was hydrolysed with 0.25 M aqueous sulphuric acid (2 ml) at 100° for 1 h, neutralized and converted into the alditol acetate. This alditol acetate had the same retention time as an authentic sample of paratitol acetate on both the OV 225 and OS 138 columns. The MS was indistinguishable from that given by the authentic sample.

A sample of II (10 mg) was acetylated with acetic anhydride/pyridine. The diacetate was isolated in the usual manner as a chromatographically pure syrup. The MS of this compound had peaks, *inter alia*, at *m/e* (peak intensities relative to the base peak in brackets): 43(100), 44(4), 45(5), 71(12), 74(18), 83(8), 84(9), 100(25), 103(7), 113(5), 116(11), 143(1.5), 155(1.1), 186(1.1) and 215(3.3). The NMR spectrum (100 MHz) (first order analysis) gave the following results: τ 5.15, 1 proton, octet, H-2, $J_{1,2}$ 3.5 Hz, $J_{2,3e}$ 5 Hz, $J_{2,3a}$ 12 Hz; τ 5.25, 1 proton, doublet, H-1, $J_{1,2}$ 3.5 Hz; τ 5.43, 1 proton, octet, H-4, $J_{4,5}$ 10 Hz, $J_{4,3e}$ 5 Hz, $J_{4,3a}$ 11 Hz; τ 6.23, 1 proton, octet, H-5, $J_{4,5}$ 10 Hz, $J_{5,6}$ 6 Hz; τ 6.58, 3 protons, singlet, OCH_3; τ 7.78, 1 proton, sextet, H-3e, $J_{3e,3a}$ 11 Hz, $J_{3e,2}$ 5 Hz, $J_{3e,4}$ 5 Hz; τ 7.93, 3 protons, singlet, *O*-acetyl; τ 7.96, 3 protons, singlet, *O*-acetyl; τ 8.10, 1 proton, sextet, H-3a, $J_{3a,3e}$ 11 Hz, $J_{3a,2}$ 12 Hz, $J_{3a,4}$ 11 Hz; τ 8.84, 3 protons, doublet, C–CH_3, $J_{5,6}$ 6 Hz. The above analysis was made on the basis of decoupling experiments and by using $Eu(fod)_3$ as shift reagent to separate overlapping protons.

In another preparation of II the reduction was performed with LAD. The MS of the acetylated, deuterium labelled II had peaks at, *inter alia*, *m/e* (peak intensities relative to the base peaks in brackets): 43(100), 44(12), 45(8), 73(13), 75(22), 85(6), 86(5), 101(3), 102(24), 104(8), 117(11), 145(9), 157(0.9), 188(0.8), 217(2.3).

The NMR spectrum (100 MHz) was similar to that obtained for the non-deuterated diacetate with the following exceptions: The 1 proton sextet at τ 7.78 (H-3e) appeared as a triplet ($J_{3e,2}$ 5 Hz, $J_{3e,4}$ 5 Hz); the 1 proton sextet at τ 8.10 had disappeared; the 3 proton doublet at τ 8.84 was changed into a 2 proton doublet; further, the multiplets of H-2, H-4 and H-5 were altered.

When the reduction mixture was processed without neutralization, the combined yield of dideoxyglycosides was increased to 50 %. GLC–MS of the acetylated reaction product and of the derived alditol acetates established a ratio between II and a methyl 4,6-dideoxyhexoside of 3:2, reprectively.

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Studies on Orchidaceae Alkaloids

XXXVII.* Dendrowardine, a Quaternary Alkaloid from *Dendrobium wardianum* Wr.

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The occurrence in various *Dendrobium*, species of fourteen alkaloids of the

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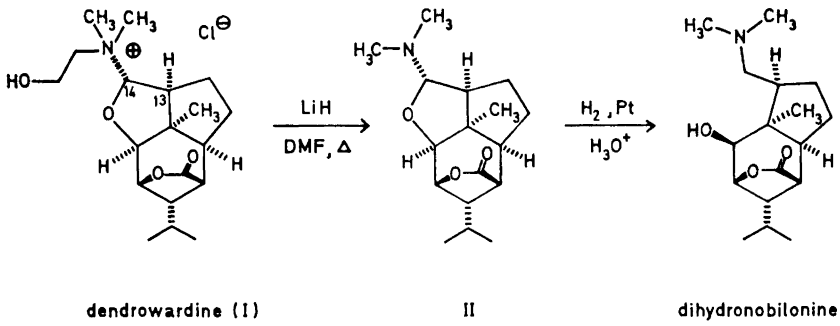

Fig. 1. Transformation of dendrowardine (I) to dihydronobilonine.

dendrobine type has previously been reported.[2,3] In this communication we report the isolation and structure determination of a quaternary alkaloid, dendrowardine (I), from *Dendrobium wardianum* Wr.

Dendrowardine was isolated as the chloride, which has the molecular formula $C_{25}H_{32}ClNO_4$. Pyrolysis of its hydroxide produced *N*,*N*-dimethylethanolamine, a small amount of a base (II), and a product of molecular weight 248 which was not further investigated. When dendrowardine was treated with lithium hydride in *N*,*N*-dimethylformamide at 100°, compound II was formed in excellent yield. Hydrogenolysis of II in aqueous hydrochloric acid over Adams catalyst gave a product indistinguishable (TLC, GLC and MS) from dihydronobilonine.[2] From the similarity between the CD curve of dendrowardine, showing a positive maximum at 228 nm, and that of dendrobine [4] it is obvious that the alkaloids have the same absolute configuration.[2] From the evidence presented above, the structure and absolute configuration of dendrowardine should be either I, or its C-14 epimer.

Information concerning the configuration at C-14 was gained from the NMR spectrum of dendrowardine. The signal from H-14 is a doublet with a coupling constant of 4.5 Hz, which is consistent with a dihedral angle between H-14 and H-13 of either 50° or 120°. The rigid structure of the dendrowardine ring system should give a dihedral angle of about 120° between H-14 and H-13 in the *exo* epimer and an angle close to 0° in the *endo* epimer. Thus, based on the Karplus equation, dendrowardine should be the *exo* epimer and possess the relative and absolute configuration depicted in Fig. 1.

Experimental. All melting points are corrected. Mass spectra were measured on an LKB 9000 spectrometer (ionization energy 70 eV), and the optical rotations on a Perkin-Elmer 141 polarimeter. The IR spectra were recorded on a Perkin-Elmer 257 instrument, the NMR spectra on a Varian A-60A spectrometer, and the CD spectra on a Cary 60 spectropolarimeter.

Isolation of dendrowardine (I). Fresh plants of *Dendrobium wardianum* Wr. (10.7 kg) were extracted with methanol (36 l). The extract was concentrated to 2 l, washed with carbon tetrachloride (5 × 0.3 l), and extracted with chloroform-ethanol (3 : 2, v/v, 11 × 0.3 l). The combined chloroform-ethanol extracts were concentrated to 100 ml, water (200 ml) was added and the solution was filtered through a column of Dowex 1-X4 (Cl^-, 2.5 × 30 cm) irrigated with water. The eluate was evaporated to dryness, and the residue was chromatographed on neutral alumina (5 × 30 cm, activity II–III) using ethanol as eluent. The first fraction contained I and the second choline together with a small amount of I.

The first fraction was evaporated to dryness. To the residue, dissolved in water (10 ml), a saturated solution of ammonium reineckate was added until no more precipitate was formed. The alkaloid reineckate was washed with ice-water (2 × 5 ml), dissolved in acetone-water (1 : 1, 3 ml) and filtered through a column of Dowex 1-X4 (Cl^-, 2 × 20 cm) irrigated with acetone-water (1 : 1). The eluate was evaporated to dryness and the residue filtered through neutral alumina (1 × 10 cm) using ethanol as eluent. The filtrate was evaporated to dryness giving crude I (0.65 g) as a glass. Crystallization from acetone gave I, m.p. 168–172° (dec.), $[\alpha]_D^{25}$ −28° (*c* 1.1, methanol), circular dichroism: $[\theta]_{228}$ +5060°.

(Found: C 60.2; H 8.69; Cl 9.87; N 3.77; O 17.6. Calc. for $C_{19}H_{32}ClNO_4$: C 61.0; H 8.63; Cl 9.48; N 3.75; O 17.1.) IR spectrum: σ_{max} (KBr) 3190 (s), 1772 (s) cm^{-1}. NMR spectrum (DMSO-d_6) τ: 4.13 (t, 1 H, $J=5.0$ Hz, exchangeable in D_2O), 4.97 (d, 1 H, $J=4.5$ Hz), 5.21 (q, 1 H, $J_1=5.0$ Hz, $J_2=3.0$ Hz), 5.68 (d, 1 H, $J=3.0$ Hz), 5.90–6.30 (m, 2 H), 6.40–7.20 (m, 3 H), 6.86 (s, 6 H), 7.60–8.45 (m, 8 H), 8.54 (s, 3 H), 9.06 (d, 6 H, $J=6.0$ Hz).

Degradation of I with lithium hydride. A mixture of I (1.5 mg) and lithium hydride (5 mg) in *N,N*-dimethylformamide (0.5 ml) was heated at 100° for 18 h, and then cooled and acidified with aqueous hydrochloric acid. The solution was washed with ether (2 × 1 ml), neutralized with sodium hydrogen carbonate and extracted with ether (2 × 1 ml). The ether solution was dried and evaporated to dryness leaving II (1.0 mg). IR spectrum: σ_{max} ($CHCl_3$) 1778 (s) cm^{-1}. Pertinent mass spectral peaks *m/e* (rel. intensity): M^+ 293 (13), 292 (9), 249 (6), 220 (6), 177 (5), 175 (4), 138 (100), 124 (9), 111 (9), 93 (11), 91 (9), 74 (24).

Hydrogenation of II. A solution of II (1.8 mg) in aqueous hydrochloric acid (2 ml, 1 %) was hydrogenated over Adams catalyst (9 mg) at room temperature and atmospheric pressure. After 20 h the catalyst was filtered off and the solution made alkaline with sodium hydrogen carbonate and extracted with ether (3 × 1 ml). The ether solution was dried and evaporated to dryness leaving a quantitative yield of dihydronobilonine, indistinguishable (TLC, GLC, MS) from an authentic sample.

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On the Polarity of the Dinitrogen Ligand in a Dinitrogen Complex of Iron

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In a previous study,[1] infrared absorption intensities of the N–N stretching vibration in some dinitrogen complexes of rhenium and iridium were reported. It was found that the intensity of the N–N stretching vibration (A_{NN}) increases with decreasing frequency (ν_{NN}) (*cf.* Fig. 2 in Ref. 1). It was concluded that the lower the ν_{NN} and the higher the A_{NN}, the greater was the disturbance of the dinitrogen ligand. Furthermore, from ESCA measurements [2] on the above mentioned dinitrogen complexes, the charge distribution on the dinitrogen ligand was determined. The presence of two peaks in the N1*s* electron spectra shows that the dinitrogen ligand has an appreciable polarity. It has been found that both the nitrogen atoms in the complexes carry a negative charge. A connection between the magnitude of the shift in N1*s* binding energy and the N–N stretching frequency has been found, *viz.* the lower the ν_{NN}, the larger the chemical shift in binding energy. Thus, when the disturbance of the dinitrogen ligand is large, *i.e.* low ν_{NN}, the more pronounced is the charge separation on the nitrogen atoms.

In order to further substantiate these observations, both infrared intensity and ESCA measurements have been performed on a dinitrogen complex of iron, *viz.* $FeH_2N_2(PPh_3)_3$. In view of the occurrence of iron in the nitrogen-fixing enzyme [3] in biological systems, such an investigation could be of added interest. $FeH_2N_2(PPh_3)_3$ was first prepared by Sacco and Aresta [4] and later by Borod'ko *et al.*[5] The complex investigated in this work has been prepared according to the procedure given by Borod'ko *et al.*[5] The purity of the compound was checked by elemental analysis and by its IR spectrum. (Found: C 74.0; H 5.69; N 3.16. Calc. C 74.3; H 5.43; N 3.21.) The IR spectrum shows a strong band at 2075 cm^{-1} (N–N stretching vibration) and a weak broad band at 1895 cm^{-1} (Fe–H stretching