107.7 (C-5′, *d*), 120.8 (C-6′, *d*), 39.0 (C-α, *t*), 134.2 (C-β, *d*), 117 6 (C-γ, *t*), 101.0 (O_2CH_2, *t*). MS *m/z* (rel. int.): 328 (7), 174 (15), 173 (100), 163 (25), 162 (59), 161 (28), 151 (12), 149 (29), 135 (68), 131 (21), 122 (12), 121 (18), 115 (21), 105 (14), 104 (20), 103 (28). *Dihydro*-**3b**. To **3a** (70 mg) in THF (40 ml), $LiAlH_4$ (15 mg) was added. The mixture was stirred (4 hr, room temp) Excess reagent was destroyed with NH_4Cl. The mixture was extracted with $CHCl_3$ The $CHCl_3$ soln was washed, dried and evapd. The residue (64 mg) was purified by TLC (silica gel, C_6H_6–EtOAc, 4 . 1) to dihydro-**3b** (40 mg). ^1H NMR (60 MHz, $CDCl_3$): δ4 40 (H-2, *d*, $J = 10$ Hz), 2.9–1.9 (H-3, 2H-4, 2H-α, *m*), 6.2–5.3 (H-5, H-6, H-7, H-β, *m*), 7.2–6.7 (3ArH, *m*), 5.97 (O_2CH_2, *s*), 5.37–4 87 (2H-γ, *m*). ^{13}C NMR (20 MHz, $CDCl_3$): δ85 9 (C-2, *d*), 49 7 (C-3, *d*), 9.5 (Me-3, *q*) 49 5 (C-3a, *s*), 28.5 (C-4, *t*), 127 1 (C-5, *d*), 127.3 (C-6, *d*), 72 5 (C-7, *d*), 100.4 (C-7a, *s*), 135.4 (C-1′, *s*), 107.8 (C-2′, *d*), 147.8 (C-3′, *s*), 147 2 (C-4′, *s*), 107.6 (C-5′, *d*), 121.0 (C-6′, *d*), 39 4 (C-α, *t*), 134.5 (C-β, *d*), 117.5 (C-γ, *t*), 101.0 (O_2CH_2, *t*).

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TWO ANTHRAQUINONES FROM *VENTILAGO CALYCULATA*

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Key Word Index—*Ventilago calyculata*; Rhamnaceae; anthraquinones.

Abstract—Two new anthraquinones have been isolated from the root bark of *Ventilago calyculata* and their structures shown to be 2,4,8-trihydroxy-1-methoxy-3-methylanthraquinone and 2,4,8-trihydroxy-1,6-dimethoxy-3-methylanthraquinone.

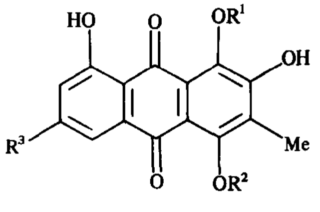
INTRODUCTION

The genus *Ventilago* is a rich source of anthraquinones [1–4]. Further investigation of the root bark of *Ventilago calyculata* afforded two more new anthraquinones, **2** and **4**, in addition to the eleven anthraquinones reported previously [2].

RESULTS AND DISCUSSION

Pigment **2**, $C_{16}H_{12}O_6$, gives a positive reduction test with $Na_2S_2O_4$, indicating its anthraquinone nature, and forms a trimethyl ether. It is soluble in aqueous sodium carbonate suggesting the presence of a β-hydroxyl group, and as there is only one IR carbonyl band, at 1630 cm^{-1}, the remaining two hydroxyl groups are in α-positions, and from the visible spectrum (λ_{max} 443 nm) it must be a 1,5 or 1,8-dihydroxyanthraquinone. The ^1H NMR spectrum confirms the presence of a β-hydroxyl and two *peri*-hydroxyl groups, and shows signals for a methoxyl and a β-methyl group. In addition an ABC pattern for three aromatic protons at δ7.26 (*d*, $J = 8$ Hz), 7.63 (*t*, $J = 8$ Hz) and 7.79 (*d*, $J = 8$ Hz) indicated that one ring carries only a *peri*-substituent. Hydrolysis of the methoxyl group with 80% H_2SO_4 indicates that it is located at a *peri* position, and as the product was 2-hydroxyislandicin **1** the new pigment must be either **2** or **3**. The latter was excluded on the basis of a negative zirconium nitrate test, and the absence of a shift in the visible spectrum on addition of NaOAc–H_3BO_3 (for alizarin the shift is 22 nm) thus demonstrating the absence of a vicinal dihydroxy system. Hence the pigment has structure **2**. The trimethyl ether of **2** was identical with the tetramethyl ether of 2-hydroxyislandicin (**1**).

The second new pigment **4**, $C_{17}H_{14}O_7$, shows all the features of **2** except that the ^1H NMR spectrum reveals the presence of a second methoxyl group and the ABC system is replaced by two *meta* protons. Demethylation of



1 $R^1 = R^2 = R^3 = H$
2 $R^1 = Me, R^2 = R^3 = H$
3 $R^1 = R^3 = H, R^2 = Me$
4 $R^1 = Me, R^2 = H, R^3 = OMe$
5 $R^1 = R^2 = H, R^3 = OMe$

4 with 80% H_2SO_4 afforded calyculatone (**5**), and the trimethyl ether of **4** was found to be identical with calyculatone tetramethyl ether. These reactions show that **4** must be the 1- or 8-monomethyl ether of **5**. A negative zirconium nitrate test and the absence of a bathochromic shift in the visible spectrum in the presence of NaOAc–H_3BO_3 indicate the absence of a vicinal dihydroxy system in the quinone. Hence the new pigment is calyculatone 1-methyl ether (**4**).

EXPERIMENTAL

For the isolation of the pigments, and other details, see ref. [2]. Fractions 57–96 afforded **2** and **4** after repeated CC (C_6H_6) and prep. TLC (C_6H_6).

Compound **2** was obtained as orange–red needles, (C_6H_6–petrol) mp 210° (Found: C, 64.10; H, 4.24. $C_{16}H_{12}O_6$ requires C, 64.00; H, 4.03%); $\lambda_{\max}^{\mathrm{MeOH}}$ nm (log ε): 225 (4.58), 255 (4.39), 280 (4.12), 443 (3.67); $\lambda_{\max}^{\mathrm{MeOH/OH^-}}$ nm: 226, 263, 325, 480; IR $\nu_{\max}^{\mathrm{CHCl_3}}$ cm^{-1}: 1630, 3400; ^{1}H NMR (220 MHz, $CDCl_3$): δ2.27 (3H, *s*, Me), 3.99 (3H, *s*, OMe), 6 95 (1H, *br s*, exchangeable with D_2O, OH-2), 7.26 (1H, *br d*, *J* = 8 Hz, H-7), 7.63 (1H, *br t*, *J* = 8 Hz, H-6), 7.79 (1H, *br d*, *J* = 8 Hz, H-5), 12.90 and 13.99 (each 1H, *s*, exchangeable with D_2O, *peri*-OH); MS (Found: M^+ 300.0634; $C_{16}H_{12}O_6$ requires M, 300.0634) *m/z* (rel. int.): 300 (100), 285 (8), 283 (11), 282 (44), 272 (7), 271 (11), 257 (37), 254 (8), 253 (11), 244 (7), 226 (12). *Methyl ether* (Me_2SO_4–K_2CO_3–Me_2CO) yellow needles (petrol), mp 149–150° (lit [2] 150°). On demethylation (80% H_2SO_4 for 90 min at 100°) **2** afforded 2-hydroxyislandicin (**1**).

Compound **4** was obtained as orange–red micro needles (C_6H_6), mp 253° (Found C, 61.72, H, 4.38 $C_{17}H_{14}O_7$ requires C, 61 82; H, 4.27%); $\lambda_{\max}^{\mathrm{MeOH}}$ nm (log ε): 227(4 56), 270 sh (4.13), 285 (4.38), 422 (4.05), 440 (3.78); $\lambda_{\max}^{\mathrm{MeOH/OH^-}}$ nm: 228, 267, 302, 490; IR $\nu_{\max}^{\mathrm{CHCl_3}}$ cm^{-1}: 1630, 3450; ^{1}H NMR (220 MHz, $CDCl_3$): δ2.28 (3H, *s*, Me), 3.95 (3H, *s*, OMe), 4.00 (3H, *s*, OMe), 6.68 (1H, *d*, *J* = 2 Hz, H-7), 6 97 (1H, *br s*, exchangeable with D_2O, OH-2), 7.36 (1H, *d*, *J* = 2 Hz, H-5), 13.20 and 13.96 (each 1H, *s*, exchangeable with D_2O, *peri*-OH); MS *m/z* (rel. int.). 330 (100), 315 (5), 313 (16), 312 (72), 302 (7), 301 (16), 300 (7), 287 (24), 284 (8), 283 (6), 268 (8), 259 (5), 256 (8). *Methyl ether* (Me_2SO_4–K_2CO_3–Me_2CO) yellow needles (petrol) mp 145–146° (lit. [3] 146°). On partial demethylation (80% H_2SO_4 for 90 min at 100°) **4** afforded calyculatone (**5**).

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