The synthesis of various cycloalkana[*d*]xanthones and conversion of the cyclohexa-analogue to a 7,7a-dimethylcyclohexa-[*d*]xanthene †

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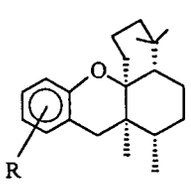
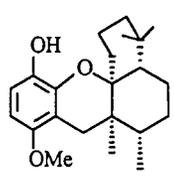
The synthesis of cyclo-penta-, -hexa- and -hepta-[*d*]xanthones **5** from (*E*)-(2-hydroxyphenyl)-5-arylpent-4-ene-1,3-diones **4**, cycloalkanones and pyrrolidine is described. Reactions to modify **5** in an attempt to synthesize analogues of the five naturally occurring cyclohexa[*d*]xanthenes (with general formula **1**) are also described: these reactions include *C*-methylations at C-7 and C-7a, hydride reduction of the 8-keto group, dehydroxylations and finally catalytic reduction to give **16**. The stereochemistry of **16** established by NOE and an X-ray crystal structure of **9aB** differs from **1** at two contiguous C-atoms.

From natural sources (fungi and sponges), five cyclohexa[*d*]-xanthenes with the general structure **1**, have been reported[1–5]



1, R = various substituents



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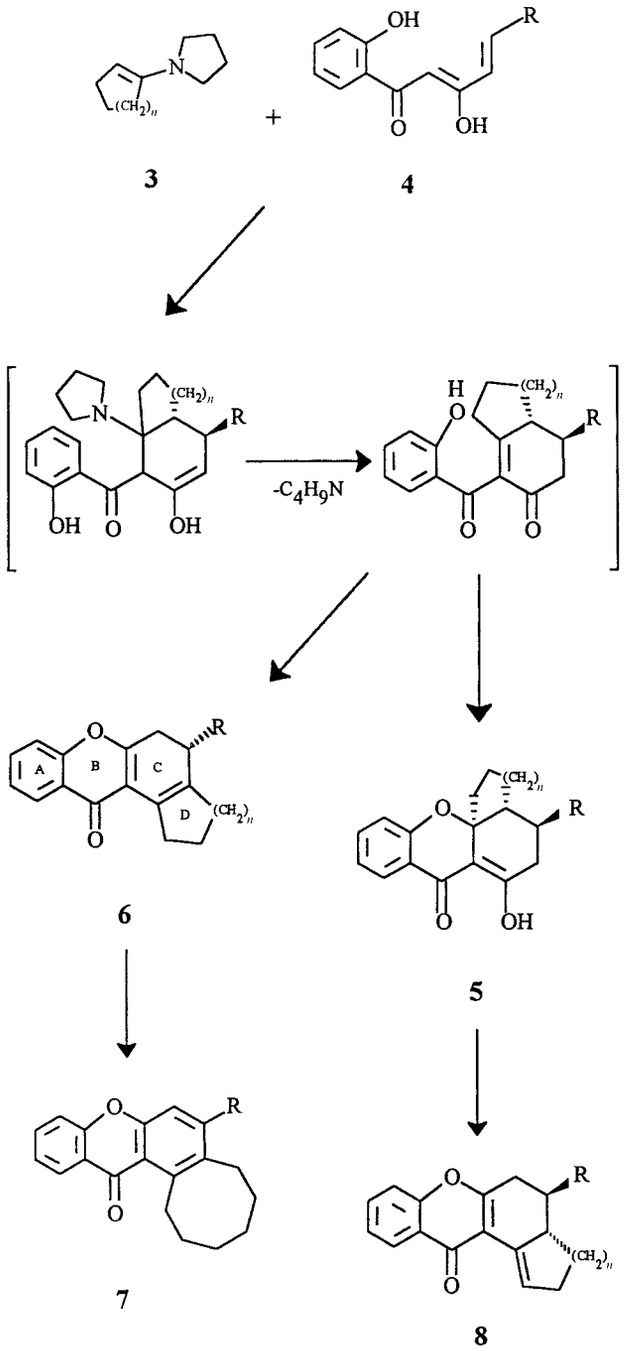
with several possessing physiological properties. For example, strongylin A **2**,[4,5] from the marine sponge *Smenospongia hartmani*, has been found to be active against P388 murine leukemia tumour cells and the influenza PR-8 strain. The total synthesis of this tetracyclic ring system including stereochemistry, is clearly a formidable challenge. We have however briefly reported[6] a one step synthesis of the tetracyclic cyclohexa[*d*]-xanthene-7,8-dione **5aB** in 62% yield from simple starting materials *viz*. the enamine **3B**, and the dione **4a** which is readily obtained *via* a Baker–Venkataraman rearrangement[7] of the ester formed from 2-hydroxyacetophenone and (*E*)-cinnamoyl chloride. In this paper the full details and generality of this cycloalkana[*d*]xanthone synthesis is reported as well as reactions of **5B** which are aimed at synthesising a closer analogue of **1**.

The synthesis of **5aB** was first extended to include **4** with other aromatic substituents *viz*. **b** and **c**, and another enamine, **3A**, in reactions which were carried out in boiling ethanol and required only half a minute (for case **A**) or five minutes (for case **B**). In this way, compounds **5aA**, **5bB**, **5cA** and **5cB** were also obtained and from a comparison of all their spectra, especially NMR resonances, with those of **5aB,** the structure of which had been established by X-ray crystallography,[6] all appeared to have the same stereochemistry as **5aB**. Thus in all cases, the stereochemistry of ring C is in the most stable arrangement with both substituents at C-3a and C-4 (in the **A** series) and C-4a and C-5 (in the **B** series), in equatorial positions and furthermore the *trans*-hydrogens at C-4a and C-5 (for the **B** series) are indicative of these [*d*] fused xanthones **5** having been formed firstly by a 4+2 cycloaddition reaction in which *exo*-addition had occurred to create ring C, followed by elimination of pyrrolidine and finally a Michael addition of the phenolic hydroxy to the resulting αβ-unsaturated ketone to give the heterocyclic ring B as shown in Scheme 1. The latter process can potentially occur *via* attack of the hydroxy from either the top or bottom face of ring C, but we appear to have only isolated adducts in which the D ring is *cis*-fused. Noting the polar nature of the reactants in these 4+2 cycloaddition reactions this process is most likely to have occurred in a stepwise manner and overall the reaction can be considered to have taken place with inverse electron demand. The procedure for the synthesis of **5** reported earlier,[6] has now been simplified by replacing the enamine with the unreacted cyclic ketone and pyrrolidine and carrying out the reaction by mixing all three reactants in refluxing dichloromethane. Using this procedure, reactants **4**(**a**–**c**) with cyclo-pentanone and -hexanone gave slightly improved yields of the corresponding compound **5** and furthermore we have succeeded in making **5aC**, **5bC** and **5cC** from **4**(**a**–**c**) and cycloheptanone. The reaction however fails to give **5D** analogues from the reaction of *N*-(cyclooct-1-en-1-yl)-pyrrolidine (or cyclooctanone and pyrrolidine) with **4**(**a**–**c**), and instead cycloocta[*a*]xanthones **6aD**, **6bD** and **6cD** are formed, presumably *via* rotation of the cyclohexenone ring before ring B is formed, as described in our earlier communication[6] except that the final elimination of water produces a double bond in ring C and not in ring D (as in **8**) which was observed with smaller rings ($n = 1,2$).[6] The change in the product formed is very likely to be due to **6D** being the thermodynamically preferred product because the cyclooctene unit contains two sp^2 centres and thus has much lower strain than the fully saturated cyclooctane found in **5D**.‡ The structures of the **6D** analogues were deduced from their spectra including the infrared absorption (at *ca.* 1641 cm^{-1}) for a chromone. Treatment of **6aD**, and **6bD** with pyrrolidine in boiling ethanol causes ring C to readily aromatise giving **7a** and **7b** respectively.

When considering dehydroxylation and *C*-methylation reactions to transform **5** into an analogue of **1** it is important to

† Full crystallographic details for crystal **9aB**, excluding structure factor tables, have been deposited at the Cambridge Crystallographic Data Centre (CCDC). For details of the deposition scheme, see 'Instructions for Authors', *J. Chem. Soc.*, *Perkin Trans. 1*, available *via* the RSC Web page (http://www.rsc.org/authors). Any request to the CCDC for this material should quote the full literature citation and the reference number 207/252.

‡ Referees comment.



Scheme 1

realize that acids and bases readily convert the [*d*]xanthone **5** into an [*a*]xanthone **8** as we reported earlier.[6,8] The first step in converting **5aB** into a 7,7a-dimethylcyclohexa[*d*]xanthene would therefore have to be a *C*-methylation reaction (at C-7a) under neutral conditions to form a non-labile product. Taylor and McKillop have shown[9,10] that on treatment with thallium(I) ethoxide, β-diketones form thallium(I) salts which react with alkylating agents to give mono-*C*-alkylation at the dicarbonyl bearing C-atom. We have found that with thallium(I) ethoxide, **5aB** formed a yellow salt which on treatment with methyl

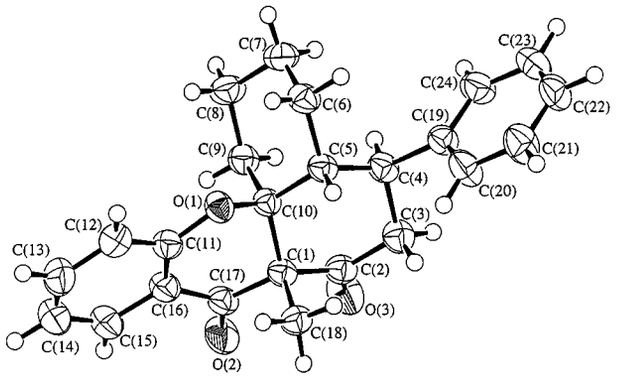


Fig. 1 X-Ray structure of compound **9aB** revealing the stereochemistry at C-13a.

iodide gave a monomethylated compound A (62%) and a dimethyl compound B (2%). This result was obtained on numerous occasions but on using a certain bottle of thallium(I) ethoxide the products were A (65%) and another monoalkylated product C (21%). Both products A and C have the formula $C_{24}H_{24}O_3$ and their ^1H and ^{13}C NMR spectra (Tables 1 and 2) reveal that they both possess methyl groups at C-7a and that they are stereoisomers. Furthermore products A and C exhibit similar NOE enhancement on irradiating the methyl group: in both cases only the H-4a and H-6′ signals are enhanced showing that the methyl group is on the same side as H-4a. Since the methylation reaction could not directly epimerise C-4a or C-5, the difference in A and C is clearly due to a difference in C-13a stereochemistry. As the relative stereochemistry at C-13a could not be solved by spectroscopic means a single crystal X-ray determination was carried out on A which revealed its structure to be **9aB** (see Fig. 1), and consequently C must have structure **10a**. The only explanation we can offer for the epimerisation at C-13a is that the somewhat basic thallium(I) ethoxide must be responsible for opening the heterocyclic ring prior to methylation as shown in Scheme 2. Analysis of the methylation reaction which gave **9aB** and **10a** reveals that it must have occurred by the more favoured axial attack in both cases. Compound B with formula $C_{25}H_{26}O_3$ having two methyl groups, one of which is a singlet and the other a doublet in the ^1H NMR spectrum exhibits NMR spectral data (Tables 1 and 2) suggesting a 6,7a-dimethylxanthone derivative. The ^1H NMR signal at δ 3.16 (double quartet) was identified as H-6 since irradiation of the methyl doublet at δ 0.84 caused the signal to collapse to a doublet (J 11.47 Hz). Furthermore the coupling constant of J 11.47 Hz, also observed at δ 2.72 (H-5), indicates that the hydrogen atoms at C-6 and C-5 are *trans* to one another. The remaining parts of the ^1H and ^{13}C NMR spectra are very similar to those of **9aB**, rather than to **10a**, and therefore we propose structure **11a** for compound B. Furthermore, on irradiating the singlet methyl NOE enhancement was observed for only the H-6 and H-4a signals. The thallium(I) ethoxide/methyl iodide *C*-methylation reaction on the analogous tetracyclic xanthones **5aA**, **5bB** and **5cB** also gave crystalline monomethylated products which from their spectra (see Tables 1 and 2) were deduced as having structures **9aA**, **9bB** and **9cB** respectively. A dimethylated derivative, **11c** analogous to **11a** was also obtained in low yield (6%) from the methylation of **5cB**. An alternative *C*-methylation procedure, using lithium diisopropylamide (LDA) and hexamethylphosphorous triamide (HMPT) was also successful in methylating analogues of **5** on the carbon atom attached to both carbonyl groups: successful reactions included the conversions of **5aA** to **9aA**, **5aB** to **9aB**, **5bB** to **9bB**, and **5cB** to **9cB** and in no case was isomer **10** or dimethyl-derivative **11** observed.

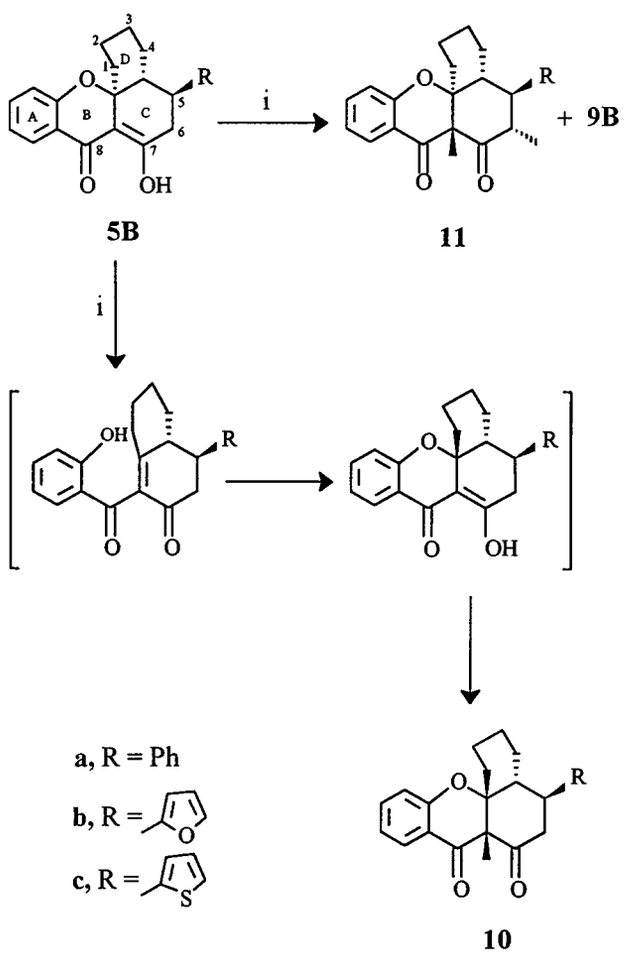
Compound **9** with two carbonyl functions would be expected to react with a methyl Grignard reagent, but with only one of the carbonyls being a ketone, the other being a vinylogous ester,

Table 1 ^{1}H NMR Spectral data of compounds **9**, **10** and **11** recorded at 300 MHz

A, **9aA**	**9aB**	**9bB**	**9cB**	C, **10a**	B, **11a**	**11c**
7.97 (1 H, dd, *J* 1.71, 7.81, Ar-H)	7.97 (1 H, dd, *J* 1.71, 7.81, Ar-H)	7.96 (1 H, dd, *J* 1.71, 7.82, Ar-H)	7.96 (1 H, dd, *J* 1.71, 7.81, Ar-H)	7.94 (1 H, dd, *J* 1.71, 7.82, Ar-H)	7.98 (1 H, dd, *J* 1.71, 7.81, Ar-H)	7.97 (1 H, dd, *J* 1.71, 7.82, Ar-H)
7.49 (1 H, ddd, *J* 1.71, 7.32, 8.30, Ar-H)	7.51 (1 H, ddd, *J* 1.71, 7.32, 8.79, Ar-H)	7.50 (1 H, ddd, *J* 1.71, 7.32, 8.30, Ar-H)	7.51 (1 H, ddd, *J* 1.71, 7.33, 8.30, Ar-H)	7.48 (1 H, ddd, *J* 1.71, 7.32, 8.79, Ar-H)	7.50 (1 H, ddd, *J* 1.71, 7.33, 8.31, Ar-H)	7.50 (1 H, ddd, *J* 1.71, 7.33, 8.30, Ar-H)
7.42–7.36 (2 H, m, Ar-H)	7.41–7.38 (2 H, m, Ar-H)	7.39 (1 H, dd, *J* 0.73, 1.95, Ar-H)	7.25 (1 H, dd, *J* 0.97, 4.89, Ar-H)	7.40–7.37 (2 H, m, Ar-H)	7.41–7.24 (5 H, m, Ar-H)	7.27 (1 H, dd, *J* 1.46, 5.13, Ar-H)
7.32–7.27 (3 H, m, Ar-H)	7.37–7.27 (3 H, m, Ar-H)	7.03 (2 H, m, Ar-H)	7.09–6.96 (3 H, m, Ar-H)	7.36–7.25 (3 H, m, Ar-H)	7.08– 6.97 (2 H, m, Ar-H)	7.06 (1 H, m, Ar-H)
7.09–7.03 (1 H, m, Ar-H)	7.09–6.99 (2 H, m, Ar-H)	6.33 (1 H, dd, *J* 1.71, 3.18, Ar-H)	6.92 (1 H, dd, *J* 1.22, 3.42, Ar-H)	7.07–6.97 (2 H, m, Ar-H)	3.16 (1 H, qd, *J* 6.35, 11.47, H-6)	6.98 (1 H, m, Ar-H)
6.94 (1 H, dd, *J* 0.49, 8.30, Ar-H)	3.31 (1 H, ddd, *J* 5.61, 12.45, 12.70, H-5)	6.14 (1 H, dd, *J* 0.74, 3.17, Ar-H)	3.66 (1 H, ddd, *J* 5.61, 12.45, 12.45, H-5)	3.34 (1 H, ddd, *J* 4.88, 11.47, 13.18, H-5)	2.90 (1 H, td, *J* 2.20, 12.45, H-4a)	6.97 (1 H, dd, *J* 3.42, 5.13, Ar-H)
3.12 (1 H, t, *J* 13.43, H-5′)	3.07 (1 H, dd, *J* 12.94, 13.67, H-6′)	3.45 (1 H, ddd, *J* 5.86, 12.45, 12.45, H-5)	3.10 (1 H, dd, *J* 12.45, 14.16, H-6′)	2.88 (1 H, dd, *J* 13.18, 14.40, H-6′)	2.72 (1 H, dd, *J* 11.47, 12.45, H-5)	6.89 (1 H, dd, *J* 1.22, 3.42, Ar-H)
2.97 (1 H, ddd, *J* 0.97, 6.10, 11.53, H-3a)	2.91 (1 H, m, H-4a)	3.22 (1 H, dd, *J* 12.45, 14.16, H-6′)	2.83 (1 H, td, *J* 2.20, 12.45, H-4a)	2.52 (1 H, dd, *J* 4.88, 14.40, H-6)	2.09 (1 H, br d, *J* 13.19)	3.14–3.01 (2 H, m, H-5, H-6)
2.65 (1 H, ddd, *J* 5.13, 11.53, 13.43, H-4)	2.52 (1 H, dd, *J* 5.61, 13.92, H-6)	2.94 (1 H, m, H-4a)	2.64 (1 H, dd, *J* 5.61, 14.16, H-6)	2.32 (1 H, dt, *J* 3.91, 11.47, H-4a)	1.95 (1 H, m)	2.85 (1 H, br d, *J* 7.33, H-4a)
2.46 (1 H, dd, *J* 5.13, 13.42, H-5)	2.12 (1 H, m)	2.50 (1 H, dd, *J* 5.86, 14.16, H-6)	2.11 (2 H, m)	1.93 (1 H, m)	1.76 (3 H, s, Me)	2.10–2.05 (2 H, m)
2.17–2.00 (2 H, m)	1.99 (1 H, m)	2.09 (2 H, m)	1.70 (3 H, s, Me)	1.68 (1 H, m)	1.71–1.29 (5 H, m)	1.72 (3 H, s, Me)
1.92–1.67 (3 H, m)	1.74 (3 H, s, Me)	1.70 (3 H, s, Me)	1.57–1.22 (6 H, m)	1.61 (3 H, s, Me)	1.23 (1 H, br d, *J* 13.92)	1.45–1.42 (5 H, m)
1.79 (3 H, s, Me)	1.45 (5 H, m)	1.47–1.26 (6 H, m)		1.59–1.33 (5 H, m)	0.84 (3 H, d, *J* 6.35, Me)	1.28–1.19 (1 H, m)
1.58–1.49 (1 H, m)	1.33 (1 H, d, *J* 14.16)			1.26–1.20 (1 H, m)		0.95 (3 H, d, *J* 5.86, Me)

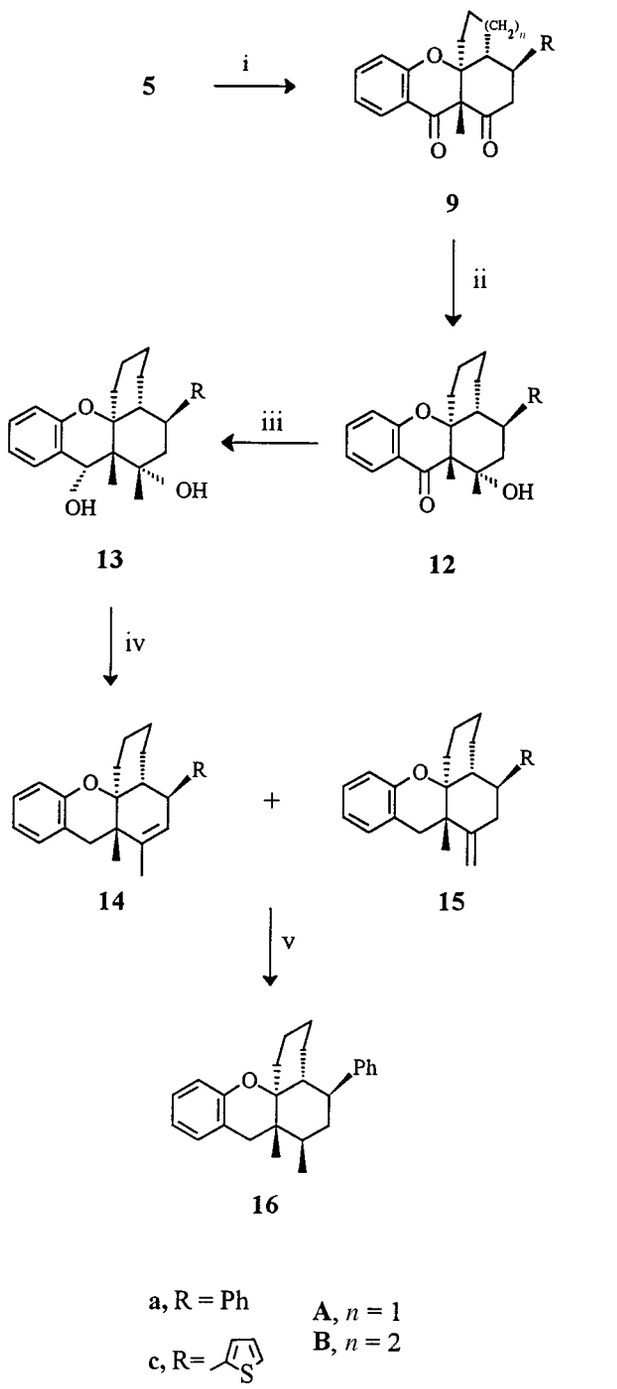
Table 2 ^{13}C NMR chemical shifts of compounds **9**, **10** and **11** recorded at 75.5 MHz

δ_C/ppm	A, **9aA**	**9aB**	**9bB**	**9cB**	C, **10a**	B, **11a**	**11c**
C=O	204.6	204.6	204.3	203.7	209.0	206.1	205.2
	189.8	190.3	190.3	190.2	192.5	190.5	190.4
sp^2-C	157.1	156.3	156.3	156.2	157.5	156.4	156.3
	141.8	142.1	154.1	146.0	142.4	141.8	145.7
	121.0	120.9	120.9	120.8	120.7	120.9	120.8
sp^2-CH	135.8	135.8	141.9	135.8	135.8	135.7	135.8
	129.0	129.1	135.8	127.7	129.0	129.0	127.8
	129.0	129.1	127.7	126.9	129.0	129.0	126.7
	128.0	127.7	121.8	124.8	127.5	129.0	125.8
	127.7	127.3	118.0	124.1	127.5	127.8	124.2
	127.7	127.3	110.2	121.8	127.1	127.8	121.8
	127.3	127.3	106.6	117.9	127.0	127.2	117.9
	121.8	121.8			121.6	121.7	
	118.2	117.9			118.2	118.0	
sp^3-C	94.8	83.8	83.3	83.4	87.6	83.6	83.2
	57.7	60.8	60.7	60.7	63.5	61.0	60.9
sp^3-CH	46.9	41.7	38.0	41.4	45.9	50.1	47.2
	44.9	39.6	35.1	37.0	43.2	45.8	45.5
						40.6	42.3
sp^3-CH_2	45.6	45.7	42.5	46.8	45.2	24.7	24.7
	29.6	24.7	24.7	24.8	27.7	21.9	22.1
	26.3	21.7	22.1	21.9	25.4	20.9	20.8
	20.0	20.9	20.8	20.8	25.3	18.8	18.7
		18.9	18.8	18.7	20.6		
sp^3-CH_3	21.2	19.0	18.9	19.0	15.7	18.9	19.0
						13.0	13.0



Scheme 2 *Reagents*: i, Tl(OEt)/MeI.

some difference in reactivity could be expected; if methylation of **9B** occurred selectively at the C-7 ketone group, this would result in the desired insertion of the C-7 methyl group which is present in **1**. In the event, treatment of **9cB** with excess methylmagnesium iodide gave only one product, with formula $C_{23}H_{26}O_3S$ (89% yield) revealing mono-methylation, and furthermore it exhibited a characteristic low field aromatic NMR signal at δ_H 7.78 (1H, dd, *J* 1.7 and 7.8 Hz) for chromanones, indicating that the C-8 carbonyl had not reacted; its stereochemistry was established in the following experiment leading to structure **12c** for the Grignard adduct (see Scheme 3). Lithium aluminium



Scheme 3 *Reagents and conditions*: i, LDA/MeI/HMPT; ii, MeMgI; iii, $LiAlH_4$; iv, $Et_3Si/HNH_4F/CF_3CO_2H$; v, H_2/Pt.

hydride reduction of **12c** gave a crystalline diol in quantitative yield, which on irradiation of the 7a-methyl signal (at δ_H 1.12 ppm) resulted in NOE enhancements of the signals at 1.53 ppm (C-7 methyl), 2.16 ppm (H-6′), 2.25 ppm (H-4a) and 5.31 ppm (H-8), showing its structure to be **13c**. Similarly **9aB** with methylmagnesium iodide gave **12a** which on lithium aluminium hydride reduction gave **13a**.

For the dehydroxylation of **13** the ionic hydrogenation method of Olah *et al.*[11] using triethylsilane, ammonium fluoride

and trifluoroacetic acid was employed. Reaction with **13c** gave a quantitative mixture of isomeric products with formula $C_{23}H_{26}OS$ and complex NMR spectra which included over 40 carbon resonances, and signals for alkene functions *viz.* at δ_H 4.82 (d, *J* 20 Hz), 5.23 (br s) and at δ_C 107.6 for a terminal methylene group. The two alkene structures **14c** and **15c** fit all the spectral data for the mixture. Similarly **13a** yielded a mixture of **14a** and **15a**. Catalytic hydrogenation (5% Pd on C) of the mixture of **14a** and **15a** gave a single crystalline product **16** ($C_{25}H_{30}O$) with stereochemistry following from an NOE experiment: irradiation at δ_H 3.08 ppm (H-5) had no effect on either of the two methyl groups showing that the two methyl groups are on the same side as the 5-phenyl group and with the methyl group at C-7 in the more stable equatorial position.

The stereochemistry of **16** unfortunately differs from the target **1** in two places, *viz.* C-13a, C-4a or at C-7, C-7a. In an attempt to obtain the stereoisomer of **16** with the correct stereochemistry, we have considered synthesizing the stereoisomers of **5** starting from the (*Z*)-dione **4**. An analysis of all the reactions involved suggests that if (*Z*)-**4** and **3B** reacted in a 4+2 cycloaddition reaction in the expected *exo*-manner to give a stereoisomer of **5**, then assuming that the large aryl group would again be in the equatorial position in ring C the product would be epimeric with **5** at both C-13a and C-4a. We also had reason to believe that the subsequent methylations, beginning with an axial methylation at C-7, would again give methyl groups on the same side as the aryl group, and hence the desired stereoisomer of **16**. Unfortunately all our attempts to obtain (*Z*)-**4** by photolysis of either (*E*)-cinnamic acid or (*E*)-**4** have been unsuccessful. For example irradiation of a solution of (*E*)-**4a**, followed by pyrrolidine and cyclopentanone yielded **5aA** and **6aA**.

Experimental

General

All melting points were determined with a Kofler hotstage microscope apparatus and are uncorrected. ^{1}H NMR (90, 270 MHz) and ^{13}C NMR (22.6 and 67.9 MHz) spectra were recorded on JEOL spectrometers, or on a Bruker DPX spectrometer at 300 and 75.5 MHz respectively, in $CDCl_3$ and were referenced against tetramethylsilane; chemical shifts are reported in ppm on the δ scale, coupling constants (*J*) are given in Hz, and multiplicity was determined from off-resonance decoupled or DEPT spectra. Mass spectra and accurate mass measurements were recorded on a Finnigan MAT-95 instrument using the EI mode with a direct inlet system and operating at 70 eV. Infrared spectra were recorded for KBr discs and UV spectra were recorded in 95% ethanol (ε values are given in dm^3 mol^{-1} cm^{-1}). Column chromatography was carried out using Merck Kieselgel 60 (70–230 mesh) and thin layer chromatography was performed on precoated silica gel 60 GF_{254} (E. Merck 7730) plates (20 cm^2) which had been activated at 120 °C for 3 hours. Thallium(I) ethoxide was obtained from the Aldrich Chemical Co., UK. All compounds reported were found to be homogeneous on TLC analysis, and their NMR spectra revealed no spurious signals.

(*E*)-1-(2-Hydroxyphenyl)-5-phenylpent-4-ene-1,3-dione 4a

A mixture of 2-hydroxyacetophenone (6.93 g, 50.96 mmol) and (*E*)-cinnamoyl chloride (8.49 g, 50.99 mmol) in dry pyridine (5 cm^3) was stirred at room temperature for 1 h before heating at 100 °C for 0.5 h under anhydrous conditions. The resulting solution was poured into 0.5 M HCl (350 cm^3) containing crushed ice (200 g) which yielded a solid cinnamate (10.79 g, 81%) as pale brown crystals, mp 69–70 °C (ethanol). Potassium *tert*-butoxide (6.88 g, 61.4 mmol) was slowly added in small portions to a magnetically stirred solution of the cinnamate (7.98 g, 30.0 mmol) in dry pyridine (10 cm^3) at 50 °C under anhydrous conditions. To the resulting mixture was added 10% acetic acid (100 cm^3) and the yellow solid which precipitated was filtered, dried and crystallised from ethanol–chloroform giving yellow needles (6.85 g, 86%) of **4a**, mp 131–132.5 °C (lit.[12] mp 133–134 °C); ν_{max}/cm^{-1} 1620 (br); λ_{max}/nm 216 (log ε 3.9), 264 (3.9), 328 (3.9); *m*/*z* 266 (M$^+$, 24%), 131 (100), 121 (53); δ_H (90 MHz) 12.23 (1 H, s, OH), 7.72–7.33 (8 H, m), 7.01–6.77 (2 H, m), 6.55 (1 H, d, *J* 15.8), 6.28 (2 H, s); δ_C (22.6 MHz) 195.9 (s, CO), 174.5 (s, CO), 162.6 (s), 139.9 (d), 135.7 (d), 135.0 (s), 130.0 (d), 128.9 (d), 128.9 (d), 128.5 (d), 128.0 (d), 128.0 (d), 122.1 (d), 119.1 (s), 119.0 (d), 118.7 (d), 97.0 (d).

(*E*)-1-(2-Hydroxyphenyl)-5-(2-furyl)pent-4-ene-1,3-dione 4b

Following the procedure described for **4a**, 2-hydroxyacetophenone and (*E*)-3-(2-furyl)acryloyl chloride gave **4b** as yellow needles (90% yield), mp 129–131 °C (ethanol–chloroform) (lit.[13] mp 122 °C); ν_{max}/cm^{-1} 1620; *m*/*z* 256 (M$^+$, 37%), 121 (100); δ_H (90 MHz) 12.24 (1 H, s, OH), 7.68 (1 H, dd, *J* 1.8, 7.9), 7.54–7.25 (3 H, m), 6.97–6.79 (2 H, m), 6.65–6.40 (3 H, m), 6.28 (2 H, s); δ_C (22.6 MHz) 195.8 (s, CO), 174.3 (s, CO), 162.6 (s), 151.7 (s), 144.8 (d), 135.7 (d), 128.5 (d), 126.2 (d), 120.1 (d), 119.2 (s), 119.0 (d), 118.7 (d), 114.7 (d), 112.6 (d), 97.0 (d).

(*E*)-1-(2-Hydroxyphenyl)-5-(2-thienyl)pent-4-ene-1,3-dione 4c

Following the procedure described for **4a**, 2-hydroxyacetophenone and (*E*)-3-(2-thienyl)acryloyl chloride gave **4c**, as yellow needles (85% yield), mp 134.5–135.5 °C (ethanol–chloroform) (HRMS: found M$^+$, 272.0509. $C_{15}H_{12}SO_3$ requires *M*, 272.0507); ν_{max}/cm^{-1} 1625; λ_{max}/nm (log ε) 229 (3.6), 278 (3.6), 328 (3.6); *m*/*z* 272 (M$^+$, 73%), 254 (44), 237 (50), 151 (69), 138 (23), 121 (100), 109 (60), 65 (36); δ_H (90 MHz) 12.23 (1 H, s, OH), 7.77 (1 H, d, *J* 17.2), 6.79–7.74 (7 H, m), 6.37 (1 H, d, *J* 17.2), 6.27 (2 H, s); δ_C (22.6 MHz) 195.8 (s, CO), 174.2 (s, CO), 162.6 (s), 140.6 (s), 135.7 (d), 132.5 (d), 130.6 (d), 128.4 (d), 128.4 (d), 128.3 (d), 121.2 (d), 119.1 (s), 119.0 (d), 118.7 (d), 96.8 (d).

(4a*RS*,5*SR*,13a*SR*)-5-Phenyl-1,2,3,4,4a,5,6,7,7a,8-decahydrobenzo[*d*]xanthene-7,8-dione 5aB

Compound **4a** (1.33 g, 5.00 mmol) and freshly prepared *N*-(cyclohex-1-en-1-yl)pyrrolidine **3B** (3.82 g, 25.30 mmol) were heated in refluxing 95% ethanol (50 cm^3) for 5 minutes, by which time all **4a** had been consumed as shown by TLC analysis. Ice–water (200 cm^3) was added and the reaction mixture extracted with chloroform (2 × 100 cm^3) and the combined organic extracts were washed with water and dried over anhydrous magnesium sulfate. Removal of solvent gave an orange gum which was purified by column chromatography [elution with light petroleum (40–60 °C)–diethyl ether 7:3] giving orange plates of **5aB** (1.1 g, 62%), mp 159–160 °C (ethanol) (HRMS: found M$^+$, 346.1562. $C_{23}H_{22}O_3$ requires *M*, 346.1568); ν_{max}/cm^{-1} 1601; λ_{max}/nm 260 (log ε 4.0), 308 (4.3), 355 (4.2); *m*/*z* 346 (M$^+$, 60%), 303 (100), 289 (33); δ_H (270 MHz) 15.29 (1 H, s, OH), 7.88 (1 H, dd, *J* 1.71, 7.81), 7.47–7.22 (6 H, m), 7.06–6.95 (2 H, m), 3.27 (1 H, dd, *J* 8.8, 8.8, 12.7, H-5), 2.70 (2 H, d, *J* 8.79), 2.50 (1 H, dd, *J* 4.64, 12.45), 2.25 (1 H, d, *J* 10.99), 2.02–1.89 (1 H, m), 1.66–1.21 (6 H, m); δ_C (67.9 MHz) 181.2 (s, CO), 180. 6 (s, CO), 158.2 (s), 142.2 (s), 135.2 (d), 128.9 (d), 127.6 (d), 127.6 (d), 127.0 (d), 126.5 (d), 121.4 (d), 120.7 (d), 118.9 (d), 118.0 (d), 109.6 (s), 79.5 (s), 43.2 (d), 39.7 (d), 39.8 (t), 32.5 (t), 22.4 (t), 21.5 (t), 19.4 (t). Compound **5aB** (69%) was also obtained as the only product after heating a mixture of **4a** (5 mmol), pyrrolidine (5 mmol) and cyclohexanone (5 mmol) in refluxing dichloromethane for 1 h following the procedure for synthesis of **5cA** below.

(3a*RS*,4*SR*,12a*SR*)-4-Phenyl-2,3,3a,4,5,6,6a,7-octahydro-1*H*-cyclopenta[*d*]xanthene-6,7-dione 5aA

Following the procedure described for **5aB**, **4a** (1.63 g, 6.13

mmol) and freshly prepared *N*-(cyclopent-1-en-1-yl)pyrrolidine **3A** (4.2 g, 30.66 mmol) after 30 s gave **5aA** (0.92 g, 45%) as pale yellow plates, mp 91–92 °C (ethanol–chloroform) (HRMS: found M^+, 332.1430. $C_{22}H_{20}O_3$ requires *M*, 332.1412); ν_{max}/cm^{-1} 1601; λ_{max}/nm 262 (log ε 3.9), 308 (4.1), 355 (4.0); *m*/*z* 332 (M^+, 41%), 303 (50), 290 (92), 289 (100); δ_H (90 MHz) 15.22 (1 H, s, OH), 7.89 (1 H, dd, *J* 7.7, 1.7), 7.53–6.86 (8 H, m), 2.70 (4 H, m), 2.64–1.37 (6 H, m); δ_C (22.6 MHz) 181.2 (s, CO), 179.5 (s, CO), 158.8 (s), 142.3 (s), 135.0 (d), 128.9 (d), 128.9 (d), 127.8 (d), 127.8 (d), 127.0 (d), 126.7 (d), 121.5 (d), 121.3 (s), 118.3 (d), 106.3 (s), 89.6 (s), 48.8 (d), 39.4 (t), 39.3 (d), 37.2 (t), 27.1 (t), 21.3 (t).

(3a*RS*,4*SR*,12a*SR*)-4-(2-Thienyl)-2,3,3a,4,5,6,6a,7-octahydro-1*H*-cyclopenta[*d*]xanthene-6,7-dione 5cA

Compound **4c** (0.2 g, 0.7 mmol) in dichloromethane (20 cm^3) was added to pyrrolidine (0.052 g, 0.7 mmol) and cyclopentanone (0.061 g, 0.7 mmol) and the mixture heated at reflux for 1 h, by which time TLC analysis showed that all **4c** had been consumed. The solvent was evaporated and the resulting gum purified by column chromatography (elution with light petroleum–diethyl ether 3:1) giving **5cA** (0.135 g, 57%) as orange plates, mp 91–93 °C (ethanol) (HRMS: found M^+, 338.0976. $C_{20}H_{18}O_3S$ requires *M*, 338.0972); ν_{max}/cm^{-1} 1602; *m*/*z* 338 (M^+, 16%), 309 (28), 296 (60), 295 (100); δ_H (300 MHz) 14.80 (1 H, s, OH), 7.88 (1 H, dd, *J* 1.7, 7.7), 7.46–7.39 (1 H, m), 7.25–7.19 (1 H, m), 7.03 (1 H, t, *J* 7.5), 6.96–6.84 (3 H, m), 3.15 (1 H, ddd, *J* 7.4, 9.4, 11.9, H-4), 2.74–2.60 (3 H, m), 2.38–2.12 (2 H, m), 1.89–1.49 (4 H, m); δ_C (75.5 MHz) 180.3 (s, CO), 180.2 (s, CO), 158.6 (s), 146.3 (s), 135.2 (d), 126.7 (d), 126.6 (d), 124.7 (d), 124.0 (d), 121.5 (d), 121.0 (s), 118.3 (d), 106.2 (s), 89.1 (s), 50.4 (d), 40.0 (t), 38.6 (d), 37.4 (t), 27.5 (t), 21.3 (t).

(4a*RS*,5*SR*,13a*SR*)-5-(2-Furyl)-1,2,3,4,4a,5,6,7,7a,8-decahydrobenzo[*d*]xanthene-7,8-dione 5bB

Following the procedure described for **5aB**, **4b** (1.28 g, 5.00 mmol) and freshly prepared *N*-(cyclohex-1-en-1-yl)pyrrolidine **3B** (3.80 g, 25.17 mmol) after 5 minutes gave **5bB** (0.84 g, 60%) as pale yellow plates, mp 124–125 °C (ethanol–chloroform) (HRMS: found M^+, 336.1364. $C_{21}H_{20}O_4$ requires *M*, 336.1362); ν_{max}/cm^{-1} 1601; λ_{max}/nm 262 (log ε 3.9), 308 (4.3), 355 (4.2); *m*/*z* 336 (M^+, 37), 293 (100), 279 (31); δ_H (90 MHz) 15.27 (1 H, s, OH), 7.85 (1 H, dd, *J* 7.8, 1.8), 7.46–7.37 (2 H, m), 7.04–6.93 (2 H, m), 6.33 (1 H, dd, *J* 3.0, 1.7), 6.15 (1 H, d, *J* 3.0), 3.43 (1 H, ddd, *J* 5.6, 12.0, 12.0, H-5), 2.84 (1 H, dd, *J* 5.7, 8.9), 2.63 (1 H, dd, *J* 9.0, 5.6), 2.47 (1 H, dt, *J* 2.5, 12.5, H-4a), 2.21 (1 H, d, *J* 10.3), 2.03–1.96 (1 H, m), 1.52–1.24 (6 H, m); δ_C (22.6 MHz) 181.0 (s, CO), 180.5 (s, CO), 158.1 (s), 154.9 (s), 141.7(d), 135.2 (d), 126.5 (s), 121.4 (d), 120.6 (s), 118.0 (d), 110.1 (d), 109.4 (s), 106.4 (d), 79.1 (s), 42.6 (d), 36.5 (t), 33.2 (d), 32.4 (t), 22.9 (t), 21.5 (t), 19.5 (t).

(4a*RS*,5*SR*,13a*SR*)-5-(2-Thienyl)-1,2,3,4,4a,5,6,7,7a,8-decahydrobenzo[*d*]xanthene-7,8-dione 5cB

Following the procedure described for **5aB**, **4c** (1.36 g, 5.00 mmol) and freshly prepared *N*-(cyclohex-1-en-1-yl)pyrrolidine **3B** (3.78 g, 25.03 mmol) after 5 minutes gave **5cB** (0.90 g, 51%) as pale yellow plates, mp 133–133.5 °C (ethanol–chloroform) (HRMS: found M^+, 352.1120. $C_{21}H_{20}O_3S$ requires *M*, 352.1133); ν_{max}/cm^{-1} 1602; λ_{max}/nm 262 (log ε 3.8), 308 (4.1), 359 (4.0); *m*/*z* 352 (M^+, 48%), 309 (100), 295 (36); δ_H (270 MHz) 15.25 (1 H, s, OH), 7.87 (1 H, dd, *J* 1.68, 7.72), 7.4–7.5 (1 H, m), 7.23 (1 H, d, *J* 5.0), 7.06–6.9 (4 H, m), 3.64 (1 H, ddd, *J* 7.1, 10.4, 12.4, H-5), 2.82 (1 H, d, *J* 1.35), 2.79 (1 H, d, *J* 4.70), 2.58 (1 H, dd, *J* 4.70, 12.42), 2.25 (1 H, d, *J* 9.74), 2.01 (1 H, m), 1.62–1.38 (6 H, m); δ_C (67.9 MHz) 180.8 (s, CO), 180.2 (s, CO), 158.1 (s), 145.9 (s), 135.3 (d), 126.7 (d), 126.5 (s), 124.7 (d), 123.9 (d), 121.5 (d), 120.5 (s), 118.0 (d), 109.5 (s), 79.2 (s), 45.1 (d), 40.6 (t), 35.2 (d), 32.6 (t), 22.4 (t), 21.4 (t), 19.4 (t).

(5a*RS*,6*RS*,14a*SR*)-6-Phenyl-2,3,4,5,5a,6,7,8,8a,9-decahydro-1*H*-cyclohepta[*d*]xanthene-8,9-dione 5aC

Following the procedure described for **5cA**, **4a** (0.50 g, 1.8 mmol), cycloheptanone (0.21 g, 1.8 mmol) and pyrrolidine (0.13 g, 1.8 mmol) gave **5aC** (0.31 g, 48%) as yellow needles, mp 137–138 °C (ethanol) (HRMS: found M^+, 360.1725. $C_{24}H_{24}O_3$ requires *M*, 360.1722); ν_{max}/cm^{-1} 1605; *m*/*z* 360 (M^+, 39%), 303 (100), 290 (18), 289 (27); δ_H (300 MHz) 15.33 (1 H, s, OH), 7.88 (1 H, dd, *J* 1.6, 7.7), 7.49–7.23 (6 H, m), 7.06–6.95 (2 H, m), 3.16 (1 H, ddd, *J* 11.5, 11.5, 6.3, H-6), 2.75–2.55 (2 H, m), 2.43–2.46 (1 H, m), 2.08 (1 H, dt, *J* 10.9, 3.7), 1.73–1.30 (9 H, m); δ_C (75.5 MHz) 181.6 (s, CO), 180.0 (s, CO), 158.2 (s), 142.7 (s), 135.5 (d), 128.8 (d), 128.8 (d), 127.8 (d), 127.8 (d), 126.8 (d), 126.4 (d), 121.4 (s), 121.4 (d), 118.1 (d), 110.5 (s), 82.6 (s), 46.7 (d), 40.7 (d), 40.3 (t), 36.7 (t), 26.9 (t), 22.9 (t), 20.5 (t), 20.3 (t).

(5a*RS*,6*SR*,14a*SR*)-6-(2-Furyl)-2,3,4,5,5a,6,7,8,8a,9-decahydro-1*H*-cyclohepta[*d*]xanthene-8,9-dione 5bC

Following the procedure described for **5cA**, **4b** (0.25 g, 0.98 mmol), cycloheptanone (0.106 g, 0.98 mmol) and pyrrolidine (0.074 g, 0.98 mmol) gave **5bC** (0.14 g, 41%) as an orange gum (HRMS: found M^+, 350.1518. $C_{22}H_{22}O_4$ requires *M*, 350.1513); ν_{max}/cm^{-1} 1601; *m*/*z* 350 (M^+, 10%), 293 (100), 279 (31); δ_H (300 MHz) 15.28 (1 H, s, OH), 7.87 (1 H, dd, *J* 1.4, 7.7), 7.45 (2 H, dt, *J* 1.6, 7.9), 7.05–6.94 (2 H, m), 6.31 (1 H, dd, *J* 1.9, 2.0), 6.13 (1 H, d, *J* 3.1), 3.28 (1 H, ddd, *J* 6.1, 11.3, 11.7, H-6), 2.88–2.60 (3 H, m), 2.33 (2 H, m), 2.11–2.03 (1 H, m), 1.74–1.25 (7 H, m); δ_C (75.5 MHz) 180.3 (s, CO), 179.6 (s, CO), 158.1 (s), 143.1 (s), 141.5 (d), 135.5 (d), 126.5 (d), 121.4 (d), 121.3 (s), 118.1 (d), 110.0 (d), 109.4 (s), 106.5 (d), 81.5 (s), 46.2 (d), 36.6 (d), 46.1 (t), 36.1 (t), 34.3 (t), 26.8 (t), 20.7 (t), 20.6 (t).

(5a*RS*,6*SR*,14a*SR*)-6-(2-Thienyl)-2,3,4,5,5a,6,7,8,8a,9-decahydro-1*H*-cyclohepta[*d*]xanthene-8,9-dione 5cC

Following the procedure described for **5cA**, **4c** (0.2 g, 0.7 mmol), cycloheptanone (0.08 g, 0.7 mmol) and pyrrolidine (0.052 g, 0.7 mmol) gave **5cC** (0.128 g, 50%) as yellow plates, mp 137–138 °C (ethanol) (HRMS: found M^+, 366.1719. $C_{22}H_{22}O_3S$ requires *M*, 366.1712); ν_{max}/cm^{-1} 1604; *m*/*z* 366 (M^+, 52%), 310 (19), 309 (100), 296 (22), 295 (48); δ_H (300 MHz) 15.27 (1 H, s, OH), 7.85 (1 H, dd, *J* 1.7, 8.8), 7.45 (1 H, dt, *J* 1.7, 6.6), 7.22 (1 H, m), 7.05–6.90 (4 H, m), 3.46 (1 H, ddd, *J* 6.6, 11.5, 11.5, H-6), 2.87–2.57 (3 H, m), 2.46 (1 H, m), 2.38–2.34 (1 H, m), 1.7–1.42 (8 H, m); δ_C (75.5 MHz) 181.7 (s, CO), 178.8 (s, CO), 158.0 (s), 146.5 (s), 135.9 (d), 126.9 (d), 126.5 (d), 124.8 (d), 121.8 (d), 120.7 (s), 118.0 (d), 110.7 (d), 110.2 (s), 82.3 (s), 48.8 (d), 41.3 (t), 36.6 (t), 36.2 (d), 27.2 (t), 23.9 (t), 20.9 (t), 20.9 (t).

7-Phenyl-1,2,3,4,5,6,7,8-octahydro-14*H*-cycloocta[*a*]xanthen-14-one 6aD and 7-phenyl-1,2,3,4,5,6-hexahydro-14*H*-cycloocta[*a*]xanthen-14-one 7a

Compound **4a** (0.5 g, 1.9 mmol) and freshly prepared *N*-(cyclooct-1-en-1-yl)pyrrolidine **3D** (1.7 g, 9.5 mmol) were heated to reflux in 95% ethanol (30 cm^3) for 24 h by which time TLC analysis showed that all **4a** had been consumed. Evaporation of the solvent and purification of the resulting gum by preparative TLC (eluted with light petroleum–diethyl ether 4:1) gave the following products. (i) The band with R_f 0.6 gave **6aD** (0.148 g, 22%) as colourless prisms, mp 145–146 °C (ethanol) (HRMS: found M^+, 356.1758. $C_{25}H_{24}O_2$ requires *M*, 356.1775); ν_{max}/cm^{-1} 1641; λ_{max}/nm 332 (log ε 3.72), 300 (3.93), 274 (4.14), 260 (4.15), 250 (4.16); *m*/*z* 356 (M^+, 100%), 273 (20), 265 (35); δ_H (300 MHz) 8.21 (1 H, dd, *J* 7.8, 1.7), 7.51 (1 H, t, *J* 7.5), 7.33–7.13 (7 H, m), 3.80 (1 H, dt, *J* 13.9, 4.2), 3.58 (1 H, dd, *J* 8.8, 1.5, H-7), 3.49 (1 H, dd, *J* 16.9, 8.8, H-8a), 2.88–2.69 (2 H, m), 2.53–2.49 (1 H, m), 1.99–1.95 (1 H, m), 1.79–1.21 (8 H, m); δ_C (75.5 MHz) 175.2 (s, CO), 164.0 (s), 155.0 (s), 140.8 (s), 135.4 (s),

132.4 (d), 128.6 (d), 128.6 (d), 128.0 (s), 127.8 (d), 127.8 (d), 126.9 (d), 126.2 (d), 125.1 (s), 124.7 (d), 117.4 (d), 117.0 (s), 43.0 (d), 36.7 (t), 32.1 (t), 30.4 (t), 29.7 (t), 27.3 (t), 26.2 (t), 25.1 (t). (ii) The band with R_f 0.5 gave **7a** (94 mg, 14%) as colourless plates, mp 157–158 °C (ethanol) (Found: C, 84.97, H, 6.37%. $C_{25}H_{22}O_2$ requires C, 84.71, H, 6.26%); ν_{max}/cm^{-1} 1648; λ_{max}/nm 345 (log ε 3.97), 265 (4.34), 248 (4.70), 238 (4.70); *m*/*z* 354 (M$^+$, 100%), 353 (90), 325 (20), 311 (28), 287 (20); δ_H (300 MHz) 8.32 (1 H, dd, *J* 8.3, 1.7), 7.86 (1 H, t, *J* 6.6), 7.46–7.22 (8 H, m), 3.67 (2 H, br t, *J* 6.1), 2.82 (2 H, br s), 1.96 (2 H, br s), 1.42 (6 H, br s); δ_C (75.5 MHz) 178.6 (s), 155.7 (s), 155.2 (s), 148.9 (s), 145.0 (s), 141.6 (s), 136.2 (s), 134.0 (d), 128.6 (d), 128.6 (d), 128.0 (d), 128.0 (d), 127.4 (d), 127.0 (d), 123.5 (d), 123.2 (s), 118.7 (s), 117.5 (d), 117.2 (d), 31.5 (t), 30.9 (t), 28.4 (t), 28.0 (t), 26.7 (t), 26.5 (t). Compound **7a** was also obtained, and in quantitative yield, by heating **6aD** in refluxing ethanol and one drop of pyrrolidine for 24 h.

7-(2-Furyl)-1,2,3,4,5,6,7,8-octahydro-14*H*-cycloocta[*a*]xanthen-14-one 6bD

Following the procedure for **5cA**, **4b** (0.5 g, 1.96 mmol), cyclooctanone (0.24 g, 1.96 mmol) and pyrrolidine (0.14 g, 1.96 mmol) gave after refluxing for 1.5 h, **6bD** (0.25 g, 37%) as colourless plates, mp 99–100 °C (ethanol) (HRMS: found M$^+$, 346.1568. $C_{23}H_{22}O_3$ requires *M*, 346.1560); ν_{max}/cm^{-1} 1648; *m*/*z* (M$^+$ 346, 100%); δ_H (300 MHz) 8.20 (1 H, dd, *J* 1.7, 8.7), 7.57 (1 H, t, *J* 7.7), 7.36–7.26 (3 H, m), 6.16 (1 H, m), 6.00 (1 H, m), 3.71–3.62 (2 H, m), 3.19 (1 H, dd *J* 7.6, 16.8), 3.03 (1 H, dd *J* 2.8, 16.8), 2.69 (1 H, dt, *J* 3.7, 12.7), 2.55 (1 H, dt, *J* 11.5, 3.1), 2.16–2.10 (1 H, m), 1.80–1.27 (8 H, m); δ_C (75.5 MHz) 175.4 (s, CO), 164.3 (s), 155.1 (s), 154.2 (s), 141.9 (d), 133.4 (s), 132.6 (d), 130.1 (s), 126.3 (d), 125.1 (s), 124.8 (d), 117.5 (d), 116.5 (s), 110.2 (d), 106.3 (d), 36.9 (d), 33.5 (t), 32.0 (t), 30.4 (t), 29.6 (t), 27.2 (t), 26.2 (t), 25.1 (t).

7-(2-Furyl)-1,2,3,4,5,6-hexahydro-14*H*-cycloocta[*a*]xanthen-14-one 7b

Compound **6bD** (0.1 g) in 95% ethanol (30 cm^3) was heated under reflux for 5 h with one drop of pyrrolidine. Evaporation of the solvent followed by column chromatography (eluted with *n*-hexane–diethyl ether 9:1) gave **7b** (0.09 g, 80%) as colourless plates, mp 130–131 °C (ethanol) (HRMS: found M$^+$, 344.1412. $C_{23}H_{20}O_3$ requires *M*, 344.1409); ν_{max}/cm^{-1} 1646; *m*/*z* 344 (M$^+$, 100%), 327 (27), 315 (30), 301 (36); δ_H (300 MHz) 8.15 (1 H, dd, *J* 1.5, 8.0), 7.54–7.49 (4 H, m), 7.47 (1 H, d, *J* 1.5), 7.27–7.16 (4 H, m), 6.57 (1 H, d, *J* 3.4), 6.43 (1 H, dd, *J* 1.8, 3.3), 2.93 (2 H, t, *J* 5.8), 1.85 (2 H, m), 1.67 (2 H, br s), 1.46–1.39 (2 H, m); δ_C (75.5 MHz) 177.2 (s), 154.7 (s), 154.3 (s), 151.3 (s), 144.1 (s), 141.1 (d), 134.8 (s), 134.2 (s), 132.9 (d), 125.8 (d), 122.3 (d), 122.0 (s), 117.5 (s), 116.0 (d), 114.4 (d), 110.6 (d), 109.7 (d), 30.1 (t), 29.6 (t), 27.2 (t), 26.8 (t), 26.2 (t), 25.0 (t).

7-(2-Thienyl)-1,2,3,4,5,6,7,8-octahydro-14*H*-cycloocta[*a*]-xanthen-14-one 6cD

Following the procedure described for **5cA**, **4c** (0.2 g, 0.73 mmol), cyclooctanone (0.092 g, 0.73 mmol) and pyrrolidine (0.052 g, 0.72 mmol) gave after heating for 2.5 h **6cD** (0.09 g, 34%) as yellow plates, mp 118–119 °C (ethanol) (HRMS: found M$^+$, 362.1340 $C_{23}H_{22}O_2S$ requires *M*, 362.1335); ν_{max}/cm^{-1} 1644; *m*/*z* (M$^+$ 362, 100%); δ_H (300 MHz) 8.22 (1 H, dd, *J* 1.6, 8.6), 7.56 (1 H, t, *J* 7.7), 7.37–7.26 (2 H, m), 7.04 (1 H, dd *J* 1.5, 4.7), 6.80 (2 H, m), 3.81–3.68 (2 H, m), 3.45 (1 H, dd, *J* 6.6, 7.9), 2.93 (1 H, dd, *J* 1.6, 16.7), 2.67 (1 H, dt, *J* 3.8, 12.8), 2.54 (1 H, t, *J* 11.2), 2.17–2.11 (1 H, m), 1.80–1.25 (8 H, m); δ_C (75.5 MHz) 175.3 (s, CO), 163.8 (s), 155.1 (s), 144.2 (s), 135.9 (s), 132.6 (d), 129.4 (s), 126.6 (d), 126.3 (d), 125.1 (s), 125.1 (d), 124.8 (d), 124.0 (d), 117.5 (d), 116.8 (s), 38.5 (d), 37.0 (t), 32.1 (t), 30.5 (t), 29.6 (t), 27.3 (t), 26.2 (t), 25.0 (t).

C-Methylation of 5aB

(a) Thallium(I) ethoxide (2.83 g, 11.3 mmol) was added to a magnetically stirred solution of compound **5aB** (0.68 g, 1.97 mmol) in benzene (20 cm^3) and the resulting mixture stirred for 5 minutes before cooling in ice. The resulting yellow precipitate was filtered and heated under reflux as a suspension in methyl iodide (15 cm^3) for 7 hours. After cooling, the mixture was filtered and the filtrate passed through a short column of Florisil (ASTM 100–200 mesh) (10 g). Concentration of the eluent gave a pale yellow gum which on column chromatography [elution with light petroleum (40–60 °C)–diethyl ether 4:1] gave two products.

(i) The less polar fraction gave (4a*RS*,5*SR*,7a*RS*,13a*RS*)-7a-methyl-5-phenyl-1,2,3,4,4a,5,6,7,7a,8-decahydrobenzo[*d*]xanthene-7,8-dione **10a** (0.15 g, 21%) as colourless plates, mp 188–189 °C (ethanol) (HRMS: found M$^+$, 360.1740. $C_{24}H_{24}O_3$ requires *M*, 360.1725); ν_{max}/cm^{-1} 1712, 1683; λ_{max}/nm 211 (log ε 4.6), 252 (4.2), 312 (3.7); *m*/*z* 360 (M$^+$, 100%), 240 (82), 228 (52); ^{1}H and ^{13}C NMR data are reported in Tables 1 and 2.

(ii) The more polar fraction gave (4a*RS*,5*SR*,7a*RS*,13a*SR*)-7a-methyl-5-phenyl-1,2,3,4,4a,5,6,7,7a,8-decahydrobenzo[*d*]-xanthene-7,8-dione **9aB** (0.46 g, 65%) as colourless rods, mp 172.5–173.5 °C (ethanol) (HRMS: found M$^+$, 360.1726. $C_{24}H_{24}O_3$ requires *M*, 360.1725); ν_{max}/cm^{-1} 1727, 1683; λ_{max}/nm 215 (log ε 4.1), 251 (4.0) and 317 (3.5); *m*/*z* 360 (M$^+$, 38%), 228 (23), 213 (29), 167 (21), 149 (47), 148 (100); ^{1}H and ^{13}C NMR data are reported in Tables 1 and 2.

The above results were obtained on two occasions but only when a particular bottle of thallium(I) ethoxide was used.

(b) Following the procedure described in (a), **5aB** (1.22 g, 3.53 mmol) gave two products.

(i) The less polar band gave (4a*RS*,5*SR*,6*SR*,7a*RS*,13a*RS*)-6,7a-dimethyl-5-phenyl-1,2,3,4,4a,5,6,7,7a,8-decahydrobenzo-[*d*]xanthene-7,8-dione **11a** (0.026 g, 2%) as colourless prisms, mp 198 °C (ethanol) (HRMS: found M$^+$, 374.1893. $C_{25}H_{26}O_3$ requires *M*, 374.1882); ν_{max}/cm^{-1} 1733, 1685; λ_{max}/nm 212 (log ε 4.2), 251 (3.8), 314 (3.4); *m*/*z* 374 (M$^+$, 29%), 227 (28), 148 (100); ^{1}H and ^{13}C NMR data are reported in Tables 1 and 2.

(ii) The more polar band gave **9aB** (0.79 g, 62%).

These results were obtained using different thallium(I) ethoxide bottles and on numerous occasions.

(c) Compound **5aB** (0.2 g, 0.57 mmol) and a hexane solution of LDA (0.74 g, 0.69 mmol) in toluene (25 cm^3) was stirred at −78 °C for 1 h before adding HMPT (0.51 g, 2.9 mmol) and stirring for a further 1 h. Methyl iodide (5 cm^3) was added and the mixture stirred at room temperature for 40 h by which time TLC analysis showed that all **5aB** had been consumed. Dilute 0.5 M hydrochloric acid (10 cm^3) was added to the mixture before extracting with chloroform (3 × 20 cm^3). Evaporation of the solvent followed by column chromatography (eluted with *n*-hexane–ether 7:3) gave **9aB** (0.12 g, 53%).

(3a*RS*,4*SR*,6a*RS*,12a*SR*)-6a-Methyl-4-phenyl-2,3,3a,4,5,6,6a,7-octahydro-1*H*-cyclopenta[*d*]xanthene-6,7-dione 9aA

(a) Following the thallium(I) ethoxide/methyl iodide procedure described for **9aB**, **5aA** (0.84 g, 2.53 mmol) yielded only one product **9aA** (0.44 g, 50%) as colourless needles, mp 160.5–161.5 °C (ethanol–chloroform) (HRMS: found M$^+$, 346.1563. $C_{23}H_{22}O_3$ requires *M*, 346.1569); ν_{max}/cm^{-1} 1736, 1689; λ_{max}/nm 216 (log ε 4.2), 251 (4.1), 318 (3.7); *m*/*z* 346 (M$^+$, 15%), 148 (100); ^{1}H and ^{13}C NMR data are reported in Tables 1 and 2.

(b) Following the LDA/MeI procedure (c) for **9aB**, **5aA** gave **9aA** (46%).

(4a*RS*,5*SR*,7a*RS*,13a*SR*)-7a-Methyl-5-(2-furyl)-1,2,3,4,4a,5,6,7,7a,8-decahydrobenzo[*d*]xanthene-7,8-dione 9bB

(a) Following the thallium(I) ethoxide/methyl iodide procedure described for the *C*-methylation of **5aB**, reaction with **5bB**

yielded only one product, **9bB** (42%) as pale orange plates, mp 169.5–170.5 °C (95% ethanol) (HRMS: found M^+, 350.1513. $C_{22}H_{22}O_4$ requires *M*, 350.1518); ν_{max}/cm^{-1} 1740, 1725, 1690, 1670; λ_{max}/nm 214 (log ε 4.9), 252 (4.4), 318 (3.9); *m*/*z* 350 (M^+, 30%), 148 (100), 121 (31); ^{1}H and ^{13}C NMR data are reported in Tables 1 and 2.

(b) Following the LDA/MeI procedure (c) for **9aB**, **5bB** gave **9bB** (44%).

C-Methylation of 5cB

(a) Following the procedure described for the *C*-methylation of **5aB** using thallium(I) ethoxide/methyl iodide, reaction with **5cB** yielded two products.

(i) The less polar band gave (4a*RS*,5*SR*,6*SR*,7a*RS*,13a*RS*)-6,7a-dimethyl-5-(2-thienyl)-1,2,3,4,4a,5,6,7,7a,8-decahydrobenzo[*d*]xanthene-7,8-dione **11c** (6%) as colourless prisms, mp 191.5–193 °C (ethanol) (HRMS: found M^+, 380.1454. $C_{23}H_{24}O_3$ requires *M*, 380.1446); ν_{max}/cm^{-1} 1730, 1680; λ_{max}/nm 215 (log ε 4.6), 235 (4.5), 310 (4.1), 356 (3.8); *m*/*z* 380 (M^+, 42%), 233 (27), 148 (100); ^{1}H and ^{13}C NMR data are reported in Tables 1 and 2.

(ii) The more polar band gave (4a*RS*,5*SR*,7a*RS*,13a*SR*)-7a-methyl-5-(2-thienyl)-1,2,3,4,4a,5,6,7,7a,8-decahydrobenzo[*d*]-xanthene-7,8-dione **9cB** (56%) as orange plates, mp 179.5–180.5 °C (95% ethanol) (HRMS: found M^+, 366.1296. $C_{22}H_{22}O_3$ requires *M*, 366.1290); ν_{max}/cm^{-1} 1744, 1728, 1692, 1677; λ_{max}/nm 230 (log ε 4.3), 317 (4.0); *m*/*z* 366 (M^+, 43%), 228 (23), 148 (100); ^{1}H and ^{13}C NMR data are reported in Tables 1 and 2.

(b) Following the LDA/MeI procedure for **9aB**, **5cB** gave **9cB** (51%).

(4a*RS*,5*SR*,7*SR*,7a*RS*,13a*SR*)-7,7a-Dimethyl-7-hydroxy-5-phenyl-1,2,3,4,4a,5,6,7,7a,8-decahydrobenzo[*d*]xanthen-8-one 12a

To a magnetically stirred mixture of magnesium turnings (0.22 g, 9.17 mmol) in dry diethyl ether (10 cm^3) was added methyl iodide (0.6 cm^3 9.63 mmol) and the resulting mixture allowed to stand until the formation of bubbles ceased. A solution of **9aB** (1.06 g, 2.94 mmol) in dry benzene (17 cm^3) and dry diethyl ether (15 cm^3) was then added dropwise and the resulting mixture stirred for 14 h at room temperature. When no further reaction was observed (from TLC analysis) the reaction mixture was poured onto crushed ice (50 g) and dilute hydrochloric acid (40 cm^3). The aqueous mixture was extracted with diethyl ether (2 × 100 cm^3) and the combined extracts washed with water (200 cm^3) and dried. Removal of solvent gave a yellow gum which on column chromatography (elution with light petroleum (40–60 °C)–diethyl ether 7:3) gave **12a** (0.91 g, 82%) as colourless rods, mp 178.5–179.5 °C (ethanol–chloroform) (HRMS: found M^+, 376.2047. $C_{25}H_{28}O_3$ requires *M*, 376.2038); ν_{max}/cm^{-1} 3540, 1685; λ_{max}/nm 215 (log ε 4.5), 247 (4.1), 320 (3.7); *m*/*z* 376 (M^+, 42%), 333 (20), 319 (44), 230 (31), 229 (100); δ_H (270 MHz) 7.79 (1 H, dd, *J* 1.71, 7.57), 7.49 (1 H, m), 7.36–7.31 (2 H, m), 7.27–7.21 (3 H, m), 7.04–6.95 (2 H, m), 3.37 (1 H, td, *J* 12.21, 5.37), 3.30 (1 H, d, *J* 1.71), 2.68 (1 H, m), 2.51 (1 H, dt, *J* 12.45, 2.20), 1.96–1.78 (4 H, m), 1.53 (3 H, s, Me), 1.44 (3 H, s, Me), 1.49–1.27 (4 H, m), 1.22 (1 H, br d, *J* 11.96); δ_C (67.9 MHz) 199.9 (s, CO), 157.5 (s), 143.9 (s), 135.7 (d), 128.7 (d), 128.7 (d), 127.5 (d), 126.7 (d), 126.5 (d), 121.8 (s), 120.7 (d), 117.7 (d), 86.0 (s), 73.9 (s), 54.4 (s), 44.6 (t), 39.4 (d), 39.4 (d) , 28.5 (q), 26.1 (t), 22.2 (t), 21.7 (t), 19.3 (t), 17.4 (q).

(4a*RS*,5*SR*,7*SR*,7a*RS*,13a*SR*)-7,7a-Dimethyl-7-hydroxy-5-(2-thienyl)-1,2,3,4,4a,5,6,7,7a,8-decahydrobenzo[*d*]xanthen-8-one 12c

Following the procedure described for **12a**, **9cB** (190 mg, 0.52 mmol), magnesium turnings (70 mg, 2.92 mmol) and methyl iodide (0.2 ml, 3.1 mmol) gave **12c** (176.5 mg, 89%) as colourless prisms, mp 169.5–171 °C (ethanol–chloroform); (HRMS, found M^+, 382.1603. $C_{23}H_{26}O_3S$ requires *M*, 382.1603); ν_{max}/cm^{-1} 3541, 1688; λ_{max}/nm 216 (log ε 4.5), 320 (3.7); *m*/*z* 382 (M^+, 47%), 339 (28), 325 (40), 230 (30), 229 (100); δ_H (270 MHz) 7.78 (1 H, dd, *J* 1.71, 7.81), 7.49 (1 H, ddd, *J* 1.71, 7.33, 9.04), 7.18 (1 H, d, *J* 4.40), 7.02 (1 H, dd, *J* 0.98, 7.81), 6.97–6.93 (2 H, m), 6.88 (1 H, dd, *J* 0.98, 3.42), 3.70 (1 H, ddd, *J* 7.08, 12.45, 17.33), 3.31 (1 H, br s, OH), 2.61 (1 H, m), 2.37 (1 H, br d, *J* 12.45), 2.01–1.94 (3 H, m), 1.84 (1 H, br d, *J* 15.63), 1.54 (3 H, s, Me), 1.51–1.36 (5 H, m), 1.41 (3 H, s, Me); δ_C (67.9 MHz) 199.8 (s, CO), 157.4 (s), 147.9 (s), 135.7 (d), 126.7 (d), 126.5 (d), 124.2 (d), 123.1 (d), 121.7 (s), 120.8 (d), 117.8 (d), 85.7 (s), 73.8 (s), 54.2 (s), 45.8 (t), 41.7 (d), 35.0 (d), CH), 28.4 (q), 26.10 (t), 22.3 (t), 21.6 (t), 19.3 (t), 17.5 (q).

(4a*RS*,5*SR*,7*SR*,7a*RS*,8*SR*,13a*SR*)-7,7a-Dimethyl-5-phenyl-1,2,3,4,4a,5,6,7,7a,8-decahydrobenzo[*d*]xanthene-7,8-diol 13a

A solution of **12a** (0.91 g, 2.42 mmol) in dry THF (25 cm^3) was slowly added to a magnetically stirred slurry of lithium aluminium hydride (0.79 g, 20.79 mmol) in dry THF (25 cm^3) over 15 minutes at room temperature under dry nitrogen. The resulting mixture was refluxed for 2 h, by which time TLC analysis showed that all **12a** had been consumed. Ice-cooled water was added to the mixture until gas evolution ceased before filtering through a thin layer of Celite and extracting the filtrate with ethyl acetate (3 × 70 cm^3). The combined organic extracts were washed with water and then dried over anhydrous magnesium sulfate. Evaporation of the solvent gave **13a** (0.91 g, 100%) as colourless needles, mp 196–197.5 °C (ethanol); (HRMS: found M^+, 378.2204. $C_{25}H_{30}O_3$ requires *M*, 378.2195); ν_{max}/cm^{-1} 3398, 3338; λ_{max}/nm 205 (log ε 4.6), 274 (3.7), 282 (3.6); *m*/*z* 379 (M+1, 25%), 378 (M^+, 94), 360 (51), 317 (46), 214 (30), 213 (100), 171 (49), 121 (88); δ_H (270 MHz) 7.53 (1 H, d, *J* 7.57), 7.36–7.31 (2 H, m), 7.27–7.18 (4 H, m), 6.97 (1 H, td, *J* 7.57, 1.22), 6.84 (1 H, dd, *J* 8.06, 1.22), 5.33 (1 H, s, H-8), 3.34 (1 H, ddd, *J* 12.94, 12.70, 4.40, H-5), 2.51 (1 H, m), 2.39 (1 H, br d, *J* 12.70), 2.11 (1 H, dd, *J* 12.94, 14.41, H-6′), 2.01–1.60 (5 H, m), 1.67 (1 H, dd, *J* 4.40, 14.40), 1.52 (3 H, s, Me), 1.41–1.34 (4 H, m), 1.15 (3 H, s, Me); δ_C (67.9 MHz) 151.8 (s), 144.4 (s), 128.9 (d), 128.7 (d), 128.7 (d), 127.4 (d), 127.3 (s), 126.3 (d), 120.7 (d), 116.8 (d), 83.0 (s), 74.9 (s), 67.5 (d), 47.1 (t), 45.2 (s), 40.1 (d), 39.6 (d), 29.5 (q), 25.8 (t), 22.6 (t), 21.6 (t), 19.6 (t), 12.0 (q).

(4a*RS*,5*SR*,7*SR*,7a*RS*,8*SR*,13a*SR*)-7,7a-Dimethyl-5-(2-thienyl)-1,2,3,4,4a,5,6,7,7a,8-decahydrobenzo[*d*]xanthene-7,8-diol 13c

Following the procedure described for **13a**, **12c** (440 mg, 1.15 mmol) and lithium aluminium hydride (410 mg, 10.79 mmol) gave **13c** (0.44 g, 100%) as colourless needles (ethanol), mp 150–151 °C; (HRMS: found M^+, 384.1764. $C_{23}H_{28}SO_3$ requires *M*, 384.1759); ν_{max}/cm^{-1} 3487, 3371; λ_{max}/nm 204 (log ε 4.4), 227 (4.3), 274 (3.6), 282 (3.5); *m*/*z* 385 (M+1, 100%), 366 (49), 323 (48), 214 (33), 213 (87), 121 (60); δ_H (270 MHz) 7.52 (1 H, d, *J* 7.81), 7.21 (1 H, dd, *J* 1.22, 7.81), 7.17 (1 H, dd, *J* 1.22, 5.13), 6.98 (1 H, dd, *J* 1.22, 7.57), 6.94 (1 H, dd, *J* 3.42, 5.13), 6.88 (1 H, dd, *J* 1.22, 3.42), 6.83 (1 H, dd, *J* 1.22, 8.06), 5.31 (1 H, s, H-8), 3.69 (1 H, ddd, *J* 12.69, 12.21, 4.15, H-5), 2.44 (1 H, m), 2.25 (1 H, br d, *J* 12.21, H-4a), 2.16 (1 H, dd, *J* 12.69, 14.41, H-6′), 1.90 (1 H, m), 1.82 (1 H, dd, *J* 4.15, 14.41), 1.71 (3 H, br s), 1.53 (3 H, s, Me), 1.50–1.30 (5 H, m), 1.12 (3 H, s, Me); δ_C (67.9 MHz) 151.7 (s), 148.7 (s), 128.9 (d), 127.5 (d), 127.3 (s), 126.5 (d), 123.9 (d), 122.9 (d), 120.7 (d), 116.8 (d), 82.8 (s), 74.8 (s), 67.5 (d), 48.2 (t), 45.1 (s), 42.5 (d), 35.1 (d), 29.3 (q), 25.8 (t), 22.7 (t), 21.6 (t), 19.6 (t), 12.0 (q).

Dehydroxylation of (4a*RS*,5*SR*,7*SR*,7a*RS*, 8*SR*,13a*SR*)-7,7a-dimethyl-5-phenyl-1,2,3,4,4a,5,6,7,7a,8-decahydrobenzo[*d*]-xanthene-7,8-diol 13a

Trifluoroacetic acid (2.1 cm^3, 27.3 mmol) was added dropwise to a magnetically stirred solution of **13a** (405 mg, 1.07 mmol), triethylsilane (811 mg, 7.0 mmol) and ammonium fluoride (270 mg, 7.3 mmol) in dichloromethane (4 cm^3) at 0 °C. The resulting mixture was stirred at 0 °C for 0.5 h and then at room temperature for 19 h, by which time TLC analysis showed that all **13a** had been consumed. Ice-cooled water (30 cm^3) was added and the reaction mixture extracted with dichloromethane (3 × 25 cm^3). The combined organic extracts were washed with 10% aqueous sodium hydrogen carbonate (160 cm^3), followed by water (200 cm^3) and dried over anhydrous magnesium sulfate. Evaporation of the solvent gave a colourless gum which on column chromatography [eluted with light petroleum (40–60 °C)–diethyl ether 7:3] gave a gum (368.6 mg, 100%) which was homogeneous by TLC analysis consisting of a mixture of (4a*RS*,5*SR*,7a*RS*,13a*SR*)-7,7a-dimethyl-5-phenyl-1,2,3,4,4a,5,7a,8-octahydrobenzo[*d*]xanthene **14a** and (4a*RS*,5*SR*,7a*RS*,13a*SR*)-7a-methyl-7-methylidene-5-phenyl-1,2,3,4,4a,5,6,7,7a,8-decahydrobenzo[*d*]xanthene **15a** in the ratio of 3:2 (from ^{1}H NMR as shown below) (HRMS: found M^+, 344.2140. $C_{25}H_{28}O$ requires *M*, 344.2140); ν_{max}/cm^{-1} 1643, 1601; *m*/*z* 344 (M^+, 60%), 238 (26), 237 (83), 212 (24), 209 (32), 133 (100); δ_H (270 MHz) 7.32–7.18 (5 H, m, **14a**+**15a**), 7.17–7.03 (2 H, m, **14a**+**15a**), 6.89–6.81 (2 H, m, **14a**+**15a**), 5.23 (0.6 × 1 H, br s, **14a**), 4.83 (0.4 × 1 H, s, **15a**), 4.76 (0.4 × 1 H, s, **15a**), 3.50 (0.6 × 1 H, br d, *J* 10.25, **14a**), 3.11 (0.6 × 1 H, d, *J* 16.36, **14a**), 3.06 (0.4 × 1 H, td, *J* 12.45, 5.13, **15a**), 2.89 (0.6 × 1 H, d, *J* 16.11, **14a**), 2.70 (0.4 × 1 H, br t, *J* 13.18, **15a**), 2.53 (0.6 × 1 H, d, *J* 16.11, **14a**), 2.52 (0.6 × 1 H, m, **14a**), 2.43 (0.4 × 1 H, d, *J* 16.36, **15a**), 2.38 (0.4 × 1 H, dd, *J* 5.13, 13.91, **15a**), 2.29 (0.4 × 1 H, br d, *J* 10.50, **15a**), 2.09 (0.6 × 3 H, s, Me **14a**), 2.05–1.85 (1 H, m, **14a**+**15a**), 1.24 (0.4 × 3 H, s, Me **15a**), 1.21 (0.6 × 3 H, s, Me **14a**).

Dehydroxylation of (4a*RS*,5*SR*,7*SR*,7a*RS*,8*SR*,13a*SR*)-7,7a-dimethyl-5-(2-thienyl)-1,2,3,4,4a,5,6,7,7a,8-decahydrobenzo-[*d*]xanthene-7,8-diol 13c

Following the procedure described for the dehydroxylation of **13a**, **13c** (400 mg, 1.05 mmol) gave a colourless solid (363 mg, 100%) consisting of a mixture of (4a*RS*,5*SR*,7a*RS*,13a*SR*)-7,7a-dimethyl-5-(2-thienyl)-1,2,3,4,4a,5,7a,8-octahydrobenzo-[*d*]xanthene **14c** and (4a*RS*,5*SR*,7a*RS*,13a*SR*)-7a-methyl-7-methylidene-5-(2-thienyl)-1,2,3,4,4a,5,6,7,7a,8-decahydrobenzo[*d*]xanthene **15c** in the ratio of 1:2 (from ^{1}H NMR data as shown below) (HRMS: found M^+, 350.1705. $C_{23}H_{26}OS$ requires M, 350.1704); *m*/*z* 350 (M^+, 75%), 243 (67), 215 (72), 133 (100), 97 (23); δ_H (270 MHz) 7.19 (3 H, m, **14c** + **15c**), 6.96–6.84 (4 H, m, **14c** + **15c**), 5.31 (0.33 × 1 H, br s, **14c**), 4.82 (0.67 × 2 H, d, *J* 20, **15c**), 3.83 (0.33 × 1 H, br dt, *J* 10.01, 2.93, **14c**), 3.43 (0.67 × 1 H, td, *J* 12.45, 5.13, **15c**), 3.11 (0.67 × 1 H, d, *J* 16.11, **15c**), 2.90 (0.33 × 1 H, d, *J* 15.60, **14c**), 2.76 (0.67 × 1 H, dd, *J* 12.45, 15.63, **15c**), 2.53 (0.33 × 1 H, d, *J* 15.61, **14c**), 2.53 (0.67 × 1 H, dd, *J* 15.63, 5.31, **15c**), 2.45 (0.67 × 1 H, d, *J* 16.12, **15c**), 2.40 (1 H, br d **14c** + **15c**), 2.09–1.96 (1 H, m, **14c** + **15c**), 1.78 (0.33 × 3 H, dd, *J* 1.22, 2.44, Me **14c**), 1.66–1.24 (7 H, m, **14c** + **15c**), 1.22 (0.67 × 3 H, s, Me **15c**), 1.18 (0.33 × 3 H, s, Me **14c**); δ_C (67.9 MHz) signals included 107.6 for an sp^2-CH_2.

(4a*RS*,5*SR*,7*RS*,7a*RS*,13a*SR*)-7,7a-Dimethyl-5-phenyl-1,2,3,4,4a,5,6,7,7a,8-decahydrobenzo[*d*]xanthene 16

The mixture of **14a** and **15a** (345 mg, 100 mmol) and 5% palladium on carbon (100 mg) in ethanol (35 cm^3) and ethyl acetate (15 cm^3) was shaken in an atmosphere of hydrogen at 40 psi for two days using a Parr hydrogenator. The resulting solution was filtered and the solvent was removed under reduced pressure giving a colourless gum which on purification by column chromatography [elution with light petroleum (40–60 °C) diethyl ether 1:1] gave **16** as colourless rods (346 mg, 100%), mp 135–136 °C (ethanol–chloroform); (HRMS: found M^+, 346.2296. $C_{25}H_{30}O$ requires *M*, 346.2297); ν_{max}/cm^{-1} 1232, 1168; λ_{max}/nm 210 (log ε 4.5), 274 (4.0), 281 (4.0); *m*/*z* 346 (M^+, 39%), 240 (20), 239 (100), 238 (23), 133 (26); δ_H (270 MHz) 7.34–7.28 (2 H, m), 7.24–7.18 (3 H, m), 7.15–7.04 (2 H, m), 6.88–6.83 (2 H, m), 3.08 (1 H, ddd, *J* 12.45, 6.84, 10.26, H-5), 2.62 (1 H, d, *J* 16.36), 2.50 (1 H, d, *J* 16.36), 2.34 (1 H, br d, *J* 12.45), 1.93–1.70 (3 H, m), 1.67–1.21 (7 H, m), 1.13 (1 H, br d, *J* 13.18), 1.01 (3 H, s, Me), 0.90 (3 H, d, *J* 6.59, Me); δ_C (67.9 MHz) 152.6 (s), 145.4 (s), 130.1 (d), 128.6 (d), 128.6 (d), 127.5 (br d), 127.1 (d), 126.2 (d), 122.4 (s), 120.0 (d), 117.2 (d), 79.9 (s), 42.9 (d), 39.4 (d), 39.4 (t), 37.9 (s), 36.2 (d), 35.7 (t), 23.2 (t), 22.5 (t), 21.4 (t), 19.3 (t), 14.3 (q), 13.2 (q).

4-Phenyl-2,3,4,5-tetrahydrocyclopenta[*a*]xanthen-11(1*H*)-one 6aA

Compound **4a** (0.2g, 0.75 mmol) in toluene was stirred under ultraviolet light for 2 h before *N*-(cyclopent-1-en-1-yl)pyrrolidine **3A** (0.053 g, 0.75 mmol) was added dropwise over a period of 1 h. The reaction was stirred under ultraviolet light for 4 days by which time TLC analysis showed that all of **4a** had been consumed. Removal of solvent gave an orange gum which on column chromatography [elution with light petroleum (40–60 °C) diethyl ether 3:1 v/v] gave two products.

(i) The less polar fraction gave **5aA** (0.068 g, 28%).

(ii) The more polar fraction yielded **6aA** as colourless prisms (0.074 g, 31%), mp 126–127 °C (ethanol) (HRMS: found M^+, 314.1334. $C_{22}H_{18}O_2$ requires *M* 314.1335); ν_{max}/cm^3 1625; *m*/*z* 314 (M^+, 100%), 312 (42), 285 (29), 237 (31), δ_H (300 MHz) 8.22 (1 H, dd, *J* 1.8, 8.6), 7.61–7.57 (1 H, m), 7.41–7.06 (7 H, m), 6.82 (1 H, m), 3.76 (1 H, m), 3.40 (1 H, dd, *J* 9.5, 17.0), 3.37 (1 H, d, *J* 9.4), 3.27 (1 H, dt, *J* 2.6, 4.8), 3.14–3.02 (1 H, m), 3.01 (1 H, d, *J* 5.8), 2.95 (1 H, d, *J* 5.9), 2.00 (1 H, d, *J* 7.2); δ_C (75.5 MHz) 174.6 (s), 163.7 (s), 155.5 (s), 142.0 (s), 136.6 (s), 132.7 (d), 128.76 (d), 128.7 (d), 127.4 (d), 127.4 (d), 126.9 (d), 126.0 (d), 124.8 (d), 124.6 (s), 120.3 (s), 117.7 (d), 114.8 (s), 40.75 (d), 36.7 (t), 33.9 (t), 33.4 (t), 23.4 (t).

X-Ray crystal structure determination of 9aB

Crystal data. Colourless prisms with dimensions 0.30 × 0.20 × 0.10 mm, $C_{24}H_{24}O_3$, $M = 360.45$, monoclinic, $a = 6.004(2)$, $b = 8.863(2)$, $c = 17.725(3)$ Å, $\beta = 95.56(2)°$, $V = 938.8(4)$ Å^3, space group P_n (No. 17), $Z = 2$, $D_x = 1.275$ g cm^{-3}, μ(Mo-Kα) = 0.83 cm^{-1}. Data were measured on a MAR diffractometer with a 300 mm image plate detector using graphite monochromatised Mo-Kα radiation ($\lambda = 0.71073$ Å) on 60 plates with 3° oscillation at 120 mm distance and 330 s exposure. 1835 unique reflections [1606 with $I > 3\sigma(I)$] were obtained from 8274 measured reflections. The structure was solved by direct methods (SIR92[14]) and refined by full-matrix least-squares refinement on *F* (TEXSAN[15]) with all non-hydrogen atoms anisotropic and 24 hydrogen atoms in calculated positions using riding model with $B_{iso}(H) = 1.3\ B(eq)$ for the attached atom. Final $R = 0.042$ and $wR = 0.047$ and GOF = 2.99 for 1606 reflections, where $w = 4F_o^2/[\sigma^2(I) + (0.022F_o^2)^2]$, maximum residual electron density 0.27 e Å^{-3}. An ORTEP[16] drawing of the molecule is shown in Fig. 1.

References

1 H. A. Weber, N. C. Baenziger and J. B. Glober, *J. Org. Chem.*, 1988 **53**, 4567.

2 P. Djura, D. B. Stierle, B. Sullivan, D. J. Faulkner, E. Arnold and J. Clardy, *J. Org. Chem.*, 1980, **45**, 1435.

3 A. Aiello, E. Fattorusso and M. Menna, *Z. Naturforsch.*, *Teil. B*, 1993, **48**, 209.

4 A. E. Wright, S. A. Rueth and S. S. Cross, *J. Nat. Prod.*, 1991, **54**, 1108.
5 M. L. B. Kondracki, M. T. Martin and M. Guyot, *Tetrahedron Lett.*, 1992, **33**, 8079.
6 R. M. Letcher, T. Y. Yue and K. K. Cheung, *J. Chem. Soc.*, *Chem. Commun.*, 1993, 159.
7 R. M. Letcher, *J. Chem. Educ.*, 1980, 220.
8 R. M. Letcher and T. Y. Yue, *J. Chem. Soc.*, *Chem. Commun.*, 1992, 1310.
9 A. McKillop and E. C. Taylor, *Chem. Br.*, 1973, 4.
10 E. C. Taylor, G. H. Hawks III and A. McKillop, *J. Am. Chem. Soc.*, 1968, **90**, 2421.
11 G. A. Olah, Q. Wang and G. K. S. Prakash, *Synlett*, 1992, 647.
12 H. L. Gaggad, K. N. Wadodkor and B. J. Ghiya, *Indian J. Chem.*, *Sect. B*, 1985, **24B**, 1244.
13 D. Desai, P. Lakhlani, D. Mendes, K. S. Varma and P. S. Fernandes, *Indian J. Chem.*, *Sect. B*, 1981, **20B**, 1005.
14 A. Altomare, M. Cascarano, C. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori and M. Camalli, *J. Appl. Cryst.*, 1994, **27**, 435.
15 TEXSAN: *Crystal Structure Analysis Package*, Molecular Structure Corporation, 3200 Research Forest Drive, The Woodland, TX, USA, 1985 and 1992.
16 C. K. Johnson: *ORTEP*II, Report ORNL-5318. Oak Ridge National Laboratory, Tennessee, USA, 1976.

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