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3,4-EPOXYPRECOCENES: THERMAL AND ACID PROMOTED DIMERISATION

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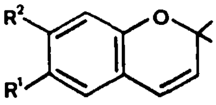
Abstract - Thermal dimerisation of 3,4-epoxyprecocene II (2b) in absence of solvents afforded high yields (65%) of tetrahydrofuran dimer 4 and minor amounts of benzopyran-3-one 3. On the other hand, two new dimers, γ-hydroxyketone 5 and dioxane 7a have also been isolated from treatment of 2b with different acids. Structural elucidations for all these dimers have been carried out by spectroscopic and analytical methods, combined with the use of selected deuteriated precursors in the corresponding dimerisation procedures.

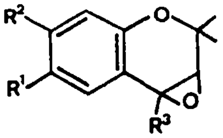
Introduction

Precocenes (1), naturally occurring substances isolated from Ageratum houstonianum, have been reported to exhibit insect antijuvenile hormone activity, when administered to sensitive species of insects[1,2]. The unique properties of these compounds have led to extensive biological and chemical investigations in this and other laboratories, to establish activity-structure relationships for evaluation of its potential application in insect control[3].



(1)

a; Precocene I : $R^1 = H$, $R^2 = OCH_3$
b; Precocene II : $R^1 = R^2 = OCH_3$



(2)

a; $R^1 = R^3 = H$, $R^2 = OCH_3$
b; $R^3 = H$, $R^1 = R^2 = OCH_3$
c; $R^3 = D$, $R^1 = R^2 = OCH_3$

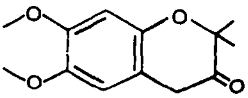
Results on mode of action and metabolism studies[4] have provided strong evidence that precocenes undergo an oxidative biotransformation into a highly reactive 3,4-epoxide intermediate 2, probably by action of mono-oxygenases of the P-450 type, within the corpora allata, the glands where the juvenile hormones are biosynthesised. This epoxide would cause the necrosis of the glands by alkylation of the cellular macromolecules with the ensuing suppression of juvenile hormone biosynthesis. The synthesis of 3,4-epoxyprecocenes revealed that they are highly reactive versus nucleophilic attack[5-7], being easily hydrolysed to mixtures of the corresponding cis- and trans-dihydrodiols, essentially through a SN1 mechanism[8].

In the context of the increasing interest in studies on the chemical and biochemical reactivities of these compounds to find analogies or differences with the reactivities of other bioactive epoxides, such as those derived from polycyclic aromatic hydrocarbons (PAH), in the present paper we report on our results of the thermal and acid promoted dimerisation of 3,4-epoxyprecocene II (2b).

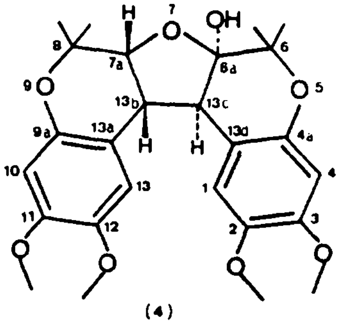
Results and Discussion

Thermal dimerisation.- Attempts of purifying crude 3,4-epoxyprecocenes by vacuum short path bulb-to-bulb distillation disclosed that major amounts of product remained as non-distillable residues, pointing out to a high thermal lability for these compounds. To shed some light on this thermal degradation process, the transformation of 3,4-epoxyprecocene II (2b) was studied, as model.

Analysis of the distilled fraction by g.l.c. revealed that epoxide 2b was impurified by the presence of variable amounts of benzopyran-3-one 3, which was identified by comparison with an authentic sample, prepared independently by an original procedure developed in this laboratory[9]. Likewise, t.l.c. fractionation of the residue afforded a major component (17% yield), which was identified by its spectral and analytical features as tetrahydrofuran dimer 4. Compound 4 (m.p. 273-5°C) had molecular formula $C_{26}H_{32}O_8$ (m/z 472, M^+100%), and exhibited the occurrence of one hydroxyl group (m/z 454, M^+-18; i.r. absorption at 3560 cm^{-1}, and its ^1H n.m.r. singlet absorption at δ 2.02, which disappeared upon addition of D_2O). Furthermore, ^1H n.m.r. spectrum showed a broad singlet absorption at δ 3.53 and an AB system at δ 3.40 and 3.84 (J_{AB}= 5 Hz), suggesting a dimer structure with a hemiacetal tetrahydrofuran ring. Formation of this structure from two epoxide molecules might be envisaged by direct linkage of the corresponding benzylic carbon atoms and concomitant bonding of the original C-3 positions of 2b through an oxygen atom bridge.



(3)



(4)

The above structure has been confirmed by X-ray diffraction analysis[10], which showed a cis-anti-cis fused ring system, with both pyran rings of the chroman systems adopting distorted boat conformations, in agreement with the observed ^1H n.m.r. couplings.

The results of experiments carried out for optimising the thermal dimerisation process showed that maximum yield of dimer 4 (65%) was achieved by heating the crude epoxide at 120°C for 20 hours in absence of solvents, whereas only low yields (<10%) were obtained by thermal treatment in the presence of solvents like toluene or chlorobenzene.

Acid promoted dimerisation

a) Dibenzyl hydrogen phosphate.- Recently, Raddo and Chan[11,12] reported that selected phosphodiesters react with epoxides of polycyclic aromatic hydrocarbons according to different pathways. In the presence of these acids, weak carcinogenic K-region arene epoxides rearranged to phenols, whereas strong mutagenic bay-region arene epoxides afforded phosphotriester adducts by a regio- and a stereospecific opening of the oxirane ring at the benzylic position. In view of the similarities suggested in the mode of action of PAH and precocene epoxides[13], we deemed interesting to ascertain the preferred reaction pathway of 3,4-epoxyprecocenes in front of dibenzyl hydrogen phosphate.

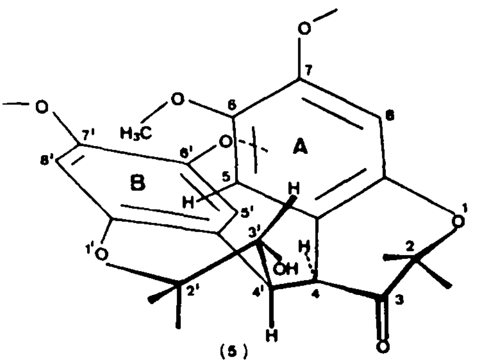
Reaction of equimolecular amounts of dibenzyl hydrogen phosphate and 3,4-epoxyprecocene II (2b) at room temperature in tetrahydrofuran, afforded a mixture in which the presence of phosphotriester was not detected. The main components of this mixture were benzopyran-3-one 3 (12%), cis- and trans-dihydrodiols derived from 2b (5%) and dimer 5 (47%).

Analytical and mass spectral data for compound 5 showed a molecular formula of $C_{26}H_{32}O_8$. The presence of one hydroxyl group was inferred from M^+-18 peak at m/z 454 in the mass spectrum and broad absorption at 3600-3000 cm^{-1} in the i.r. spectrum, being further confirmed by a doublet at δ 2.05 (J= 6 Hz), attributable to H-C-O<u>H</u> in the ^1H n.m.r. spectrum, which disappeared upon addition of D_2O. Likewise, the occurrence of a ketone moiety was deduced from i.r. carbonyl absorption at 1720 cm^{-1} and a peak at 211.65 ppm in the ^{13}C n.m.r. spectrum. Other particular features in the ^1H n.m.r. spectrum showed one aromatic proton singlet and one aromatic methoxy group absorption at δ 5.93 and 3.36 ppm, shifted abnormally upfield, when compared to the corresponding absorptions in related benzopyranic derivatives prepared in this and other laboratories (cf. Table). In addition, the spectrum also revealed the presence of one AMX system, appearing H_A as a double doublet at δ 3.59 ppm (J_{AM}= 2 Hz, J_{AX}= 11 Hz), and H_M and H_X as doublets, at δ 4.07 and 3.20 respectively, being H_X also coupled to the hydroxyl proton. The assignation of δ 3.59 and 4.07 signals to benzylic protons H-4' and H-4, respectively, was substantiated by the disappearance of these absorptions in the ^1H n.m.r. spectrum of the corresponding dideuteriated analog of dimer 5, prepared by reaction of 4-^2H-3,4-epoxyprecocene II 2c[14] with dibenzyl hydrogen phosphate.

Table.- Significant chemical shifts (ppm) of ^1H n.m.r. spectra of dimer 5 and of related benzopyran systems

Proton	Observed chemical shifts	Chemical shift range in related benzopyran systems[3,5,14].
H-5	5.93	6.5-6.7
CH_3O (C-6)	3.36	3.7-3.9
<u>H</u>COR (H-3')(R= H)	3.20	3.7-3.9
HCCO (H-4)	4.07	3.4-3.6
H-4'	3.59	2.7-3.0

All above data were consistent with dimer structure 5, in which the linkage between both 3,4-epoxyprecocene moieties was through C-4 and C-4' and one carbonyl and one hydroxyl groups were located at C-3 and C-3', respectively. Furthermore, the occurrence of a preferred conformation of 5 may substantiate the assignation of signals at δ 5.93 and 3.36 to H-5 and CH_3O (C-6), respectively, being the 0.5-0.8 ppm upfield shifts observed for these absorptions, plausibly, promoted by diamagnetic shielding of aromatic ring A. Likewise, the analogous displacement on the signal at δ 3.20, attributed to H-3', would be originated by the proximity of this proton to aromatic ring B. Conversely, the paramagnetic deshielding effect of C-3 carbonyl group on coplanar H-4' shifts downfield the absorption of this proton which appears at δ 3.59. A similar deshielding shift is observed on the corresponding absorption of H-4 proton at δ 4.07, due to the relative spatial positions between aromatic ring B and this proton. In addition, the coupling constant between H-3' and H-4' (J= 11 Hz) suggested an antiperiplanar arrangement of the corresponding C-H bonds, whereas the small value of the coupling constant between H-4 and H-4' (J= 2 Hz) pointed to a dihedral angle of ca. 70°, in this case.



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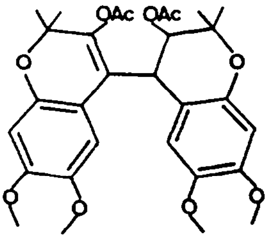
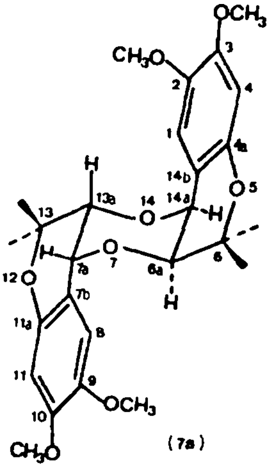


(6)

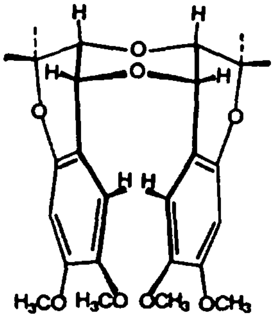
The structure of dimer 5 was further substantiated by treatment of 5 with acetic anhydride in the presence of pyridine to give diacetate 6 (m/z 556 (M^+) and M^+-60; i.r. absorption at 1750 cm^{-1} and ^1H n.m.r. singlets at δ 2.06 and 2.28). A comparative study of the ^1H n.m.r. spectra of compounds 5 and 6 revealed several differences, probably associated to partial loss of the above conformational preference caused by the acetylation reaction. While this conversion promoted an unusually large downfield shift (2.2 ppm) on the H-3' proton absorption, only small to moderate shifts in the same direction (0.07-0.35 ppm) were observed for H-5, CH_3O (C-6) and H-4 absorptions.

b) Reaction with other acids.- Reaction of 3,4-epoxide 2b with other classical acid catalysts, such as p-toluenesulphonic acid and boron trifluoride etherate, was also investigated. Results obtained in both cases were similar to those observed with dibenzyl hydrogen phosphate, but the formation of a new dimer 7, in 10% yield, could be ascertained from the reaction mixture of the treatment of epoxide 2b with boron trifluoride.

Compound 7 had molecular formula $C_{26}H_{32}O_8$; its i.r. spectrum did not show hydroxyl or carbonyl absorptions and its ^1H n.m.r. spectrum revealed a high symmetry with the signals attributable to C-6a, C-7a, C-13a and C-14a protons, appearing as doublets at δ 4.07 and 4.71, with a relative cis stereochemistry (J= 6 Hz) between both type of protons. All these data pointed to a 1,4-dioxane structure for this dimer, with a cis,cis configuration, in which two different modes of linkage between both building moieties, cis,anti,cis (7a) or cis,syn,cis (7b) might be anticipated.



(7a)



(7b)

Examination of both possibilities with space filling models suggested a severe encumbrance for the second arrangement 7b, in which H-5 and H-5' should also be subjected to diamagnetic shielding by ring currents of aromatic rings, in contrast to the normal chemical shifts observed for these protons in the ^1H n.m.r. spectrum. On the other hand, all the ^1H n.m.r. absorptions were in agreement with the cis,anti,cis arrangement. It is worth of note that this mode of linkage has also recently been assigned by Anastasis and Brown[15] to a dimer isolated from treatment of 3,4-dihydro-3.4-diol derivative of precocene I (1a) with p-toluenesulphonic acid in boiling benzene. However, these authors attributed an asymmetric cis,trans configuration to this compound, on the basis of the complexity of its ^1H n.m.r. spectrum.

To shed some light on the possible interconversion of the different dimers and on the putative intermediates participating in its formation starting from 3,4-epoxyprecocene 2b, several complementary experiments were carried out.

As anticipated from the stereochemical differences of the benzylic bonds in the corresponding structures, cyclisation of dimer 5 to afford 4 did not take place under any of the conditions which led to compound 4 from epoxide 2b, suggesting independent mechanistic pathways leading to the formation of both compounds.

On the other hand, the isolation of benzopyran-3-one 3 as by-product in some of the above dimerisation reactions, advised to ascertain the potential role of this compound in the formation of the different dimers. However, when ketone 3 was subjected to either the thermal or acid catalysed conditions, above depicted for 3,4-epoxyprecocene 2b, it failed to give any detectable amounts of dimers 4, 5 or 7a. In addition, the reaction of 3 with 4-(^{2}H)-3,4-epoxyprecocene II (2c) in the presence of dibenzyl hydrogen phosphate afforded an analog of dimer 5, with deuterium label at the benzylic positions, and over 100% recovery of 3. . These results indicated that ketone 3 can be ruled out as intermediate precursor in the formation of dimers 4, 5 or 7a.

In summary, results herein reported on the reactivity of 3,4-epoxyprecocene II (2b) have shown its thermal dimerisation to tetrahydrofuran dimer 4, in high conversion yields, and its transformation to two additional dimer compounds, γ-hydroxyketone 5, as main product and dioxane 7a, as minor component, in the presence of acid catalysts.

On the other hand, the suggested parallelism in the reactivity of 3,4-epoxyprecocenes and bay-region PAH diol epoxides might be apparently questioned from the above results of the reaction of epoxide 2b with dibenzyl hydrogen phosphate, in which the formation of phosphotriester adducts was not detected. In fact, as inferred from studies of hydrolysis of 3,4-epoxyprecocenes by previous authors, these compounds are more reactive than PAH diol epoxides[7].

Experimental Part

General Methods.- Melting points were determined on a Kofler apparatus and are uncorrected. Elemental analyses were carried out with a 1106 Carlo Erba analyser. I.r. spectra were recorded on a 399B Perkin Elmer apparatus. Mass spectra were obtained with an updated MS-9 instrument coupled to a Digital PDP 11/24 computer system. The ^{1}H and ^{13}C n.m.r. spectra were registered on a Varian XL20 (200 MHz for ^{1}H) and a Bruker WP 80 SY (80 MHz for ^{1}H and 20 MHz for ^{13}C) spectrometers. Samples were observed in 5 mm spinning tubes at ca. 20% solutions in deuteriochloroform at normal temperature probe, the solvent providing the lock signal. All chemical shifts are given in ppm downfield from internal tetramethylsilane.

6a,7a,13b,13c-Tetrahydro-6a-hydroxy-2,3,11,12-tetramethoxy-6,6,8,8-tetramethyl-6H,8H-bischromeno [3,4-b:4',3'-d]furan (4). Epoxyprecocene 2b[5] (0.18 g, 0.76 mmol) was heated for 20 h at 120°C. The crude was allowed to cool, diluted in chloroform and purified by preparative thin layer chromatography (silica gel; hexane:diethyl ether/1.5:4.5), to afford 0.117 g (R_f 0.4, 65% yield) of the dimer 4, which crystallised on standing and was recrystallised from methanol. m.p. 273-5°C (Found: C, 65.75; H, 6.79. $C_{26}H_{32}O_8$ requires C, 66.09; H, 6.83); m/z 472 (M^+, 100%), 454 (23.5) and 439 (47.4); $\nu_{max.}$ (KBr) 3560, 2930, 2830, 1620, 1510, 1450, 1410, 1260, 1200, 1160, 1130, 1075, 1055, 950, 860 and 835 cm^{-1}; δ_H 1.07 (3H,s,CH_3), 1.21 (3H,s,CH_3), 1.50 (6H,s,CH_3), 2.02 (1H,s,OH), 3.40 (1H,d,J=5Hz,C_{13b}-H), 3.53 (1H,s,C_{13c}-H), 3.83 (3H,s,CH_3O), 3.84 (3H,s,CH_3O), 3.84 (1H,d,J=5Hz, C_{7a}-H), 3.91 (3H,s,CH_3O), 3.92 (3H,s,CH_3O), 6.46 (2H,s,ArH), 6.74 (1H,s,ArH) and 6.80 (1H,s,ArH) ppm; δ_C 21.42 (CH_3), 21.90 (CH_3), 22.23 (CH_3), 25.56 (CH_3), 45.02 (C-13b), 52.54 (C-13c), 55.87 (2 CH_3O), 56.86 (CH_3O), 57.04 (CH_3O), 75.40, 77.55 (C-6,C-8), 81.58 (C-7a), 101.88, 102.24 (C-4,C-10), 105.88 (C-13d), 111.42, 111.49 (C-1,C-13), 112.29, 113.43 (C-6a,C-13a), 144.06, 144.40 (C-3,C-11) and 146.50, 146.99, 149.56, 149.72 (C-2,C-4a,C-9a,C-12) ppm.

3,3',4,4'-Tetrahydro-3'-hydroxy-6,6',7,7'-tetramethoxy-2,2,2',2'-tetramethyl-3-oxo-4,4'-2H,2'H-bichromene (5) A solution of epoxyprecocene 2b (0.18 g, 0.76 mmol) in tetrahydrofuran (1 ml) was treated with a solution of dibenzyl hydrogen phosphate (0.21 g, 0.76 mmol) in the same amount of solvent, and the mixture was stirred for 20 h at room temperature. The residue obtained after solvent removal was purified by preparative thin layer chromatography (silica gel; dichloromethane:ethyl acetate/95:5), to yield 0.085 g (R_f 0.4, 47% yield) of a pale yellowish solid which crystallised on standing and was characterised as dimer 5, and 0.022 g (R_f 0.6, 12% yield) of a yellowish oil which was identified as benzopyran-3-one 3 by comparison with an authentic sample independently prepared[9]. Compound 5 had m.p. 164-5°C (Found: C, 65.92; H, 7.13. $C_{26}H_{32}O_8$ requires C, 66.09; H, 6.83); m/z 472 (M^+, 1.9%), 454 (0.9) and 237 (100); $\nu_{max.}$ (KBr) 3480, 2980, 2940, 1720, 1620, 1515, 1445, 1270, 1230, 1205, 1130, 1080, 1015 and 875 cm^{-1}; δ_H 1.10 (3H,s,CH_3), 1.28 (3H,s,CH_3), 1.29 (3H,s,CH_3), 1.58 (3H,s,CH_3), 2.05 (1H,d,J=6Hz,OH), 3.20 (1H,dd,J_1=6Hz, J_2= 11Hz, CHOH), 3.36 (3H,s,CH_3O), 3.59 (1H,dd,J_2=11Hz,J_3=2Hz,$C_{4'}$-H), 3.80 (3H.s.CH_3O), 3.83 (3H,s,CH_3O), 3.89 (3H,s,CH_3O), 4.07 (1H,d,J_3=2Hz,C_4-H), 5.93 (1H,s,ArH), 6.32 (1H,s,ArH), 6.52 (1H,s,ArH) and 6.93 (1H,s,ArH) ppm; δ_C 17.57 (CH_3), 24.14 (CH_3), 24.24 (CH_3), 26.52 (CH_3), 46.42 (C-4'), 48.35 (C-4), 55.76 (CH_3O), 55.95 ($2CH_3O$), 57.13 (CH_3O), 72.62 (C-2'), 77.04 (C-2), 82.37 (C-3'), 101.93, 102.49 (C-8,C-8'), 110.63, 111.07 (C-5,C-5'), 112.99, 113.60 (C-4a,C-4'a), 143.73, 144.64 (C-6,C-6'), 147.01. 148.47, 149.32, 149.56 (C-7,C-7',C-8a,C-8'a) and 211.65 (C-3) ppm.

4,4'-(^{2}H)-3,3',4,4'-Tetrahydro-3'-hydroxy-6,6',7,7'-tetramethoxy-2,2,2',2'-tetramethyl-3-oxo-4,4'--2H,2'H-bichromene. A solution of 4-(^{2}H)-epoxyprecocene II (2c, 0.15 g, 0.63 mmol), prepared in 80% overall yield from 4-(^{2}H)-precocene II[14] according to the general procedure previously reported[5], in tetrahydrofuran (1.5 ml), was treated with dibenzyl hydrogen phosphate as above described, to yield, after preparative thin layer chromatography purification, 0.83 g (55% yield) of expected dimer 5 deuterated at C-4 and C-4'. m/z 474 (M^+,1.7%), 473 (2.3), 239 (41) and 238 (100); δ_H 1.10 (3H,s,CH_3), 1.29 (6H,s,CH_3), 1.58 (3H,s,CH_3), 2.13 (1H,d,J=6Hz,OH), 3.20 (1H,d,J=6Hz,CHOH), 3.35 (3H,s,CH_3O), 3.80 (3H,s,CH_3O), 3.83 (3H,s,CH_3O), 3.88 (3H,s,CH_3O), 4.07 (1H,s,H-4), 5.92 (1H,s,ArH), 6.32 (1H,s,ArH), and 6.93 (1H,s,ArH) ppm.

3',4'-Dihydro-3,3'-diacetoxy-6,6',7,7'-tetramethoxy-2,2,2',2'-tetramethyl-4,4'-2H,2'H-bichromene (6). A solution of dimer 5 (0.040 g, 0.08 mmol) in pyridine (2 ml), was treated with acetic anhydride (1 ml) and the mixture was stirred for 30 min at room temperature. The residue obtained after elimination of reagents under vacuum was purified by preparative thin layer chromatography (silica gel; dichloromethane:ethyl acetate/9:1), to afford 0.032 g (R_f 0.6, 64% yield) of a pale yellow oil which was identified as diacetate 6. m/z 556 (M^+,10%) and 195 (100); $\nu_{max.}$ (film) 3980, 3940, 1750 (br.), 1620, 1510, 1450, 1370, 1270, 1220, 1195, 1105, 1040, 1015 and 865 cm^{-1}; δ_H 1.29 (3H,s,CH_3), 1.37 (3H,s,CH_3), 1.45 (6H,s,CH_3), 2.06 (3H,s,CH_3CO), 2.28 (3H,s,CH_3CO), 3.43 (3H,s, CH_3O), 3.68 (3H,s,CH_3O), 3.79(3H,s,CH_3O), 3.82 (3H,s,CH_3O), 3.94 (1H,d,J=10Hz,H-4'), 5.42 (1H,d,J=10Hz,H-3'), 6.20 (1H,s,ArH), 6.41 (1H,s,ArH), 6.45 (1H,s,ArH) and 6.72 (1H,s,ArH) ppm.

6a,13,13a,14a-Tetrahydro-2,3,9,10-tetramethoxy-6,6,13,13-tetramethyl-6H,7aH-bischromeno {3,4-b:3',4'-e}-{1,4}dioxin (7a). A mixture of 3,4-epoxyprecocene II (2b) (0.18 g, 0.76 mmol) in tetrahydrofuran (4 ml) and boron trifluoride etherate (0.1 ml, 0.80 mmol) was allowed to react for 20 h at room temperature. The residue obtained after solvent removal was purified by preparative thin layer chromatography (silica gel; hexane:diethyl ether/1:3), to afford four compounds: 0.018 g of dimer 4 (R_f 0.4, 10%), 0.045 g of dimer 5 (R_f 0.3, 25%). 0.040 g of compound 3 (R_f 0.7, 21%) and 0.018 g (R_f 0.5, 10%) of a pale yellow solid which was recrystallised from diethyl ether/hexane and characterised as dimer 7a. m.p. 224-6°C (Found C, 66.09; H, 6.91. $C_{26}H_{32}O_8$ requires C, 66.09; H, 6.83); m/z 472 (M^+,100%), 236 (16.3) and 205 (97.6); $\nu_{max.}$ (CCl_4) 2910, 2820, 1500, 1225, 1195, 1130, 1100 and 1015 cm^{-1}; δ_H1.27 (6H,s,CH_3), 1.48 (6H,s,CH_3), 3.83 (6H,s,CH_3O), 3.86 (6H,s,CH_3O), 4.07 (2H,d,J=6Hz,CH), 4.71 (2H,d,J=6Hz,CH), 6.39 (2H,s,ArH) and 6.84 (2H,s,ArH) ppm.

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