Synthesis of 2-Methoxystypandrone: Comments on the Structure of Ventilaginone

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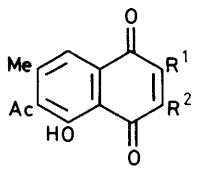
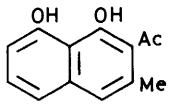
The structure of 2-methoxystypandrone a naphthoquinone isolated from *Polygonum cuspidatum*, *Rhamnus fallax*, and *Ventilago calyculata* is confirmed by synthesis as 6-acetyl-5-hydroxy-2-methoxy-7-methylnaphthalene-1,4-dione (**1**). The structure proposed for ventilaginone, an unusual naphthalene isolated from *Ventilago maderaspatana*, 8,9-dimethoxy-5-methylnaphtho[1,8-*de*]-1,3-dioxin-4-yl methyl ketone (**17**), is shown by synthesis to be erroneous. Alternative structures are considered.

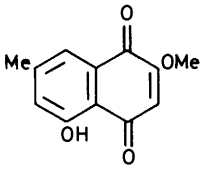
The naphthoquinone 2-methoxystypandrone (**1**), a compound closely related to both dianellidin (**4**) and stypandrone (**2**),[1] has recently been isolated from a number of plant sources. Kimura and his co-workers[2] isolated 2-methoxystypandrone (**1**) from the dried roots of *Polygonum cuspidatum* Sieb. et Zucc., a nostrum in traditional Chinese and Japanese medicine. Their structural determination relied heavily on the interpretation of spectroscopic data and the deacetylation of 2-methoxystypandrone (**1**) to the naphthoquinone (**5**). Miething and



(**1**) R^1 = OMe, R^2 = H
(**2**) R^1 = R^2 = H
(**3**) R^1 = H, R^2 = OMe



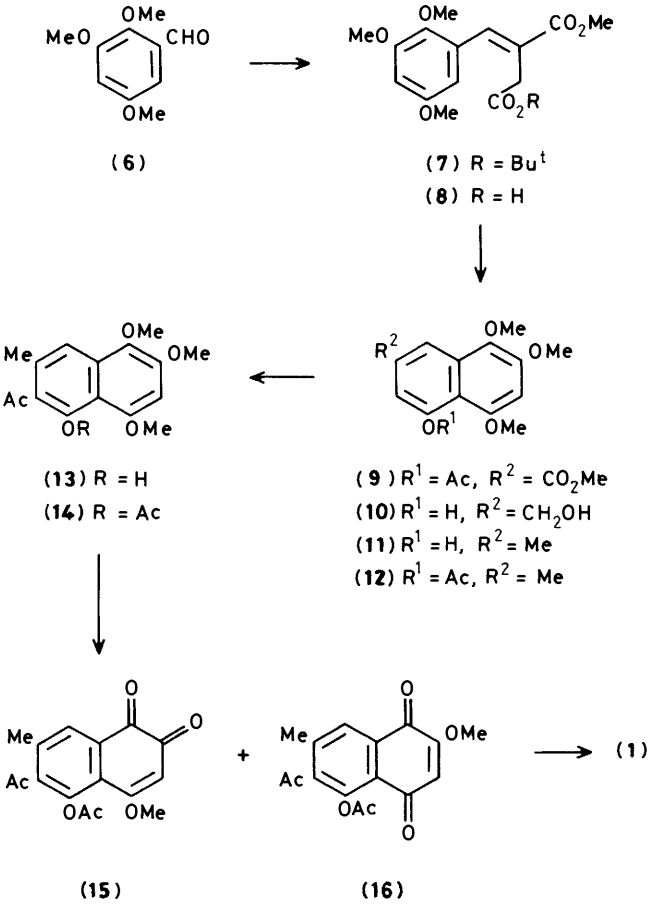
(**4**)



(**5**)

Rauwald[3] isolated 2-methoxystypandrone from the stem bark of *Rhamnus fallax* Boiss., and Rao and Thomson and their co-workers[4] isolated it from the root bark of *Ventilago calyculata*. These groups also relied heavily on spectroscopic evidence for the structural determination. Apparently none of these samples of 2-methoxystypandrone has been directly compared. It has also been suggested that orientalone, a compound claimed to have structure (**3**),[5] is in fact 2-methoxystypandrone.[4]

We have now confirmed the structure of 2-methoxystypandrone by synthesis. Thus, the readily available benzaldehyde (**6**) was caused to undergo a Wittig reaction in boiling benzene with 2-t-butoxycarbonyl-1-methoxycarbonylethylidenetriphenylphosphorane[6] and the resultant itaconic ester (**7**) was deprotected by exposure to trifluoroacetic acid. The itaconic half-acid (**8**), so obtained, underwent ring-closure on treatment with potassium acetate in boiling acetic anhydride. The resultant naphthalene (**9**) was reduced first with lithium aluminium hydride which supplied the diol (**10**), and then catalytic reduction with hydrogen over palladized charcoal afforded the naphthol (**11**). The derived acetate (**12**) on subjection to Fries rearrangement under mild conditions gave solely the ketone (**13**) as shown by its spectroscopic properties, in particular the presence of a lowfield signal ascribed to an intramolecularly hydrogen-bonded hydroxy group in its ^{1}H n.m.r. spectrum. The derived acetate (**14**) on oxidation with ammonium cerium(IV) nitrate yielded both an *o*- (**15**) and a *p*-quinone (**16**) which were differentiated on the grounds of their electronic spectra. Naphthalene-1,2-diones absorb at longer

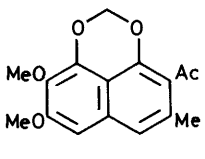


(**6**)
(**7**) R = Bu^t
(**8**) R = H
(**9**) R^1 = Ac, R^2 = CO_2Me
(**10**) R^1 = H, R^2 = CH_2OH
(**11**) R^1 = H, R^2 = Me
(**12**) R^1 = Ac, R^2 = Me
(**13**) R = H
(**14**) R = Ac
(**15**)
(**16**)
(**1**)

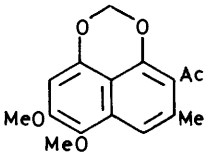
wavelengths than the isomeric 1,4-quinones. Thus 4-methoxynaphthalene-1,2-dione absorbs at 404 nm[7] whereas the longest wavelength absorption in the electronic spectrum of the isomeric 2-methoxynaphthalene-1,4-dione is at 333 nm.[8] The major isomer proved to be the *p*-isomer (**16**) and on hydrolysis of the acetate it provided synthetic 2-methoxystypandrone which was identical with an authentic sample by all the usual criteria so that structure (**1**) is confirmed.

Thomson and Rao and their co-workers[4] isolated a naphthalene ventilaginone, from *Ventilago maderaspatana* to which they ascribe the unusual structure (**17**). The 1,8-methylenedioxy group appears to be unique among naphthalenoid natural products. The orientation of the methylenedioxy group was deduced from a comparison of the ^{1}H n.m.r. spectra of the three possible methylenedioxy isomers in the naphthalene series and the conclusion is in accord with similar data.[9] Information

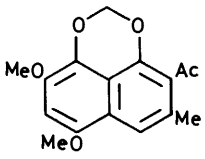
about the arrangement of substituents was sought from n.O.e experiments and these showed that a methoxy group and the methyl group were each adjacent to different aromatic protons. If the substitution pattern of the ring bearing the acetyl group is correct, and it is common to many naphthalenoid natural products, there are then three possible structures for ventilaginone: (**17**), (**18**), and (**19**). Structure (**17**) was preferred



(**17**)



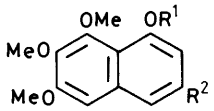
(**18**)



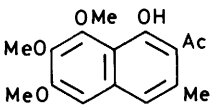
(**19**)

on the grounds that only one methoxy group signal in the ^1H n.m.r. spectrum suffered a benzene induced solvent shift, and it was also argued that the chemical shift, δ 6.69, of the proton adjacent to a methoxy group was too low field for a β-proton. We now show, by synthesis, that structure (**17**) is erroneous.

The known naphthalene (**20**)[10] was converted *via* the diol (**21**) into the naphthol (**22**). The derived acetate (**23**) again yielded only one ketone, ascribed structure (**24**), on Fries



(**20**) R^1 = Ac, R^2 = CO_2Me
(**21**) R^1 = H, R^2 = CH_2OH
(**22**) R^1 = H, R^2 = Me
(**23**) R^1 = Ac, R^2 = Me



(**24**)

rearrangement. We have previously shown that in naphthalenes hindered α-methoxy groups can often be cleaved by boron trichloride in the presence of β-methoxy groups.[11] Consequently treatment of the ketone (**24**) with boron trichloride gave an unstable diol which on methylenation provided compound (**17**). The m.p. and ^1H n.m.r. spectrum of compound (**17**) were different to those published for ventilaginone so that structure (**17**) is incorrect. In an attempt to synthesize compound (**18**), a possible alternative structure, we treated the naphthol (**13**) with boron trichloride and subjected the product to methylenation but we were unable to isolate any pure product from this reaction. It is likely, then, that ventilaginone is either compound (**18**) or (**19**). The benzene-induced solvent shift data[4] would favour structure (**18**).

Experimental

General directions have been given previously.[12] ^{13}C N.m.r. spectra were recorded at 20.1 MHz on a Bruker WP-80 instrument or at 75.5 MHz on a Bruker AM-300 instrument for solutions in deuteriochloroform.

2,3,5-*Trimethoxybenzaldehyde* (**6**).—A solution of 2,3,5-trimethoxybenzoic acid (18.3 g)[13] in anydrous tetrahydrofuran (330 ml) was added to a stirred suspension of lithium aluminium hydride (5.0 g) in tetrahydrofuran (100 ml) and the mixture was then heated under reflux for 2 h. The cooled solution was treated with an excess of saturated aqueous sodium sulphate and the product was isolated with ethyl acetate. The crude alcohol was stirred and heated under reflux in benzene (500 ml) with activated manganese dioxide (64.0 g) in a Dean-Stark apparatus for 18 h. The manganese dioxide was separated by filtration and the residue left on removal of the solvent was crystallized from light petroleum which gave the aldehyde (**6**) (13.0 g, 81%) as pale yellow needles, m.p. 62—64 °C (lit.,[14] 62—63 °C).

(E)-3-*Methoxycarbonyl*-4-(2,3,5-*trimethoxyphenyl*)*but*-3-*enoic Acid* (**8**).—A solution of the aldehyde (**6**) (5.0 g) and 2-t-butoxycarbonyl-1-methoxycarbonylethylidenetriphenylphosphorane (17.1 g) in anhydrous benzene was heated under reflux under an atmosphere of argon. At intervals of 29, 16, and 45 h successive additions of the phosphorane (2.3, 5.7, and 2.3 g) were made, and the reaction was worked up after a further 29 h. The crude product was passed through a column of silica gel with 20% ethyl acetate–light petroleum as eluant and the eluate was further purified by radial chromatography with 15% ethyl acetate–light petroleum as eluant. The ester (**7**) (7.33 g, 78%) was obtained as a viscous oil which was dissolved in trifluoroacetic acid (20 ml) and stirred at room temperature for 21 h. The solvent was removed under diminished pressure and the last traces were removed by azeotroping with benzene. The crude product was dissolved in ethyl acetate and purified by extraction with aqueous sodium hydrogen carbonate in the usual way. It was then recrystallized from dichloromethane–light petroleum to give needles (5.03 g, 81%) of the *acid* (**8**), m.p. 128—129 °C (Found: C, 58.3; H, 5.9%; M^+, 310. $C_{15}H_{18}O_7$ requires C, 58.05; H, 5.85%; *M*, 310); δ_H(80 MHz) 3.53 (2 H, s, CH_2), 3.71 and 3.76 (each 3 H, s, OMe), 3.85 (6 H, s, 2 × OMe), 6.38 and 6.53 (2 H, AB, *J* 2.7 Hz, ArH), and 7.92 (1 H, br, OH).

Methyl 4-*Acetoxy*-5,7,8-*trimethoxynaphthalene*-2-*carboxylate* (**9**).—The acid (**8**) (4.14 g) and anhydrous potassium acetate (2.5 g) were heated under reflux in acetic anhydride (35 ml) for 1.5 h. The solution was poured into water and after the acetic anhydride had hydrolysed the crude product was isolated by extraction with ethyl acetate in the usual way. It was purified by radial chromatography with 40% ethyl acetate–light petroleum as eluant. The *ester* (**9**) (4.34 g, 96%) crystallized from dichloromethane–light petroleum as yellow needles, m.p. 144—146 °C (Found: C, 61.15; H, 5.5%; M^+, 334. $C_{17}H_{18}O_7$ requires C, 61.05; H, 5.45%; *M*, 334) δ_H(80 MHz) 2.32 (3 H, s, COMe), 3.86 (3 H, s, OMe), 3.93 (9 H, s, 3 × OMe), 6.72 (1 H, s, 6-H), and 7.50 and 8.70 (2 H, AB, $J_{1,3}$ 1.7 Hz, 1- and 3-H).

3-(*Hydroxymethyl*)-5,6,8-*trimethoxy*-1-*naphthol* (**10**).—A solution of the foregoing ester (**9**) (4.6 g) in anhydrous tetrahydrofuran (150 ml) was added dropwise at 0 °C to a stirred suspension of lithium aluminium hydride (1.32 g) in tetrahydrofuran (50 ml). The solution was then stirred at room temperature for 2 h after which the excess of lithium aluminium hydride was destroyed by the addition of saturated aqueous sodium sulphate followed by dilute hydrochloric acid. The crude product was isolated by extraction with ethyl acetate and then crystallized from chloroform–light petroleum to give needles (3.28 g, 89%) of the *diol* (**10**), m.p. 127—128 °C (Found: C, 63.6; H, 6.4%; M^+, 264. $C_{14}H_{16}O_5$ requires C, 63.65; H, 6.1%; M^+, 264); δ_H(300 MHz) 2.03 (1 H, br, OH), 3.84, 3.95, and 3.98 (each 3 H, s, OMe), 4.70 (2 H, s, CH_2), 6.49 (1 H, s, 7-H), 6.68 (1 H, d, $J_{2,4}$ 1.5 Hz, 2-H), 7.43 (1 H, s, *w*/2 3.5 Hz, 4-H), and 9.13 (1 H, s, OH).

5,6,8-*Trimethoxy*-3-*methyl*-1-*naphthol* (**11**).—A solution of the foregoing diol (**10**) (408 mg) in ethyl acetate (100 ml) containing concentrated hydrochloric acid (1 drop) was stirred with palladized charcoal (10%; 10 mg) under an atmosphere of hydrogen until absorption ceased. Work-up gave a crude product which was purified by radial chromatography with 20%

ethyl acetate–light petroleum as eluant. The naphthol (**11**) (373 mg, 88%) crystallized from dichloromethane–light petroleum as prisms, m.p. 144—145 °C (Found: C, 67.55; H, 6.75%; M^+, 248. $C_{14}H_{16}O_4$ requires C, 67.75; H, 6.5%; *M*, 248); δ_H(80 MHz) 2.43 (3 H, s, Me), 3.89, 3.96, and 4.00 (each 3 H, s, OMe), 6.51 (1 H, s, 7-H), 6.62 (1 H, d, $J_{2,4}$ 1.5 Hz, 2-H), 7.33 (1 H, br s, 4-H), and 9.10 (1 H, s, OH). The derived *acetate* (**12**) (acetic anhydride–pyridine, 95%) formed needles (from dichloromethane–light petroleum), m.p. 131—132 °C (Found: C, 66.3; H, 6.5%; M^+, 290. $C_{16}H_{18}O_5$ requires C, 66.2; H, 6.25%; *M*, 290); δ_H(300 MHz) 2.34 (3 H, s, COMe), 2.47 (3 H, apparent d, Me), 3.88, 3.89, and 3.95 (each 3 H, s, OMe), 6.57 (1 H, s, 7-H), 6.79 (1 H, d, $J_{2,4}$ 1.6 Hz, 2-H), and 7.74 (1 H, apparent q, 4-H).

1-*Hydroxy*-5,6,8-*trimethoxy*-3-*methyl*-2-*naphthyl Methyl Ketone* (**13**).—The acetate (**12**) (200 mg) was stirred at 50 °C (bath) for 1 h with boron trifluoride–diethyl ether (2.0 ml). The solution was then poured into water and the crude product was isolated by extraction with ethyl acetate in the usual way. It was then purified by radial chromatography with 30% ethyl acetate–light petroleum as eluant. The *ketone* (**13**) (144 mg, 72%) crystallized from dichloromethane–light petroleum as needles, m.p. 129—130 °C (Found: C, 66.2; H, 6.45%; M^+, 290. $C_{16}H_{18}O_5$ requires C, 66.2; H, 6.25%; *M*, 290); δ_H(300 MHz) 2.38 (3 H, d, $J_{Me,4}$ 0.7 Hz, Me), 2.60 (3 H, s, COMe), 3.85 (3 H, s, OMe), 3.93 (6 H, s, 2 × OMe), 6.47 (1 H, s, 7-H), 7.29 (1 H, apparent d, 4-H), and 9.80 (1 H, s, OH). The derived *acetate* (**14**) (acetic anhydride–pyridine, 95%) formed needles (from dichloromethane–light petroleum), m.p. 143—144 °C (Found: C, 65.25; H, 6.05%; M^+, 332. $C_{18}H_{20}O_6$ requires C, 65.05; H, 6.05%; *M*, 332); δ_H(80 MHz) 2.31 (3 H, s, OAc), 2.39 (3 H, d, $J_{Me,4}$ 0.6 Hz, Me), 2.50 (3 H, s, Ac), 3.88 (6 H, s, 2 × OMe), 3.95 (3 H, s, OMe), 6.61 (1 H, s, 7-H), and 7.77 (1 H, narrow q, 4-H).

Oxidation of the Acetate (**14**).—A solution of ammonium cerium(IV) nitrate (600 mg) in the minimum volume of water was added dropwise to a solution of the acetate (**14**) (210 mg) in acetonitrile (2.0 ml). The solution was stirred at room temperature for 1 h and then diluted with water and extracted with dichloromethane. The crude product was subjected to radial chromatography with 60% ethyl acetate–light petroleum as eluant. The first band to be eluted gave 5-*acetoxy*-6-*acetyl*-2-*methoxy*-7-*methylnaphthalene*-1,4-*dione* (**16**) (68 mg, 38%) which crystallized from benzene–light petroleum as yellow prisms, m.p. 143—145 °C (lit.,[2] 138—140 °C) (Found: C, 63.7; H, 4.7. $C_{16}H_{14}O_4$ requires C, 63.55; H, 4.65%); δ_H(300 MHz) 2.39 (3 H, d, $J_{Me,8}$ 0.6 Hz, Me), 2.41 and 2.49 (each 3 H, s, Ac and OAc), 3.88 (3 H, s, OMe), 6.04 (1 H, s, 3-H), and 7.94 (1 H, narrow q, 8-H); δ_C (75.5 MHz) 19.47 and 21.09 (OCO*Me* and Me), 31.60 (CO*Me*), 56.47 (OMe), 111.53 (C-8), 127.06 (C-3), 120.91, 132.17, 141.23, 142.32, 145.45, and 159.27 (C-2, -5, -6, -4a, -8a), 168.91 (O*C*OMe), 179.26 and 183.06 (C-1, -4), and 201.64 (*C*OMe); $\nu_{max.}$(KBr) *inter alia*, 1 780, 1 700, 1 650, 1 615, and 1 595 cm^{-1}; $\lambda_{max.}$(MeOH) 250, 282, and 340 nm (ε 21 100, 13 800, and 3 800 respectively); *m*/*z* 275 (15%), 260 (100), 245 (95), and 231 (52). Further elution provided 5-*acetoxy*-6-*acetyl*-4-*methoxy*-7-*methylnaphthalene*-1,2-*dione* (**15**) (29 mg, 16%) which crystallized from dichloromethane–light petroleum as orange prisms, m.p. 225—229 °C (decomp.) (Found: C, 63.85; H, 4.55. $C_{16}H_{14}O_4$ requires C, 63.55; H, 4.65%); δ_H(80 MHz) 2.29 (3 H, s, OAc), 2.35 (3 H, s, Me), 2.48 (3 H, s, Ac), 3.55 (3 H, s, OMe), 5.96 (1 H, s, 3-H), and 7.93 (1 H, s, 8-H); δ_C(75.5 MHz) 18.92 and 20.50 (OCO*Me* and Me), 31.46 (CO*Me*), 57.29 (OMe), 104.29 (C-8), 129.93 (C-3), 122.02, 131.34, 139.94, 143.27, and 143.72 (C-5, -6, -7, -4a, and -8a), 168.61 and 168.67 (C-4 and O*C*OMe), 178.41 and 178.59 (C-1, -2); and 201.74 (*C*OMe), $\nu_{max.}$(KBr) *inter alia*, 1 780, 1 715, 1 665, and 1 600 cm^{-1}; $\lambda_{max.}$(MeOH) 213, 258, 289infl, 337, and 410 nm (ε 15, 100, 20, 700, 5 200, 1 600, and 1 700 respectively); *m*/*z* 274 (11%), 260 (2), 232 (56), and 217 (100).

6-*Acetyl*-5-*hydroxy*-2-*methoxy*-7-*methylnaphthalene*-1,4-*dione* (2-*Methoxystypandrone*) (**1**).—Potassium hydroxide (100 mg) was added under argon to a stirred solution of the acetate (**16**) (22 mg) in methanol (10 ml) and water (1 ml). After 1 min an excess of dilute hydrochloric acid was added and the crude product was isolated by extraction with ethyl acetate. The *stypandrone* (**1**) (17 mg, 93%) crystallized from benzene–light petroleum as golden yellow needles, m.p. and mixed m.p. 198—199 °C (lit.,[2–4] 193—194 °C, 181.5—183.5 °C,187 °C) (Found: C, 64.3; H, 4.8. $C_{14}H_{12}O_5$ requires C, 64.6; H, 4.65%); δ_H(80 MHz) 2.35 (3 H, s, Me), 2.58 (3 H, s, Ac), 3.98 (3 H, s, OMe), 6.10 (1 H, s, 8-H), 7.51 (1 H, s, 3-H), and 12.50 (1 H, s, OH): δ_C(75.5 MHz) 20.00 (Me), 31.66 (CO*Me*), 56.77 (OMe), 109.61 (C-3), 121.66 (C-8), 112.42 (C-4a), 130.53 (C-6), 136.70 (C-8a), 143.53 (C-7), 158.17 (C-5), 161.05 (C-2), 179.10 (C-1), 190.32 (C-4), and 202.91 (*C*OMe), $\nu_{max.}$(KBr) *inter alia*., 1 700, 1 680, 1 630, and 1 590 cm^{-1}; $\lambda_{max.}$(MeOH), 222, 250infl, 288, and 412 nm (ε 19 500, 10 900, 11 100, and 4 300 respectively); *m*/*z* 261 (13%), 260 (85, M^+), 246 (15), 245 (100), 231 (34), 217 (48), 215 (12), 174 (16), 161 (12), 146 (12), 133 (14), 118 (12), and 105 (11). It was identical with an authentic sample (mixed m.p., R_F values in three different solvent systems, mass and i.r. spectra).

6,7,8-*Trimethoxy*-3-*methyl*-1-*naphthol* (**22**).—Reduction of methyl 4-acetoxy-5,6,7-trimethoxynaphthalene-2-carboxylate (**20**) (2.2 g)[10] with lithium aluminium hydride in a manner similar to that described for the preparation of compound (**10**) gave the diol (**21**) (1.25 g, 72%) as a viscous oil which was hydrogenolysed in a manner similar to that described in the preparation of compound (**11**). The *naphthol* (**22**) (975 mg, 84%) crystallized from ethanol–light petroleum as needles, m.p. 82—83 °C (Found: C, 67.95; H, 6.65%; M^+, 248. $C_{14}H_{16}O_4$ requires C, 67.75; H, 6.4%; *M*, 248); δ_H(80 MHz) 2.36 (3 H, s, Me), 3.89 (6 H, s, 2 × OMe), 4.09 (3 H, s, OMe), 6.59 (1 H, br s, 2-H), 6.78 (1 H, s, 5-H), 6.90 (1 H, br s, 4-H), and 9.31 (1 H, s, OH). The *acetate* (**23**) (acetic anhydride–pyridine, 95%) formed prisms (from dichloromethane–light petroleum), m.p. 82—84 °C (Found: C, 65.9; H, 6.05%; M^+, 290. $C_{16}H_{18}O_5$ requires C, 66.2; H, 6.25%; *M*, 290); δ_H(80 MHz) 2.36 (3 H, s, COMe), 2.43 (3 H, s, Me), 3.92 (9 H, s, 3 × OMe), 6.80 (1 H, br s, 2-H), 6.88 (1 H, s, 5-H), and 7.33 (1 H, br s, 4-H).

1-*Hydroxy*-6,7,8-*trimethoxy*-3-*methyl*-2-*naphthyl Methyl Ketone* (**24**).—The acetate (**23**) (1.26 g) and boron trifluoride–diethyl ether (13 ml) were allowed to react in a manner similar to that described for the preparation of compound (**13**). The *ketone* (**24**) (1.03 g, 82%) crystallized from dichloromethane–light petroleum as needles, m.p. 72—73 °C (Found: C, 66.2; H, 6.3%; M^+, 290. $C_{16}H_{18}O_5$ requires C, 66.2; H, 6.25%; *M*, 290); δ_H(80 MHz) 2.33 (3 H, s, Me), 2.62 (3 H, s, COMe), 3.90 (6 H, s, 2 × OMe), 4.10 (3 H, s, OMe), 6.76 (1 H, s, 5-H), 6.90 (1 H, s, 4-H), and 10.22 (1 H, s, OH).

8,9-*Dimethoxy*-5-*methylnaphtho*[1,8-de]-1,3-*dioxin*-4-*yl Methyl Ketone* (**17**).—All the operations in the following experiment were carried out under an atmosphere of argon. A solution of boron trichloride (200 mg) in dichloromethane (1 ml) was added at 0 °C to a stirred solution of the ketone (**24**) (100 mg) in dichloromethane (4 ml). The solution was then stirred at room temperature for 1.5 h after which it was poured into water. The crude product was isolated by extraction with ether and then dissolved in *N*,*N*-dimethylformamide (3.5 ml). Anhydrous potassium fluoride (60 mg) and dibromomethane (100 mg) were added and the mixture was stirred and heated at 120—130 °C (bath) for 4 h. The cooled mixture was then poured

into water and the crude product was extracted with ethyl acetate and purified by radial chromatography with 10% ethyl acetate–light petroleum as eluant. The *ketone* (**17**) (17 mg, 17%) crystallized from dichloromethane–light petroleum as needles, m.p. 148—149 °C (Found: C, 66.3; H, 5.55. $C_{16}H_{16}O_5$ requires C, 66.65; H, 5.6%); δ_H(80 MHz) 2.41 (3 H, d, $J_{Me,6}$ 0.9 Hz, Me), 2.61 (3 H, s, COMe), 3.97 (6 H, s, 2 × OMe), 5.59 (2 H, s, 2-H), 6.75 (1 H, s, 5-H), and 7.14 (1 H, br s, 6-H); δ_C (20.1 MHz) 20.78 (Me), 33.00 (CO*Me*), 56.12 and 61.68 (OMe), 91.17 (C-2), 99.81 (C-7), 109.11 (C-5), 120.87 (C-6), 121.48, 131.64, 131.64, 134.27, 141.89, and 148.17 (each ArC), 155.20 (C-4), and 202.8 (C=O); $\nu_{max.}$(KBr) *inter. ilia.*, 1 680, 1 640, 1 610, and 1 590 cm^{-1}; *m/z* 288 (72%, M^+), 273 (100), 245 (15), 230 (8), 144 (11), 136.5 (9), 129 (9), and 115 (13).

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