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BENZISOCHROMANQUINONES IN *VENTILAGO* SPECIES

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Key Word Index—*Ventilago calyculata*, *V. maderaspatana*; Rhamnaceae; benzisochromanquinone; ventiloquinone.

Abstract—From the acetone extract of the root bark of *Ventilago maderaspatana* eight new benzisochromanquinones, ventiloquinones A, B, C, D, E, F, G and H, have been isolated. Ventiloquinones I, J and K are three more new benzisochromanquinones isolated from the root bark of *V. calyculata*. The majority are 3,4,5,10-tetrahydro-*cis*-1,3-dimethyl-1H-naphtho[2,3-c]pyran-5,10-quinones related to eleutherin, but F, H, I, J and K are 6,9-quinones related to ventilagone.

INTRODUCTION

In pursuing our interest in the quinone constituents of *Ventilago* species [1–6] we have continued our investigations of *V. maderaspatana* and *V. calyculata*. In addition to the anthraquinones [1–4], naphthoquinones [5] and isofuranonaphthoquinones [6] reported earlier, we have encountered a new group of eight benzisochromanquinones in the acetone extract of the root bark of *V. maderaspatana*, designated ventiloquinones A–H, and from the acetone extract of the root bark of *V. calyculata* three more quinones of the same type, ventiloquinones I–K, were isolated. The structure elucidation of these quinones is the subject of this paper.

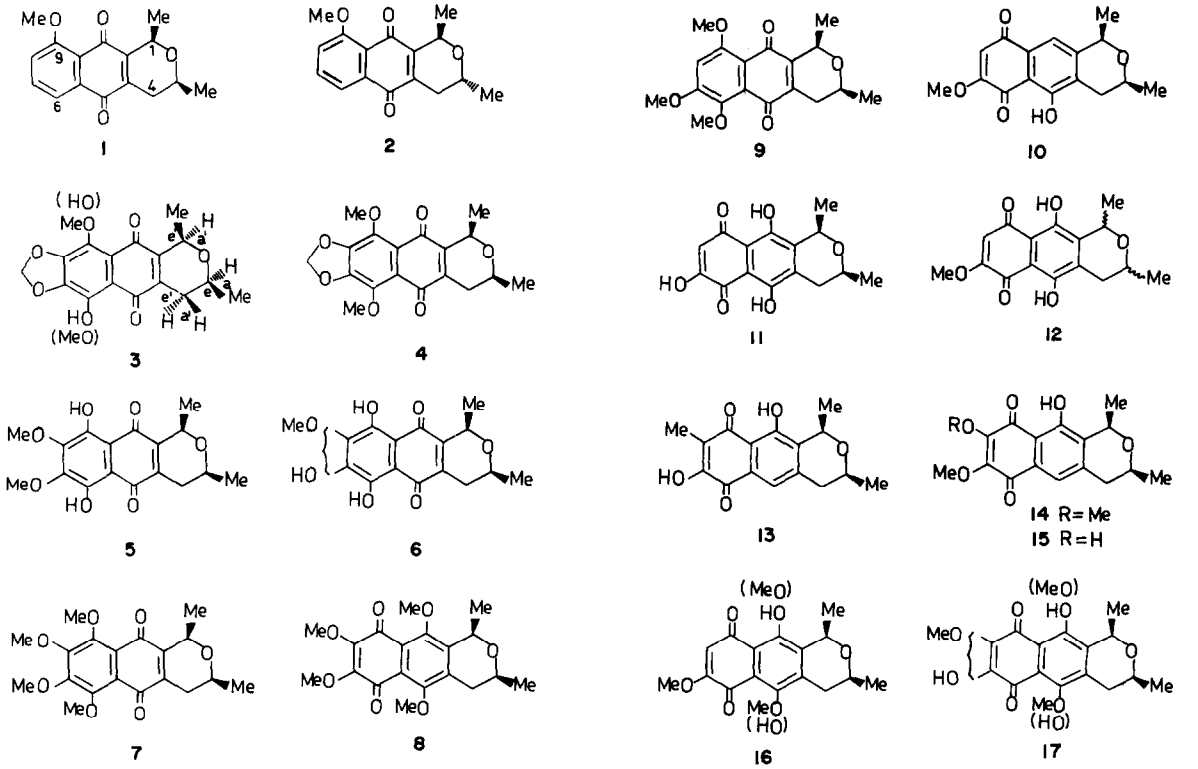
RESULTS AND DISCUSSION

Ventiloquinone-A, $C_{17}H_{16}O_7$, forms a methyl ether and an acetate, and its ^{1}H NMR spectrum includes singlets for methoxyl-, *peri*-hydroxyl and methylenedioxy groups, but benzenoid and quinonoid protons are absent. The demethylated product shows a characteristic naphthazarin VIS absorption [7] and ^{1}H NMR signals for two *peri* hydroxyls; hence the methoxyl group of A is in a *peri* position. In addition to the above signals, the ^{1}H NMR spectrum shows signals for a fused dihydro-1,3-dimethyl[2,3-c]pyran system which was corroborated by spin decoupling studies. Considerable fine structure for two non-equivalent methylene protons and two methine protons was observed due to geminal, vicinal and long-range couplings which can be interpreted as an ABXY pattern [8,9] ($\delta_A = 2.16$, $\delta_B = 2.70$, $\delta_X = 3.55$, $\delta_Y = 4.79$). Comparison of δ and J values for the pyran ring protons with those of eleutherin (**1**) [10] and isoeleutherin (**2**) [10] showed excellent agreement with the former. From the magnitude of the long range ($J_{AY} = 3.5$ Hz, $J_{BY} = 3$ Hz) and vicinal ($J_{AX} = 9$ Hz, $J_{BX} = 3$ Hz) coupling constants [11] it can be inferred that the C-1 and C-3 protons are axial and the signals at δ2.16 and 2.70, with larger and smaller coupling constants, can be attributed to axial and equatorial protons, respectively, at C-4. It follows that ventilone-A has one of the structures **3**.

Ventiloquinone-B is the methyl ether of ventiloquinone-A and has the structure **4**. Both A and B gave the same naphthazarin on demethylation (with HBr), and methylation of ventiloquinone-A afforded B.

Ventiloquinone-D, $C_{17}H_{18}O_7$, is a naphthazarin as indicated by its characteristic UV-VIS absorption and ^{1}H NMR spectrum at low field. The ^{1}H NMR spectrum also shows signals for two symmetrical methoxyl groups and a dihydro-1,3-dimethyl[2,3-c]pyran system. The long range coupling constants are smaller than those observed for ventiloquinones A and B consistent with fusion of the pyran ring to a tautomeric (i.e. partially benzenoid) system. Tautomerism also accounts for the formation of two dimethyl ethers (see below) one of which has J values close to those of A and B thus confirming the *cis* configuration of ventiloquinone-D. Thus D has structure **5**; like other members of this family it has a large positive optical rotation.

Diazomethane methylation [12] of ventiloquinone-C gives ventiloquinone-D. Thus ventiloquinone-C has structure **6**; in fact both isomers are present. TLC examination (multiple development) showed two very closely moving spots with R_f difference less than 0.1 cm and these compounds could not be separated. It is also clear from the observation of *two* pairs of signals (2:1 ratio) in the ^{1}H NMR spectrum for *peri*-hydroxyl protons, indicating the presence of two isomers in the same ratio. Moreover, the methylene proton (H_a-4 and H_e-4) signals appear to be doubled and, on scale expansion, the lower field methyl doublet further split into another doublet. On methylation (Me_2SO_4–K_2CO_3) of the isomeric mixture two trimethyl ethers were obtained, and these were identical with the two dimethyl ethers derived similarly from ventiloquinone-D. One of these, mp 113°, is regarded as **7** since it shows only two methoxyl signals at δ3.88 (6H) and 4.00 (6H), and the pyran ring resonances are very close to those of B. The other isomer, a semi-solid, is **8**; it shows three methoxyl signals at δ3.80 (3H), 3.84 (3H) and 4.05 (6H), and the H-1 and H-4 proton resonances are broadened and shifted downfield relative



to those of **7**. 1,5-Naphthoquinone structures can be excluded as they would be expected to show four methoxyl signals (see also ventiloquinone-K).

Ventiloquinone-E, $C_{18}H_{20}O_6$, forms a leucodiacetate showing characteristic naphthalenic UV absorption. The ^{1}H NMR spectrum of ventiloquinone-E revealed three methoxyl groups and an aromatic proton, and signals for a dihydrodimethylpyran ring very similar to those of previous compounds. The chemical shift of the aromatic proton (δ6.72) clearly indicates that it is located between two oxygen functions on the benzenoid ring [13], and hence the heterocyclic ring is fused to the quinone ring. As complete demethylation (HBr) afforded a naphthopurpurin derivative (UV-VIS, NMR) ventiloquinone-E is regarded as **9**, the β-methoxyl being assigned to C-7 on biogenetic grounds, assuming an acetate–malonate origin, and analogy with F (see below). In agreement the ^{1}H NMR spectrum of E is very similar to that of 6-hydroxy-7-methoxyeleutherin [14] found in *Karwinskia humboldtiana* (Rhamnaceae). As the CD curve of ventiloquinone-E is similar to that of eleutherin the chirality at the asymmetric centres must be 1*R*,3*S* (presumably this is the case for all the ventiloquinones).

Ventiloquinone-F, $C_{16}H_{16}O_5$, is a juglone derivative (UV) and its ^{1}H NMR spectrum shows signals for a methoxyl and a *peri*-hydroxyl group, a 1,3-dimethyl[2,3-c]pyran system, and two 1H singlets at δ5.87 and 7.18. The signal at δ5.87 must be assigned to a quinonoid proton adjacent to the methoxyl group, and that at δ7.18 can be attributed to a *peri*-proton. Thus ventiloquinone-F is a 2- or 3-methoxyjuglone with the pyran system fused to the benzenoid ring, and that is reflected in the smaller $J_{1,4}$ coupling constants (2.2 and 1.7 Hz) which are normally observed in such compounds [15, 16]. As the signals for the H-4 protons are well separated the *peri*-hydroxyl must be at C-5 (see section below on ventiloquinone-H). Ventiloquinone-F therefore has structure **10** or the 8-methoxy isomer. The proton coupled ^{13}C NMR spectrum shows that the chelated quinone carbonyl signal at δ182.60 is a doublet (J = 5.1 Hz) and the other carbonyl signal at δ179.20 is also a doublet (J = 1.8 Hz). Although relatively small these couplings are consistent only with structure **10**; the sample was small and $^2J_{C-H}$ was not resolved.

Ventiloquinone-G, $C_{15}H_{14}O_6$, is a naphthopurpurin (UV-VIS, ^{1}H NMR, soluble aq. $NaHCO_3$) with a fused dihydro-1,3-dimethyl[2,3-c]pyran ring as indicated by its ^{1}H NMR spectrum; the remaining ring proton appears at δ6.34 (6.37 in naphthopurpurin [17]). The splitting pattern for the heterocyclic ring protons is virtually the same as in ventiloquinone-D so that ventiloquinone-G has the tautomeric structure **11**, assigning the β-hydroxyl to C-7 on biogenetic grounds. Attempts to correlate G with E were unsuccessful. The product obtained by vigorous demethylation of E (see above) was different from G and is probably the *trans* epimer (inadequate resolution of its ^{1}H NMR spectrum precluded confirmation in that way). Methylation of G with diazomethane gave a monomethyl ether **12** which was also different from the monomethyl ether derived from E by *peri*-demethylation with BBr_3. The implication is that **12** derived from G is *cis* but the BBr_3 reaction also effected epimerization so forming the *trans* isomer of **12**. The ^{1}H NMR spectrum of the former confirmed its *cis* configuration. In the spectrum of **12** derived from E the resolution was inadequate to obtain long range coupling constants but it could be observed that the splitting pattern for the H-4$_e$ proton was *dd* and not *dt* as found for the epimer. This implies that $J_{1,4}$ is very small, consistent with a *trans* structure for **12** derived from E. Efforts to

epimerize *cis* **12** under various acidic conditions were not fruitful.

Ventiloquinone-H, $C_{17}H_{18}O_6$, is identified as a juglone from its UV-VIS, IR and ^1H NMR spectra. The ^1H NMR spectrum shows signals for a *peri* hydroxyl, a *peri* proton and two methoxyl groups whose chemical shifts (δ4.06 and 4.09) are consistent with their location on the quinone ring [17]. Ventiloquinone-H is thus a 2,3-dimethoxyjuglone and this is in accordance with the monodemethylation which occurs on heating in ethanolic hydrochloric acid for 30 min. Only the methoxyl group at C-3 (naphthoquinone numbering) was hydrolysed [12] and further demethylation did not occur when the reaction was continued for 1 hr more. A dihydro-1,3-dimethyl[2,3-c]pyran system is again present (NMR) in ventiloquinone-H but the splitting pattern for the pyran ring protons differs from the previous compounds, in particular the signals from the two H-4 protons overlap (in $CDCl_3$ solution) at δ2.68. A comparison shows that the pattern is very similar to that of ventilagone (**13**) [18, 19] where the methylene (H-4) protons appear as an irregular multiplet at δ2.68 ($CDCl_3$). However, in C_6D_6 solution the H-4 signals are well separated so that coupling constants could be measured. The $J_{1,4}$ values were close to those of F confirming that in ventiloquinone-H also the 1,3-dimethyl groups are in the *cis*-configuration, with the pyran ring fused to the benzenoid ring. Thus ventiloquinone-H has structure **14**. Overlap of the H-4 signals (in $CDCl_3$) is a feature of these benzisochromanquinones which have no oxygen function at C-5. Evidently a *peri*-substituent enhances the non-equivalence of the methylene protons; a similar *peri* effect has been observed in dihydroisocoumarins [20, 21].

Ventiloquinone-I is the mono-desmethyl ether of ventiloquinone-H. The structures were correlated by methylation of ventiloquinone-I with diazomethane to give H, and further, the mono-demethylated product of ventiloquinone-H (see above) is identical with ventiloquinone-I, which is assigned structure **15**.

Ventiloquinone-J, $C_{17}H_{18}O_6$, contains a *peri*-hydroxyl and two methoxyl groups, and a 1H singlet at δ6.04 must be ascribed to a proton on the quinone ring adjacent to a methoxyl group. Consequently the central ring is benzenoid with the second methoxyl occupying a *peri*-position. The presence of a dihydro-1,3-dimethyl[2,3-c]pyran system fused to the benzene ring was clearly evident from the ^1H NMR spectrum, and the coupling constants and splitting pattern were similar to those of ventiloquinone-F (but less well resolved at 220 MHz). Ventiloquinone-J can thus be assigned the structure **16** assuming that the β-methoxyl is located at C-7 as in F. Unfortunately it was not possible to correlate J with G owing to lack of material but a *peri*-demethylation of J with BCl_3 gave a product identical (TLC, MS, only) with *trans* **12** obtained from E with BBr_3.

Ventiloquinone-K, $C_{17}H_{18}O_7$, is a fully substituted naphthoquinone as indicated by its ^1H NMR spectrum which shows the presence of two methoxyls, one *peri*-hydroxyl, and another hydroxyl which must be placed on the quinone ring as the pigment is soluble in aq. $NaHCO_3$. The chemical shift (δ4.13) of one methoxyl suggests that it is adjacent to the hydroxyl on the quinone ring [17]. The central ring is therefore benzenoid with the other methoxyl group in a *peri*-position. The dihydro-1,3-dimethyl[2,3-c]pyran system is again indicated by its ^1H NMR spectrum, the splitting pattern being similar to those of ventiloquinones F and J, the $J_{1,4}$ values corresponding to the usual 1,3-*cis*-diequatorial geometry with the pyran ring fused to the benzene ring (a *trans* arrangement is excluded because $J_{e'e'}$ would then be < 1 Hz). Thus ventiloquinone-K is one of the structures **17**. The dimethyl ether (Me_2SO_4–K_2CO_3–Me_2CO) of ventiloquinone-K was found to be identical with the tetramethyl ether **8** derived from ventiloquinone-C. Ventiloquinone-K was unaffected by BCl_3 and BBr_3 under conditions where J was *peri*-demethylated. This suggests that in K (**17**) the *peri*-methoxyl occupies the more hindered position at C-10 whereas in J (**16**) the *peri*-methoxyl is at C-5.

EXPERIMENTAL

Silica gel-G and silica gel (100–200 mesh), Acme, India were used for prep. TLC and CC respectively.

Plant material. Voucher specimens, *V. calyculata* No. NUH238 and *V. maderaspatana* No. NUH171 are deposited at Nagarjuna University Herbarium.

Extraction and purification. Air dried, powdered root bark (2.5 kg) of *V. maderaspatana* was extracted with Me_2CO. Part of the dark brown residue (50 g) was subjected to CC on silica gel (300 g). The column was eluted with C_6H_6–petrol (1:1) (fractions 1–90), C_6H_6 (fractions 92–172), C_6H_6–EtOAc (9:1) (fractions 173–212), C_6H_6–EtOAc (4:1) (fractions 213–240). Fractions 91–120 (4 g) were rechromatographed on silica gel (60 g) and eluted with C_6H_6 collecting 75 ml fractions. The earlier fractions did not yield any solid. Fractions 13–26 on prep. TLC (C_6H_6–EtOAc, 9:1) gave ventiloquinone-A as bright red needles (MeOH), mp 148° (46 mg). Fractions containing ventiloquinones D and H (fractions 11–58) were separated by prep. TLC (C_6H_6–EtOAc, 9:1). Ventiloquinone-D crystallized from MeOH as dark red microcrystals (74 mg), mp 101°, ventiloquinone-H separated from petrol as orange red crystals (29 mg), mp 95–96°. Fractions 157–172 were subjected to CC (C_6H_6, C_6H_6–EtOAc, 19:1). Ventiloquinone-C was eluted with C_6H_6; it crystallized from aq. MeOH as dark red needles (62 mg), mp 137°. The C_6H_6–EtOAc (19:1) eluate containing ventiloquinone-B was purified by prep. TLC (C_6H_6–EtOAc, 4:1), and crystallized from MeOH as yellow needles (56 mg), mp 134°. Fractions 173–196 were subjected to CC (C_6H_6–EtOAc, 9:1). Ventiloquinone-G eluted in the latter fractions together with C. They were separated by prep. TLC on silica gel-1% $(CO_2H)_2$ plates (C_6H_6–EtOAc, 19:1). Ventiloquinone-G crystallized from MeOH–petrol as orange red crystals (10 mg), mp 183°. Fractions 197–212 were subjected to rechromatography (CC: C_6H_6–EtOAc, 9:1). Fractions containing ventiloquinone-F on prep. TLC (C_6H_6–EtOAc, 9:1) followed by crystallization from MeOH–petrol gave orange red needles (34 mg), mp 213°. Fractions 214–219 on CC (C_6H_6–EtOAc, 4:1) and repeated crystallization from C_6H_6 gave ventiloquinone-E as orange red needles (110 mg), mp 119°.

For a preliminary separation of the quinones from the Me_2CO extract of *V. calyculata* see ref. [2]. Fractions 97–112 were subjected to CC (C_6H_6–EtOAc, 9:1). Ventiloquinones I, J and K were eluted together in C_6H_6–EtOAc (9:1). They were separated by repeated prep. TLC (C_6H_6–EtOAc, 19:1) on silica gel–2% $(CO_2H)_2$ plates. Ventiloquinone-I crystallized from MeOH–petrol as red flakes (29 mg), mp 189°; ventiloquinone-J from C_6H_6–petrol as dark red flakes (21 mg), mp 141°; and ventiloquinone-K (from MeOH–petrol) as red needles, (18 mg), mp 157°.

Ventiloquinone-A (**3**). Found: C, 62.08; H, 4.90%; $[M]^+$, 332.0896. $C_{17}H_{16}O_7$ requires C, 61.44; H, 4.85%; $[M]^+$,

332.0895; $[\alpha]_D^{25}$ +299° ($CHCl_3$, *c* 0.22); UV λ_{max}^{EtOH} nm (log ε): 225 (4.46), 270 (4.23), 294 (3.80), 435 (3.57); IR ν_{max}^{nujol} cm^{-1}: 920, 1632, 1662; ^1H NMR (360 MHz, $CDCl_3$): δ1.35 (3H, *d*, *J* = 6.1 Hz, Me-3), 1.50 (3H, *d*, *J* = 6.4 Hz, Me-1), 2.17 (1H, *ddd*, *J* = 18.3, 10.2, 3.9 Hz, H_a-4), 2.69 (1H, *dt*, *J* = 18.3, 2.65, 2.65 Hz, H_e-4), 3.55 (1H, *m*, 14 lines H-3), 3.98 (3H, *s*, OMe), 4.81 (1H, *m*, 13 lines H-1), 6.18 (2H, *s*, $-OCH_2O-$), 12.51 (1H, *s*, exch. with D_2O, *peri*-OH); (C_6D_6, 100 MHz): δ1.19 (3H, *d*), 1.71 (3H, *d*), 2.00 (1H, *ddd*), 2.55 (1H, *dt*), 3.22 (1H, *m*), 3.88 (3H, *s*), 4.85 (1H, *m*), 5.30 (2H, *s*); MS *m/z*: 322 (100%), 317 (45), 303 (32), 299 (9), 289 (20), 274 (16). The *acetate* (Ac_2O–C_5H_5N) was obtained as bright yellow needles (petrol), mp 172°. Found: C, 61.18; H, 4.82%. $C_{19}H_{18}O_8$ requires C, 60.96; H, 4.85%; ^1H NMR (100 MHz, $CDCl_3$): δ1.32 (3H, *d*, *J* = 7 Hz, Me-3), 1.48 (3H, *d*, *J* = 7 Hz, Me-1), 2.04 (1H, *ddd*, *J* = 18, 10, 3.5 Hz, H_a-4), 2.40 (3H, *s*, OAc), 2.66 (1H, *dt*, *J* = 18, 3, 3 Hz, H_e-4), 3.48 (1H, *m*, H-3), 4.00 (3H, *s*, OMe), 4.75 (1H, H-1), 6.13 (2H, *s*, $-OCH_2O-$). The *methyl ether* (Me_2SO_4–K_2CO_3–Me_2CO or MeI–Ag_2O–$CHCl_3$) forms yellow needles (MeOH), mp 134°, identical with ventiloquinone-B (co-TLC, mmp and IR). The *demethylated product* (HBr–AcOH) of ventiloquinone-A was identical with the demethylated product of ventiloquinone-B (see below) (co-TLC, IR, UV).

Ventiloquinone-B (**4**). Found: C, 62.50; H, 5.20%; $[M]^+$, 346.1050. $C_{16}H_{18}O_7$ requires C, 62.42; H, 5.24%; M, 346.1052. $[\alpha]_D^{25}$ +350° ($CHCl_3$, *c* 0.12); UV λ_{max}^{EtOH} nm (log ε): 222 (4.19), 273 (4.10), 294 sh (3.37), 400 (3.28); IR ν_{max}^{nujol} cm^{-1}: 920, 1628, 1650, 1662; ^1H NMR (360 MHz, $CDCl_3$): δ1.33 (3H, *d*, *J* = 6.2 Hz, Me-3), 1.48 (3H, *d*, *J* = 6.6 Hz, Me-1), 2.08 (1H, *ddd*, *J* = 18.4, 10.2, 3.8 Hz, H_a-4) 2.77 (1H, *dt*, *J* = 18.4, 2.66, 2.66 Hz, H_e-4), 3.52 (1H, *m*, 14 lines, H-3), 3.98 (3H, *s*, OMe), 3.99 (3H, *s*, OMe), 4.77 (1H, *m*, 13 lines, H-1), 6.13 (2H, *s*, $-OCH_2O-$); ^{13}C NMR (25.2 MHz, $CDCl_3$): δ20.40 (*q*, C-3a), 21.36 (*q*, C-1a), 29.67 (*t*, C-4), 61.0 (*q*, OMe), 61.1 (*q*, OMe), 69.04 (*d*, C-3), 69.86 (*d*, C-1), 103.0 (*t*, OCH_2O), 120.79 (*s*, C-5a)[a], 121.65 (*s*, C-9a)[a], 140.13 (*s*, C-6)[b], 140.37 (*s*, C-7)[b], 141.10 (*s*, C-8)[b], 144.22 (*s*, C-9)[b], 144.60 (*s*, 10a)[c], 146.48 (*s*, C14a)[c], 182.50 (*s*, CO), 183.29 (*s*, CO) (assignments with the same superscript may be interchangeable). MS *m/z* (rel. int.): 346 (100%), 331 (82), 317 (23), 316 (27), 313 (33), 303 (16), 301 (16), 289 (17), 288 (23), 273 (22). The *demethylated* product (HBr–AcOH) was obtained as dark red needles (MeOH), mp 127°. Found: C, 60.44; H, 4.49%. $C_{16}H_{14}O_7$ requires C, 60.38; H, 4.43%; UV λ_{max}^{MeOH} nm: 250, 290, 460, 485, 510, 520, 568; $\lambda_{max}^{MeOH-HO^-}$ nm: 557, 593; IR ν_{max}^{KBr} cm^{-1}: 1610. This naphthazarin was the *trans* epimer. The *cis* epimer was obtained by treating **A** (12 mg) in CH_2Cl_2 (5 ml) at −78° with molar BCl_3 in CH_2Cl_2 (0.15 ml) for 1 hr. The crude product was separated from starting material by prep. TLC ($CHCl_3$) and then sublimed at 115°/0.001 mm Hg to give red needles, mp 142.5–143.5°; Found: $[M]^+$, 318.0731. $C_{16}H_{14}O_7$ requires 318.0739; IR ν_{max}^{KBr} cm^{-1}: 1610; ^1H NMR (220 MHz, $CDCl_3$): δ1.34 (3H, *d*, *J* = 8 Hz, Me-3), 1.57 (3H, *d*, *J* = 8 Hz, Me-1), 2.29 (1H, *ddd*, *J* = 18, 9, 3.5 Hz, H_a-4), 2.80 (1H, *ddd*, *J* = 18, 3.5, 2.5 Hz, H_e-4), 3.58 (1H, *m*, 3H), 4.87 (1H, *m*, H-1), 6.21 (2H, *s*, $-OCH_2O-$), 12.67 and 12.79 (each 1H, *s*, exch. with D_2O, *peri*-OH).

Ventiloquinone-C (**6**). Found: C, 59.84; H, 4.98%; $[M]^+$, 320.0896. $C_{16}H_{16}O_7$ requires C, 60.00; H, 5.04%; $[M]^+$, 320.0893; UV λ_{max}^{EtOH} nm (log ε): 250 (4.10), 308 (3.68), 461 (3.65), 488 (3.71), 526 (3.58), 565 (3.14); IR ν_{max}^{nujol} cm^{-1}: 1590, 3300; ^1H NMR (220 MHz, $CDCl_3$): δ1.39 (3H, *d*, *J* = 7 Hz, Me-3), 1.64 (3H, *d*, *J* = 7 Hz, Me-1), 2.42 (1H, *ddd*, *J* = 18, 10, 2.5 Hz, H_a-4 overlapped by similar signals) 2.90 (1H, *dt*, *J* = 18, 3, ~ 2 Hz, H_e-4 overlapped by similar signals), 3.64 (1H, *m*, H-3), 4.20 (3H, *s*, OMe), 5.0 (1H, *m*, H-1), 12.23/12.90; 11.97/13.17 (2:1 ratio, total 2H, all *s*, exch. with D_2O, 2 × *peri*-OH); MS *m/z*: 320 (100%), 305 (80), 302 (6), 290 (14), 289 (14), 287 (16), 277 (24), 276 (54), 261 (17).

The monomethyl ether (CH_2N_2 in Et_2O for 1 min) was identical with ventiloquinone-D (co-TLC, IR and mmp). Methylation (Me_2SO_4–K_2CO_3–Me_2CO) of ventiloquinone-C afforded two *trimethyl ethers* separated by prep. TLC ($CHCl_3$).

Methyl ether **7** was obtained as yellow needles (C_6H_6–petrol), mp 113°; Found: C, 63.08; H, 6.20%. $C_{19}H_{22}O_7$ requires C, 62.98; H, 6.12%; ^1H NMR (100 MHz, $CDCl_3$): δ1.34 (3H, *d*, *J* = 7 Hz, Me-3), 1.48 (3H, *d*, *J* = 7 Hz, Me-1), 2.06 (1H, *ddd*, *J* = 18, 10, 3.5 Hz, H_a-4), 2.78 (1H, *dt*, *J* = 18, 3, 3 Hz, H_e-4), 3.52 (1H, *m*, H-3), 3.88 (6H, *s*, 2 × OMe), 4.0 (6H, *s*, 2 × OMe), 4.76 (1H, *m*, H-1); *Methyl ether* **8** was obtained as an orange red viscous liquid; Found: $[M]^+$, 362.1364. $C_{19}H_{22}O_7$ requires M, 362.1365; ^1H NMR (100 MHz, $CDCl_3$): δ1.38 (3H, *d*, *J* = 7 Hz, Me-3), 1.58 (3H, *d*, *J* = 7 Hz, Me-1), 2.40 (1H, *s* (*br*), H_a-4), 2.90 (1H, *s* (*br*), H_e-4), 3.52 (1H, *m*, H-3), 3.80 (3H, *s*, OMe), 3.84 (3H, *s*, OMe), 4.05 (6H, *s*, 2 × OMe), 5.0 (1H, *q* (*br*), H-1); MS *m/z*: 362 (84%), 347 (100), 332 (20), 331 (16), 317 (24), 303 (29), 287 (17), 273 (13).

Ventiloquinone-D (**5**). Found: C, 61.20: H, 5.47%; $[M]^+$, 334.1047. $C_{17}H_{18}O_7$ requires C, 61.07; H, 5.43%; $[M]^+$, 334.1052; $[\alpha]_D^{25}$ +308° ($CHCl_3$, *c* 0.17); UV λ_{max}^{EtOH} nm (log ε): 232 (4.58), 310 (3.94), 465 (3.94), 500 (4.04), 535 (3.84), 585 (2.97); IR ν_{max}^{KBr} cm^{-1} 1610; ^1H NMR (360 MHz, $CDCl_3$): δ1.37 (3H, *d*, *J* = 6.1 Hz, Me-3), 1.61 (3H, *d*, *J* = 6.4 Hz, Me-1), 2.38 (1H, *ddd*, *J* = 17.8, 10.4, 2.6 Hz, H_a-4), 2.87 (1H, *ddd*, *J* = 17.8, 2.3, 2.1 Hz, H_e-4), 3.60 (1H, *ddq*, *J* = 10.4, 6.1, 2.3 Hz, H-3), 4.10 (6H, *s*, 2 × OMe), 4.97 (1H, *ddq*, *J* = 6.4, 2.6, 2.3 Hz, H-1), 12.89 and 13.12 (each 1H, *s*, exch. with D_2O, *peri*-OH); ^{13}C NMR (25.2 MHz, $CDCl_3$): δ20.84 (*q*, C-3a), 21.31 (*q*, C-1a), 30.82 (*t*, C-4), 61.47 (*q*, 2 × OMe), 68.51 (*d*, C-3), 70.51 (*d*, C-1), 107.6 (*s*, C-5a, 9a), 137.5 (*s*, C-4a)[a], 140.79 (*s*, C-10a)[a], 147.48 (*s*, C-7, 8), 158.1 (C-6, 9), 181.47 (*s*, 2 × CO) (assignments with the same superscript may be interchanged); MS *m/z*: 334 (100%), 319 (60), 305 (11), 304 (23), 303 (27), 291 (28), 290 (28), 275 (16), 261 (11).

Ventiloquinone-E (**9**). Found: C, 65.10; H, 6.03%; $[M]^+$, 332.1257. $C_{18}H_{20}O_6$ requires C, 65.06; H, 6.07%; $[M]^+$, 332.1259; $[\alpha]_D^{25}$ +438° ($CHCl_3$, *c* 0.13); UV λ_{max}^{EtOH} nm (log ε): 220 (4.46), 270 (4.11), 417 (3.48); IR ν_{max}^{KBr} cm^{-1}: 1637, 1645, 1667; ^1H NMR (360 MHz, $CDCl_3$): δ1.33 (3H, *d*, *J* = 6.2 Hz, Me-3), 1.49 (3H, *d*, *J* = 6.6 Hz, Me-1), 2.10 (1H, *ddd*, *J* = 18.3, 10.2, 3.7 Hz, H_a-4), 2.80 (1H, *dt*, *J* = 18.3, 2.6, 2.6 Hz, H_e-4), 3.52 (1H, *ddq*, 10.2, 6.2, 2.6 Hz, H-3), 3.86 (3H, *s*, OMe-7), 3.96 (6H, *s*, OMe-6 and 9), 4.79 (1H, *ddq*, 6.6, 3.7, 2.6 Hz, H-1), 6.72 (1H, *s*, H-8); C_6D_6 (100 MHz): δ1.18 (3H, *d*), 1.76 (3H, *d*), 2.0 (1H, *ddd*), 2.80 (1H, *dt*), 3.2 (1H, *m*), 3.28 (3H, *s*), 3.50 (3H, *s*), 4.04 (3H, *s*), 4.96 (1H, *m*), 6.24 (1H, *s*); ^{13}C NMR (25.2 MHz, $CDCl_3$): δ20.63 (C-3a), 21.31 (C-1a), 29.69 (C-4), 56.26, 56.85, 61.35 (3 × OMe), 68.96 (C-3), 70.13 (C-1), 101.65 (C-8), 113.75 (C-5a)[a], 126.64 (C-9a)[a], 140.73 (C-10a)[b], 143.49 (C-4a)[b], 147.63 (C-7), 157.66 (C-6), 159.44 (C-9), 182.50, 183.75 (2 × CO) (assignments with the same superscript may be interchanged). MS *m/z*: 332 (89%), 317 (100), 303 (11), 302 (28), 299 (14), 289 (8), 287 (10), 274 (18), 259 (14); CD λ_{max}^{MeOH} Δε (nm): −7.59 (221), +8.38 (287), +1.55 (408), [eleutherin (**1**) −3.34 (240), +3.92 (277), +3.06 (330), +1.67 (390)].

The leucodiacetate (Ac_2O, Zn, NaOAc) was obtained as needles (MeOH), mp 140°. Found: C, 63.02; H, 6.84%; $C_{22}H_{26}O_8$ requires C, 63.15; H, 6.26%; UV λ_{max}^{MeOH} nm: 305, 317, 342; IR ν_{max}^{KBr} cm^{-1}: 1765; ^1H NMR (100 MHz, $CDCl_3$): δ1.31 (3H, *d*, *J* = 7 Hz, Me-3), 1.56 (3H, *d*, *J* = 7 Hz, Me-1), 2.08 (1H, *m*, H-4), 2.30 (3H, *s*, OAc), 2.33 (3H, *s*, OAc), 2.60 (1H, *m*, H-4), 3.68 (1H, *m*, H-3), 3.75 (3H, *s*, OMe), 3.82 (3H, *s*, OMe), 3.88 (3H, *s*, OMe), 4.92 (1H, *m*, H-1), 6.72 (1H, *s*, H-7). *The demethylated product, trans* **11** (HBr–AcOH), was obtained as red microcrystals (MeOH), mp 219°. Found: C, 62.24; H, 4.98%. $C_{15}H_{14}O_6$ requires C, 62.07; H, 4.86%. UV λ_{max}^{MeOH}: 315, 474, 495, 520 sh, 540 sh; IR ν_{max}^{KBr} cm^{-1}: 1600, 3400; ^1H NMR (100 MHz, $CDCl_3$): δ 1.43 (3H, *d*, *J* = 7 Hz,

Me-3), 1.65 (3H, *d*, J = 6 Hz, Me-1), 2.42 (1H, 4 *s* (*br*), H_a-4), 2.94 (1H, 2 *s* (*br*), H_e-4), 4.12 (1H, *m*, H-3), 5.23 (1H, *m*, H-1), 6.40 (1H, *s*, H-8), 12.00 and 13.34 (each 1H, *s*, exch. with D_2O, *peri*-OH). Demethylation as for ventiloquinone B, but using BBr_3, gave, after prep. TLC ($CHCl_3$–petrol, 2:1), *trans* **11** as a red solid; ^{1}H NMR (220 MHz, $CDCl_3$): δ 1.40 (3H, *d*, J = 8 Hz, Me-3), 1.61 (3H, *d*, J = 8 Hz, Me-1), 2.40 (1H, *dd* (*br*), H_a-4), 2.90 (1H, *dd*, H_e-4), 3.95 (3H, *s*, OMe), 4.07 (1H, *m*, H-3), 5.17 (1H, *q*, H-1), 6.18 (1H, *s*, H-8), 12.75 and 13.20 (each 1H, *s*, *peri*-OH).

Ventiloquinone-F (**10**). Found: C, 66.39; H, 5.32%; $[M]^+$, 288.0996. $C_{16}H_{16}O_5$ requires C, 66.66; H, 5.59%; $[M]^+$, 288.0997; $[\alpha]_D^{25}$ +350° (MeOH, *c* 0.14); UV λ_{max}^{MeOH} nm (log ε): 256 (4.38), 299 (3.84), 422 (3.70); $\lambda_{max}^{MeOH-HO^-}$ nm: 511; IR ν_{max}^{KBr} cm^{-1}: 1645, 1662 sh; ^{1}H NMR (360 MHz, $CDCl_3$): δ 1.38 (3H, *d*, J = 6.2 Hz, Me-3), 1.54 (3H, *d*, J = 6.6 Hz, Me-1), 2.43 (1H, *ddd*, J = 17.5, 10.9, 2.2 Hz, H_a-4), 2.83 (1H, *ddd*, J = 17.6, 3.0, 1.7 Hz, H_e-4), 3.75 (1H, *ddq*, J = 10.9, 6.2, 3.0 Hz, H-3), 3.95 (3H, *s*, OMe), 4.77 (1H, *ddq*, J = 6.6, ~ 1.95, ~ 1.95 Hz, H-1), 5.87 (1H, *s*, H-8), 7.18 (1H, *s*, H-10), 12.38 (1H, exch. with D_2O, *peri*-OH); ^{13}C NMR (90.6 MHz, $CDCl_3$): δ 20.87 (*q*, C-3a), 21.51 (*q*, C-1a), 29.99 (*t*, C-4), 56.55 (*q*, OMe), 69.77 (*d*, C-3), 72.97 (*d*, C-1), 102.59 (*d*, C-8)[a], 111.39 (*s*, C-5a), 113.72 (*d*, C-10)[a], 128.18 (*s*, C-9a)[b], 128.73 (*s*, C-4a)[b], 150.01 (*s*, C-10a), 162.83 (*s*, C-5)[c], 168.02 (*s*, C-7)[c], 179.20 (*s*, C-9), 182.60 (*s*, C-6) (assignments with the same superscript may be interchanged); MS *m/z*: 288 (17%), 260.1036 ($C_{15}H_{16}O_4$ requires 260.1041, 38), 246 (13), 245.0814 ($C_{14}H_{13}O_4$ requires 245.0814, 62), 232 (6), 229 (7), 218 (30), 216 (100), 215 (12), 203 (31), 201 (35).

Ventiloquinone-G (**11**). Found: C, 62.00; H, 4.82%; $[M]^+$, 290.0795. $C_{15}H_{14}O_6$ requires C, 62.07; H, 4.86%; $[M]^+$, 290.0790; $[\alpha]_D^{18}$ +720° (MeOH, *c* 0.10); UV λ_{max}^{MeOH} nm (log ε): 230 (4.22), 258 (4.11), 300 (3.87), 478 sh (3.82), 500 (3.83), 526 sh (3.74), 540 sh (3.60); $\lambda_{max}^{MeOH-HO^-}$ nm: 500, 530, 568; $\lambda_{max}^{MeOH-AlCl_3}$ nm: 240, 343, 492 sh, 524, 564; IR ν_{max}^{KBr} cm^{-1}: 1600, 1622, 3300; ^{1}H NMR (360 MHz, $CDCl_3$): δ 1.38 (3H, *d*, J = 6.2 Hz, Me-3), 1.63 (3H, *d*, J = 6.4 Hz, Me-1), 2.40 (1H, *ddd*, J = 17.6, 10.4, 2.6 Hz, H_a-4), 2.87 (1H, *dt*, J = 17.6, 2.1, 2.1 Hz, H_e-4), 3.62 (1H, *ddq*, J = 10.4, 6.2, 2.1 Hz, H-3), 5.02 (1H, *qt*, J = 6.4, ~ 2.3, ~ 2.3 Hz, H-1), 6.34 (1H, *s*, H-8), 7.40 (1H, *s* (*br*), exch with D_2O, HO-7), 11.95 and 13.46 (each 1H, *s*, exch. with D_2O, *peri*-OH); MS *m/z*: 290 (100%), 275 (55), 261 (13), 248 (29), 247 (24), 246 (27), 245 (10), 232 (13), 231 (10), 228 (10). Methylation (CH_2N_2) gave, after prep. TLC ($CHCl_3$) a red solid; ^{1}H NMR (220 MHz, $CDCl_3$): δ 1.41 (3H, *d*, J = 6 Hz, Me-3), 1.65 (3H, *d*, J = 6 Hz, Me-1), 2.42 (1H, *ddd*, H_a-4), 2.90 (1H, *ddd*, H_e-4), 3.63 (1H, *m*, H-3), 3.95 (3H, *s*, OMe), 5.01 (1H, *m*, H-1), 6.19 (1H, *s*, H-8), 12.77 and 13.37 (each 1H, exch. with D_2O, *peri*-OH).

Ventiloquinone-H (**14**). Found: C, 64.38; H, 5.62%; $[M]^+$, 318.1097. $C_{17}H_{18}O_6$ requires C, 64.14; H, 5.70%; $[M]^+$, 318.1103; $[\alpha]_D^{25}$ +330° (MeOH, *c* 0.13); UV λ_{max}^{MeOH} nm (log ε): 258 (4.25), 300 (4.02), 423 (3.69); $\lambda_{max}^{MeOH-HO^-}$ nm 530; IR ν_{max}^{KBr} cm^{-1}: 1620, 1670; ^{1}H NMR (360 MHz, $CDCl_3$): δ 1.33 (3H, *d*, J = 6.1 Hz, Me-3), 1.60 (3H, *d*, J = 6.3 Hz, Me-1), 2.68 (2H, 5*q*, irregular, CH_2-4), 3.64 (1H, *m*, 11 lines, H-3), 4.06 (3H, *s*, OMe), 4.09 (3H, *s*, OMe), 5.02 (1H, *qt*, J = 6.3, ~ 1.8, ~ 1.7 Hz, H-1), 7.32 (1H, *s*, H-5), 12.45 (1H, *s*, exch. with D_2O *peri*-OH); (360 MHz, C_6D_6): δ 1.14 (3H, *d*, J = 6.1 Hz, Me-3), 1.81 (3H, *d*, J = 6.4 Hz, Me-1), 2.05 (1H, *ddd*, J = 16.5, 10.4, 2.0 Hz, H_a-4), 2.34 (1H, *ddd*, J = 16.5, 1.8, 1.0 Hz, H_e-4), 3.29 (1H, *m*, 14 lines, H-3), 3.60 (3H, *s*, OMe), 3.70 (3H, *s*, OMe), 5.06 (1H, *qdd*, 6.3, 1.9, 1.9 Hz, H-1) [in ventilagone H_a-4 and H_e-4 appear at δ 2.04 and 2.34 (in C_6D_6), respectively]. MS *m/z*: 318 (22%), 303.0852 ($C_{16}H_{15}O_6$ requires 303.0868, 100), 275 (8), 261 (10). Ventiloquinone-H (10 mg) was demethylated with conc. HCl (10 ml) in refluxing EtOH (10 ml) for 30 min. The product was obtained as bright red flakes (MeOH–petrol), mp 184°, and found to be identical with ventiloquinone-I (co-TLC, mmp, ^{1}H NMR).

Ventiloquinone-I (**15**). Found: C, 62.96; H, 5.20%; $[M]^+$, 304.0937, $C_{16}H_{16}O_6$ requires C, 63.15; H, 5.30%; $[M]^+$, 304.0947; UV λ_{max}^{MeOH} nm (log ε): 235 (4.22), 280 (4.08), 408 (3.82); IR ν_{max}^{KBr} cm^{-1}: 1625, 1660, 3380; ^{1}H NMR (220 MHz, $CDCl_3$): δ 1.37 (3H, *d*, J = 7 Hz, Me-3), 1.64 (3H, *d*, J = 7 Hz, Me-1), 2.72 (2H, *m*, CH_2-4) (the H-4 signals separate in C_6D_6 soln), 3.67 (1H, *m*, H-3), 4.19 (3H, *s*, OMe), 5.04 (1H, *q* (*br*), J = 7 Hz, H-1), 6.80 (1H, *s* (*br*), exch. with D_2O, OH), 7.37 (1H, *s*, H-5), 11.68 (1H, *s*, exch. with D_2O, *peri*-OH); MS *m/z*: 304 (26%), 289.0702 ($C_{15}H_{13}O_6$ requires 289.0712, 100), 271(7), 261 (6), 247 (7). The monomethyl ether of ventiloquinone-I (CH_2N_2 in Et_2O) was found to be identical with ventiloquinone-H (co-TLC, mmp, ^{1}H NMR). Methylation with Me_2SO_4–K_2CO_3–Me_2CO gave two trimethyl ethers identical (co-TLC) with those obtained from ventiloquinone-C.

Ventiloquinone-J (**16**). Found: C, 64.07; H, 5.64%; $[M]^+$, 318.1112. $C_{17}H_{18}O_6$ requires C, 64.14; H, 5.70%; $[M]^+$, 318.1103. $[\alpha]_D^{22}$ +215° (MeOH, *c* 0.10); UV λ_{max}^{MeOH} nm (log ε): 232 (4.20), 250 sh (3.80) 295 (3.77), 435 (3.48); IR ν_{max}^{KBr} cm^{-1}: 1620, 1668; ^{1}H NMR (220 MHz, $CDCl_3$): δ 1.49 (3H, *d*, J = 7 Hz, Me-3), 1.74 (3H, *d*, J = 7 Hz, Me-1), 2.50 (1H, *ddd*, J = 18, 2, ~ 2.5 Hz, H_a-4), 2.97 (1H, *dt*, J = 18, ~ 1 Hz, H_e-4), 3.61 (1H, *m*, H-3), 3.84 (3H, *s*, OMe), 3.93 (3H, *s*, OMe), 5.04 (1H, *q* (*br*), J = 7 Hz, H-1), 6.04 (1H, *s*, H-8), 13.42 (1H, *s*, exch. with D_2O, *peri*-OH); MS *m/z*: 318 (76%), 303.0868 ($C_{16}H_{15}O_6$ requires 308.0868, 100), 288 (12), 275 (14), 274 (15), 271 (17), 261 (17), 257 (16), 243 (13). Demethylation with BCl_3, as above, gave after prep. TLC, a red solid, mp 130°, identical (TLC, MS) with *trans* **12**; Found: $[M]^+$, 304.0950. $C_{16}H_{16}O_6$ requires M, 304.0947; MS *m/z*: 304 (100%), 289 (85), 260 (45).

Ventiloquinone-K (**17**). Found: C, 60.88; H, 5.46%; $[M]^+$, 334.1047. $C_{17}H_{18}O_7$ requires C, 61.07; H, 5.43%; $[M]^+$, 334.1052; $[\alpha]_D^{17}$ +565° (MeOH, *c* 0.085); UV λ_{max}^{MeOH} nm (log ε): 218 (4.85), 245 (4.69), 260 (4.38), 310 (3.97), 435 (3.84); IR ν_{max}^{KBr} cm^{-1}: 1605, 1650, 3300; ^{1}H NMR (220 MHz, $CDCl_3$): δ 1.37 (3H, *d*, J = 6.1 Hz, Me-3), 1.61 (3H, *d*, J = 6.3 Hz, Me-1), 2.41 (1H, *ddd*, J = 17.2, 10.5, 2.1 Hz, H_a-4), 2.89 (1H, *dt*, J = 17.2, 1.9, 1.9 Hz, H_e-4), 3.58 (1H, *m*, 12 lines, H-3), 3.82 (3H, *s*, OMe), 4.13 (3H, *s*, OMe), 5.02 (*ddt*, J = 6.3, 1.9, 1.9 Hz, H-1), 7.34 (1H, *s* (*br*), exch. with D_2O, OH), 13.28 (*s*, exch. with D_2O, *peri*-OH); MS *m/z*: 334 (81%), 319.0808 ($C_{16}H_{15}O_7$ requires 319.0817, 100), 304 (11), 302 (14), 291 (13), 290 (17), 286 (13), 277 (25), 275 (18), 273 (17), 259 (16). The methyl ether (CH_2N_2 in Et_2O) obtained from ventiloquinone-K was identical (co-TLC, ^{1}H NMR) with ventiloquinone-C trimethyl ether (**8**).

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