The Stereoselective Formation of Naphtho[1,2-*c*]pyrans, Angular Analogues of the Aphin-derived Glucoside B, by an Intramolecular Version of the Mukaiyama Reaction of 4-Naphthyldioxolanes

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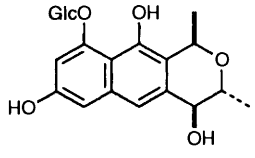
Stereoselective isomerisation of the pair of epimers *rel*-(2*R*,4*S*,5*S*)- and *rel*-(2*S*,4*S*,5*S*)-4-(4-isopropoxy-5,7-dimethoxynaphthalene-2-yl)-2,5-dimethyl dioxolane **12** with an excess of a mixture of titanium tetrachloride and titanium tetraisopropoxide afforded the two products *rel*-(1*R*,3*S*,4*S*)-3,4-dihydro-4-hydroxy-6-isopropoxy-7,9-dimethoxy-1,3-dimethylnaphtho[1,2-*c*]pyran **13**, and the C-1 epimer **15**. Isomerisation of *rel*-(2*S*,4*R*,5*S*)-4-(8-bromo-4-isopropoxy-5,7-dimethoxynaphthalen-2-yl)-2,5-dimethyl dioxolane **36** with an excess of titanium tetrachloride alone afforded *rel*-(1*S*,3*S*,4*R*)-3,4-dihydro-4-hydroxy-6-isopropoxy-7,9-dimethoxy-1,3-dimethylnaphtho[1,2-*c*]pyran **38** and its 5-bromo derivative **39**, the latter being formed through bromine migration on the aromatic nucleus.

Our interest in the synthesis of naphthopyrans related to the aphin-derived glucoside B **1**[1] and the results described in the preceding paper[2] led to our formulating a new strategy for the construction of naphthopyrans through the stereoselective isomerisation of naphthyldioxolanes using titanium tetrachloride.[3] Several other entirely unrelated intramolecular examples[4–11] of the Mukaiyama reaction[12,13] have been reported both prior to and during the course of this investigation. In this paper we describe a preliminary study of the titanium tetrachloride-induced isomerisation of 2,5-dimethyl-4-(2-naphthyl)dioxolanes.‡



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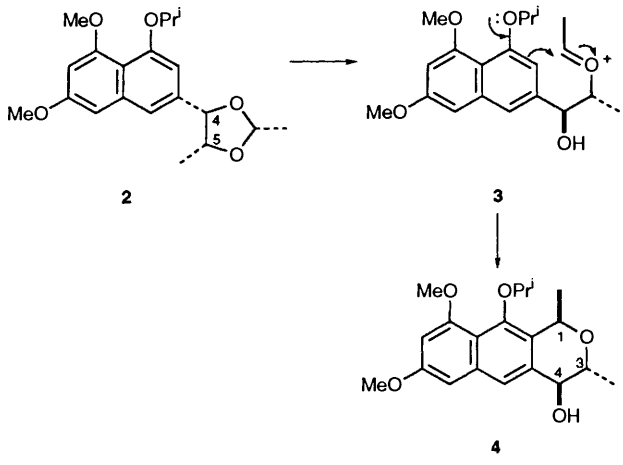
Results and Discussion

The desired isomerisation is that depicted in Scheme 1, in which the relative stereochemistry at C-4 and C-5 in the initial dioxolane **2**§ determines that established at C-3 and C-4 in the product naphthopyran **4**. At the inception of this work,[14] it was expected that the C-1 methyl in the product naphthopyran **4** would assume the pseudoaxial orientation through the intermediacy of the planar oxocarbenium ion **3** in order to minimize *peri* interaction with the neighbouring isopropoxy substituent, although recent work[15] has shown that other factors may be implicated.

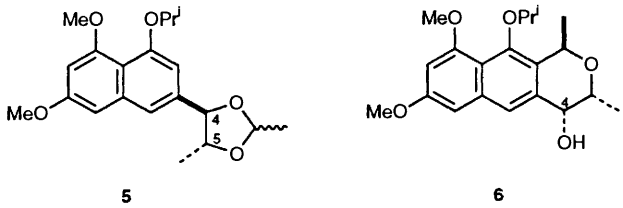
Isopropyl was chosen to protect the C-10 oxygen of the target naphthopyran **4** since it was intended to selectively remove it with boron trichloride[16] and oxidise the derived phenol to the racemate of the dimethyl ether of Quinone A[17] to



Scheme 1

confirm the structure of product **4** including the relative stereochemistry.

To test this isomerisation hypothesis, the naphthyldioxolanes **5** were chosen as the synthetic targets, as their relative stereochemistry at C-4 and C-5 was deemed the easiest to construct, even though it was appreciated that the derived naphthopyran **6**, if formed, would have the incorrect stereochemistry for the C-4 hydroxy group of Glucoside B (Scheme 2).



Scheme 2

The alcohol **7** was oxidised with activated manganese dioxide[18] to afford the aldehyde **8**. This was treated with ethylidenetriphenylphosphorane to afford a stereochemical mixture of the olefins **9** which reacted, in turn, with bis(acetonitrile)dichloropalladium(II) to yield the (*E*)-isomer **10** as the sole product in high yield.[19] This stereochemically pure olefin

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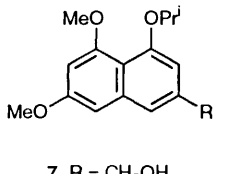
‡ For clarity, the numbering of the naphthalenic substituents is consistent with that used for the naphthalenes in the preceding two papers.

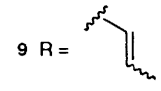
§ Structures of synthetic compounds depicted as single enantiomers represent racemates.

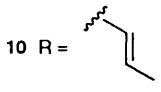
reacted with osmium tetroxide to afford the diol **11** as a single racemate in a yield of 91%. Attempted conversion of the *E*-olefin **10** into the corresponding epoxide failed with *meta*-chloroperbenzoic acid. Several products were formed two of which were chromatographically separated from the mixture and identified as the 1,2- and 1,4-naphthoquinones, **16** and **17**, formed in yields of 13 and 10% respectively. Preferential electrophilic attack on the dimethoxy-substituted aromatic ring rather than the olefin precluded the facile formation of the desired epoxide, which could have been subjected to stereoselective ring-opening to form the *erythro*-diol (*cf.* **35**) required for the formation of the dioxolane **2**, and thence **4**, the Glucoside B analogue.

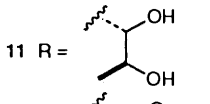
The dioxolane **12** corresponding to the diol **11** was prepared by reaction of the latter with acetaldehyde, either using trifluoroacetic acid in ether, which gave the product **12** in a yield of 63%, or using toluene-*p*-sulfonic acid in benzene which afforded the same product in a yield of 76%. In each case, the dioxolane obtained was a single stereoisomer, although the relative stereochemistry at C-2 was not established, since it was considered irrelevant if C-2 was to become planar (*cf.* **3**) in the subsequent reaction of the dioxolane **5**.

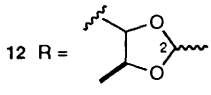


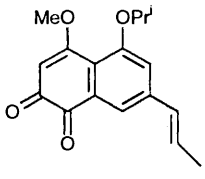
7 R = CH_2OH
8 R = CHO











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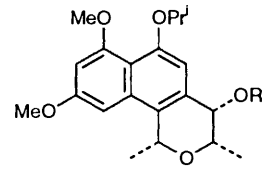
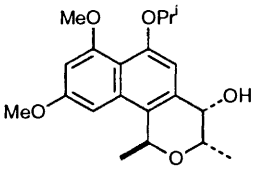


13 R = H
14 R = Ac



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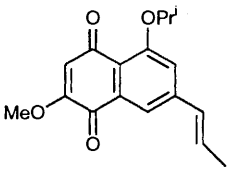

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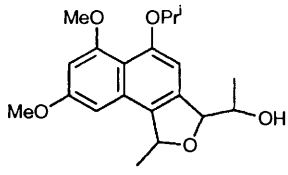
The dioxolane **12** was treated with an excess of both titanium tetrachloride and titanium tetraisopropoxide, whereupon two new compounds were isolated, as well as the starting dioxolane **12** and its precursor, the diol **11**. The molecular ion in the mass spectrum of each new compound appeared at *m/z* 346, confirming that both were isomeric with dioxolane **12**. The gross features of ^{1}H NMR spectra of the new compounds were also very similar. In addition to three aromatic protons for each (two *meta* coupled doublets and a singlet), and signals for one isopropoxy and two methoxy substituents, each compound showed two three-proton methyl doublets, three methine protons and an exchangeable proton. For the higher R_F compound, obtained in a yield of 39% and assigned structure **13**, 1-H appeared as a quartet (*J* 7 Hz) at δ 5.38, 3-H as a doublet of quartets (*J* 1 and 7 Hz) at δ 3.84, and 4-H as a doublet (*J* 1 Hz) at δ 4.16, broadened through further coupling to the adjacent alcohol proton. For the lower R_F compound, obtained in a yield of 13% and assigned structure **15**, the corresponding methine protons appeared at δ 5.33 (q, *J* 6.5 Hz), 4.24 (dq, *J* 1.5 and 6.5 Hz) and 4.21 (dd, *J* 1.5 and 8 Hz), respectively. The latter coupling was to the OH proton at δ 1.92 (d, *J* 8 Hz).

In order to establish that each product was a naphthopyran rather than a naphthofuran of the general structure **18**, the alcohol function of each isomer was acetylated, which resulted in the marked deshielding, by about 1.6 ppm in each case, of the 4-H signals at δ 4.16 and 4.21 in the compounds **13** and **15**, respectively. Similar treatment of the isomeric naphthofurans **18** would have led to deshielding of the doublet of quartets (at δ 3.84 and 4.24).

The fact that the coupling constants between 3-H and 4-H were small (1–1.5 Hz) in each case confirmed that, with the 3-methyl equatorial, the hydroxy (or acetoxy) group was pseudoaxial.[1,20] With the relative stereochemistry established at C-3 and C-4, it only remained to determine the configurations at C-1 and also whether the products were linear or angular naphthopyrans.



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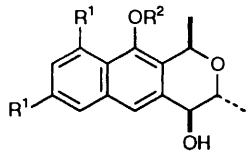


19 R^1 = H, R^2 = Me
20 R^1 = OMe, R^2 = Pr^i

Two factors supported the major product of higher R_F, possessing the pseudoequatorial 1-methyl substituent as for structure **13**, and the minor product, of lower R_F, the pseudoaxial 1-methyl as for **15**. The first was the values for the chemical shifts of 3-H for each isomer, at δ 3.84 for **13** and δ 4.24 for **15**. It is known that for benzopyrans and linear naphthopyrans, 3-H appears in the range δ 3.5–3.9 for *cis* 1,3-dimethyl isomers, while for the *trans* analogues, 3-H resonates in the range δ 3.9–4.3.[21,22] However, there were, hitherto, too few examples involving a 4-hydroxy substituent in both series to be able to generalise, and the possibility that either or both naphthopyrans were angular led to further uncertainties.

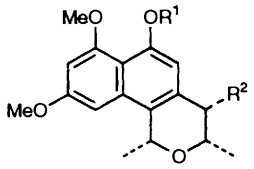
The second factor was that a nuclear Overhauser difference spectrum run on the minor isomer after exchange with deuterium oxide showed enhancement for the pseudoaxial proton 3-H on irradiation of 1-methyl at δ 1.62.

This same experiment also suggested the proximity of the aromatic protons 8-H and 10-H to the 1-methyl. This observation supported the assignment of the angular naphthopyran **15** to the minor product. The assignment of angular structures to both isomers was further indicated by the positions of the resonances for 5-H in each product; that for **13** at δ 6.74 and that for **15** at δ 6.78. The corresponding resonances for the related linear naphthopyrans **19** and **20** were observed at much lower field, *viz.* at δ 7.84 and 7.61, respectively,[2] although the analogy was not entirely secure in view of the difference in stereochemistry at the adjacent ring atom, C-4.

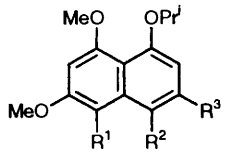
The assignments of structures **13** and **15** to the major (higher R_F) and minor (lower R_F) products were confirmed through X-ray crystallographic analysis on the crystalline acetate **14** of the oily **13** and on the minor alcohol **15** itself.[23]

Sufficient material remained to attempt a small-scale deisopropylation of compound **13**, using an excess of boron trichloride. In addition to starting material, three products were

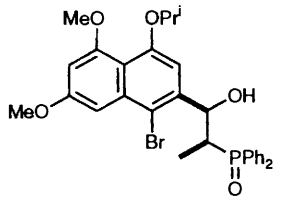
identified. The major product (30%) was the derived phenol **21**. However, chlorination of the starting alcohol **13** gave rise to its C-4 pseudoaxial chloro derivative **22** (15%) and the corresponding chlorinated phenol **23** (15%).



21 R^1 = H, R^2 = OH
22 R^1 = Pr^i, R^2 = Cl
23 R^1 = H, R^2 = Cl



24 R^1 = H, R^2 = Br, R^3 = CH_2OAc
25 R^1 = Br, R^2 = H, R^3 = CH_2OAc
26 R^1 = H, R^2 = Br, R^3 = CH_2OH
27 R^1 = Br, R^2 = H, R^3 = CH_2OH
28 R^1 = H, R^2 = Br, R^3 = CHO
29 R^1 = Br, R^2 = H, R^3 = CHO



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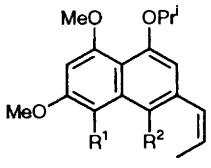


31 R^1 = H, R^2 = Br
32 R^1 = Br, R^2 = H

This first experiment, therefore, indicated that it was possible to isomerise naphthyldioxolanes into naphthopyrans. A second isomerisation was then attempted with a *cis* 4,5-disubstituted dioxolane related to compound **2**, to provide the correct relative stereochemistry at C-3 and C-4 required for Glucoside B **1**. A bromine atom would be attached at either of the unsubstituted α-positions of compound **2** to discourage formation of the angular naphthopyran through steric crowding. The syntheses of both the 1- and 8-monobromo derivatives of compound **2** were investigated simultaneously.

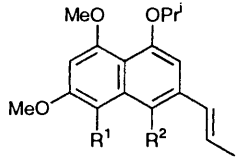
The 1-bromonaphthyl acetate **24** was hydrolysed to the corresponding alcohol **26**, which was, in turn, oxidised as before to the related aldehyde **28**. Wittig reaction of this compound **28** with ethylidenephosphorane afforded a roughly 1 : 1 mixture of the *Z*-olefin **31** and *E*-olefin **33**.

Alternatively, Warren's method[24] for obtaining *Z*-olefins using the Horner–Wittig reaction was investigated. Ethyldiphenylphosphine oxide was thus treated with the 1-bromonaphthaldehyde **28** according to the conditions stipulated for *erythro* selectivity. The *erythro* adduct **30** was obtained in a 42% yield after repeated recrystallisation in order to separate the *threo* adduct formed simultaneously. Elimination of diphenylphosphinate under optimised conditions provided the *Z*-olefin **31** in a yield of 82% from the *erythro* adduct **30**. Small quantities (< 10%) of the *E*-olefin **33** were also obtained.

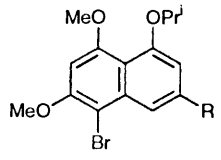
The modest yield for the formation of the pure *erythro* adduct **30** and other considerations militated against further investigations on the 1-bromonaphthalene series, and in favour of the isomeric 8-bromo analogues.

Thus, the 8-bromonaphthyl acetate **25** was converted *via* the alcohol **27** into the corresponding aldehyde **29**. In contrast to the reaction of the 1-bromonaphthaldehyde **28** with ethylidenetriphenylphosphorane, which gave a 1 : 1 ratio of *Z*- and *E*-olefins **31** and **33**, similar reaction with the 8-bromonaphthaldehyde **29** afforded largely the (*Z*)-olefin **32**, contaminated by only 8% of the minor (*E*)-isomer **34**. These assignments were based on the respective olefinic coupling constants of 13 and 15.6 Hz. Since the former value was at the upper limit for *Z*-olefins, confirmation was sought through reaction with bis(acetonitrile)dichloropalladium(II).[19] Such a reaction for 2 h did convert the major into the minor product of the Wittig reaction, thereby confirming the assignment. However, longer reaction times converted the product **34** into the *E*-1-bromo olefin **33**, bromine migration having occurred.[25] The same result was obtained if the oily *Z*-olefin **32** was left in sunlight for 4 days, isomerisation to the *E*-olefin **34** preceding radical migration of bromine from C-8 to C-1 to afford **33**. Furthermore, chromatography of the *Z*-olefin **32** for purification returned the olefin enriched in the *E*-isomer **34**.

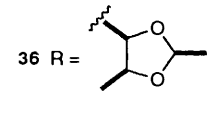
The crude *Z*-olefin **32** was, therefore, converted, without any purification, into the corresponding diol **35** in an overall yield of 59% from the aldehyde **29**. This diol was, in turn, converted into the dioxolane **36** as a single diastereoisomer, using acetaldehyde dimethyl acetal in the presence of toluene-*p*-sulfonic acid. A nuclear Overhauser effect difference spectrum, obtained by irradiation of the 5-H heterocyclic ring proton, showed the proximity of both 2-H and 4-H, thereby supporting the formulation of the product stereochemistry as *cis*, *syn*. Similar irradiation of 2-H and 4-H supported this assignment. This isomer is, no doubt, favoured as the one with least non-bonded interactions, in the conformation **37**.



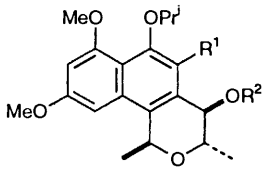
33 R^1 = H, R^2 = Br
34 R^1 = Br, R^2 = H



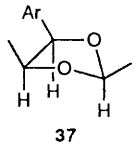
35 R =



36 R =



38 R^1 = R^2 = H
39 R^1 = Br, R^2 = H
40 R^1 = H, R^2 = Ac
41 R^1 = Br, R^2 = Ac



37

The naphthyldioxolane **36** was treated with 10 molar equiv. of titanium tetrachloride in methylene dichloride at −78 °C. Aside from minor quantities of the starting dioxolane **36** (12%), the diol **35** (14%) and the alcohol **27** (4%), two new compounds were identified. These were the debrominated angular naphthopyran **38** and its 5-bromo derivative **39**, isolated in 45 and 18%, respectively (calculated on starting dioxolane consumed).

The mass spectrum of the major product showed a molecular ion at *m/z* 346, indicating loss of bromine; the minor product gave rise to a molecular ion pair at *m/z* 426 and 424 in a ratio of approximately 1 : 1, indicating that it was an isomer of the starting dioxolane **36**.

The aromatic regions of the ^{1}H NMR spectra of each were instructive. The major product **38** showed a 2 H singlet at δ 6.50 and a 1 H singlet at δ 6.97. The minor product **39** showed a pair of 1 H *meta*-coupled doublets at δ 6.55 and 6.60, indicating the migration of bromine to the alternate aromatic ring.

In addition to signals due to an isopropoxy and two methoxy groups as well as two methyl doublets, each spectrum showed

three 1-H signals due to the three methine protons on each heterocyclic ring. For the major product, **38**, these were a quartet (J 6.5 Hz) at δ 5.32 due to 1-H, a doublet of quartets (J 8.3 and 6.3 Hz) at δ 3.89 due to 3-H, a triplet (J 8.3 Hz) at δ 4.38 due to 4-H and a doublet (J 8.3 Hz) at δ 1.89 for the hydroxy group. Deuterium oxide exchange collapsed 4-H to a doublet (J 8.3 Hz) and removed the alcohol signal. Related signals were observed for the minor product **39**.

That each compound was a naphthopyran rather than a naphthofuran was confirmed by the conversion of each into its acetate, to form **40** and **41**, whereupon the 4-H signal of each was deshielded by well over 1 ppm.

The ^{1}H NMR spectra of the minor product **39** and its acetate **41** showed the doubling of some of the signals, which was ascribed to the existence of two conformations of the pyran ring as a consequence of considerable crowding of the substituents attached to all adjacent atoms from C-3 to C-7 of the ring system. This effect was more pronounced for the acetate. This notwithstanding, the product **39** was shown to be a single compound since it was smoothly converted in high yield (81%) into the debrominated angular pyran **38** on reaction with an excess of butyllithium, a process in which the intermediate lithio derivative of metal–halogen exchange was, no doubt, well stabilized by both the neighbouring alkoxide and isopropoxy substituents.

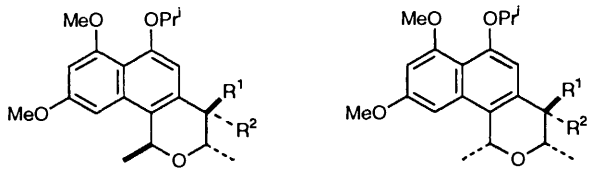
The large coupling constant (J 8.3 Hz) between 3-H and 4-H in the naphthopyran **38** was consistent with their being almost *trans*-diaxial; the 3-methyl was, therefore, equatorial and the 4-hydroxy pseudoequatorial.

Nuclear Overhauser effect difference spectroscopy supported the 1-methyl being pseudoaxial. Thus, its irradiation enhanced the 3-H signal significantly.

The chemical shift of the aromatic 5-H (δ 6.97) was comparable with those (δ 6.74 and 6.78) for the angular stereoisomers **13** and **15**, and quite different from that (δ 7.61) of the known[2] linear regioisomer **4**.

These data led to the assignment of structure **38** to the major product and **39** to the minor brominated derivative. However, since the C-1 stereochemistry of both compounds rested solely on NOE experiments, a method of relating these structures to those of the stereoisomers **13** and **15**, determined through X-ray crystallography, was sought. This was achieved by converting each of the angular naphthopyrans **13** and **15** into their 4-deoxy derivatives and comparing the products, as follows.

Compound **15** was treated with phosphorus tribromide, whereupon a mixture of the two benzylic bromides **42** and **43** was produced. For the former, **42**, the C-4 bromine was pseudoequatorial as the coupling constant between 3-H and 4-H was 8.5 Hz while that for the stereoisomer **43** was 2 Hz. The respective chemical shifts for the neighbouring 5-H aromatic protons were δ 6.92 and 6.65 indicating the closer proximity of bromine to 5-H in the former case.



42	R^1 = Br, R^2 = H	**45**
43	R^1 = H, R^2 = Br	**46**
44	R^1 = R^2 = H	**47**

Treatment of the mixture of these isomers with aqueous ethanolic Raney nickel catalyst yielded the *trans*-1,3-dimethylnaphthopyran **44** as a single product.

The naphthopyranol **13** was similarly converted into the pair of bromides **45** and **46**, whose individual stereochemistries were once again assigned as above from the 4-H coupling constants and 5-H chemical shifts. These stereoisomers were hydrogenolysed as above with Raney nickel to afford the *cis*-1,3-dimethylnaphthopyran **47**, stereoisomeric with the previous product **44**.

It is noteworthy that the chemical shift for 3-H in the *cis* compound **47** was δ 3.74 and for the *trans* isomer **44** was δ 4.25. These values are entirely consistent with the ranges δ 3.5–3.9 and 3.9–4.3 for *cis* and *trans* compounds reported previously[21,22] (and earlier, tentatively, in this paper for compounds **13** and **15**).

The naphthopyran **38** was then treated with phosphorus tribromide to afford the pair of isomeric bromides **42** and **43** identical with those previously obtained from the epimeric alcohol **15**. Hydrogenolysis of this mixture of bromides once again afforded the *trans*-1,3-dimethyl compound **44**. As a consequence, the stereochemistries of the pyrans **38** and **39** were confirmed.

Conclusions.—The major objective of the work described in this paper was achieved in that it was shown first that appropriately substituted naphthyldioxolanes may be stereoselectively isomerised to angular naphthopyrans related to Glucoside B 1, although conversion into the desired linear naphthopyrans has not yet been achieved. The formation of the angular analogues may arise through steric crowding leading to ring closure of intermediate oxonium ions such as **3** *para* rather than *ortho* to the sterically demanding isopropoxy substituent. Such observed ring closure may also be favoured as a consequence of the well known preference for electrophilic substitution of naphthalenes at the α- rather than the β-position.

Secondly, it was shown that the stereochemistry at C-3 and C-4 in the product could be controlled by choice of stereochemistry at the vicinal centres C-4 and C-5 in the starting dioxolane. The factors determining the control of stereochemistry at C-1 have not yet been established and may be regulated by either steric or other factors, such as the nature of the transition state.[15]

Other problems that remain to be solved include construction of linear rather than angular naphthopyrans, perhaps by replacing isopropoxy by methoxy or hydroxy groups, and/or blocking the α-position to discourage formation of the angular ring system. Furthermore, there had been insufficient material available in this study to optimise the yields of the products by varying conditions such as temperature and the proportion of titanium tetrachloride required. Such experiments would best be performed on benzenoid models, which would be less difficult to synthesize. The design and synthesis of suitable substrates is currently under active investigation to provide answers to these questions.

Finally, it is assumed that the desired naphthopyrans were formed to the exclusion of isomeric naphthofurans such as **18**, since formation of the former occurs *via* the 6-*endo-trig* ring-closure of oxonium ions such as **3** rather than through the less favoured 5-*endo-trig* ring-closures that would lead to the isomeric naphthofurans.[26,27]

Experimental

General Details.—See preceding paper in this issue.

4-Isopropoxy-5,7-dimethoxynaphthalene-2-carbaldehyde **8**.—A solution of the alcohol **7**[25] (463 mg, 1.69 mmol) in benzene (25 cm^3) was boiled with activated manganese dioxide (2 g, 23

mmol) for 5 h. The reaction mixture was then cooled, filtered and the filtrate evaporated. The residue obtained upon work-up was chromatographed (eluent 10% ethyl acetate–light petroleum) to afford the *product* (335 mg, 73%), m.p. 73–75 °C (ethyl acetate–light petroleum) (Found: C, 70.2; H, 6.5. $C_{16}H_{18}O_4$ requires C, 70.1; H, 6.6%); ν_{max}/cm^{-1} 1690 (C=O); δ(90 MHz) 1.41 [6 H, d, *J* 7, $CH(CH_3)_2$], 3.88 (6 H, s, OCH_3), 4.67 [1 H, sept., *J* 7, $CH(CH_3)_2$], 6.58 and 6.80 (each 1 H, d, *J* 2, 6- and 8-H), 7.12 and 7.65 (each 1 H, *J* 1.5, 3- and 1-H) and 9.97 (1 H, s, CHO); *m/z* 274 (M^+, 32%), 232 (100) and 189 (32).

rel-(1S,2S)-1-(4-*Isopropoxy*-5,7-*dimethoxynaphthalen*-2-*yl*)-*propane*-1,2-*diol* **11**.—To a solution of the alkene **10**[19] (194 mg, 0.68 mmol) in pyridine was added a solution of osmium tetroxide (200 mg, 0.79 mmol) in ether (2 cm^3). After the mixture had been stirred at room temperature for 45 min, thin layer chromatography (TLC) showed the presence of some starting material and so more osmium tetroxide (100 mg, 0.39 mmol) was added to it; the mixture was then stirred for a further 15 min. A solution of water (5 cm^3) pyridine (5 cm^3) and sodium metabisulphite (700 mg) was added to the stirred reaction mixture which, after 30 min, was acidified (dilute hydrochloric acid) and extracted with methylene dichloride. The residue obtained upon work-up was chromatographed (eluent 30% ethyl acetate–light petroleum increasing to neat ethyl acetate) to afford the *product* (191 mg, 88%) as colourless needles, m.p. 91–92 °C (ethyl acetate–light petroleum) (Found: C, 67.5; H, 7.35. $C_{18}H_{24}O_5$ requires C, 67.5; H, 7.5%); ν_{max}/cm^{-1} 3315 (OH) and 1627 and 1608 (C=C); δ(90 MHz) 1.00 (3 H, d, *J* 7, 1′-CH_3), 1.33 [6 H, d, *J* 7, $CH(CH_3)_2$], 3.36 (2 H, s br, OH), 3.80 and 3.84 (each 3 H, s, OCH_3), 3.85 (1 H, m, 2′-H), 4.29 (1 H, d, *J* 7, 1′-H), 4.47 [1 H, sept., *J* 7, $CH(CH_3)_2$], 6.39 and 6.54 (each 1 H, d, *J* 2, 6- and 8-H) and 6.64 and 7.08 (each 1 H, d, *J* 1.5, 3- and 1-H); *m/z* 320 (M^+, 66%), 274 (32), 232 (100), 205 (79), 189 (32), 174 (11), 149 (15), 57 (15) and 43 (29).

rel-(2R *or* 2S,4S,5S)-4-(4-*Isopropoxy*-5,7-*dimethoxynaphthalen*-3-*yl*)-2,5-*dimethyldioxolane* **12**.—A solution of the diol **11** (94 mg, 0.29 mmol), acetaldehyde (38 mg, 0.86 mmol) and toluene-*p*-sulfonic acid (37 mg, 0.21 mmol) in benzene (20 cm^3) was heated under reflux in a Dean-Stark apparatus for 30 min. The cooled solution was washed with aqueous sodium hydrogen carbonate and then water. The residue obtained upon work-up was chromatographed (eluent 5% ethyl acetate–light petroleum) to afford the oily *product* (77 mg, 76%) (Found: C, 69.5; H, 7.5. $C_{20}H_{26}O_5$ requires C, 69.4; H, 7.6%); δ(90 MHz) 1.38 [6 H, d, *J* 7, $CH(CH_3)_2$], 1.41 (3 H, d, *J* 7, 5′-CH_3), 1.50 (3 H, d, *J* 5, 2′-CH_3), 3.88 and 3.90 (each 3 H, s, OCH_3), 3.86–3.90 (1 H, dq, *J* 7 and 9, 5′-H), 4.54 (1 H, d, *J* 9, 4′-H), 4.56 [1 H, sept., *J* 7, $CH(CH_3)_2$], 5.50 (1 H, q, *J* 5, 2′-H), 6.49 and 6.72 (each 1 H, d, *J* 2, 6- and 8-H) and 6.76 and 7.28 (each 1 H, d, *J* 1.5, 1- and 3-H); *m/z* 346 (M^+, 72%), 260 (32), 245 (100), 244 (93), 72 (23) and 43 (53).

rel-(1R,3S,4S)-3,4-*Dihydro*-4-*hydroxy*-6-*isopropoxy*-7,9-*dimethoxy*-1,3-*dimethylnaphtho*[1,2-c]*pyran* **13** and rel-(1S,3S,4S)-3,4-*Dihydro*-4-*hydroxy*-6-*isopropoxy*-7,9-*dimethoxy*-1,3-*dimethylnaphtho*[1,2-c]*pyran* **15**.—To a solution of the dioxolane **12** (97 mg, 0.28 mmol) in methylene dichloride (2 cm^3) was added titanium tetraisopropoxide (0.17 cm^3, 162 mg, 0.57 mmol) at −78 °C under nitrogen. The solution was stirred for 5 min after which titanium tetrachloride (0.06 cm^3, 103 mg, 0.55 mmol) was added to it. The dark reaction mixture was stirred for 15 min at room temperature then quenched with saturated aqueous sodium hydrogen carbonate. The residue obtained upon work-up was purified by preparative thin layer (PLC) chromatography (eluent 30% ethyl acetate–light petroleum) to afford the oily *product* **13** (31 mg, 32%, or 39% based on unrecovered starting material) with R_F 0.49 in the solvent system quoted (Found: C, 69.5; H, 7.6. $C_{20}H_{26}O_5$ requires C, 69.3; H, 7.6%); δ(90 MHz) 1.39 [9 H, d, *J* 7, $CH(CH_3)_2$ and 3-CH_3], 1.64 (3 H, d, *J* 7, 1-CH_3), 1.92 (1 H, s br, OH), 3.84 (1 H, dq, *J* 1 and 7, 3-H), 3.87 and 3.88 (each 3 H, s, OCH_3), 4.16 (1 H, d br, *J* 1, 4-H), 4.57 [1 H, sept., *J* 7, $CH(CH_3)_2$], 5.38 (1 H, q, *J* 7, 1-H), 6.49 and 6.59 (each 1 H, d, *J* 2, 8- and 10-H) and 6.74 (1 H, s, 5-H); *m/z* 346 (M^+, 58%), 331 (32), 289 (100), 259 (19) and 245 (15). This was followed (R_F 0.41) by the *product* **15** (10 mg, 10%, or 13% based on unrecovered starting material) m.p. 136–137 °C (light petroleum) (Found: M^+, 346.177195. $C_{20}H_{26}O_4$ requires *M*, 346.177994); δ 1.39 [6 H, d, *J* 6, $CH(CH_3)_2$], 1.42 (3 H, d, *J* 6.5, 3-CH_3), 1.62 (3 H, d, *J* 6.5, 1-CH_3), 1.92 (1 H, d, *J* 8, OH), 3.89 and 3.91 (each 3 H, s, OCH_3), 4.21 (1 H, dd, *J* 1.5 and 8, 4-H), 4.24 (1 H, dq, *J* 1.5 and 6.5, 3-H), 4.57 [1 H, sept., *J* 6, $CH(CH_3)_2$], 5.33 (1 H, q, *J* 6.5, 1-H), 6.48 and 6.51 (each 1 H, d, *J* 2, 8- and 10-H) and 6.78 (1 H, s, 5-H); *m/z* 346 (M^+, 63%), 331 (32), 301 (25), 289 (100), 259 (43) and 245 (15).

rel-(1R,3S,4S)-4-*Acetoxy*-3,4-*dihydro*-6-*isopropoxy*-7,9-*dimethoxy*-1,3-*dimethylnaphtho*[1,2-c]*pyran* **14**.—A solution of the naphthopyran **13** (11 mg, 0.03 mmol) in acetic anhydride (2 cm^3) and pyridine (0.5 cm^3) was stirred at 55 °C for 1 h after which it was diluted with methylene dichloride and washed successively with saturated aqueous sodium hydrogen carbonate, dilute hydrochloric acid and water. The residue obtained upon work-up was chromatographed (PLC, eluent 15% ethyl acetate–light petroleum) to afford the *product* **14** (12 mg, 97%), m.p. 134–136 °C (light petroleum) (Found: M^+, 388.189686. $C_{22}H_{28}O_6$ requires *M*, 388.188556); δ 1.31 (3 H, d, *J* 6.5, 3-CH_3), 1.39 [6 H, d, *J* 6, $CH(CH_3)_2$], 1.65 (3 H, d, *J* 6, 1-CH_3), 2.15 (3 H, s, $COCH_3$), 3.89 (6 H, s, OCH_3), 3.95 (1 H, dq, *J* 1.5 and 6.5, 3-H), 4.55 [1 H, sept., *J* 6, $CH(CH_3)_2$], 5.45 (1 H, q, *J* 6, 1-H), 5.75 (1 H, d, *J* 1.5, 4-H), 6.53 and 6.63 (each 1 H, d, *J* 2, 8-and 10-H) and 6.78 (1 H, s, 5-H); *m/z* 388 (M^+, 23%), 271 (84), 259 (17), 149 (17), 71 (17), 43 (100) and 41 (37).

Reaction of Compound **13** *with Boron Trichloride*.—Compound **13** (29 mg, 0.084 mmol) in methylene dichloride (2 cm^3) was treated with boron trichloride (21 mg, 0.18 mmol) in methylene dichloride (0.1 cm^3) at −78 °C and then stirred for 30 min. The temperature of the reaction mixture was raised to −10 °C after which it was stirred for a further 30 min. The reaction was quenched by addition of water to the mixture and the products were extracted with methylene dichloride. The residue obtained upon work-up afforded, in order of decreasing R_F, first, compound **22** [3 mg, 10% (15%†)] δ(90 MHz) 1.40 [6 H, d, *J* 7, $CH(CH_3)_2$], 1.44 (3 H, d, *J* 7, 3-CH_3), 1.61 (3 H, d, *J* 7, 1-CH_3), 3.87 (6 H, s, OCH_3), 4.01 (1 H, dq, *J* 1.5 and 7, 3-H), 4.56 [1 H, sept., *J* 7, $CH(CH_3)_2$], 4.76 (1 H, d, *J* 1.5, 4-H), 5.48 (1 H, q, *J* 7, 1-H), 6.53 (1 H, d, *J* 2, 8-H), 6.61 (1 H, d, *J* 2, 10-H) and 6.66 (1 H, s, 5-H); *m/z* 366 (M^+, 15), 364 (M^+, 41), 351 (7), 349 (19), 309 (34) and 307 (100). This was followed by compound **23** [3 mg, 10% (15%†)]; δ(90 MHz) 1.44 (3 H, d, *J* 7, 3-CH_3), 1.65 (3 H, d, *J* 7, 1-CH_3), 3.87 and 4.20 (each 3 H, s, OCH_3), 3.92 (1 H, dq, *J* 1.5 and 7, 3-H), 4.72 (1 H, d, *J* 1.5, 4-H), 5.44 (1 H, q, *J* 7, 1-H), 6.51 and 6.60 (each 1 H, d, *J* 2, 8- and 10-H), 6.62 (1 H, s, 5-H) and 9.20 (1 H, s, OH); *m/z* 324 (M^+, 11%), 322 (M^+, 30), 309 (35), 307 (100), 273 (9) and 271 (28). Unchanged starting material **12** was recovered (10 mg, 35%). Finally compound **21** was isolated [5 mg, 20% (30%†)] δ (90 MHz) 1.39 (3 H, d, *J* 7, 3-CH_3), 1.63 (3 H, d, *J* 7, 1-CH_3), 3.78 (1 H, dq, 1.5 and 7, 3-H), 3.88 and 4.02 (each 3 H, s, OCH_3), 4.08

† Yields in parentheses are based on unrecovered starting material.

(1 H, d, *J* 1.5, 4-H), 5.36 (1 H, q, *J* 7, 1-H), 6.49 and 6.61 (each 1 H, d, *J* 2, 8- and 10-H), 6.72 (1 H, s, 5-H) and 9.18 (1 H, s, OH, disappears with D_2O wash); *m/z* 304 (M^+, 37%), 289 (100), 271 (25), 245 (19) and 243 (9).

Reaction of Compound **10** *with* meta-*Chloroperbenzoic Acid.*—The olefin **10** (68 mg, 0.24 mmol) was dissolved in methylene dichloride (20 cm^3) and saturated aqueous sodium hydrogen carbonate (1 cm^3) added to the solution. This was followed by *m*-chloroperbenzoic acid (144 mg, 0.96 mmol) added to this solution over 20 min. The mixture was stirred vigorously at room temperature during which it became dark red. After 24 h, TLC of the reaction mixture indicated formation of a number of products. The mixture was diluted with water and extracted with methylene dichloride. The residue obtained upon work-up was chromatographed (eluent 20% ethyl acetate–light petroleum) to provide two major products. The product of higher R_F was the quinone **17** (7 mg, 10%); δ_H 1.42 [6 H, d, *J* 6.1, $CH(CH_3)_2$], 1.93 (3 H, d, *J* 6, 3′-CH_3), 3.84 (3 H, s, OCH_3), 4.65 [1 H, sept., *J* 6.1, $CH(CH_3)_2$], 6.03 (1 H, s, 3-H), 6.35–6.59 (2 H, m, 1′- and 2′-H) and 7.18 and 7.71 (each 1 H, d, *J* 2, 6- and 8-H); *m/z* 286 (M^+, 95%), 271 (100) and 244 (80). The product of lower R_F was the quinone **16** (9 mg, 13%); δ 1.37 [6 H, d, *J* 6.1, $CH(CH_3)_2$], 1.92 (3 H, d, *J* 6, 3′-CH_3), 3.91 (3 H, s, OCH_3), 4.59 [1 H, sept., *J* 6.1, $CH(CH_3)_2$], 5.90 (1 H, s, 3-H), 6.30–6.50 (2 H, m, 1′- and 2′-H) and 7.14 and 7.82 (each 1 H, d, *J* 2, 6- and 8-H); *m/z* 286 (M^+, 95%), 271 (100) and 244 (79).

1-*Bromo*-2-*hydroxymethyl*-4-*isopropoxy*-5,7-*dimethoxynaphthalene* **26**.—The acetate **24** (200 mg, 0.50 mmol) was dissolved in 1% (w/v) methanolic potassium hydroxide (42 mg, 0.75 mmol) and the mixture stirred for 10 min at room temperature. Dilute hydrochloric acid was added to the mixture to quench the reaction and the organic material was extracted into ether and the extract washed with water. The residue obtained upon work-up was chromatographed (eluent 10% ethyl acetate–light petroleum) to afford *product* **26** (142 mg, 80%) as white feather-like needles, m.p. 106–107 °C (light petroleum) (Found: C, 53.9; H, 5.35. $C_{16}H_{19}BrO_4$ requires C, 54.1; H, 5.35%); ν_{max}/cm^{-1} 3389 (OH) and 1619 and 1599 (C=C); δ_H 1.39 [6 H, d, *J* 6.2, $CH(CH_3)_2$], 2.18 (1 H, t, *J* 6.4, OH, D_2O exchangeable), 3.91 and 3.94 (each 3 H, s, OCH_3), 4.57 [1 H, sept., *J* 6.2, $CH(CH_3)_2$], 4.88 (1 H, d, *J* 6.4, CH_2), 6.51 (1 H, d, *J* 2.4, 6-H), 7.23 (1 H, d, *J* 2.4, 8-H) and 7.26 (1 H, s, 3-H); δ_C 22.06 (2 × CH_3), 55.22 and 56.11 (2 × OCH_3), 65.72 (CH_2), 73.25 (CH), 98.20 (C-6)[a], 99.14 (C-3)[a], 110.31 (C-8)[a], 112.42 (C-4a)[b], 115.29 (C-8a)[b], 135.99 (C-1), 139.05 (C-2), 154.80 (C-4)[c], 158.31 (C-5)[c] and 158.88 (C-7)[c]; *m/z* 356 (M^+, 35%), 354 (M^+, 35%), 314 (100), 312 (100), 271 (12) and 269 (12). (Assignments with identical superscripts are interchangeable.)

1-*Bromo*-4-*isopropoxy*-5,7-*dimethoxynaphthalene*-2-*carbaldehyde* **28**.—A solution of the alcohol **26** (125 mg, 0.35 mmol) in benzene (10 cm^3) was boiled with activated manganese dioxide[18] (1 g) for 1 h. The reaction mixture was cooled, filtered and concentrated. The residue was purified by chromatography (eluent 10% ethyl acetate–light petroleum) to afford the *aldehyde* **28** (100 mg, 81%) as yellow needles, m.p. 111–112 °C (light petroleum) (Found: C, 54.5; H, 4.85. $C_{16}H_{17}BrO_4$ requires C, 54.4; H, 4.8%); ν_{max}/cm^{-1} 1680 (C=O) and 1617 and 1593 (C=C); δ_H 1.42 [6 H, d, *J* 6.1, $CH(CH_3)_2$] 3.92 and 3.98 (each 3 H, s, OCH_3), 4.70 [1 H, sept., *J* 6.1, $CH(CH_3)_2$], 6.68 (1 H, d, *J* 2.3, 6-H), 7.20 (1 H, s, 3-H), 7.42 (1 H, d, *J* 2.3, 8-H) and 10.60 (1 H, s, CHO); δ_C 21.95 (2 × CH_3), 55.37 and 56.41 (2 × OCH_3), 72.24 (CH), 99.22 (C-6), 102.29 (C-3)[a], 105.37 (C-8)[a], 118.41 (C-4a)[b], 120.42 (C-8a)[b], 131.98 (C-2), 136.32 (C-1), 155.49 (C-4)[c], 158.49 (C-5)[c], 159.82 (C-7)[c] and 193.07 (CHO); *m/z* 354 (M^+, 34%), 352 (M^+, 34%), 312 (100), 310 (100), 269 (24) and 267 (24).

(Z)- *and* (E)-1-(1-*Bromo*-4-*isopropoxy*-5,7-*dimethoxynaphthalen*-2-*yl*)*prop*-1-*ene* **31** *and* **33**.—To a stirred suspension of ethyltriphenylphosphonium bromide (400 mg, 1.10 mmol) in dry tetrahydrofuran (10 cm^3) under nitrogen at 0 °C, was added butyllithium (1.10 mmol, 1.3 mol equiv.). The orange solution was stirred at 0 °C for 5 min, and then cooled to −78 °C. The aldehyde **28** (300 mg, 0.85 mmol) dissolved in dry tetrahydrofuran (2 cm^3) was then slowly dripped into the solution so that its temperature did not rise above −78 °C. The mixture was then stirred at −78 °C for 15 min after which it was allowed to warm to room temperature over 1 h. The reaction was quenched by the addition of water to the mixture after which it was diluted with ether. The organic layer was separated and washed several times with brine. The residue obtained upon work-up was chromatographed on alumina (eluent 15% ethyl acetate–light petroleum) to afford a mixture (~1:1) of the olefins **31** and **33** (248 mg, 80%) as a yellow oil; δ_H 1.34 and 1.36 [each 6 H, d, *J* 6.1, $CH(CH_3)_2$ of each isomer], 1.80 (3 H, dd, *J* 7 and 1.5, 3′-CH_3 of isomer **31**), 1.97 (3 H, dd, *J* 6.5 and 1.7, 3′-CH_3 of isomer **33**), 3.90, 3.91, 3.95 and 3.99 (each 3 H, s, OCH_3 of each isomer), 4.50 and 4.54 [each 1 H, sept., *J* 6.1, $CH(CH_3)_2$ of each isomer], 5.91 (1 H, dq, *J* 11.5 and 7, 2′-H of isomer **31**), 6.24 (1 H, dq, *J* 15.5 and 6.5, 2′-H of isomer **33**), 6.51 (1 H, d, *J* 1.5, 6-H of isomer **31**), 6.54 (1 H, d, *J* 1.5, 6-H of isomer **33**), 6.65 (1 H, dq, *J* 11.5 and 1.5, 1′-H of isomer **31**), 6.72 (1 H, s, 3-H of isomer **31**), 6.94 (1 H, s, 3-H of isomer **33**), 6.98 (1 H, dq, *J* 15.5 and 1.7, 1′-H of isomer **33**), 7.29 (1 H, d, *J* 1.5, 8-H of isomer **31**) and 7.34 (1 H, d, *J* 1.5, 8-H of isomer **33**).

rel-(1R,2S)-1-(1-*Bromo*-4-*isopropoxy*-5,7-*dimethoxynaphthalen*-2-*yl*)-2-*diphenylphosphinoylpropan*-1-*ol* **30**.—To ethyldiphenylphosphine oxide (131 mg, 0.57 mmol) in dry tetrahydrofuran (4 cm^3) at 0 °C under nitrogen, was added butyllithium (0.57 mmol, 1 mol equiv.). The dark orange solution was immediately cooled to −78 °C and the aldehyde **28** (200 mg, 0.57 mmol) in dry tetrahydrofuran (2 cm^3) added dropwise at such a rate that the temperature of the solution did not rise above −78 °C. The solution was allowed to warm to room temperature over 1 h after which it was diluted with water to quench the reaction. The organic material was extracted into ether and flash chromatography (eluent 70% ethyl acetate–light petroleum) of the residue obtained upon work-up yielded a mixture of *erythro* and *threo* adducts (212 mg, 63%). Repeated crystallisation (light petroleum) afforded the erythro *adduct* **30** (140 mg, 42%) as white needles, m.p. 204–205 °C (light petroleum) (Found: C, 61.65; H, 5.4. $C_{30}H_{32}BrO_5P$ requires C, 61.7; H, 5.5%); ν_{max}/cm^{-1} 3190 (OH) and 1615 and 1593 (C=C); δ_H 1.05 (3 H, dd, *J* 16.1 and 7.1, 3′-CH_3), 1.37 [6 H, d, *J* 6.1, $CH(CH_3)_2$], 2.94 (1 H, quint., *J* 7.1, 2′-H), 3.91 (6 H, s, OCH_3), 4.62 [1 H, sept., *J* 6.1, $CH(CH_3)_2$], 5.01 (1 H, s, OH), 5.59 (1 H, d, *J* 8.3, 1′-H), 6.51 and 7.19 (each 1 H, d, *J* 2, 6- and 8-H), 7.22 (1 H, s, 3-H) and 7.50–8.14 (10 H, m, Ph_2PO); *m/z* 584 (M^+, 8%), 582 (M^+, 8%), 503 (100) and 461 (65).

(Z)-1-(1-*Bromo*-4-*isopropoxy*-5,7-*dimethoxynaphthalen*-2-*yl*)*prop*-1-*ene* **31**.—The *erythro* adduct **30** (29 mg, 0.05 mmol) was dissolved in dry dimethylformamide (3 cm^3) at 55 °C under nitrogen and sodium hydride (0.1 mmol) was added in one portion to this solution. After the mixture had been stirred at 55 °C for 20 min it was diluted with water and the organic material was extracted into ether. The extract was washed with brine and the residue obtained upon work-up was chromatographed on alumina (eluent 15% ethyl acetate–light petroleum) to afford the (*Z*)-olefin **31** (15 mg, 82%) as an oil (Found: C, 59.3; H, 5.6. $C_{18}H_{21}BrO_3$ requires C, 59.2; H, 5.75%);

ν_{max}(film)/cm^{-1} 1615 and 1590 (C=C); δ_H 1.36 [6 H, d, *J* 6.1, CH(C*H*)$_3$)$_2$], 1.80 (3 H, dd, *J* 7 and 1.5, 3'-CH$_3$), 3.90 and 3.95 (each 3 H, s, OCH$_3$), 4.50 [sept., *J* 6.1, C*H*(CH$_3$)$_2$], 5.91 (1 H, dq, *J* 11.5 and 7, 2'-H), 6.51 (1 H, d, *J* 1.5, 6-H), 6.65 (1 H, dq, *J* 11.5 and 1.5, 1'-H), 6.72 (1 H, s, 3-H) and 7.29 (1 H, d, *J* 1.5, 8-H); *m/z* 366 (M$^+$, 42%), 364 (M$^+$, 42%), 324 (100), 322 (100), 285 (20) and 243 (80).

8-*Bromo*-2-*hydroxymethyl*-4-*isopropoxy*-5,7-*dimethoxynaphthalene* **27**.—The acetate **25** (500 mg, 0.50 mmol) was dissolved in 1% (w/v) methanolic potassium hydroxide (105 mg, 1.88 mmol) and the solution stirred for 10 min at room temperature. The reaction was quenched by the addition of dilute hydrochloric acid to the mixture and the organic material was extracted into ether. The extract was washed with water and the residue obtained upon work-up was chromatographed (eluent 10% acetate–light petroleum) to afford the *product* **27** (399 mg, 90%) as white needles, m.p. 97–98 °C (light petroleum) (Found: C, 54.0; H, 5.15. $C_{16}H_{19}BrO_4$ requires C, 54.1; H, 5.35%); ν_{max}/cm^{-1} 3419 (OH) and 1622 and 1596 (C=C); δ_H 1.38 [6 H, d, *J* 6.1, CH(C*H*$_3$)$_2$], 2.23 (1 H, t, *J* 6.1, OH, D_2O exchangeable), 3.98 and 4.03 (each 3 H, s, OCH$_3$), 4.55 [1 H, sept., *J* 6.1, C*H*(CH$_3$)$_2$], 5.77 (1 H, d, *J* 6.1, CH$_2$), 6.62 (1 H, s, 6-H), 6.82 (1 H, d, *J* 1.5, 3-H) and 7.71 (1 H, d, *J* 1.5, 1-H); δ_C 22.04 (2 × CH$_3$), 56.47 and 56.72 (2 × OCH$_3$), 65.39 (CH$_2$), 72.96 (CH), 95.28 (C-6), 99.75 (C-4a)[a], 109.44 (C-3)[b], 114.80 (C-8a)[a], 116.81 (C-1)[b], 135.26 (C-8), 140.87 (C-2), 153.88 (C-4)[c], 155.16 (C-5)[c] and 159.84 (C-7)[c]; *m/z* 356 (M$^+$, 38%), 354 (M$^+$, 38%), 314 (100), 312 (100), 299 (16), 297 (16), 271 (19) and 269 (20).

8-*Bromo*-4-*isopropoxy*-5,7-*dimethoxynaphthalene*-2-*carbaldehyde* **29**.—The alcohol **27** (150 mg, 0.42 mmol) was dissolved in benzene (10 cm^3) and boiled with activated manganese dioxide[18] (1 g) for 1 h. The reaction mixture was cooled, filtered and concentrated, and the residue was chromatographed (eluent 10% ethyl acetate–light petroleum) to yield the *aldehyde* **29** (127 mg, 85%) as yellow needles, m.p. 127–128 °C (methylene dichloride–light petroleum) (Found: C, 54.2; H, 4.85. $C_{16}H_{17}BrO_4$ requires C, 54.4; H, 4.8%); ν_{max}/cm^{-1} 1685 (C=O) and 1595 (C=C); δ_H 1.43 [6 H, d, *J* 6.1, CH(C*H*$_3$)$_2$], 3.96 and 4.03 (each 3 H, s, OCH$_3$), 4.74 [1 H, sept., *J* 6.1, C*H*-(CH$_3$)$_2$], 6.75 (1 H, s, 6-H), 7.19 and 8.31 (each 1 H, d, *J* 1.5, 3- and 1-H) and 10.08 (CHO); δ_C 21.99 (2 × CH$_3$), 56.82 and 56.93 (2 × OCH$_3$), 71.99 (CH), 98.27 (C-6), 101.21 (C-4a)[a], 102.53 (C-3)[b], 118.18 (C-8a)[a], 126.42 (C-1)[b], 135.25 (C-2)[c], 135.74 (C-8)[c], 154.79 (C-4)[d], 156.49 (C-5)[d], 158.49 (C-7)[d] and 192.29 (CHO); *m/z* 354 (M$^+$, 40%), 352 (M$^+$, 40%), 312 (100), 310 (100), 297 (19), 295 (19), 269 (36) and 267 (36).

Catalytic Isomerization of the Z-Olefin **32**.—A solution of methylene dichloride (5 cm^3) containing bis(acetonitrile)dichloropalladium(II) (25 mg) and the (Z)-olefin **32** (200 mg, 0.55 mmol) was stirred at room temperature for 2 h. The solution was filtered and concentrated. The residue was chromatographed (eluent 5% ethyl acetate–light petroleum) to afford the *E*-olefin **34** (170 mg, 85%) as an oil; ν_{max}(film)/cm^{-1} 1615 and 1590 (C=C); δ_H 1.30 [6 H, d, *J* 6.1, CH(C*H*$_3$)$_2$], 1.84 (3 H, dd, *J* 6 and 1.8, 3-CH$_3$), 3.87 and 3.92 (each 3 H, s, OCH$_3$), 4.49 [1 H, sept., *J* 6.1, C*H*(CH$_3$)$_2$], 6.29 (1 H, dq, *J* 15.6 and 6, 2'-H), 6.47 (1 H, dq, *J* 15.6 and 1.8, partially obscured by 6-H, 1'-H), 6.51 (1 H, s, 6-H) and 6.84 and 7.65 (each 1 H, d, *J* 1.5, 3- and 1-H); *m/z* 366 (M$^+$, 44%), 364 (M$^+$, 44%), 324 (100), 322 (100), 285 (22) and 243 (80).

rel-(1R,2S)-1-(8-*Bromo*-4-*isopropoxy*-5,7-*dimethoxynaphthalen*-2-*yl*)*propane*-1,2-*diol* **35**.—To a stirred suspension of ethyltriphenylphosphonium bromide (400 mg, 1.10 mmol) in dry tetrahydrofuran (10 cm^3) cooled to 0 °C, was added butyllithium (1.08 mmol, 1.3 mol equiv.) under nitrogen. The orange solution was stirred at 0 °C for 5 min and then cooled to −78 °C. The aldehyde **29** (300 mg, 0.85 mmol) dissolved in dry tetrahydrofuran (3 cm^3) was slowly dripped in at such a rate that the temperature of the solution did not rise above −78 °C. After 15 min at this temperature, the reaction mixture was warmed to room temperature and the reaction monitored by TLC. When no starting material remained (*ca.* 1.5 h) water was added to the mixture and the organic material extracted into ether. The organic layer was washed several times with brine and the residue obtained upon work-up contained (*Z*)-1-(8-bromo-4-isopropoxy-5,7-dimethoxynaphthalen-2-yl)-prop-1-ene **32** together with triphenylphosphine oxide. This mixture was immediately converted into the diol **35**; δ_H(on chromatographed olefin) 1.38 [6 H, d, *J* 6.5, CH(C*H*$_3$)$_2$], 1.92 (3 H, dd, *J* 8 and 1.8, 3'-CH$_3$), 3.92 and 3.98 (each 3 H, s, OCH$_3$), 5.54 [1 H, sept., *J* 6.5, C*H*(CH$_3$)$_2$], 5.86 (1 H, dq, *J* 13 and 8, 2'-H), 6.54 (1 H, dq, *J* 13 and 1.8, 1'-H), 6.58 (1 H, s, 6-H) and 6.72 and 7.75 (each 1 H, d, *J* 2, 3- and 1-H). To the solution of crude *Z*-olefin **32** in dry pyridine (4 cm^3), was added a solution of osmium tetroxide (250 mg, 0.98 mmol) in dry ether (6 cm^3). The black solution was stirred at room temperature for 30 min after which sodium metabisulphite (1.2 g), water (10 cm^3) and pyridine (10 cm^3) were added to it and the whole stirred for 10 min. The reaction mixture was acidified with dilute hydrochloric acid and the organic material extracted with methylene dichloride. The residue obtained upon work-up was purified by chromatography (eluent 30% ethyl acetate–light petroleum) to yield the *diol* **35** (200 mg, 59% from aldehyde **32**) as off-white needles, m.p. 128–129 °C (ethyl acetate–light petroleum) (Found: C, 54.1; H, 5.8. $C_{18}H_{23}BrO_5$ requires C, 54.1; H, 5.8%); ν_{max}/cm^{-1} 3346 (OH) and 1616 and 1596 (C=C); δ_H 1.06 (3 H, d, *J* 6.4, 3'-CH$_3$), 1.32 [6 H, d, *J* 6.2, CH(C*H*$_3$)$_2$], 1.89 and 2.61 (each 1 H, s br, OH, D_2O exchangeable), 3.89 and 3.94 (each 3 H, s, OCH$_3$), 4.15 (1 H, dq, *J* 4.6 and 6.4, partially obscured by OCH$_3$, 2'-H), 4.48 [1 H, sept., *J* 6.2, C*H*(CH$_3$)$_2$], 4.71 (1 H, d, *J* 4.6, 1'-H), 6.54 (1 H, s, 6-H) and 6.78 and 7.27 (each 1 H, s, 3- and 1-H); δ_C 17.55 (CH$_3$), 22.13 [CH(*C*H$_3$)$_2$], 56.68 and 56.92 (2 × OCH$_3$), 71.26 (2 × CH), 72.99 [*C*H-(CH$_3$)$_2$], 95.65 (C-6), 96.02 (C-4a)[a], 109.07 (C-3)[b], 110.05 (C-8a)[a], 117.26 (C-1)[b], 135.28 (C-8), 140.42 (C-2), 154.17 (C-4)[c], 155.24 (C-5)[c] and 158.51 (C-7)[c]; *m/z* 400 (M$^+$, 79%), 398 (M$^+$, 79%), 354 (19), 352 (19), 313 (100), 311 (100), 285 (41), 283 (39), 232 (28) and 204 (76).

rel-(2S,4R,5S)-4-(8-*Bromo*-4-*isopropoxy*-5,7-*dimethoxynaphthalen*-2-*yl*)-2,5-*dimethyldioxolane* **36**.—To a solution of the diol **35** (60 mg, 0.15 mmol) in benzene (20 cm^3) was added acetaldehyde dimethyl acetal (40 mg, 0.45 mmol) and a catalytic amount of toluene-*p*-sulfonic acid. The solution was boiled for 30 min in a Dean-Stark apparatus after which it was cooled and washed with aqueous sodium hydrogen carbonate and water. The residue obtained upon work-up was chromatographed (eluent 40% ethyl acetate–light petroleum) to yield the *dioxolane* **36** (47 mg, 74%) as colourless cubes, m.p. 89–90 °C (light petroleum) (Found: C, 56.2; H, 5.65. $C_{20}H_{25}BrO_5$ requires C, 56.5; H, 5.9%); ν_{max}/cm^{-1} 1620 and 1597 (C=C); δ_H 0.86 (3 H, d, *J* 6.4, 5'-CH$_3$), 1.36 [6 H, d, *J* 6, CH(C*H*$_3$)$_2$], 1.59 (3 H, d, *J* 4.6, 2'-CH$_3$), 3.93 and 3.96 (each 3 H, s, OCH$_3$), 4.41 (1 H, dq, *J* 7.1 and 6.4, 5'-H), 4.54 [1 H, sept., *J* 6, C*H*(CH$_3$)$_2$], 5.09 (1 H, d, *J* 7.1, 4'-H), 5.21 (1 H, q, *J* 4.6, 2'-H), 6.61 (1 H, s, 6-H) and 6.74 and 7.70 (each 1 H, s, 3- and 1-H); δ_C 16.29 and 19.96 (2 × CH$_3$), 22.14 [CH(*C*H$_3$)$_2$], 56.75 and 56.93 (2 × OCH$_3$), 72.73 [*C*H(CH$_3$)$_2$], 77.00 and 81.02 (2 × CH), 95.67 (C-6), 100.22 (CH), 101.01 (C-4a)[a] 109.49 (C-3)[b], 115.41 (C-8a)[a], 117.45 (C-1)[b], 135.29 (C-8), 138.77 (C-2), 154.06 (C-4)[c], 155.02 (C-5)[c] and 158.12 (C-7)[c]; *m/z* 426 (M$^+$, 100%), 424 (M$^+$, 100%), 384

(18), 382 (18), 340 (90), 338 (90), 325 (39), 323 (40), 259 (22) and 72 (50).

rel-(1S,3S,4R)-3,4-*Dihydro*-4-*hydroxy*-6-*isopropoxy*-7,9-*dimethoxy*-1,3-*dimethylnaphtho*[1,2-c]*pyran* **38** *and* rel-(1S,3S,4R)-5-*Bromo*-3,4-*dihydro*-4-*hydroxy*-6-*isopropoxy*-7,9-*dimethoxy*-1,3-*dimethylnaphtho*[1,2-c]*pyran* **39**.—To a stirred solution of the dioxolane **36** (113 mg, 0.26 mmol) in dry methylene dichloride (10 cm^3) at −78 °C under nitrogen, was added titanium tetrachloride (0.3 cm^3, 2.6 mmol). The dark solution was immediately warmed to room temperature and stirred for 1 h. The reaction was quenched by the addition of saturated aqueous sodium hydrogen carbonate to the mixture, and the aqueous layer separated and extracted with methylene dichloride and washed with water. The residue obtained upon work-up was chromatographed (eluent 25% ethyl acetate–light petroleum) to afford *product* **39** [18 mg, 15% (18%†)] as a yellow oil (Found: M^+, 424.0866. $C_{20}H_{25}BrO_5$ requires *M*, 424.0886); ν_{max}(film)/cm^{-1} 3413 (OH) and 1618 and 1594 (C=C); δ_H 1.28 (3 H, d, *J* 6.1, 3-CH_3), 1.32 [6 H, d, *J* 6.1, CH(CH_3)$_2$], 1.72 (3 H, d, *J* 6.6, 1-CH_3), 3.14 (1 H, s br, OH, D_2O exchangeable), 3.89 and 3.93 (each 3 H, s, OCH_3), 4.27 (1 H, sext., *J* 6.1, 3-H), 4.43 [1 H, dsept., *J* 2.8 and 6.1, C*H*(CH$_3$)$_2$], 4.71 (1 H, s br, becomes d on D_2O exchange, *J* 5.4, 4-H), 5.25 (1 H, q, *J* 6.6, 1-H), 6.55 (1 H, d, *J* 2.1, 8-H), and 6.60 (1 H, d, *J* 2.1, 10-H); *m*/*z* 426 (M^+, 20%), 424 (M^+, 20%), 384 (21), 382 (20), 369 (94), 367 (94) and 323 (100). *Compound* **38** with lower R_F was obtained as white needles [36 mg, 40%, (45%†)], m.p. 128–129 °C (light petroleum) (Found: C, 69.4; H, 7.3. $C_{20}H_{26}O_5$ requires C, 69.4; H, 7.5%); ν_{max}/cm^{-1} 3393 (OH) and 1616 and 1594 (C=C); δ_H 1.35 [6 H, d, *J* 6.1, CH(CH_3)$_2$], 1.41 (3 H, d, partially obscured by isopropoxy, *J* 6.3, 3-CH_3), 1.64 (3 H, d, *J* 6.5, 1-CH_3), 1.89 (1 H, d, *J* 8.3, OH, D_2O exchangeable), 3.86 and 3.88 (each 3 H, s, OCH_3), 3.89 (1 H, dq, partially obscured by OCH_3, *J* 8.3 and 6.3, 3-H), 4.38 (1 H, t, *J* 8.3, collapses to d on D_2O exchange, *J* 8.3, 4-H), 4.54 [1 H, sept., *J* 6.1, C*H*(CH$_3$)$_2$], 5.32 (1 H, q, *J* 6.5, 1-H), 6.50 (2 H, s, 8- and 10-H) and 6.97 (1 H, s, 5-H); δ_C 18.78 and 20.22 (2 × CH_3), 22.16 [CH(*C*H$_3$)$_2$], 55.20 and 56.20 (2 × OCH_3), 68.90, 69.43 and 71.26 (3 × CH), 72.79 [*C*H(CH$_3$)$_2$], 95.25 (C-5a)[a], 98.25 (C-8)[a], 108.43 (C-10a)[a], 114.56 (C-6a)[b], 126.58 (C-10a)[b], 133.65 (C-1a)[b], 134.32 (C-4a)[b], 154.75 (C-6)[c], 158.17 (C-7)[c] and 159.04 (C-9)[c]; *m*/*z* 346 (M^+, 47%), 331 (32), 289 (100), 271 (25) and 245 (30). A further three compounds isolated from the mixture were the dioxolane **36** (14 mg, 12%), diol **35** (14 mg, 14%) and alcohol **27** (3 mg, 4%), each identical with original material.

rel-(1S,3S,4R)-4-*Acetoxy*-3,4-*dihydro*-4-*hydroxy*-6-*isopropoxy*-7,9-*dimethoxy*-1,3-*dimethylnaphtho*[1,2-c]*pyran* **40**.—A solution of compound **38** (41 mg, 0.12 mmol) in acetic anhydride (2 cm^3) and pyridine (0.5 cm^3) was stirred at 55 °C for 1 h. Methylene dichloride and water were added to the mixture and this solution was washed with dilute hydrochloride acid and then finally with water. The residue obtained upon work-up was chromatographed (eluent 15% ethyl acetate–light petroleum) to yield the *acetate* **40** (45 mg, 97%) as colourless rhomboids, m.p. 135–136 °C (light petroleum) (Found: C, 67.85; H, 7.0. $C_{22}H_{28}O_5$ requires C, 68.0; H, 7.2%); ν_{max}/cm^{-1} 1733 (C=O) and 1616 and 1593 (C=C); δ_H (3 H, d, *J* 6.2, 3-CH_3), 1.37 [6 H, d, *J* 6.1, CH(CH_3)$_2$], 1.70 (3 H, d, *J* 6.5, 1-CH_3), 2.19 (3 H, s, $COCH_3$), 3.89 (6 H, s, OCH_3), 4.18 (1 H, dq, *J* 7.6 and 6.2, 3-H), 4.45 [1 H, sept., *J* 6.1, C*H*(CH$_3$)$_2$], 5.36 (1 H, q, *J* 6.5, 1-H), 5.82 (1 H, d, *J* 7.6, 4-H), 6.48–6.53 (2 H, m, 8- and 10-H) and 6.55 (1 H, s, 5-H); *m*/*z* 388 (M^+, 30%), 373 (12), 313 (21) and 271 (100).

† Yields in parentheses are based on unrecovered starting material.

Conversion of Compound **39** *into* **38**.—The naphthopyran **39** (51 mg, 0.12 mmol) was dissolved in dry tetrahydrofuran (20 cm^3) at −78 °C under nitrogen and butyllithium (0.59 mmol, 5 mol equiv.) was added to the solution. After this had been stirred for 1 h at −78 °C it was allowed to warm to room temperature over 15 min. The reaction was quenched by the addition of water to the mixture which was then extracted with ether. The extract was washed exhaustively with water and the residue obtained upon work-up was chromatographed (eluent 20% ethyl acetate–light petroleum) to afford the *naphthopyran* **38** (33 mg, 81%) whose TLC behaviour and ^1H NMR, MS and IR spectra were identical with those of original material described above.

trans-3,4-*Dihydro*-6-*isopropoxy*-7,9-*dimethoxy*-1,3-*dimethylnaphtho*[1,2-c]*pyran* **44**.—The naphthopyran **15** (50 mg, 0.14 mmol) was dissolved in dry benzene (5 cm^3) and treated with phosphorus tribromide (0.05 cm^3, 0.53 mmol). The solution was stirred at room temperature for 30 min after which the reaction was quenched by addition of dilute aqueous sodium hydrogen carbonate to the mixture. The organic material was extracted into methylene dichloride and the residue obtained upon work-up chromatographed (eluent 10% ethyl acetate–light petroleum) to afford two products. The first fraction yielded *compound* **42** (22 mg, 38%); δ_H 1.40 [6 H, d, *J* 6, CH(CH_3)$_2$], 1.49 (3 H, d, *J* 6.1, 3-CH_3), 1.73 (3 H, d, *J* 6.5, 1-CH_3), 3.89 (6 H, s, OCH_3), 4.32 [1 H, dq, partially obscured by C*H*(CH$_3$)$_2$, *J* 8.5 and 6.1, 3-H], 4.51 [1 H, sept., *J* 6, C*H*(CH$_3$)$_2$], 5.06 (1 H, d, *J* 8.5, 4-H), 5.37 (1 H, q, *J* 6.5, 1-H), 6.51 (2 H, s, 8- and 10-H) and 6.92 (1 H, s, 5-H); *m*/*z* 410 (M^+, 45%), 408 (M^+, 45%), 395 (20), 393 (20), 353 (72), 351 (72), 329 (25), 314 (38), 287 (56), 271 (100) and 257 (46). The second fraction contained *compound* **43** (22 mg, 39%); δ_H 1.39 [6 H, d, *J* 6.1, CH(CH_3)$_2$], 1.46 (3 H, d, *J* 6.1, 3-CH_3), 1.64 (3 H, d, *J* 6.6, 1-CH_3), 3.89 (6 H, s, OCH_3), 4.17 (1 H, dq, *J* 2 and 6.1, 3-H), 4.53 [1 H, sept., *J* 6.1, C*H*(CH$_3$)$_2$], 5.11 (1 H, d, *J* 2, 4-H), 5.49 (1 H, q, *J* 6.6, 1-H), 6.54 (2 H, s, 8- and 10-H) and 6.65 (1 H, s, 5-H); *m*/*z* 410 (M^+, 45%), 408 (M^+, 45%), 395 (20), 353 (75), 351 (75), 329 (27), 314 (38), 287 (57), 271 (100) and 257 (43). A mixture of compounds **42** and **43** (44 mg, 0.11 mmol) was dissolved in ethanol (7.5 cm^3) and water (2.5 cm^3). To this mixture was added Raney nickel catalyst (50% in water; 100 mg) and the solution stirred at 60 °C for 15 min. The reaction was quenched by filtering off the catalyst and washing the filtrate exhaustively with methylene dichloride. The residue obtained upon work-up was chromatographed (eluent 10% ethyl acetate–light petroleum) to yield the *naphthopyran* **44** (25 mg, 69%) as white cubes, m.p. 83–84 °C (light petroleum) (Found: C, 72.5; H, 7.75. $C_{20}H_{26}O_4$ requires C, 72.7; H, 7.9%); ν_{max}/cm^{-1} 1616 (C=C); δ_H 1.35 (3 H, d, *J* 6.1, 3-CH_3), 1.37 [6 H, d, *J* 6.1, CH(CH_3)$_2$], 1.66 (3 H, d, *J* 6.6, 1-CH_3), 2.71 (2 H, apparent d, *J* 7.2, pseudoequatorial and pseudoaxial 4-H), 3.89 (6 H, s, OCH_3), 4.25 (1 H, apparent sext., *J* 6.1, 3-H), 4.48 [1 H, sept., *J* 6.1, C*H*(CH$_3$)$_2$], 5.40 (1 H, q, *J* 6.6, 1-H), 6.46 (1 H, d, *J* 2.2, 8-H), 6.50 (1 H, s, 5-H) and 6.54 (1 H, d, *J* 2.2, 10-H); δ_C 20.35 and 21.94 (2 × CH_3), 22.13 [CH(*C*H$_3$)$_2$], 36.69 (CH_2), 55.15 and 56.11 (2 × OCH_3), 62.46 and 69.80 (2 × CH), 72.95 [*C*H(CH$_3$)$_2$], 94.79 (C-5a)[a], 97.67 (C-8)[a], 112.28 (C-10)[a], 114.05 (C-4a)[b], 126.17 (C-6a)[b], 131.64 (C-10a)[b], 134.02 (C-10b)[b], 153.68 (C-6)[c], 157.93 (C-7)[c] and 158.89 (C-9)[c]; *m*/*z* 330 (M^+, 39%), 315 (29) and 273 (100).

cis-3,4-*Dihydro*-6-*isopropoxy*-7,9-*dimethoxy*-1,3-*dimethylnaphtho*[1,2-c]*pyran* **47**.—The naphthopyran **13** (40 mg, 0.12 mmol) dissolved in dry benzene (5 cm^3) was treated with phosphorus tribromide (0.04 cm^3, 0.45 mmol). The solution was stirred at room temperature for 30 min after which dilute aqueous sodium hydrogen carbonate was added to it. The

organic material was extracted with methylene dichloride and the residue obtained upon work-up chromatographed (eluent 10% ethyl acetate–light petroleum) to afford two products. *Compound* **45** (15 mg, 30%) of higher R_F; δ_H 1.40 [6 H, d, *J* 6, $CH(CH_3)_2$], 1.54 (3 H, d, *J* 6.1, 3-CH_3), 1.56 (3 H, d, *J* 6.1, 1-CH_3), 3.87 (1 H, dq, partially obscured by OCH_3, *J* 8.5 and 6.1, 3-H), 3.88 and 3.94 (each 3 H, s, OCH_3), 4.54 [1 H, sept., *J* 6, $CH(CH_3)_2$], 5.10 (1 H, d, *J* 8.5, 4-H), 5.42 (1 H, q, *J* 6.1, 1-H), 6.50 and 6.56 (each 1 H, d, *J* 2.2, 8- and 10-H) and 7.00 (1 H, s, 5-H); *m/z* 410 (M^+, 46%), 408 (M^+, 46%), 395 (20), 393 (21), 353 (75), 351 (75), 329 (24), 314 (38), 287 (55), 271 (100) and 257 (40).

Compound **46** (17 mg, 35%) of lower R_F; δ_H 1.40 [6 H, d, *J* 6, $CH(CH_3)_2$], 1.42 [3 H, d, partially obscured by $CH(CH_3)_2$, *J* 6, 3-CH_3], 1.69 (3 H, d, *J* 6.1, 1-CH_3), 3.76 (1 H, q, *J* 6, 3-H), 3.88 and 3.89 (each 3 H, s, OCH_3), 4.58 [1 H, sept., *J* 6, $CH(CH_3)_2$], 4.79 (1 H, s br, 4-H), 5.58 (1 H, q, *J* 6.1, 1-H), 6.51 and 6.58 (each 1 H, d, *J* 2.2, 8- and 10-H) and 6.62 (1 H, s, 5-H); *m/z* 410 (M^+, 45%), 408 (M^+, 45%), 395 (20), 393 (20), 353 (76), 351 (76), 329 (25), 314 (38), 287 (55), 271 (100) and 257 (42). A mixture of compounds **45** and **46** (32 mg, 0.08 mmol) was dissolved in ethanol (7.5 cm^3) and water (2.5 cm^3). To this mixture was added Raney nickel catalyst (50% in water; 100 mg) and the solution was stirred at 60 °C for 15 min. The reaction was quenched by filtering off the catalyst and washing the filtrate exhaustively with methylene dichloride. The residue obtained upon work-up was chromatographed (eluent 10% ethyl acetate–light petroleum) to yield the *naphthopyran* **47** (17 mg, 64%) as white cubes, m.p. 74–75 °C (light petroleum) (Found: M^+, 330.1835. $C_{20}H_{26}O_4$ requires *M*, 330.1831); ν_{max}/cm^{-1} 1617 (C=C); δ_H 1.81 [9 H, d, *J* 6.1, $CH(CH_3)_2$ and 3-CH_3], 1.59 (3-H, d, *J* 6.1, 1-CH_3), 2.56 (1 H, dd, *J* 15.6 and 2.2, pseudoequatorial 4-H), 2.79 (1 H, dd, *J* 15.6 and 10, pseudoaxial 4-H), 3.74 (1 H, ddq, *J* 2.2, 10 and 6.1, 3-H), 3.88 and 3.89 (each 3 H, s, OCH_3), 4.48 [1 H, sept., *J* 6.1, $CH(CH_3)_2$], 5.44 (1 H, q, *J* 6.1, 1-H), 6.46 (1 H, d, *J* 2.1, 8-H), 6.51 (1 H, s, 5-H) and 6.58 (1 H, d, *J* 2.1, 10-H); *m/z* 330 (M^+, 37%), 315 (29) and 273 (100).

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