Naphthopyranquinones. Confirmation of the Structures of the Ventiloquinones E, G and J by Synthesis

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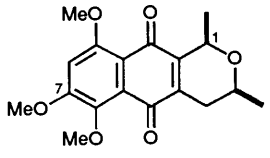
Both ventiloquinone E (*cis*-3,4-dihydro-6,7,9-trimethoxy-1,3-dimethyl-1*H*-naphtho[2,3-*c*]pyran-5,10-quinone) **1** and ventiloquinone G (*cis*-3,4-dihydro-5,7,10-trihydroxy-1,3-dimethyl-1*H*-naphtho[2,3-*c*]pyran-6,9-quinone) **3** have been synthesised and shown to be identical with natural samples isolated from the root bark of *Ventilago maderaspatana*. *cis*-3,4-Dihydro-5-hydroxy-7,10-dimethoxy-1,3-dimethyl-1*H*-naphtho[2,3-*c*]pyran-6,9-quinone **5** has also been synthesised and found to be different to ventiloquinone J, which must then be *cis*-3,4-dihydro-10-hydroxy-5,7-dimethoxy-1,3-dimethyl-1*H*-naphtho[2,3-*c*]pyran-6,9-quinone **4**.

The elegant syntheses[1] of the naphtho[2,3-*c*]pyran-6,9-quinones (±)-ventilagone[2] and (±)-ventiloquinone H[3] recently reported by Brassard and co-workers prompt us to report our assembly of other ventiloquinones, also isolated[3] from *Ventilago maderaspatana* and *V. calyculata* by a route which can readily provide either 6,9- or isomeric 5,10-quinones.[4] Specifically, we now report the formation of ventiloquinone E **1** and ventiloquinone G **3**, and also show that,



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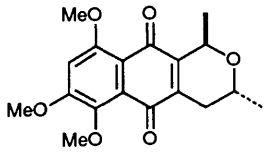

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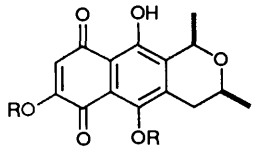
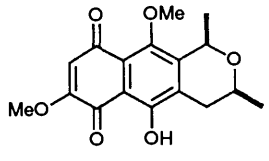


3; R = H
4; R = Me



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of the two possible structures **4** or **5** proposed for ventiloquinone J,[3] the C-10 *O*-methyl ether **4** is correct since the latter, derived by an unambiguous synthesis, is different to the natural product.

Results and Discussion

The desired regioselectivity in the present study was achieved by the recently reported[5] specificity in the acetylation of 1,2,4,5,8-pentamethoxynaphthalene to afford solely the 6-acetyl derivative **7**. This ketone **7** is known[5] to undergo oxidation in the more electron-rich ring to afford the corresponding methoxy-substituted 1,4-naphthoquinone **14**. In order to achieve oxidation of the less electron-rich acetyl-substituted ring, naphthalene **7** was treated with limited quantities of boron trichloride, which permitted selective removal of the methyl group *ortho* to the acetyl function to afford the *ortho*-acetylnaphthol **8** in high yield. In particular, the structural assignment was confirmed by its ^{1}H NMR spectrum, which showed a hydrogen-bonded proton at δ 14.08. This naphthol **8** was oxidised with ceric ammonium nitrate[6] to yield the quinone **15**, which darkened on isolation and was therefore not characterised but was immediately allylated with allyltrimethylstannane,[7,8] and the derived adduct was benzylated to afford the dibenzyl ether **16** in an overall yield of 51% from the naphthol **8**. Reduction of this ketone with lithium aluminium hydride gave rise to the alcohol **18** which was cyclised exclusively to the isomeric *trans* 1,3-dimethylnaphthopyran **20** using potassium *tert*-butoxide in dimethylformamide in a yield of 92%.[8,9] The stereochemistry was assigned on the basis of the ^{1}H NMR spectrum, in which the proton 3-H appeared as a multiplet at δ 4.0–4.2.[9,10] None of the *cis* stereoisomer was detected, which was consistent with our earlier finding[8] that greater crowding by the C-10 benzyloxy group in the product leads to the C-1 methyl substituent solely adopting the less hindered pseudoaxial configuration. Furthermore, cyclisation of the allylic alcohol **18** with mercuric acetate followed by sodium borohydride[10] afforded only the *trans* stereoisomer **20** of the pyran, even though it is known[10] that both *cis* and *trans* isomers are obtained in analogous products bearing a C-10 methoxy substituent. Removal of the benzyl protecting groups in pyran **20** followed by aerial oxidation provided the quinone **2**, the C-1 epimer of ventiloquinone E **1**. Its ^{1}H NMR spectrum gave unequivocal confirmation of the *trans* stereochemistry as expected for an isoeleutherin derivative.[11] In our hands, attempted partial isomerisation of the *trans* compound **2** into the *cis* epimer **1** using phosphoric acid was unsuccessful.[12]

The experiments described above pointed to the use of as small an alkoxy group as possible *ortho* to acetyl in the precursor acetylnaphthalenes in order to maximise yields of *cis* dimethylnaphthopyrans in the cyclisation step. A methoxy group was therefore chosen. However, it was still imperative that, at least for the synthesis of ventiloquinone E **1**, the central ring be subsequently preferentially oxidised. This necessitated the use of a selectively removable protecting group from the alternative oxygen at C-5, and benzyl was chosen for this purpose.

Differential protection on the oxygens at C-5 and C-10 was achieved as follows. The quinone **15** was reduced and acetylated to afford the diacetate **9**. This diacetate was subjected to selective hydrolysis of the acetate *ortho* to the aromatic acetyl group, and the derived phenolic hydroxy group, the hydrogen of which resonated in the ^{1}H NMR spectrum at δ 14.10, was methylated to yield the tetramethoxy acetate **10**, in an overall yield of 87% from the diacetate **9**. Hydrolysis of the remaining acetate and allylation of the intermediate naphthol gave rise to the allyl ether **11**. Claisen rearrangement of this ether followed

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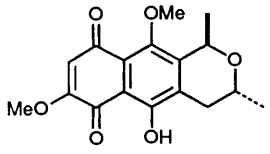

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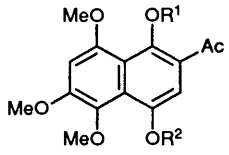
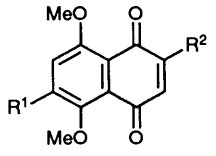
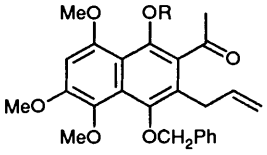


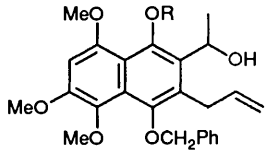
7; $R^1 = R^2 = Me$
8; $R^1 = H$, $R^2 = Me$
9; $R^1 = R^2 = Ac$
10; $R^1 = Me$, $R^2 = Ac$
11; $R^1 = Me$, $R^2 = CH_2CH{=}CH_2$
12; $R^1 = CH_2Ph$, $R^2 = Ac$
13; $R^1 = CH_2Ph$, $R^2 = CH_2CH{=}CH_2$



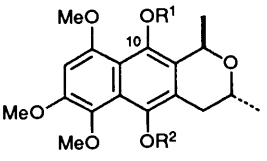
14; $R^1 = Ac$, $R^2 = OMe$
15; $R^1 = OMe$, $R^2 = Ac$



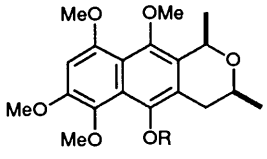
16; $R = CH_2Ph$
17; $R = Me$



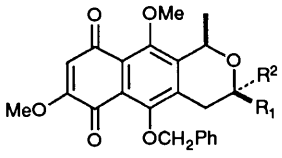
18; $R = CH_2Ph$
19; $R = Me$



20; $R^1 = R^2 = CH_2Ph$
21; $R^1 = Me$, $R^2 = CH_2Ph$
22; $R^1 = Me$, $R^2 = H$



23; $R = CH_2Ph$
24; $R = H$



25; $R^1 = Me$, $R^2 = H$
26; $R^1 = H$, $R^2 = Me$

by benzylation of a second intermediate naphthol provided the monobenzyloxynaphthyl ketone **17** in an overall yield of 66% from the diacetate **9**. The fact that the Claisen rearrangement had taken place from phenolic oxygen to aromatic carbon confirmed the order in which the acetates had undergone hydrolysis. Reduction of the ketone **17** with lithium aluminium hydride provided the alcohol **19**, whose cyclisation with potassium *tert*-butoxide in dimethylformamide occurred in high yield to afford solely the *trans*-dimethylnaphthopyran **21**. Alternatively, cyclisation of alcohol **19** with mercuric acetate followed by sodium borohydride provided a 1:1 mixture of the *cis*- and *trans*-pyrans **23** and **21**, in a combined yield of 56%. The two stereoisomers were separated by careful preparative chromatography. For the *cis*-compound **23** hydrogenolysis of the benzyl protecting group afforded the naphthol **24**, which was oxidised with ceric ammonium nitrate to the racemate 1 of natural ventiloquinone E, identical (except for optical purity) with an authentic natural sample. In particular, its ^1H NMR spectrum showed that it possessed the *cis* stereochemistry of a substituted eleutherin,[11] and was different from its epimer **2** described above. The synthesis also confirmed Thomson and co-worker's biogenetically based assignment[3] of the methoxy at C-7 rather than C-8 for ventiloquinone E.

As described above, the dibenzyl ether **16** was obtained in two steps from the quinone **15** by allylation with allyltrimethylstannane followed by benzylation, and the overall yield for the three steps from the naphthol **8** to the ether **16** was 51%. Although this is a short sequence, its disadvantages were that the expensive allylstannane had to be prepared and the yield is not outstanding for this quinone. This was therefore compared with the five-step sequence naphthol **8**→**15**→**9**→**12**→**13**→**16** for which all steps were easy to perform, yields were good (40% overall yield), and use of the stannane was avoided.

Ventiloquinone J was assigned one of the two possible structures **4** or **5** by Thomson and co-workers[3] on the basis of its spectral characteristics, but a distinction was not made between these. We have synthesised compound **5** (see below), which was clearly different to ventiloquinone J, and this confirms the assignment of structure **4** for this natural product. Oxidation of the *cis* compound **23** with silver(II) oxide[13] afforded the corresponding 6,9-quinone **25**. This compound showed long-range coupling between the pseudoaxial 1-H and each of the protons at C-4 ($J_{1a',4a'}$ 1.8 Hz and $J_{1a',4e'}$ 1.5 Hz). Selective removal of the benzyl group from pyran **25** yielded the quinone **5**, m.p. 163–164 °C (lit.,[3] 141 °C for ventiloquinone J) and for which compound other physical properties do not correspond with those reported for ventiloquinone J. Unfortunately, no natural material was available for direct comparison with synthetic **5**.

Oxidation of the *trans* product **21** with silver(II) oxide afforded the 6,9-quinone **26**, for which long-range coupling between the pseudoequatorial 1-H and pseudoaxial 4-H (0.8 Hz) was very much weaker than for the *cis* compound **25**, and negligible to the pseudoequatorial 4-H (as expected for $J_{1e',4e'}$). Removal of benzyl from quinone **26** afforded the new quinone **6** ($J_{1e',4a'}$ 0.9 Hz), isomeric with compound **5**.

Treatment of the *cis*-quinone **25** with ethanolic hydrochloric acid gave rise to racemic ventiloquinone G **3**, identical (other than for optical purity) with a natural sample. This confirmed the structure of this natural product by synthesis.

Experimental

^1H (200 MHz) and ^{13}C (50 MHz) NMR spectra were measured on a Varian VXR spectrometer, in [^2H]chloroform with tetramethylsilane as internal reference. *J* Values are given in Hz. IR spectra were measured for Nujol mulls using a Perkin-Elmer 983 spectrophotometer. Mass spectra were recorded on a VG Micromass 16 F mass spectrometer. Preparative layer chromatography (PLC) was performed on glass plates coated with Merck Kieselgel 60 F_{254}, while column chromatography refers to dry-packed columns using the same gel (70–230 mesh). Light petroleum refers to the fraction of b.p. 60–80 °C, and ether to diethyl ether. The phrase 'residue obtained upon work-up' refers to the residue when the organic layer was separated, dried ($MgSO_4$), and the solvent evaporated under reduced pressure.

2-Acetyl-4,5,6,8-tetramethoxy-1-naphthol **8**.—The naphthalene **7**[5] (1.099 g, 3.43 mmol) in dry methylene dichloride (50 cm^3) was treated at −78 °C with boron trichloride (0.403 g, 3.43 mmol) in the same solvent (8 cm^3). After 30 min the solution was allowed to warm to room temperature and then hydrolysed with an excess of water. The organic material was extracted into methylene dichloride (200 cm^3). The residue obtained upon work-up was chromatographed (eluent 40% ethyl acetate–light petroleum) to afford the *naphthol* **8** (0.920 g, 88%) as off-yellow needles, m.p. 157–158 °C (propan-2-ol) (Found: C, 62.55; H, 5.95. $C_{16}H_{18}O_6$ requires C, 62.75; H, 5.9%); ν_{max}/cm^{-1} 1688 (C=O) and 1616 (C=C); δ_H 2.62 (3 H, s, $COCH_3$), 3.77, 3.88,

3.97 and 3.99 (each 3 H, s, OCH_3), 6.67 (1 H, s, 7-H), 6.96 (1 H, s, 3-H) and 14.08 (1 H, s, OH, D_2O exchangeable); *m/z* 306 (M^+, 100%), 291 (40), 277 (9), 262 (12) and 43 (25).

2-*Acetyl*-3-*allyl*-1,4-*dibenzyloxy*-5,6,8-*trimethoxynaphthalene* **16**.—The naphthol **8** (500 mg, 1.63 mmol) in acetonitrile (120 cm^3) and water (50 cm^3) was treated with cerium(IV) ammonium nitrate (2.33 g, 4.24 mmol) in water (20 cm^3) during 8 min, and stirring was continued for a further 15 min. The mixture was poured into water, extracted with methylene dichloride, and the solution evaporated under reduced pressure to afford a residue. To this was added dry methylene dichloride (100 cm^3) and the solution was then cooled to −78 °C and the flask flushed with nitrogen. Boron trifluoride–ether (0.22 cm^3, 1.63 mmol) was added, whereupon the solution turned dark brown. Allyltrimethylstannane (880 mg, 2.45 mmol) was added, and the reaction mixture stirred for 1 h at −78 °C and then warmed to room temperature. Water (100 cm^3) was then rapidly added and the organic product extracted with methylene dichloride (4 × 50 cm^3). The dried extract was filtered, and the resulting oil, on evaporation of the solvent, was dissolved in dry acetone (100 cm^3) and treated with potassium carbonate (2.25 g, 16.3 mmol) and benzyl bromide (2.80 g, 1.94 cm^3, 16.3 mmol). The mixture was boiled with vigorous stirring for 12 h. The mixture was cooled and filtered, the solvent evaporated and the residue chromatographed (eluent 10–20% ethyl acetate–light petroleum) to yield the *product* **16** (427 mg, 51%), identical in all spectroscopic aspects with the material synthesised below.

3-*Allyl*-1,4-*dibenzyloxy*-2-(1′-*hydroxyethyl*)-5,6,8-*trimethoxynaphthalene* **18**.—The ketone **16** (342 mg, 0.67 mmol) in dry ether (20 cm^3) was added to a stirred suspension of lithium aluminium hydride (38 mg, 1.0 mmol) in ether (20 cm^3). When TLC showed that all the starting material had been converted into product (*ca.* 5 min), the reaction was worked up by the addition of saturated aqueous ammonium chloride, followed by anhydrous magnesium sulphate. Work-up of the filtrate gave a residue which was chromatographed (eluent 20% ethyl acetate–light petroleum) to afford the *product* **18** (342 mg, 99%), m.p. 124–125 °C (methylene dichloride–cyclohexane) (Found: C, 74.65; H, 6.85. $C_{32}H_{34}O_6$ requires C, 74.7; H, 6.6%); ν_{max}/cm^{-1} 3433 (OH) and 1604 (C=C); δ_H 1.62 (3 H, d, *J* 6.8, CH_3CHOH), 3.5–3.7 (2 H, m, $ArCH_2$), 3.72, 3.85 and 4.02 (each 3 H, s, OCH_3), 4.92 (4 H, s, OCH_2Ph), 4.96 (1 H, dd, *J* 17 and 1.7, vinyl CH_2), 5.10 (1 H, dd, *J* 10.1 and 1.7, vinyl CH_2), 5.23 (1 H, q, *J* 6.8, $CHCH_3$), 4.9–5.3 (1 H, OH, D_2O exchangeable), 6.11 (1 H, m, vinyl CH), 6.75 (1 H, s, 7-H) and 7.3–7.6 (10 H, m, $PhCH_2$); δ_C 29.75 (CH_3C), 30.50 (CH_2CH=), 56.75, 57.00 and 62.75 (3 × OCH_3), 67.25 (CHOH), 76.5 and 77.5 (2 × OCH_2), 97.25 (C-7), 115.75 (=CH_2), 116.5 (C-8a)[a], 125.35 (C-4a)[a], 127.5–129.7 (C of 2 × Ph), 136.70 (C-2)[b], 132.50 (C-3), 137.5 (=CH), 138.20 (C-1)[b], 148.4 (C-4), 149.5 (C-6), 150.00 (C-5) and 153.00 (C-8), (assignments with the same superscript may be interchanged); *m/z* 514 (M^+, 3%), 422 (15), 315 (22) and 91 (100).

trans-5,10-*Dibenzyloxy*-3,4-*dihydro*-6,7,9-*trimethoxy*-1,3-*dimethyl*-1H-*naphtho*[2,3-c]*pyran* **20**.—Compound **18** (121 mg, 0.24 mmol) dissolved in dry dimethylformamide (DMF) (10 cm^3) and dry nitrogen was passed through the solution for 10 min. Potassium *tert*-butoxide (0.21 g, 1.92 mmol) was added and the mixture stirred under nitrogen at an oil bath temperature of 70 °C for 2 h. The mixture was cooled, poured into water, and extracted exhaustively with ether (4 × 30 cm^3). The residue obtained upon work-up was chromatographed (eluent 20% ethyl acetate–light petroleum) to afford the *naphthopyran* **20** (111 mg, 92%) as white grains, m.p. 125–126 °C (crystallised after subjection to PLC and left to stand, then washed with cyclohexane) (Found: C, 74.4; H, 6.35. $C_{32}H_{34}O_6$ requires C, 74.7; H, 6.65%); ν_{max}/cm^{-1} 1616 and 1595 (C=C); δ_H 1.35 (3 H, d, *J* 6.0, 3-CH_3), 1.64 (3 H, d, *J* 6.6, 1-CH_3), 2.57 (1 H, dd, *J* 17.0 and 11.0, 4-H_a), 3.13 (1 H, dd, *J* 17.0 and 3.3, 4-H_e), 3.74, 3.87 and 4.02 (each 3 H, s, OCH_3), 4.0–4.2 (1 H, m, partly obscured by OCH_3 protons, 3-H), 4.75 and 4.80 (each 1 H, d, *J* 20.3, CH_2Ph) 5.00 and 5.05 (each 1 H, d, *J* 14.1, CH_2Ph), 5.34 (1 H, q, *J* 6.6, 1-H), 6.70 (1 H, s, 8-H) and 7.3–7.7 (10 H, m, Ph); δ_C 20.75 (3-CH_3), 22.05 (1-CH_3), 30.94 (C-4), 56.57, 56.80, 62.17 (3 × OCH_3), 62.54 (C-3), 68.77 (C-1), 75.50 and 76.26 (2 × CH_2Ph), 96.41 (C-8), 116.11 (C-9a)[a], 124.70 (C-4a)[b], 126.78 (C-5a)[a], 127.42–128.39 (C of Ph × 2), 138.05 (C-10a)[b], 138.10 (C-10)[b], 146.69 (C-7)[c], 146.83 (C-5)[c], 149.36 (C-6) and 153.05 (C-9) (assignments with the same superscript may be interchanged); *m/z* 514 (M^+, 5%), 423 (13), 331 (17), 285 (10), 91 (100) and 43 (45).

trans-3,4-*Dihydro*-6,7,9-*trimethoxy*-1,3-*dimethyl*-1H-*naphtho*[2,3-c]*pyran*-5,10-*quinone* **2**.—The pyran **20** (49 mg, 0.095 mmol) in ethyl acetate (10 cm^3) was stirred together with 10% Pd–C (100 mg) and a drop of concentrated hydrochloric acid at room temperature under an atmosphere of hydrogen for 1 h. After filtration and evaporation of the solvent under reduced pressure the residue was chromatographed (eluent 50% ethyl acetate–light petroleum) to yield the *product* **2** (28 mg, 87%) as pale orange needles, m.p. 177.5–178.5 °C (methylene dichloride–cyclohexane) (Found: C, 64.9; H, 6.0. $C_{18}H_{20}O_6$ requires C, 65.05; H, 6.0%); ν_{max}/cm^{-1} 1651 and 1636 (C=O) and 1579 and 1551 (C=C); δ_H 1.31 (3 H, d, *J* 6.0, 3-CH_3), 1.50 (3 H, d, *J* 6.8, 1-CH_3), 2.19 (1 H, ddd, *J* 18.9, 10.1 and 1.85, 4-H_a), 2.64 (1 H, dd, *J* 18.9 and 3.5, 4-H_e), 3.9–4.0 (1 H, m, partly obscured by OCH_3 protons, 3-H), 4.96 (1 H, dq, *J* 6.8 and 1.85, 1-H) and 6.72 (1 H, s, 8-H); δ_C 19.62 (3-CH_3), 21.47 (1-CH_3), 29.50 (C-4), 56.17, 56.63 and 61.23 (3 × OCH_3), 62.51 (C-3), 67.16 (C-1), 101.15 (C-8), 112.93 (C-5a)[a], 126.41 (C-9a)[a], 140.73 (C-10a)[b], 143.41 (C-4a)[b], 146.65 (C-7), 158.03 (C-6), 159.55 (C-9) and 181.56 and 184.08 (2 × CO) (assignments with the same superscript may be interchanged); *m/z* 332 (M^+, 100%), 317 (86), 302 (32), 289 (19), 259 (21), 137 (10), 115 (12), 65 (10) and 43 (36).

1,4-*Diacetoxy*-2-*acetyl*-5,6,8-*trimethoxynaphthalene* **9**.—A solution of cerium(IV) ammonium nitrate (3.84 g) in water (70 cm^3) was added dropwise with stirring over a period of 15 min to a solution of the naphthol **8** (0.82 g, 2.68 mmol) in acetonitrile (100 cm^3) and water (30 cm^3). The solution was stirred for a further 15 min and then poured into water (200 cm^3). This was extracted twice with methylene dichloride (2 × 200 cm^3). The organic layer was separated and then shaken with an aqueous solution (200 cm^3) containing sodium dithionite (5 g, an excess) in a separating funnel. The residue obtained upon work-up of the fluorescent green organic phase was immediately dissolved in dry pyridine (50 cm^3), and acetic anhydride (5 cm^3) was added. The mixture was heated at 80 °C for 2 h. The cooled reaction mixture was added to an excess of water. The organic material was then extracted with methylene dichloride keeping the pyridine in the aqueous layer by carefully acidifying with dilute hydrochloric acid. The residue obtained upon work-up was chromatographed (eluent 20% ethyl acetate–light petroleum) to afford the *diacetate* **9** (695 mg, 69%) as pale yellow rectangles, m.p. 170–171 °C (methylene dichloride–light petroleum) (Found: C, 60.55; H, 5.35. $C_{19}H_{20}O_8$ requires C, 60.65; H, 5.3%); ν_{max}/cm^{-1} 1763 and 1754 (OAc) and 1680 (C=O); δ_H 2.34 and 2.39 (each 3 H, s, $OCOCH_3$), 2.57 (3 H, s, $CCOCH_3$), 3.77, 3.90 and 3.95 (each 3 H, s, OCH_3), 6.69 (1 H, s, 7-H) and 7.43 (1 H, s, 3-H); δ_C 20.60 and 21.38 (CH_3CO_2) 30.74 (CH_3COC), 56.09, 56.48 and 61.55 (3 × OCH_3), 97.32 (C-7), 115.37 (C-8a)[b], 119.85 (C-3), 124.73 (C-2)[a], 126.29 (C-4a)[b],

135.45 (C-1)[a], 142.47 (C-4)[a], 144.81 (C-6), 152.03 (C-5), 154.37 (C-8), 169.38 (2 × CO) and 195.95 (CO) (assignments with the same superscript may be interchanged); *m/z* 376 (M^+, 23%), 334 (35), 292 (80), 277 (100) and 43 (43).

4-*Acetoxy*-2-*acetyl*-1,5,6,8-*tetramethoxynaphthalene* **10**.—The acetate **9** (684 mg, 1.82 mmol) was dissolved by warming in methanol (70 cm^3). To the cooled solution was added a methanolic solution of potassium hydroxide (to give a 1% w/v solution, 2.18 mmol) and the solution was stirred at room temperature for 10 min. To the reaction mixture was added water (100 cm^3) and methylene dichloride (150 cm^3) and the whole was then carefully acidified with dilute hydrochloric acid. The residue obtained upon work-up was immediately dissolved in dry acetone (150 cm^3), and dry potassium carbonate (1.25 g, 9.06 mmol) and dimethyl sulphate (1.15 g, 9.06 mmol) were added, and the mixture boiled with stirring for 3 h. The cooled reaction mixture was filtered and evaporated. The residue was chromatographed (eluent 50% ethyl acetate–light petroleum) to afford the *product* **10** (551 mg, 87%) as prisms, m.p. 158–160 °C (propan-2-ol) (Found: C, 62.15; H, 5.7. $C_{18}H_{20}O_7$ requires C, 62.1; H, 5.8%); ν_{max}/cm^{-1} 1758 (OAc) and 1646 (C=O); δ_H 2.21 (3 H, s, $OCOCH_3$), 2.61 (3 H, s, $CCOCH_3$), 3.67, 3.71, 3.87 and 3.90 (each 3 H, s, OCH_3), 6.64 (1 H, s, 3-H) and 7.27 (1 H, s, 7-H); δ_C 20.63 (CH_3CO_2) and 31.20 (CH_3COC), 56.44, 56.73, 61.82 and 63.87 (4 × OCH_3), 96.96 (C-7), 116.30 (C-8a)[a], 120.18 (C-3), 126.53 (C-4a)[a], 126.73 (C-2)[a], 135.5 (C-1), 140.97 (C-4), 152.06 (C-6), 154.72 (C-5), 156.81 (C-8), 169.64 (CH_3CO_2) and 198.70 (CH_3COC) (assignments with the same superscript may be interchanged); *m/z* 348 (M^+, 35%), 306 (53), 291 (100), 263 (12) and 42 (43).

2-*Acetyl*-4-*allyloxy*-1,5,6,8-*tetramethoxynaphthalene* **11**.—Compound **10** (551 mg, 1.04 mmol) was dissolved by warming in methanol (100 cm^3). To the cooled solution was added a methanolic solution of potassium hydroxide (to give a 5% w/v solution, 5.20 mmol) and the solution was stirred for 10 min. To the reaction mixture was added water (70 cm^3) and methylene dichloride (100 cm^3) and the whole was then carefully acidified with dilute hydrochloric acid. The residue obtained upon work-up was dissolved in dry acetone (100 cm^3). Dry potassium carbonate (1.1 g, 8.0 mmol) and allyl bromide (0.96 g, 7.9 mmol) were added and the mixture was boiled with stirring for 16 h. The cooled reaction mixture was filtered and evaporated. The residue was chromatographed (eluent 30% ethyl acetate–light petroleum) to afford the *product* **11** (507 mg, 92%) m.p. 85.5–86.5 °C (cyclohexane) (Found: C, 66.25; H, 6.3. $C_{19}H_{22}O_6$ requires C, 65.90; H, 6.35%); ν_{max}/cm^{-1} 1657 (C=O); δ_H 2.73 (3 H, s, $COCH_3$), 3.77, 3.78, 4.00 and 4.01 (each 3 H, s, OCH_3), 4.62 (2 H, dt, *J* 5.3 and 1.4, $ArCH_2$), 5.29 (1 H, ddd, *J* 10.5, 3.2 and 1.4, vinyl CH_2), 5.53 (1 H, ddd, *J* 17.3, 3.2 and 1.7, vinyl CH_2), 6.16 (1 H, ddd, *J* 17.3, 10.5 and 5.3, vinyl CH), 6.74 (1 H, s, 3-H) and 7.09 (1 H, s, 7-H); δ_C 31.32 (CH_3C), 56.71, 56.78, 61.93 and 63.64 (4 × OCH_3), 70.82 (OCH_2), 97.56 (C-7), 107.84 (=CH), 116.51 (C-8a)[b], 117.44 (=CH_2), 126.59 (C-4a)[b], 126.67 (C-1)[b], 133.27 (C-3), 138.03 (C-2), 150.66 (C-4)[a], 152.21 (C-6)[a], 153.02 (C-5), 154.20 (C-8) and 200.05 (CO) (assignments with the same superscript may be interchanged); *m/z* 346 (M^+, 75%), 305 (100), 289 (36), 275 (20), 270 (12), 245 (17), 43 (56) and 41 (58).

2-*Acetyl*-3-*allyl*-4-*benzyloxy*-1,5,6,8-*tetramethoxynaphthalene* **17**.—Compound **11** (507 mg, 1.47 mmol) was heated under nitrogen at 125 °C for 24 h. The product was immediately dissolved in dry acetone (50 cm^3) and dry potassium carbonate (1.00 g, 7.35 mmol) and benzyl bromide (1.25 g, 0.87 cm^3, 7.35 mmol) were added and the mixture was boiled with stirring for 27 h. The cooled reaction mixture was filtered and evaporated. The residue was chromatographed (eluent 5–30% ethyl acetate–light petroleum) to afford the *product* **17** (525 mg, 82%) as a pale yellow oil. (Found: M^+, 436.1877. $C_{26}H_{28}O_6$ requires *M*, 436.1886); ν_{max}/cm^{-1} (film) 1696 (C=O); δ_H 2.58 (3 H, s, $COCH_3$), 3.57 (2 H, br d, *J* 6.0 $ArCH_2$), 3.68 and 3.74 (each 3 H, s, OCH_3), 4.02 (6 H, s, 2 × OCH_3), 4.89 (2 H, s, CH_2Ph), 4.95 (1 H, dd, *J* 16.4 and 1.7, vinyl CH_2), 5.03 (1 H, dd, *J* 10.4 and 1.5, vinyl CH_2), 5.95 (1 H, ddt, *J* 16.4, 10.4 and 6.0, vinyl CH), 6.74 (1 H, s, 7-H) and 7.3–7.6 (5 H, m, $PhCH_2$); *m/z* 436 (M^+, 7%), 345 (100), 314 (23), 286 (13), 91 (47) and 49 (23).

3-*Allyl*-4-*benzyloxy*-2-(1-*hydroxyethyl*)-1,5,6,8-*tetramethoxynaphthalene* **19**.—The ketone **17** (172 mg, 0.39 mmol) in dry ether (15 cm^3) was added to a stirred suspension of lithium aluminium hydride (23 mg, 0.61 mmol) in ether (10 cm^3). When TLC showed that all the starting material had been converted into product (*ca.* 5 min), the reaction was worked up by addition of saturated aqueous ammonium chloride, followed by anhydrous magnesium sulphate. Work-up of the filtrate gave a residue which was chromatographed (eluent 30% ethyl acetate–light petroleum) to afford the *product* **19** (160 mg, 93%) as a pale brown oil, (Found: M^+, 438.207. $C_{26}H_{30}O_6$ requires *M*, 438.204); ν_{max}(film)/cm^{-1} 3468 (OH), and 1604 and 1585 (C=C); δ_H 1.62 (3 H, d, *J* 6.6, CH_3CHOH), 3.40–3.59 (2 H, m, CH_2CH=), 3.68, 3.87, 3.99 and 4.01 (each 3 H, s, OCH_3), 4.83 and 4.86 (each 1 H, d, *J* 10.3, CH_2Ph), 4.95 (1 H, dd, *J* 17.3 and 1.7, vinyl CH_2), 5.07 (1 H, dd, *J* 10.3 and 1.6, vinyl CH_2), 5.16 (1 H, br q, *J* 6.6, $CHCH_3$), 6.07 (1 H, ddd, *J* 17.3, 10.3 and 5.2, vinyl CH), 6.74 (1 H, s, 7-H) and 7.30–7.56 (5 H, m, $PhCH_2$); δ_C 25.46 (CH_3C), 30.45 (CH_2C=), 56.92, 57.02, 62.36 and 63.70 (4 × OCH_3), 67.58 (CHOH), 76.66 (OCH_2), 97.27 (C-7), 115.83 (=CH_2), 116.12 (C-8a)[a], 125.35 (C-4a)[a], 127.60–129.25 (C of Ph), 132.36 (C-3), 136.68 (C-2)[b], 137.38 (=CH), 138.21 (C-1)[b], 147.71 (C-4), 149.96 (C-6), 151.37 (C-5) and 152.75 (C-8) (assignments with the same superscript may be interchanged); *m/z* 438 (M^+, 11%), 347 (100), 329 (24), 298 (15) and 91 (37).

trans-5-*Benzyloxy*-3,4-*dihydro*-6,7,9,10-*tetramethoxy*-1,3-*dimethyl*-1H-*naphtho*[2,3-c]*pyran* **21** *and* cis-5-*benzyloxy*-3,4-*dihydro*-6,7,9,10-*tetramethoxy*-1,3-*dimethyl*-1H-*naphtho*[2,3-c]-*pyran* **23**.—A mixtue of the alcohol **19** (160 mg, 0.37 mmol) and mercury(II) acetate (134 mg, 0.37 mmol) in tetrahydrofuran (THF) (5 cm^3) and water (5 cm^3) was stirred for 1 h. Sodium hydroxide (3 mol dm^{-3}; 3.0 cm^3) was added and the mixture stirred for 1 h, after which sodium borohydride (3 mol dm^{-3} solution in 3 mol dm^{-3} aqueous sodium hydroxide; 3.0 cm^3) was added. The mixture was stirred at room temperature for 40 min, then diluted with water and extracted with ethyl acetate (3 times). The residue obtained upon work-up was flash chromatographed (eluent 50% ethyl acetate–light petroleum), and the resulting residue was subjected to PLC (eluent 7% ethyl acetate–light petroleum) to give firstly the cis-*compound* **23** (45 mg, 28%) as an oil. (Found: M^+, 438.2052. $C_{26}H_{30}O_6$ requires *M*, 438.2042); ν_{max}(film)/cm^{-1} 1606 and 1590 (C=C); δ_H 1.35 (3 H, d, *J* 6.1, 3-CH_3), 1.64 (3 H, d, *J* 6.3, 1-CH_3), 2.49 (1 H, dd, *J* 16.2 and 10.7, 4-H_a), 3.10 (1 H, dd, *J* 16.2 and 1.4, 4-H_e), 3.60 (1 H, ddq, *J* 10.7, 6.1 and 1.4, 3-H), 3.72, 3.74, 4.00 and 4.01 (each 3 H, s, OCH_3), 4.86 and 4.94 (each 1 H, d, *J* 10.4, CH_2Ph), 5.20 (1 H, q, *J* 6.3, 1-H), 6.69 (1 H, s, 8-H) and 7.3–7.6 (5 H, m, Ph); *m/z* 438 (M^+, 11%), 347 (100), 303 (87), 91 (68) and 43 (19). The second fraction afforded the trans-*compound* **21** (45 mg, 28%) as opaque clusters, m.p. 139–140.5 °C (light petroleum) (Found: C, 71.05; H, 7.2. $C_{26}H_{30}O_6$ requires C, 71.25; H, 6.9%); ν_{max}/cm^{-1} 1609 and 1591 (C=C); δ_H 1.33 (3 H, d, *J* 6.3, 3-CH_3), 1.60 (3 H, d, *J* 6.6, 1-CH_3), 2.53 (1 H, dd, *J* 17.3 and 11.2, 4-H_a), 3.10 (1 H, dd, *J* 17.3 and 3.4, 4-H_e), 3.71 and 3.76 (each 3 H, s, OCH_3), 4.00 (6 H, s, 2 × OCH_3), 3.9–4.15 (1 H, m, obscured by OCH_3 peaks, 3-H), 4.79 and 4.94 (each 1 H, d, *J* 10.0, CH_2Ph), 5.29 (1 H, q, *J*

6.6, 1-H), 6.68 (1 H, s, 8-H) and 7.3–7.6 (5 H, m, Ph); *m/z* 438 (M^+, 9%), 347 (100), 303 (67), 91 (58) and 43 (23).

cis-3,4-*Dihydro*-6,7,9-*trimethoxy*-1,3-*dimethyl*-1H-*naphtho*-[2,3-c]*pyran*-5,10-*quinone* (*ventiloquinone E*) **1**.—Compound **23** (22 mg, 0.05 mmol) in ethyl acetate (10 cm^3) was stirred together with 10% Pd–C (20 mg) and a drop of concentrated hydrochloric acid at room temperature under an atmosphere of hydrogen for 30 min. After filtration and evaporation of the solvent under reduced pressure the residue was flash chromatographed (eluent ethyl acetate) to afford the naphthol **24**, which was immediately dissolved in a mixture of acetonitrile (5 cm^3) and water (2 cm^3). A solution of cerium(IV) ammonium nitrate (70 mg, 1.28 mmol) in water (5 cm^3) was added dropwise with stirring over a period of 10 min. The solution was stirred for a further 15 min and then poured into water (20 cm^3). This was extracted with methylene dichloride (2 × 40 cm^3). The residue obtained upon work-up was chromatographed (eluent 30% ethyl acetate–light petroleum) to afford the *quinone* **1** (13 mg, 78%) as orange crystals, which proved to be identical in spectroscopic and physical properties with a sample of natural origin m.p. 129–130 °C (sample of natural origin, supplied by Prof. R. H. Thomson, m.p. 130–130.5 °C) (Found: M^+, 332.1278. Calc. for $C_{18}H_{20}O_6$: *M*, 332.1260); spectroscopic[3] and thin layer chromatographic comparison of the synthetic with the naturally derived sample of ventiloquinone E showed them to be identical; δ_H 1.33 (3 H, d, *J* 6.2, 3-CH_3), 1.49 (3 H, d, *J* 6.6, 1-CH_3), 2.10 (1 H, ddd, *J* 18.3, 10.3 and 3.7, 4-H_a), 2.78 (1 H, dt, *J* 18.3, 2.6 and 2.6, 4-H_e), 3.53 (1 H, ddq, *J* 10.3, 6.2 and 2.6, 3-H), 3.86 (3 H, s, OCH_3), 3.96 (6 H, s, 2 × OCH_3), 4.80 (1 H, ddq, *J* 6.6, 3.7 and 2.6, 1-H) and 6.71 (1 H, s, 8-H); *m/z* 332 (M^+, 89%), 317 (100), 303 (10), 302 (29) and 299 (14).

4-*Acetoxy*-2-*acetyl*-1-*benzyloxy*-5,6,8-*trimethoxynaphthalene* **12**.—The diacetate **9** (181 mg, 0.48 mmol) was dissolved by warming in methanol (30 cm^3). To the cooled solution was added a methanolic solution of potassium hydroxide (to give a 1% w/v solution, 0.58 mmol) and the solution was stirred for 10 min. To the reaction mixture was added water (50 cm^3) and methylene dichloride (100 cm^3) and the whole was then carefully acidified with dilute hydrochloric acid. The residue obtained upon work-up was flash chromatographed (50% ethyl acetate–light petroleum) to yield 4-acetoxy-2-acetyl-5,6,8-trimethoxy-1-naphthol which was immediately dissolved in dry acetone (50 cm^3). Dry potassium carbonate (330 mg, 2.39 mmol) and benzyl bromide (410 mg, 2.40 mmol) were added, and the mixture was boiled with stirring for 1 h. The cooled reaction mixture was filtered and the solution was evaporated. The residue was chromatographed (eluent 10% ethyl acetate–light petroleum) to afford the *product* **12** (173 mg, 85%) as white grains, m.p. 147–148 °C (propan-2-ol) (Found: C, 68.05; H, 5.8. $C_{24}H_{24}O_7$ requires C, 67.9; H, 5.65%); ν_{max}/cm^{-1} 1754 (OAc) and 1662 (C=O); δ_H 2.35 (3 H, s, $OCOCH_3$), 2.62 (3 H, s, $CCOCH_3$), 3.81, 3.84 and 3.99 (each 3 H, s, OCH_3), 4.93 (2 H, s, CH_2Ph), 6.73 (1 H, s, 7-H), 7.35 (1 H, s, 3-H) and 7.34–7.47 (5 H, m, $PhCH_2$); δ_C 20.61 (CH_3CO_2), 31.41 (CH_3COC), 56.47, 56.69 and 61.86 (3 × OCH_3), 78.81 (CH_2Ph), 97.12 (C-7), 116.65 (C-8a)[b], 120.21 (C-3), 124.84 (C-4a)[b], 126.5–128.45 (C of Ph), 135.92 (C-2)[a], 137.03 (C-1)[a], 141.25 (C-4)[a], 152.08 (C-6), 154.93 (C-5), 155.01 (C-8), 169.79 (CH_3CO_2) and 199.39 (CH_3COC) (assignments with the same superscript may be interchanged); *m/z* 424 (M^+, 28%), 382 (17), 340 (23), 325 (12), 291 (100), 234 (18), 233 (12), 91 (69) and 43 (61).

2-*Acetyl*-4-*allyloxy*-1-*benzyloxy*-5,6,8-*trimethoxynaphthalene* **13**.—Compound **12** (131 mg, 0.31 mmol) was dissolved by warming in methanol (30 cm^3). To the cooled solution was added a methanolic solution of potassium hydroxide (to give a 5% w/v solution, 1.55 mmol) and the solution was stirred for 10 min. To the reaction mixture was added water (50 cm^3) and methylene dichloride (100 cm^3) and then the whole was carefully acidified with dilute hydrochloric acid. The residue obtained upon work-up was dissolved in dry acetone (50 cm^3), and dry potassium carbonate (210 mg, 1.52 mmol) and allyl bromide (200 mg, 1.65 mmol) were added, and the mixture was boiled with stirring for 16 h. The cooled reaction mixture was filtered and evaporated. The residue was chromatographed (eluent 40% ethyl acetate–light petroleum to afford the *product* **13** (107 mg, 82%) as pale yellow plates, m.p. 105–106 °C (propan-2-ol) (Found: C, 71.2; H, 6.4. $C_{25}H_{26}O_6$ requires C, 71.1; H, 6.15%); ν_{max}/cm^{-1} 1646 (C=O); δ_H 2.72 (3 H, s, $COCH_3$), 3.89, 3.92 and 4.08 (each 3 H, s, OCH_3), 4.72 (2 H, br d, *J* 5.2, allyl CH_2), 4.96 (2 H, s, CH_2Ph), 5.39 (1 H, dd, *J* 10.5 and 1.4, vinyl CH_2), 5.64 (1 H, dd, *J* 17.2 and 1.7, vinyl CH_2), 6.27 (1 H, ddd, *J* 17.2, 10.5 and 5.2, vinyl CH), 6.85 (1 H, s, 7-H), 7.18 (1 H, s, 3-H) and 7.37–7.58 (5 H, m, Ph); δ_C 31.62 (CH_3C), 56.54, 56.80 and 61.96 (3 × OCH_3), 70.83 (OCH_2), 78.57 (CH_2Ph), 97.60 (C-3), 107.72 (=CH), 116.70 (C-8a)[b], 117.48 (=CH_2), 126.53 (C-4a)[b], 127.49–128.40 (C of Ph), 133.27 (C-7), 137.30 (C-1)[a], 138.07 (C-2)[a], 150.82 (C-4)[c], 150.94 (C-6)[c], 152.11 (C-5), 154.26 (C-8) and 200.51 (CO) (assignments with the same superscript may be interchanged); *m/z* 422 (M^+, 22%), 331 (47), 282 (15), 272 (10), 91 (100), 65 (13), 43 (29) and 41 (26).

2-*Acetyl*-3-*allyl*-1,4-*dibenzyloxy*-5,6,8-*trimethoxynaphthalene* **16**.—The allyl compound **13** (189 mg, 0.45 mmol) was heated under nitrogen at 125 °C for 24 h. The Claisen rearranged product of slightly higher R_f value was immediately dissolved in dry acetone (50 cm^3), and dry potassium carbonate (330 mg, 2.39 mmol) and benzyl bromide (410 mg, 2.40 mmol) was added and the mixture was boiled with stirring for 7 h. The cooled reaction mixture was filtered and evaporated. The residue was chromatographed (eluent 20% ethyl acetate–light petroleum) to afford the *product* **16** (190 mg, 83%) as white needles, m.p. 93–94 °C (propan-2-ol) (Found: C, 75.1; H, 6.0. $C_{32}H_{32}O_6$ requires C, 75.0; H, 6.25%); ν_{max}/cm^{-1} 1695 (C=O); δ_H 2.60 (3 H, s, $COCH_3$), 3.61 (2 H, br d, *J* 5.0, $ArCH_2$), 3.73, 3.91 and 4.04 (each 3 H, s, OCH_3), 4.87 and 4.95 (each 2 H, s, OCH_2Ph), 4.95–5.10 (2 H, m, partly obscured by peak at δ 4.95, vinyl CH_2), 5.90–6.10 (1 H, m, vinyl CH), 6.75 (1 H, s, 7-H) and 7.34–7.61 (10 H, m, Ph); δ_C 30.69 (CH_3C), 33.40 (CH_2–CH=), 56.38, 56.68 and 62.25 (3 × OCH_3), 76.74 and 78.38 (2 × CH_2Ph), 96.48 (C-7), 115.81 (C-8a)[b], 116.03 (=CH_2), 126.04 (C-4a)[b], 127.45–128.21 (C of 2 × Ph), 133.15 (C-3), 136.62 (=CH), 137.24 (C-1)[b], 137.71 (C-2)[b], 147.83 (C-4)[c], 147.96 (C-6)[c], 150.60 (C-5), 153.34 (C-8) and 205.53 (CO) (assignments with the same superscript may be interchanged); *m/z* 512 (M^+, 5%), 421 (21), 330 (9), 280 (13), 91 (81) and 57 (95).

cis-5-*Benzyloxy*-3,4-*dihydro*-7,10-*dimethoxy*-1,3-*dimethyl*-1H-*naphtho*[2,3-c]*pyran*-6,9-*quinone* **25**.—The naphthalene **23** (31 mg, 0.071 mmol), silver(II) oxide (45 mg, 0.36 mmol) and dioxane (5 cm^3) were stirred together at room temperature. Nitric acid (6 mol dm^{-3}; 0.4 cm^3) was added and the reaction mixture stirred for 5 min. A mixture of methylene dichloride (10 cm^3) and water (3 cm^3) was added and the organic layer was separated and washed with more water. The residue obtained upon work-up was chromatographed (eluent 50% ethyl acetate–light petroleum), to afford the *quinone* **25** (25 mg, 87%) as orange needles, m.p. 180–182 °C (methanol) (Found: C, 70.2; H, 5.8. $C_{24}H_{24}O_6$ requires C, 70.55; H, 5.9%); ν_{max}/cm^{-1} 1676 and 1636 (C=O) and 1623 (C=C); δ_H 1.29 (3 H, d, *J* 6.2, 3-CH_3), 1.57 (3 H, d, *J* 6.4, 1-CH_3), 2.32 (1 H, ddd, *J* 17.0, 10.6 and 1.8, 4-H_a), 2.87 (1 H, ddd, *J* 17.0, 2.0 and 1.5, 4-H_e), 3.47 (1 H, ddq, *J* 10.6, 6.2 and 2.0, 3-H), 3.79 and 3.85 (each 3 H, s, OCH_3), 4.84 and 4.96 (each 1 H, d, *J* 10.2, CH_2Ph), 5.02 (1 H, ddq, *J* 6.4,

1.8 and 1.5, 1-H), 6.05 (1 H, s, 8-H) and 7.3–7.6 (5 H, m, Ph); *m/z* 408 (M^+, 17%), 317 (7), 273 (23) and 91 (100).

cis-3,4-*Dihydro*-5-*hydroxy*-7,10-*dimethoxy*-1,3-*dimethyl*-1H-*naphtho*[2,3-c]*pyran*-6,9-*quinone* **5**.—The naphthalene **25** (14 mg, 0.034 mmol) in ethyl acetate (7 cm^3) was stirred together with 10% Pd–C (15 mg) and a drop of concentrated hydrochloric acid at room temperature under an atmosphere of hydrogen for 1 h. After filtration and evaporation of the solvent under reduced pressure the residue was flash chromatographed (eluent 50% ethyl acetate–light petroleum) to afford the *naphthol* **5** (9 mg, 82%) as orange needles, m.p. 163–164 °C (light petroleum) (Found: M^+, 318.1108. $C_{17}H_{18}O_6$ requires *M*, 318.1103); ν_{max}/cm^{-1} 3394 (OH), and 1646 and 1638 (C=O); δ_H 1.35 (3 H, d, *J* 6.1, 3-CH_3), 1.56 (3 H, d, *J* 6.4, 1-CH_3), 2.38 (1 H, ddd, *J* 17.5, 10.5 and 1.9, 4-$H_{a'}$), 2.88 (1 H, ddd, *J* 17.5, 1.9 and 1.9, 4-$H_{e'}$) 3.58 (1 H, ddq, *J* 10.5, 6.1 and 1.9, 3-H), 3.76 and 3.85 (each 3 H, s, OCH_3), 4.97 (1 H, qt, *J* 6.4 and 1.9, 1-H), 6.02 (1 H, s, 8-H) and 12.79 (1 H, s, OH, D_2O exchangeable); *m/z* 318 (M^+, 100%), 303 (77), 288 (50), 273 (29), 258 (50), 245 (25), 231 (19), 167 (15), 115 (23), 69 (40) and 43 (76).

trans-5-*Benzyloxy*-3,4-*dihydro*-7,10-*dimethoxy*-1,3-*dimethyl*-1H-*naphtho*[2,3-c]*pyran*-6,9-*quinone* **26**.—The naphthalene **21** (31 mg, 0.071 mmol), silver(II) oxide (45 mg, 0.36 mmol), and dioxane (5 cm^3) were stirred together at room temperature. Nitric acid (6 mol dm^{-3}; 0.4 cm^3) was added and the reaction mixture was stirred for 5 min after which a mixture of methylene dichloride (10 cm^3) and water (3 cm^3) was added and the organic layer was separated and washed with more water. The residue obtained upon work-up was chromatographed (eluent 50% ethyl acetate–light petroleum) to afford the *quinone* **26** (22 mg, 76%) as yellow needles, m.p. 128.5–129.5 °C (methanol) (Found: M^+, 408.1592. $C_{24}H_{24}O_6$ requires *M*, 408.1573); ν_{max}/cm^{-1} 1676 and 1637 (C=O) and 1628 (C=C); δ_H 1.27 (3 H, d, *J* 6.1, 3-CH_3), 1.53 (3 H, d, *J* 6.6, 1-CH_3), 2.30 (1 H, ddd, *J* 17.8, 10.8 and 0.8, 4-$H_{a'}$), 2.89 (1 H, dd, *J* 17.8 and 3.4, 4-$H_{e'}$), 3.83 and 3.85 (each 3 H, s, OCH_3), 3.75–4.05 (1 H, m, partly obscured by OCH_3 peaks, 3-H), 4.80 and 4.98 (each 1 H, d, *J* 10.2, CH_2Ph), 5.13 (1 H, br q, *J* 6.6, 1-H), 6.03 (1 H, s, 8-H) and 7.3–7.6 (5 H, m, Ph); *m/z* 408 (M^+, 9%), 317 (5), 273 (12), 91 (100) and 57 (55).

trans-3,4-*Dihydro*-5-*hydroxy*-7,10-*dimethoxy*-1,3-*dimethyl*-1H-*naphtho*[2,3-c]*pyran*-6,9-*quinone* **6**.—The quinone **26** (21 mg, 0.05 mmol) in ethyl acetate (10 cm^3) was stirred together with 10% Pd–C (20 mg) and a drop of concentrated hydrochloric acid at room temperature under an atmosphere of hydrogen for 1 h. After filtration and evaporation of the solvent under reduced pressure, the residue was flash chromatographed (eluent 50% ethyl acetate-light petroleum) to afford the *naphthol* **6** (15 mg, 92%) as orange needle clusters, m.p. 219–220 °C (light petroleum) (Found: C, 63.85; H, 5.35. $C_{17}H_{18}O_6$ requires C, 64.15; H, 5.65%); ν_{max}/cm^{-1} 3368 (OH), 1634 (C=O) and 1611 (C=C); δ_H 1.38 (3 H, d, *J* 6.2, 3-CH_3), 1.58 (3 H, d, *J* 6.6, 1-CH_3), 2.39 (1 H, ddd, *J* 18.3, 10.7 and 0.9, 4-$H_{a'}$), 2.89 (1 H, dd, *J* 18.3 and 3.6, 4-$H_{e'}$), 3.82 and 3.88 (each 3 H, s, OCH_3), 4.07 (1 H, ddq, *J* 10.7, 6.2 and 3.6, 3-H), 5.12 br. (1 H, q, *J* 6.6, 1-H), 6.06 (1 H, s, 8-H) and 12.83 (1 H, s, OH, D_2O exchangeable); *m/z* 318 (M^+, 100%), 303 (97), 288 (70), 259 (35), 245 (27), 231 (16), 167 (13), 115 (15), 69 (20) and 43 (31).

cis-3,4-*Dihydro*-5,7,10-*trihydroxy*-1,3-*dimethyl*-1H-*naphtho*-[2,3-c]*pyran*-6,9-*quinone* (*ventiloquinone G*) **3**.—The naphthoquinone **25** (23 mg, 0.06 mmol) was treated with concentrated hydrochloric acid (10 cm^3) in boiling ethanol (10 cm^3) for 30 min. The reaction was quenched by the addition of water (30 cm^3) and the mixture was extracted with methylene dichloride (2 × 20 cm^3). The residue obtained upon work-up was chromatographed on deactivated silica (eluent 40% ethyl acetate–light petroleum) to afford (±)-*ventiloquinone G* (13 mg, 74%) as orange–red crystals, m.p. 183 °C (sample of natural origin, m.p. 183 °C) (Found: C, 62.35; H, 4.80%; M^+ 290.0808. $C_{15}H_{14}O_6$ requires C, 62.05; H, 4.85%; *M*, 290.0790); λ_{max}/nm (log ε) ($CHCl_3$) 258 (4.07), 317 (3.84), 480 (3.73), 500 (3.74) and 510 (3.76); ν_{max}/cm^{-1} 3349 (OH), 1630 (C=O) and 1608 (C=C); δ_H 1.37 (3 H, d, *J* 6.2, 3-CH_3), 1.62 (3 H, d, *J* 6.4, 1-CH_3), 2.40 (1 H, ddd, *J* 17.6, 10.3 and 2.6, $H_{4a'}$) 2.87 (1 H, ddd, *J* 17.6, 2.1 and 2.0, $H_{4e'}$), 3.62 (1 H, ddq, *J* 10.3, 6.2 and 2.1, 3-H), 5.02 (1 H, qt, *J* 6.4, 2.2 and 2.0, 1-H), 6.34 (1 H, s, 8-H), 7.40. (1 H, br s, 7-OH) and 11.96 and 13.46 (each 1 H, s, 6- and 9-OH); *m/z* 290 (M^+, 100%), 275 (53), 248 (30), 247 (25) and 246 (26). This product had the same TLC behaviour as the natural material.

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