Quinoline Alkaloids. Part 27.[1] Synthesis of the *Ptelea* Alkaloids Pteleflorine, Neohydroxylunine, *O*-Methylhydroxyluninium salt and Hydroxylunine

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Methods for the racemic syntheses of the *Ptelea* alkaloids, pteleflorine **12**, neohydroxylunine **14**, *O*-methylhydroxyluninium salt **15**, hydroxylunine **16** and related compounds, are described. A more convenient method for the preparation of 1,3-benzodioxol-4-amine **3** is also reported.

The dimethyldihydropyranoquinolines, pteleflorine **13** and neohydroxylunine **14**, and the isopropyldihydrofuroquinolines, *O*-methylhydroxyluninium salt **15** and hydroxylunine **16**, have been isolated on numerous occasions[2–5] from the rutaceous species *Ptelea trifoliata*. All of these alkaloids have structures characterised by the occurrence of a 1,3-dioxolo(7,8-methylenedioxy) group in their homocyclic rings. Detailed studies on the biosynthesis and synthesis of these alkaloids have not yet been reported. In our laboratory, a study of the biosynthesis of pteleflorine **12** in *P. trifoliata* was planned. An authentic sample of the alkaloid was needed to help to characterise and act as 'cold carrier' in the isolation of the alkaloid from crude extracts resulting from the feeding experiments. We now report the methods adopted and successfully employed for the synthesis of **12** and the related alkaloids **13–16**.

Previous synthetic[6,7] and biosynthetic[8] studies have demonstrated that both dihydropyranoquinolines and isopropyldihydrofuroquinolines can be obtained by the oxidative cyclisation of 4-methoxy-3-(3-methylbut-2-enyl)quinolin-2-one skeletons. The methoxyquinolinone **10**, which could be involved in the biosynthesis of **12** and **14–16**, was earlier isolated[9] from *P. trifoliata*. We recognised that this methoxyquinolinone may also be a suitable starting point in our syntheses. Our synthetic routes, hence biomimetic in design, to **12–16** are outlined in Schemes 1 and 2. In summary, they involve synthesis and peracid cyclisation of **10** to afford pteleflorine **12** and the corresponding isomeric furanoquinoline **13**. Appropriate rearrangements of **12** and **13** would then give neohydroxylunine **14**, *O*-methylhydroxyluninium salt **15** and hydroxylunine **16**.

Discussion

6-Methoxy-7-(3-methylbut-2-enyl)-1,3-dioxolo[4,5-h]-*quinoline-8-one* **10**.—The synthesis of **10** involved diazomethane methylation of the hydroxyquinolinone **7** which can be prepared[10] by condensation of 1,3-benzodioxol-4-amine **3** and the diethyl malonate ester **6** (Scheme 1). The amine **3** is not available commercially but it has been previously obtained[11,12] by the Hofmann degradation of the amide **2**. Our attempts to prepare **3** by such traditional methods were unsatisfactory as low yields were realised. An alternative method for this synthesis was thus desired. After checking the literature, it was observed[13,14] that primary aromatic amines may be synthesised by the hydrolysis of carbamate esters that are obtained, in a modified Curtius rearrangement,[15–18] by reaction of the corresponding aromatic carboxylic acids with the phosphorus reagent diphenylphosphoryl azide (DPPA).

When 1,3-benzodioxole-4-carboxylic acid **1** was treated with DPPA using a typically reported procedure,[18] in refluxing t-butyl alcohol, a colourless solid soon separated from the reaction mixture. When isolated by filtration, this solid was identified as the urea derivative **5**. Its ^{1}H NMR spectrum showed it contained two 1,3-benzodioxole moieties (4 H singlet at δ 6.04) plus resonances for six aromatic protons; two of which were shifted downfield to δ 7.58 and were thus being deshielded by a neighbouring carbonyl function. IR absorptions at 3 280 and 1 645 cm^{-1} denoted the presence of an amide NH and urea carbonyls, respectively. After removal of the solid, work-up of the remaining filtrate and chromatography resulted in isolation of the expected ester product **4** in 23% yield. The ^{1}H NMR spectrum of this derivative was characterised by the occurrence of a 9 H singlet at δ 1.55 which was confirmative of a t-butyl group. An IR absorption observed at 1710 cm^{-1} was in agreement with that reported[18] for the carbonyls in esters of this type. When the reaction was repeated employing 1,4-dioxane as solvent the yield of urea by-product **5** was reduced (26%) and the ester **4** was obtained as principal product (58%). This suggests the use of a solvent with a higher boiling point helped to reduce the stability of the isocyanate intermediate, which is also involved in this modified rearrangement, and promotes its conversion into the ester product **4**.

The urea **5** was resistant to hydrolysis by acids or bases. In contrast, treatment of **4** at room temperature with 5M HCl gave the desired amine **3** in good yield (82%) sufficiently pure for subsequent use. This method proved to be much more convenient than the traditional Hofmann degradation for a large-scale synthesis of **3**. It should be equally adoptable for the preparation of most primary amines and in particular those which form relatively stable isocyanate intermediates in reactions of this type.

Reaction of **3** and **6**, as previously reported,[10] afforded the hydroxyquinolinone **7**.

In a study on the stereospecific synthesis of the alkaloid orixine, Grundon and co-workers[10] showed that prolonged methylation (48 h) of the hydroxyquinolinone **7**, with ethereal diazomethane, yielded a mixture of the dimethyl ethers **8** and **9**. When we treated **7** with a 4 molar excess of diazomethane, after 6 h a mixture of three products was obtained which was separated by chromatography. Two of the products again proved to be the dimethyl ethers **8** and **9**. The third product was identified to be the monomethyl compound **10** that we desired. Its ^{1}H NMR spectrum distinguished it from the dimethyl ethers; in particular only one 3 H singlet for an ether methoxy occurred at δ 3.90 whilst in **8** a 6 H singlet at δ 3.85 is attributed to overlapping

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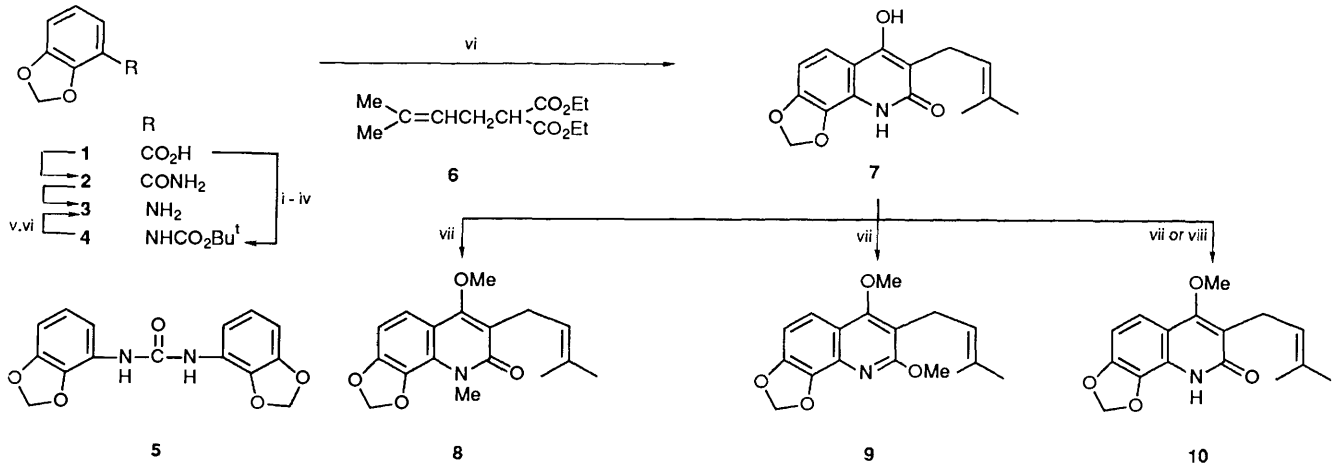
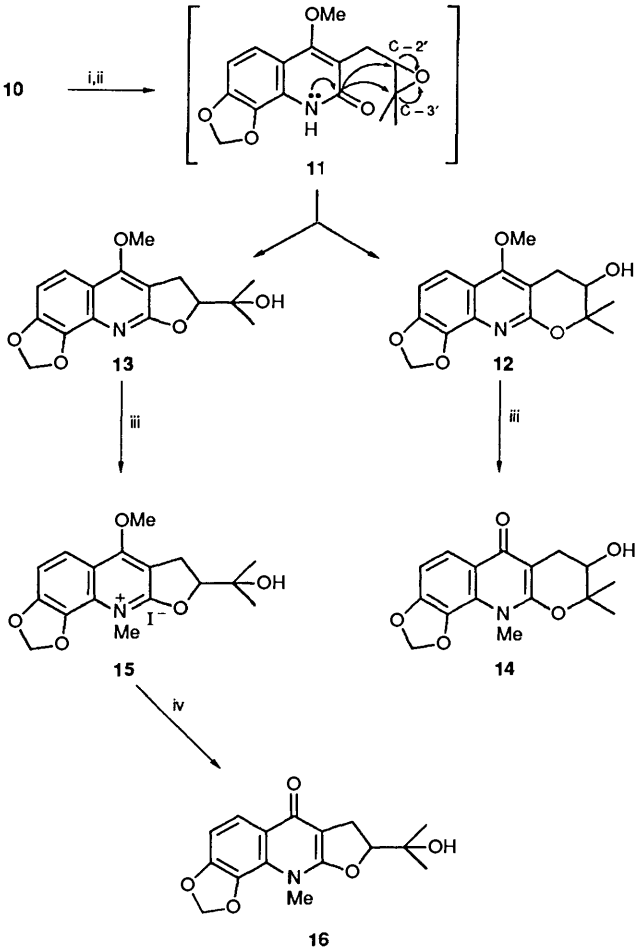


Scheme 1 *Reagents and conditions:* i, DPPA; ii, Et_3N; iii, Bu^tOH; iv, reflux in 1,4-dioxane; v, 5M HCl; vi, stir in EtOH, room temp. 48 h; vi, reflux in Ph_2O; vii, 4 mol equiv. CH_2N_2, 6 h; viii, 10 mol equiv. CH_2N_2, 1 min

OMe and NMe groups. The IR spectrum of **10** also exhibited a carbonyl absorption at 1645 cm^{-1} which confirmed its quinolinone structure. The ethers **8** and **10** have both been previously isolated from *P. trifoliata*;[7,19] the former compound is now commonly known as pteleprenine. This is the first reported synthesis of the monomethyl ether **10**.

Previous synthetic studies[6,7] have also shown that brief treatment (1 min) of hydroxyquinolinones, of the type **7**, with an excess of diazomethane (10 mol dm^{-3}) results in selective methylation of the phenolic hydroxy group to furnish the corresponding monomethoxyquinolinones. When **7** was treated in an analogous fashion **10** was obtained as sole product.



Scheme 2 *Reagents and conditions:* i, *m*-$ClC_6H_4CO_3H$; ii, stir in dry $CHCl_3$, room temp. 40 h; iii, reflux in MeI, 15 h; iv, heat in pyridine, 85–90 °C, 3 h

Syntheses of Pteleflorine **12**, *Neohydroxylunine* **14**, *O-Methylhydroxyluninium Salt* **15** *and Hydroxylunine* **16**.—Peracid oxidative cyclisation of the methoxyquinolinone **10** in ethanol-free chloroform with *m*-chloroperbenzoic acid gave pteleflorine **12** and an isomeric furanoalcohol **13** (Scheme 2). Reactions of this type are thought[20] to proceed *via* an intermediate epoxide of the type **11**, which then spontaneously undergoes an intramolecular cyclisation, with its quinolinone oxygen, at the adjacent (C-3′) tertiary carbocation centre (electronically favoured 6-*endo* process) or at the secondary C(2′) carbocation centre (stereochemically favoured 5-*exo* process) to give a binary isomeric mixture of pyrano and furano isomers. A similar process also probably accounts for the results which we observed in which **12** and **13** were obtained in yields of 20 and 38%, respectively. This is the first reported synthesis of these two compounds. The NMR spectra of these isomers were readily distinguishable. In the spectrum of the pyranoquinoline **12**, the CMe_2 group appeared as a 6 H singlet at δ 1.44 whilst the analogous CMe_2OH in **13** occurs as two distinct 3 H singlets at δ 1.40 and 1.28. The chemical shifts of the methine protons in the furano and pyrano rings also differed, occurring at δ 3.74 in **12** and δ 4.61 in **13**. Pteleflorine **12** has been isolated[2] from the flowers of *P. trifoliata* but the furanoalcohol **13** has not yet been obtained from a rutaceous source.

Reaction of pyranoquinolines with methyl iodide gave the corresponding *N*-methylquinolones.[6] When **12** was similarly heated at reflux in methyl iodide, neohydroxylunine **14** was obtained in quantitative yield. The occurrence of a low-field aromatic proton at δ 7.90 in the ^1H NMR spectrum of **14**, and an IR absorption apparent at 1635 cm^{-1} was further evidence for a quinolone structure. The precise mechanisms operating in reactions of this type have recently been reinvestigated.[1] An American group[3] earlier isolated this alkaloid from both the quaternary and non-quaternary extracts of *P. trifoliata*. In contrast, methyl iodide treatment of the furanoalcohol **13** gave *O*-methylhydroxyluninium iodide **15**; salts of this type have also been found[3] in *P. trifoliata*. The Grundon group[6] obtained similar methiodide salts and observed they could be readily transformed to *N*-methylfuroquinolones when they are heated above their melting points. In our studies however, an attempted thermal degradation of the iodide salt **15** (m.p. 161 °C) was unsuccessful. Substantial charring of the material occurred and only trace amounts of the expected product

hydroxylunine **16** could be isolated. Several authors have also reported[3,21,22] that quinolinium salts can also undergo this rearrangement if they are heated in the presence of pyridine. Treatment of **15** in pyridine at 80 °C gave hydroxylunine **16** in more satisfactory yield (78%). This alkaloid was isolated in independent studies from both *P. trifoliata*[4,5] and the rutaceous species *Lunasia amara*.[23]

All of the natural products synthesised in this study displayed physical and spectral properties comparable to those reported for the isolated alkaloids.

Experimental

General Directions.—M.p.s were recorded on a Kofler hot-stage apparatus and are uncorrected. IR spectra were recorded (KBr discs) on a Perkin-Elmer 457 spectrophotometer. ^{1}H NMR spectra were obtained from a Perkin-Elmer R32 (90 MHz). Unless otherwise indicated, deuteriochloroform was employed as solvent; chemical shifts are assigned on the δ scale with tetramethylsilane as internal standard and all *J* values are in Hz. High resolution mass spectra were obtained from an AEI MS9 instrument fitted with an Elliot 905 computer system. Elemental analyses were carried out by the Butterworth Microanalytical Consultancy Ltd, Middlesex, UK.

Preparative TLC (PLC) was performed with plates (200 × 200 mm) that were prepared 'in house' from Merck Kieselgel $HF_{254+366}$ (Type 60). Column chromatography was carried out on silica gel, 50–100 mesh.

All commercial solvents and reagents were purified, when necessary, by standard laboratory procedures.[24] Ether refers to diethyl ether and light petroleum to the boiling fraction 40–60 °C. Diazomethane was generated by the alkaline decomposition of *N*-methyl-*N*-nitrosotoluene-*p*-sulphonamide (Diazald ®).

1,3-*Benzodioxole*-4-*carboxylic Acid* **1**.—This acid was prepared using the earlier reported methods of Perkin *et al.*[25]

t-Butyl-1,3-*Benzodioxol*-4-*ylcarbamate* **4**.—The acid **1** (15 g, 0.09 mmol) was heated under reflux in a mixture of 1,4-dioxane (250 ml) and t-butyl alcohol (75 ml). Diphenylphosphoryl azide (DPPA) (26 g, 0.09 mol) and triethylamine (9.75 g, 0.095 mol) were added in one batch to the mixture and reflux continued for a further 8 h. The dioxane solvent was removed under reduced pressure and the residue taken up in chloroform (250 ml). An insoluble white solid was isolated by filtration and identified as N,N′-*di*-(1,3-*benzodioxol*-4-*yl*)*urea* **5** (3.5 g, 26%), m.p. 260–264 °C (with sublimation) (Found M^+, 300.0753. $C_{15}H_{12}N_2O_5$ requires M, 300.0746); ν_{max}/cm^{-1} 3280 (NH) and 1645 (C=O); δ_H[$(CD_3)_2SO$] 6.04 (4 H, s, 2 × OCH_2O), 6.56–6.87 (4 H, m, 4 × ArH) and 7.58 (2 H, br d, 2 × ArH); *m/z* (EI) 300 (M^+, 52%), 163 (42) and 137 (100).

The remaining organic filtrate was washed successively with portions of 5% aqueous citric acid (3 × 70 ml), water, saturated aqueous sodium hydrogen carbonate and finally with saturated brine. The organic layer was dried ($MgSO_4$), column-type silica gel (15 g) was added and the solvent was carefully evaporated. The resulting powder was placed in a Soxhlet thimble and exhaustively extracted with a refluxing ether–light petroleum (30:70 v/v) solvent mixture (500 ml). Evaporation of the solvents gave the ester **4** as a colourless solid (12.5 g, 58%), m.p. 92–93 °C; ν_{max}/cm^{-1} 3350 (N–H) and 1710 (C=O); δ_H 1.55 (9 H, s, Bu^t), 5.92 (2 H, s, OCH_2O) and 6.45–6.87 (3 H, m, ArH): *m/z* (EI) 237 (M^+, 34%), 181 (48) and 137 (77) (Found: C, 60.8; H, 6.3; N, 5.9. $C_{12}H_{15}NO_4$ requires C, 60.7; H, 6.3; N, 5.9%).

1,3-*Benzodioxol*-4-*amine* **3**.—The ester **4** (12.4 g, 0.005 mol) was dissolved in ethanol (250 ml) and treated with a solution of 5M hydrochloric acid (200 ml). The mixture was stirred at room temperature for 48 h. After evaporation of the ethanol solvent, the remaining aqueous layer was washed with ether (3 × 50 ml). The acid layer was then cooled in an ice-bath and solid potassium hydroxide was carefully added until a pH of 7 was realised. Undissolved inorganic salts were filtered off and the filtrate was thoroughly extracted with ether (6 × 50 ml). The combined ether layers were briefly washed with water (3 × 30 ml), dried ($MgSO_4$) and evaporated to yield the amine **3** as an almost colourless viscous oil (5.85 g, 84%). It displayed spectral properties identical to those reported[10] and was sufficiently pure for further use.

6-*Hydroxy*-7-(3-*methylbut*-2-*enyl*)-1,3-*dioxolo*[4,5-h]-*quinolin*-8-*one* **7**.—Reaction of 1,3-benzodioxol-4-amine **3** (5.5 g, 0.04 mol) and the malonate ester **6** (11.5 g, 0.05 mol) by the reported procedure of Grundon *et al.*[10] gave **7** as a cream-coloured solid (3.5 g, 30%), m.p. 195–198 °C (from aqueous ethanol) (lit.,[10] 196–199 °C).

Diazomethane Methylation of the Hydroxyquinolinone **7**.—(*a*) The quinolinone **7** (1.4 g, 0.004 mol) dissolved in methanol (50 ml) was treated with a 4 molar excess of ethereal diazomethane and stirred at room temperature for 6 h. Excess of reagent was then destroyed by the addition of glacial acetic acid. Evaporation of the solvents gave a gum which was dissolved in chloroform (100 ml) and the solution washed with 2M sodium hydroxide (4 × 40 ml) and then with water (3 × 30 ml), dried ($MgSO_4$) and evaporated under reduced pressure to give a thick viscous gum which was subjected to column chromatography on silica gel. Elution with ether–light petroleum (5:95 v/v) yielded a colourless oil which was shown by NMR spectroscopy to be the known[10] dimethyl ether 6,8-dimethoxy-7-(3-methylbut-2-enyl)-1,3-dioxolo[4,5-*h*]quinoline **9** (230 mg, 15%). Further elution with ether–light petroleum (35:65 v/v) gave 6-methoxy-9-methyl-7-(3-methylbut-2-enyl)-1,3-dioxolo[4,5-*h*]quinolin-8(9*H*)-one **8** (now commonly known as pteleprenine) as a colourless solid (570 mg, 37%), m.p. 72–74 °C (from ether–light petroleum ether) (lit.,[10] 73–75 °C); ν_{max}/cm^{-1} 1640 (C=O); δ_H 1.71, 1.80 [each 3 H, s, $C(Me_2)$], 3.33 (2 H, d, CH_2CH), 3.85 (6 H, s, OMe, NMe), 5.23 (1 H, br t, CH_2CH), 6.01 (2 H, s, OCH_2O), 6.79 (1 H, d, *J* 9, ArH) and 7.35 (1 H, d, *J* 9, ArH). Finally, elution with light petroleum ether (30:70 v/v) afford the desired 6-*methoxy*-7-(3-*methylbut*-2-*enyl*)-1,3-*dioxolo*[4,5-h]*quinolin*-8-*one* **10** as colourless plates (220 mg, 14%), m.p. 159–162 °C (from ether–light petroleum) (lit.,[7] 159–161 °C) (Found: M^+, 287.1162. $C_{16}H_{17}NO_4$ requires M, 287.1157); ν_{max}/cm^{-1} 3410 (NH) and 1640 (CO); δ_H 1.70, 1.81 [each 3 H, s, $=C(Me_2)$], 3.55 (2 H, d, CH_2CH), 3.90 (3 H, s, OMe), 5.27 (1 H, br t, CH_2CH), 6.09 (2 H, s, OCH_2O), 6.78 (1 H, d, *J* 10, ArH) and 7.28 (1 H, d, *J* 10, ArH); *m/z* (EI) 287 (M^+, 98%), 272 (100), 244 (75) and 218 (39).

(*b*) Treatment of **7** (1.2 g) in AnalaR methanol with a 10 molar excess of ethereal diazomethane for 1 min and work-up as described in (*a*) yielded the monomethyl ether **10** as the sole product (450 mg, 36%). Acidification of the alkaline extracts gave unchanged quinolinone **7** (400 mg, 33%).

Peracid Treatment of the Methoxyquinolinone **10**.—The monomethoxyquinolinone **10** (160 mg, 0.55 mol) in dry chloroform (20 ml) was treated with *m*-chloroperbenzoic acid (160 mg, 0.92 mmol; 80% active oxygen content) and stirred at room temperature, in the absence of light, for 40 h. The mixture was then first washed with 2M aqueous sodium hydrogen carbonate (3 × 30 ml), and thoroughly extracted with 4M hydrochloric acid (4 × 30 ml). The combined acid layers were neutralised by the careful addition of solid sodium carbonate and extracted with ether (3 × 30 ml). When dried (Na_2SO_4),

evaporation of the ethereal extracts gave an oily residue. PLC on silica gel and successive elutions (× 3) with ethyl acetate–chloroform (5:95 v/v) and then (× 3) ethyl acetate–chloroform (10:90 v/v), yielded two components: pteleflorine **12** as an oil (35 mg, 20%), R_F 0.65 which was crystallised as colourless plates, m.p. 88–91 °C (from benzene–hexane) (lit.,[2] 93–96 °C) (Found: M, 303.1106. $C_{16}H_{17}NO_3$ requires M, 303.1107); ν_{max}/cm^{-1} 3450 (OH); δ_H 1.44 (6 H, s, CMe_2), 3.02 (2 H, dd, *J* 16 and 5, CH_2CHOH), 3.74 (1 H, br t, CH_2CHOH), 3.8 (3 H, s, OMe), 6.1 (2 H, s, OCH_2O), 6.95 (1 H, d, *J* 10, ArH) and 7.38 (1 H, d, *J* 10, ArH); *m/z* (EI) 303 (M^+, 89%) and 232 (45); and the furanoalcohol 7,8-*dihydro*-8-(2-*hydroxypropan*-2-*yl*)-6-*methoxy*-1,3-*dioxolo*[4,5-h]*furo*[2,3-b]*quinoline* **13** as a colourless solid (65 mg, 38%), R_F 0.5, m.p. 163–166 °C (from ether–diisopropyl ether) (Found: M^+, 303.1104. $C_{16}H_{17}NO_5$ requires M, 303.1104); ν_{max}/cm^{-1} 3400 (OH); δ_H 1.28, 1.40 (each 3 H, s, CMe_2OH), 3.56 (2 H, q, *J* 14 and 8, CH_2CHCMe_2OH), 4.18 (3 H, s, OMe), 4.61 (1 H, dd, *J* 16, CH_2CHCMe_2OH), 6.11 (2 H, s, OCH_2O), 6.91 (1 H, d, *J* 10, ArH) and 7.55 (1 H, d, *J* 10, ArH); *m/z* (EI) 303 (M^+, 100%) and 244 (79).

Methyl Iodide Treatment of Pteleflorine.—The pyranoquinoline **12** (15 mg, 0.05 mmol) and methyl iodide (2 ml) were heated under reflux for 15 h. Evaporation under reduced pressure gave 7,8-*dihydro*-8-*hydroxy*-9,9,11-*trimethyl*-1,3-*dioxolo*[4,5-h]*pyrano*[2,3-b]*quinolin*-6(11H)-*one* (*neohydroxylunine*) **14** (15 mg, 100%) crystallising as fine colourless needles, m.p. 223–225 °C (from hexane–dichloromethane) (lit.,[3] 228–231 °C) (Found: M^+, 303.1143, $C_{16}H_{17}NO_5$ requires M, 303.1107; ν_{max}/cm^{-1} 3360 (OH) and 1635 (C=O); δ_H 1.37, 1.50 (each 3 H, s, CMe_2), 2.57 (2 H, dd, *J* 16 and 5, CH_2CHOH), 3.77 (3 H, s, NMe), 3.70 (1 H, q, CH_2CHOH), 6.00 (2 H, s, OCH_2O), 6.80 (1 H, d, *J* 10, ArH) and 7.90 (1 H, d, *J* 10, ArH); *m/z* (EI) 303 (M^+, 38%), 233 (29), 232 (100) and 231 (18).

Methyl Iodide Treatment of the Furano Alcohol **13**.—In a similar manner to that described for **12**, the furano alcohol **13** (65 mg, 0.21 mmol) was heated at reflux with methyl iodide (5 ml) for 15 h. Evaporation gave O-*methylhydroxyluninium iodide* **15** (94 mg, 98%) which was obtained, after repeated crystallisation, as colourless plates, m.p. 159–161 °C (methanol–ether); ν_{max}/cm^{-1} 3400 (OH); δ_H 1.32, 1.49 (each 3 H, s, CMe_2OH), 4.23 (3 H, s, OMe), 4.45 (3 H, s, NMe), 5.16 (1 H, br t, $CHCMe_2OH$), 6.23 (2 H, s, OCH_2O), 7.20 (1 H, d, *J* 10, ArH) and 7.84 (1 H, d, *J* 10, ArH); *m/z* (EI) 317 (M^+ − HI, 70%), (M^+ − CH_3I, 4), 286 (12) and 258 (100).

7,8-*Dihydro*-8-(2-*hydroxypropan*-2-*yl*)-1,3-*dioxolo*[4,5-h]-*furo*[2,3-b]*quinolin*-6(10H)-*one* (*Hydroxylunine*) **16**.—The iodide salt **15** (35 mg, 0.07 mmol) was heated in pyridine (1 ml) at 85–90 °C (oil bath) for 3.5 h. After evaporation under reduced pressure, the residue was suspended in chloroform (10 ml) and washed with water (3 × 30 ml). The chloroform layer was dried (Na_2SO_4) and evaporated to yield *hydroxylunine* **16** (18 mg, 78%), crystallising as colourless needles, m.p. 222–225 °C (from methanol–ether) (lit.,[5] 224–227 °C) (Found: M^+, 303.1095. $C_{16}H_{17}NO_5$ requires M, 303.1107); ν_{max}/cm^{-1} 3340 (OH) and 1640 (C=O); $\delta_H(CD_3OH)$ 1.24, 1.34 (each 3 H, s, CMe_2OH), 3.12 (2 H, q, *J* 14 and 8, CH_2CHCMe_2OH), 3.92 (3 H, s, NMe), 4.80 (1 H, dd, *J* 17, CH_2CHCMe_2OH), 6.08 (2 H, s, OCH_2O), 6.92 (1 H, d, *J* 10, ArH) and 7.82 (1 H, d, *J* 10, ArH); *m/z* (EI) 303 (M^+, 84%), 288 (27), 270 (74), 245 (58) and 244 (100).

Acknowledgements

The authors are grateful to the Ministry for Science and Research of Nordrhein-Westfalen (Germany) for providing a Heinrich Hertz-Stiftung (fellowship) in support of these studies.

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Paper 0/04091F
Received 7*th September* 1990
Accepted 8*th October* 1990