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TETRAHEDRON

Transformations of Lignans, Part V.[1] Reactions of DDQ with a Gmelinol Hydrogenolysis Product and its Derivatives

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Abstract : Hydrogenolysis of gmelinol **8** with sodium in liquid ammonia gives a triol **9**, which is converted under various reaction conditions into a range of derivatives including the di- and tri-*O*-methyl ethers **10** and **11**, a 3,4-dibenzyl-3-hydroxy-tetrahydrofuran **12**, and its acetate **13**. These derivatives undergo oxidative cyclisation with DDQ in acetic acid or trifluoroacetic acid to yield 1-aryltetralin, 1-arylnaphthalene, dibenzocyclooctadiene and spirodienone derivatives in reactions which provide biomimetic analogies for biogenetic transformations of lignans.

INTRODUCTION

In our studies of lignan transformations, we have shown that dihydrocubebin **1** and its 3,4-dibenzyltetrahydrofuran derivative **2** are converted into lignans such as **3-7** by oxidative coupling reactions with DDQ (2,3-dichloro-5,6-dicyano-1,4-benzoquinone) in acetic acid or trifluoroacetic acid media.[1b] We now report that **9**,[2,3] obtained from gmelinol **8** by hydrogenolysis with sodium in liquid ammonia, and its derivatives **10-15**, can be transformed into the 1-aryltetralins **18, 19, 22, 28** and **30**, the 1-arylnaphthalenes **27** and **32**, the dibenzocyclooctadienes **20** and **24**, and the spirodienone **26**, by oxidative coupling with DDQ in acetic acid or trifluoroacetic acid. These reactions lend support to the mechanistic pathways proposed for the biogenesis of lignans from simple dibenzylbutane precursors.

RESULTS AND DISCUSSION

Hydrogenolysis of gmelinol **8** with 10 equivalents of sodium in liquid ammonia produced the triol **9** (99%), which formed a mixture of monoacetate **14** (30%) and diacetate **15** (28%) when refluxed with aqueous acetic acid, and gave **15** alone (75%) when treated with acetic anhydride in pyridine (Scheme 1). The triol **9**

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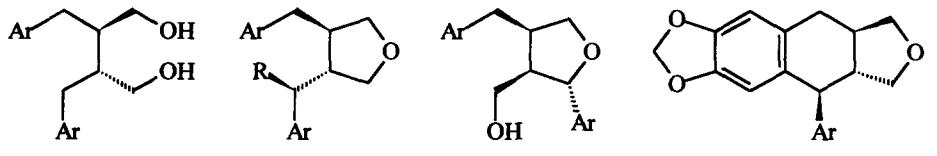
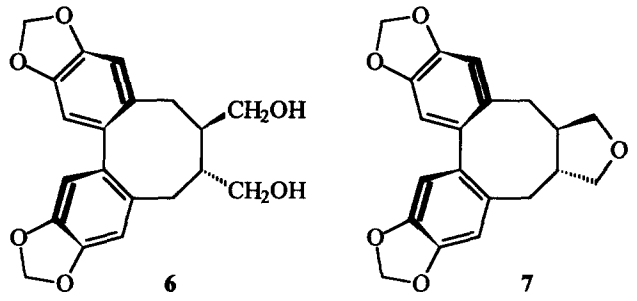
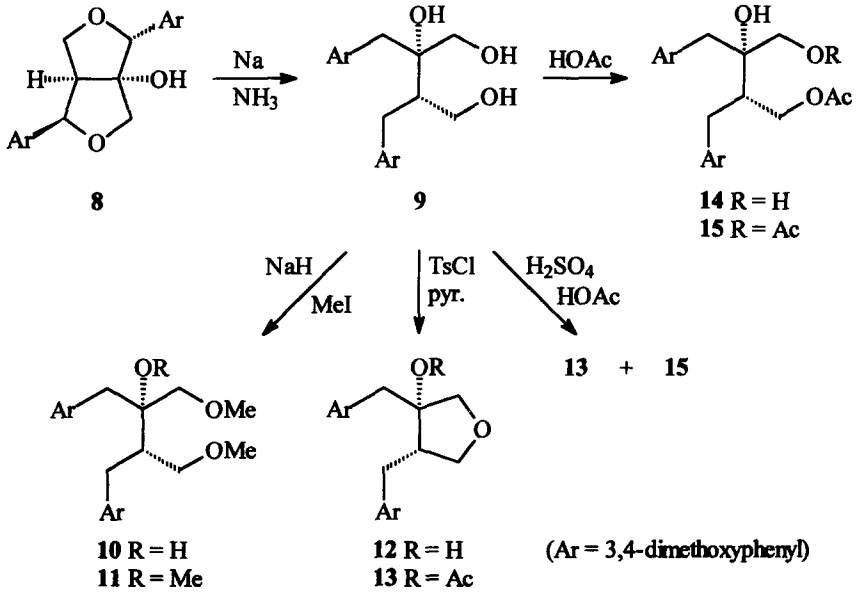


1 2 R = H 3 R = OAc 4 5



6 7 (Ar = 3,4-methylenedioxyphenyl)

gave a mixture of the dimethyl ether **10** (28%) and the trimethyl ether **11** (54%) when treated with sodium hydride and methyl iodide in THF. The triol **9** also gave 3,4-dibenzyl-3-hydroxytetrahydrofuran **12** (73%), when refluxed with p-toluenesulfonyl chloride in pyridine. It produced a mixture of 3,4-dibenzyl-3-acetoxytetrahydrofuran **13** (71%) and diacetate **15** (12%), when treated with conc. H_2SO_4 in glacial acetic acid.

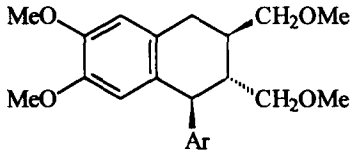


8 **9** **14** R = H **15** R = Ac

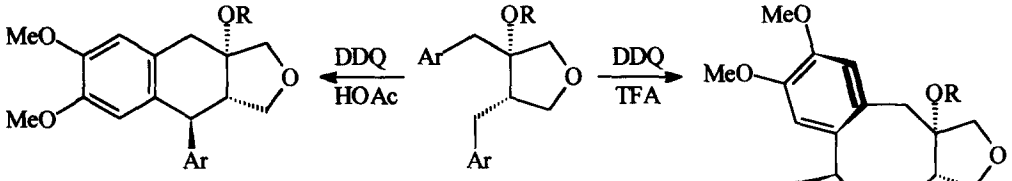
10 R = H **11** R = Me **12** R = H **13** R = Ac (Ar = 3,4-dimethoxyphenyl)

Scheme 1

When **12** was treated with 3.5 equivalents of DDQ in acetic acid, a single product (83%) was obtained which had the molecular formula $C_{22}H_{26}O_6$, corresponding to dehydrogenation having occurred (Scheme 2). Analysis of the ^1H and ^{13}C NMR spectra of this compound (Tables 5 and 6) and comparison with data in the literature[1b] led to the conclusion that it was the 1-aryltetralin **18**. In particular, this was supported by the loss, as compared with **12**, of one benzylic proton and one aromatic proton leaving a doublet at δ 3.96 (H-1) and two singlets at δ 6.35 and 6.65 p.p.m (H-5 and H-8). Furthermore, the large coupling constant (11.6 Hz) between H-1 and H-2 indicated a *trans*-configuration as in phyltetralin **16**[4] and lintetralin **17**.[5] Acetylation of **18** with acetic anhydride in pyridine produced the monoacetate **19**.



16 Ar = 3,4-dimethoxyphenyl
17 Ar = 3,4-methylenedioxyphenyl



18 R = H
19 R = Ac

12 R = H
13 R = Ac

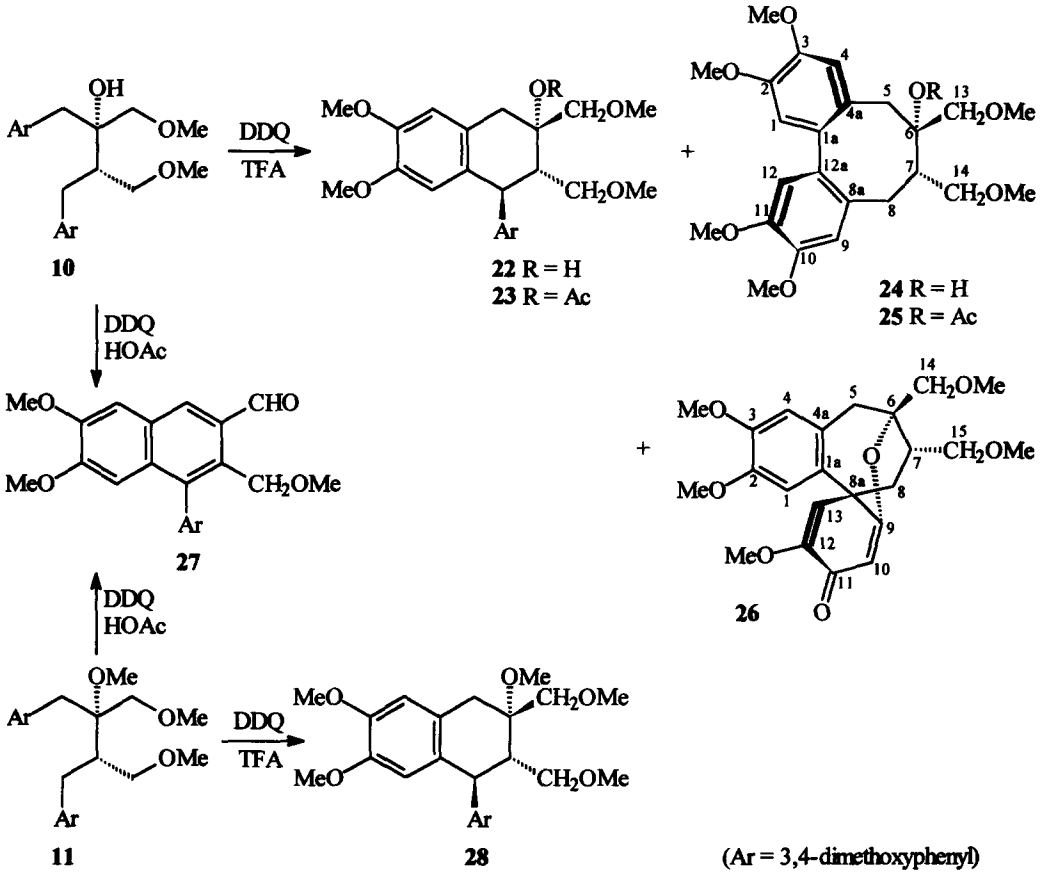
20 R = H
21 R = Ac

Scheme 2 (Ar = 3,4-dimethoxyphenyl)

When **12** was treated with 2 equivalents of DDQ in trifluoroacetic acid a single product (70%), isomeric with **18**, was obtained. Analysis of the ^1H NMR spectrum of this compound (Table 7) showed that the aromatic region contained four singlets. This led to the proposal that oxidative coupling had taken place to give the dibenzocyclooctadiene **20**. This conclusion was supported by 2D COSY experiments and by comparison of the ^1H and ^{13}C NMR spectra with those of compound **7** prepared earlier.[1b] Acetylation of **20** with acetic anhydride in pyridine produced the monoacetate **21**.

When **10** was reacted with 2 equivalents of DDQ in trifluoroacetic acid a mixture of three products **22** (25%), **24** (40%) and **26** (16%) was obtained (Scheme 3). Analysis of the ^1H NMR spectrum of **22** showed a doublet at δ 4.32 for one benzylic proton and two doublets at δ 2.68 and 3.27 for two benzylic protons. Again

the loss of one benzylic proton and one aromatic proton leaving a doublet at δ 4.32 (H-1) and two singlets at δ 6.22 and 6.59 suggested the formation of a 1-aryltetralin. Heating compound **22** under reflux with acetic anhydride and pyridine for a period of 18 h yielded a monoacetate **23** in 30% yield, which suggested that a tertiary hydroxyl was present in **22**. The mass spectra of **22** and **23** also showed an ion at *m/z* 269 which is characteristic of the 1-aryltetralin series.[6]



Scheme 3

Analysis of the ^{1}H NMR spectrum of **24** indicated that the aromatic region contained four singlets. This led to the proposal that oxidative coupling had taken place to give the dibenzocyclooctadiene **24**. This conclusion was supported by 2D COSY experiments and by comparison of the ^{1}H and ^{13}C NMR spectra with those of compound **6** prepared earlier.[1b] Treatment of **24** with acetic anhydride and pyridine afforded the monoacetate **25** in low yield.

The third product, which had molecular formula $C_{23}H_{28}O_7$, *m/z* 416 (M^+), was assigned structure **26**, since it contained only three aromatic methoxyl groups and gave a carbonyl signal at δ 182.5 in its ^{13}C NMR spectrum. It also gave a low field signal at δ 176.5 which, on the basis of structure **26**, is assigned to C-9. The structure of **26** was eventually confirmed by X-ray crystallography (Figure 1). A possible mechanism leading to **26** is shown in Scheme 4. The structure of **26** bears some resemblance to the eupodienone series[7] and also resembles the spirodienones produced by oxidation of dibenzylbutyrolactones using phenyliodonium *bis*-(trifluoroacetate).[8]

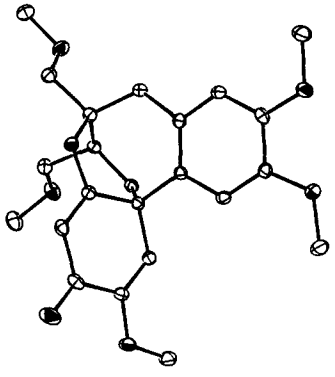
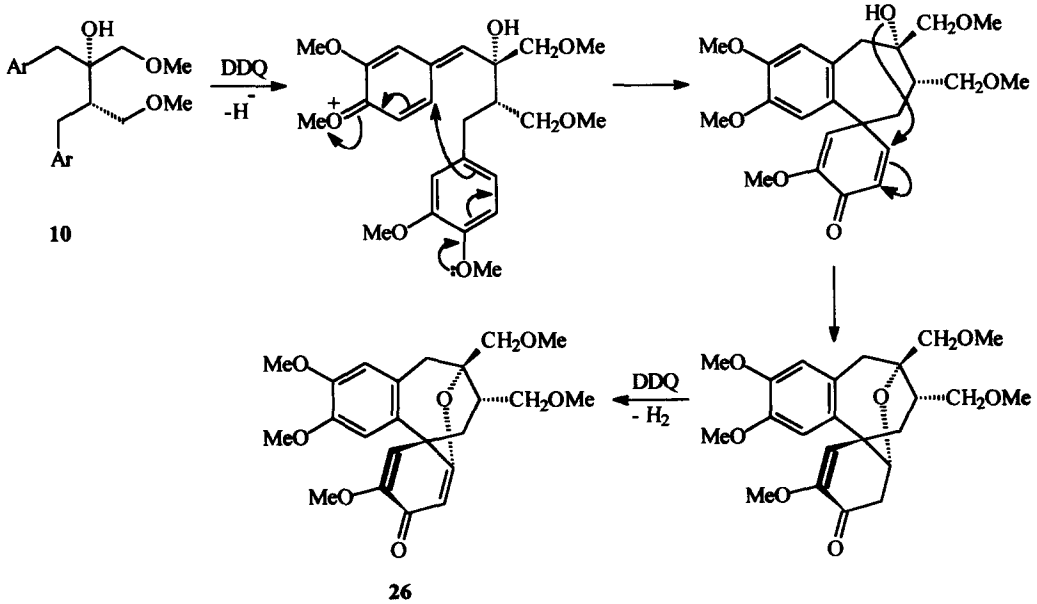


Figure 1. X-ray structure of 26



10

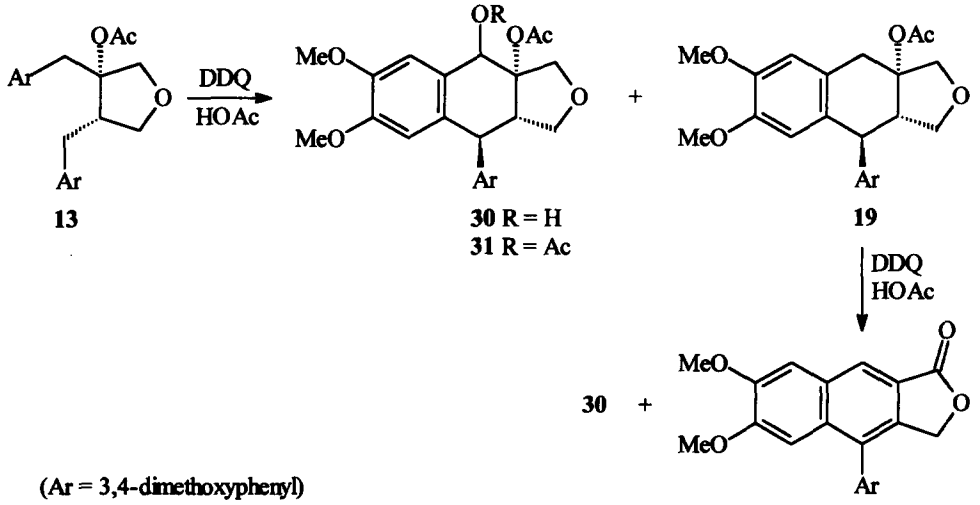
26

Scheme 4

When **10** was treated with 3 equivalents of DDQ in acetic acid a new product **27** (27%) was obtained along with the aryltetralin **22** (Scheme 3). Analysis of the ^{1}H NMR spectrum of **27** showed a singlet at δ 10.40 corresponding to an aldehyde proton and also the characteristic pattern of aromatic protons for a 1-arylnaphthalene. Based on its ^{1}H and ^{13}C NMR spectra it was identified as the 1-arylnaphthalene **27** which was prepared earlier by Satyanarayana *et al.*[9] starting from phyllanthin.

When **11** was reacted with 2 equivalents of DDQ in trifluoroacetic acid compound **28** (59%) was obtained (Scheme 3). Based on its ^{1}H and ^{13}C NMR spectra, and also on the presence of the ion at *m/z* 269 in its mass spectrum, it was identified as the 1-aryltetralin **28**. When **11** was reacted with 4 equivalents of DDQ in acetic acid the 1-arylnaphthalene **27** (96%) was again obtained.

The 3,4-dibenzyl-3-acetoxytetrahydrofuran **13** on treatment with 2 equivalents of DDQ in acetic acid produced a new product **30** (16%), and the previously isolated aryltetralin acetate **19** (66%) (Scheme 5). The molecular formula of **30**, $C_{24}H_{28}O_8$, indicates that it contains one more oxygen than **19**. Furthermore, **30** gave a diacetate **31**, on treatment with acetic anhydride, indicating that the additional oxygen is in the form of a secondary hydroxyl since the α-H which appeared as a singlet at δ 3.61 in compound **30** moves downfield to δ 3.71 in its acetate **31**. Based upon analysis of the ^{1}H and ^{13}C NMR spectra of **30** and its acetate **31** (Tables 5 and 6), and comparison with **19**, the secondary hydroxyl in **30** has been placed at C-4. The fact that the carbon chemical shift at δ 34.7 present in **19** was absent in the ^{13}C NMR spectra of **30** and **31** also supports placing the hydroxyl at C-4 in **30**. The structure of **30** is further supported by the fact that it was prepared directly from **19**

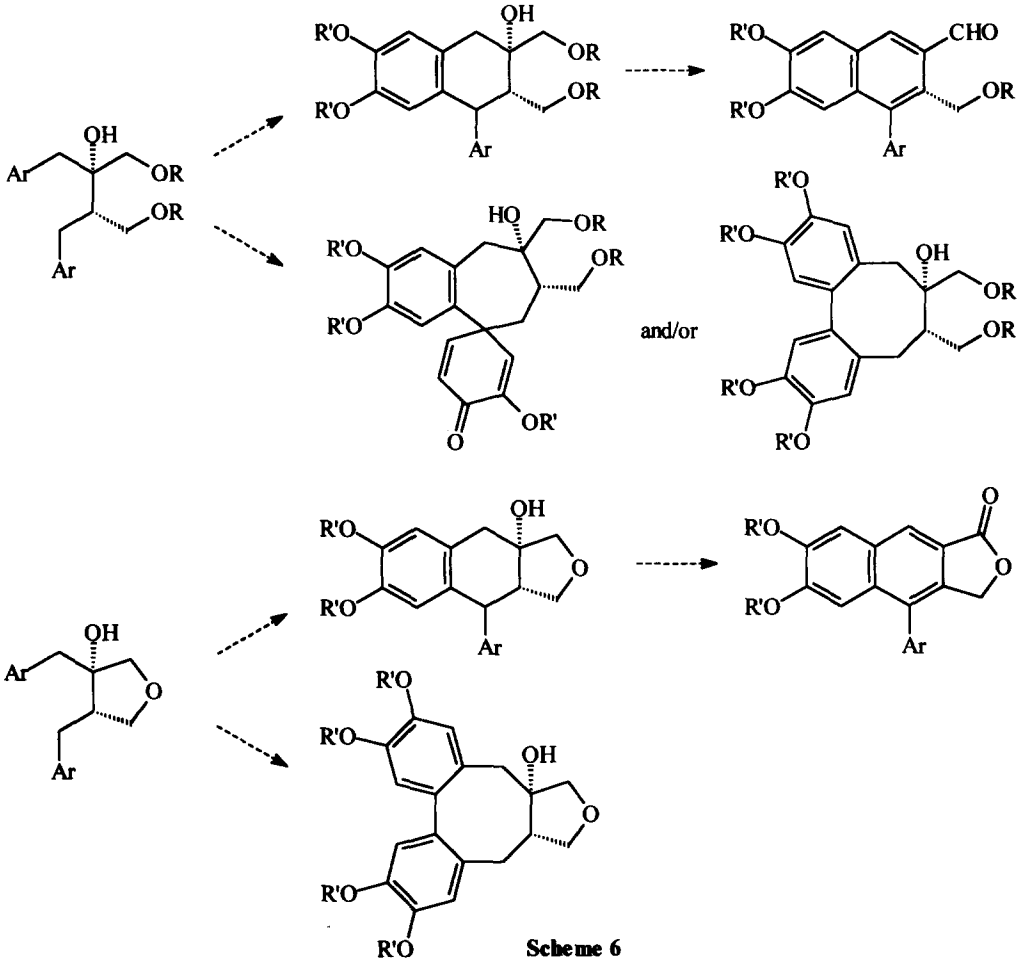


(Ar = 3,4-dimethoxyphenyl)

Scheme 5

by the action of DDQ in acetic acid. A by-product (26%) obtained in the reaction of **19** with 9 equivalents of DDQ in acetic acid was identified as the 1-arylnaphthalene lactone **32** based upon the analysis of its ^{1}H and ^{13}C spectra and by comparison with spectral data given in the literature.[9]

In conclusion, gmelinol **8**, a readily available naturally occurring lignan of the furofuran type,[10] can be transformed into various lignans through hydrogenolysis and oxidative coupling reactions with DDQ in acetic acid and trifluoroacetic acid media. These reactions illustrate the facile interconversion of the different lignan series under oxidative conditions and lend support to the mechanistic schemes proposed for the chemical[1d] and biochemical[11] generation of more complicated lignan types from the parent dibenzylbutane skeleton (Scheme 6).



Scheme 6

Table 1 : ^{1}H NMR spectra of 2,3-dibenzylbutane-1,2,4-triol derivatives

	9	14	15	10	11	1
H-1a	3.47 d (11.4)	3.80 m.	4.13 d (11.7)	3.20 s	3.25 d (8.0)	3.73 dd (2,11)
H-1b	3.53 d (11.4)	3.65 dd (5.5, 11.5)	4.01 d (11.7)	--	3.31 d	--
H-2	--	--	--	--	--	1.82 m
H-3	2.09 m	2.21m	2.22 m	2.05 m	2.27 m	1.82 m
H-4a	3.65 dd (5.8,11.2)	4.03 d (11.74)	3.83 m	3.27 dd (4.2, 9.7)	3.34 dd (2.7, 10.8)	-
H-4b	3.72 dd (9.25)	4.17 m	4.20 m	3.47 dd (2.7,9.7)	3.43 d (10.6)	3.43 dd (4,11)
2-CH_2	2.90 d (13.7)	2.84 d (13.9)	2.85 d (14.0)	2.77 d (13.6)	2.80 d (14.2)	-
	2.94 d (13.7)	2.94 d (13.9)	2.99 d (14.0)	3.08 d (13.6)	3.09 d (14.2)	2.64 m
3-CH_2	2.53 dd (13.7, 11.8)	2.66 dd (11.45, 13.9)	2.61 dd (10.9, 14.0)	2.73 dd (11.8, 13.7)	2.60 dd (11.1,13.5)	--
	2.99 dd (13.7, 3.0)	3.08 dd (3.7, 13.9)	3.03 dd (3.3, 14.0)	3.02 dd (3.6, 13.7)	2.83 dd (13.5)	2.64m
ArOMe	3.84 s	3.86 s	3.86 s	3.86 s	3.85 s	--
	3.85 s	3.87 s	3.87 s	3.87 s (x2)	3.86 s	--
	3.86 s	3.88 s	--	3.88 s	3.87 s	--
	3.87 s	3.89 s	--	--	--	--
ROMe	--	--	--	3.25 s	3.20 s	3.25 s
	--	--	--	3.33 s	3.32 s	3.33 s
	--	--	--	--	3.38 s	--
OH	2.08 m	2.52 m	2.34 m	3.58 s	--	3.88 br.s
Arom.	6.74-6.87 m	6.83-7.4 m	6.68-6.83 m	6.68-6.88 m	6.7-6.9 m	6.4-6.7 m
OAc	--	2.08 s	2.02 s	--	--	--
OAc	--	--	2.08 s	--	--	--

EXPERIMENTAL

^{1}H and ^{13}C NMR spectra were recorded on Bruker AC 400 instrument at 400 and 100 MHz respectively. All spectra used tetramethylsilane as internal standard and were run in $CDCl_3$. Mass spectra were recorded either on a VG 12-250 quadropole instrument or on a VG Micromass Quattro II instrument. Accurate mass measurements were made using either a ZAB-E high resolution double focussing instrument or Finnigan Mat 900 instrument. Infra-red spectra were recorded either as a nujol mull or as films on NaCl plates using a Perkin-Elmer Fourier transform 1725X spectrometer. Dichloromethane was purified by passing it down an alumina column and distillation over calcium hydride. Silica gel-G was used for column chromatography and for tlc. Melting points were recorded on an Electrothermal 9100 melting point apparatus and are uncorrected.

Crystal structure determination

Cell dimensions and intensity data were recorded at 293K, using an Enraf Nonius KappaCCD area detector diffractometer mounted at the window of a rotating anode operating at 50KV, 50mA with

Table 2 : ^{13}C NMR spectra of 2,3-dibenzylbutane-1,2,4-triol derivatives

	9	14	15	10	11	1
C-3'	147.4	147.4	147.6	147.2	147.0	147.3
C-3"	147.9	148.0	148.1	147.5	147.3	--
C-4'	148.8	148.8	148.9	148.4	148.3	145.5
C-4"	148.9	148.9	149.0	148.8	148.6	--
C-1'	128.8	128.7	128.1	130.3	130.4	--
C-1"	133.0	132.7	132.6	133.5	134.3	134.3
C-6'	121.0	120.9	120.9	121.1	121.0	--
C-6"	122.6	122.4	122.6	122.6	122.5	121.7
C-2'	111.1	111.1	111.2	110.7	110.6	--
C-2"	111.2	111.2	111.4	111.1	110.9	109.2
C-5'	112.2	112.0	111.2	112.3	112.4	--
C-5"	113.8	113.7	113.7	113.9	113.9	107.8
C-1	65.0	65.7	63.1	71.3	70.4	59.8
C-2	76.8	75.7	74.7	76.1	80.5	44.1
C-3	47.5	45.1	45.6	44.7	50.9	44.1
C-4	60.8	63.5	67.5	75.6	75.3	59.8
2-CH_2	31.6	32.6	32.5	31.5	32.3	35.7
3-CH_2	40.2	40.7	40.7	40.6	38.2	35.7
Ar-OMe	55.9	55.8	55.8	55.8	55.7	--
	55.9	55.9	55.9	55.8	55.7	--
	--	--	55.9	55.9	55.8	--
	--	--	--	--	55.8	--
R-OMe	--	--	--	58.8	58.4	--
	--	--	--	58.9	58.6	--
OCH_2O	--	--	--	--	--	100.6
OAc	--	21.0	20.9	--	--	--
	--	170.7	170.7	--	--	--
OAc	--	--	21.0	--	--	--
	--	--	170.8	--	--	--

a molybdenum anode (λ(Mo-Kα) = 0.71073 Å). The crystal-to-detector distance was 30mm and ϕ and Ω scans (2° increments, 10s exposure time) were carried out to fill the Ewald sphere. Data collection and processing were carried out using the programs collect[12], DENZO[13] and maXus[14] and an empirical absorption correction was applied using SORTAV.[15,16] The structure was solved via direct methods[17] and refined by full matrix least squares[17] on F^2. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were treated using a riding model. Full details have been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition number 127364.

Preparation of 9

To freshly distilled liquid ammonia (200 ml) was added a solution of gmelinol **8** (1 g, 2.45 mmol) in dry THF (50

Table 3 : ^{1}H NMR spectra of 3,4-dibenzyltetrahydrofuran derivatives

	12	13	2
H-2a	3.5d (9.47)	4.20d(10.5)	3.84dd (6,9)
H-2b	3.89d	4.16d(10.5)	--
H-4	2.37m	2.50m	2.09m
H-5a	3.72dd (9.5, 8.5)	3.53dd (7.9, 8.5)	3.33dd (6,9)
H-5b	3.9dd(8.55)	3.83dd(6.1)	--
H-6a	2.78d(13.7)	3.10d(14.2)	2.48m
H-6b	2.91d(13.7)	3.50d(14.2)	--
H-7a	2.58dd(10.3, 13.8)	2.39dd(11.0, 12.6)	2.48m
H-7b	2.81dd(4.9, 13.8)	2.54dd(2.3, 12.6)	--
H-3	--	--	2.09m
OMe	3.7s	3.83s	--
	3.85s	3.84s	
	3.88s	3.85s	
	3.92s	3.88s	
OCH_2O	--	--	5.81s
Arom.	6.66-6.83m	6.4-6.89 m	6.4-6.7m
OAc	--	2.15s	--

ml) and then sodium metal (1 g) was added and the mixture was stirred at -190°C for 1 h. The reaction was quenched carefully by adding NH_4Cl (10 g) and excess liquid ammonia was allowed to evaporate at room temperature. The reaction mixture was then extracted with ethyl acetate (3x30 ml) and the combined ethyl acetate extracts were washed with brine (3x20 ml), then dried ($MgSO_4$) and filtered. Evaporation of the solution under reduced pressure gave a pale yellow residue (1 g, 99%), which crystallised from methanol to give colourless crystals of **9**, m.p.140°C (lit.[2,3] 143-4°C), $[\alpha]_D^{25}$ –15.94 (c 0.175, $CHCl_3$). *m/z*(EI) 406(M^+, 2%), 254(12), 238(4), 220(6) 189(5), 151(100), 137(9). *m/z*(CI) 407(M+H$^+$, 2%), 389(1), 372(10), 353(15), 233(10), 151(100). ν_{max}(Nujol) 3400(OH), 1600(arom.) cm^{-1}. Acc. Mass 406.1992. $C_{22}H_{30}O_7$ requires 406.1992. For NMR spectra see Tables 1 and 2.

Preparation of monoacetate 14 and diacetate 15

A mixture of **9** (0.3 g, 0.74 mmol) in aqueous acetic acid (18 ml) was refluxed for 24 h at 100°C. The reaction mixture was then poured into ice-water and extracted with ethyl acetate (3x30 ml). The combined ethyl acetate extracts were washed successively with $NaHCO_3$ (3x20 ml) and brine (3x20 ml), then dried ($MgSO_4$) and filtered. Removal of the solvent under reduced pressure gave a reddish brown residue (0.29 g). Column chromatography (eluent, CH_2Cl_2 - EtOAc 4:1) yielded **14** (0.1 g, 30%) as a pale yellow gum, *m/z*(EI) 448(M^+, 3%), 353(2), 296(12), 279(3), 261(3), 219(21), 206(2), 191(8), 151(100), 137(10). *m/z*(CI) 466(M+NH_4^+, 5%),

Table 4 : ^{13}C NMR spectra of 3,4-dibenzyltetrahydrofuran derivatives

	12	13	2
C-3'	147.4	147.4	147.5
C-4'	148.1	148.1	--
C-3"	148.9	148.8	145.7
C-4"	148.1	148.9	--
C-1'	129.3	128.7	
C-1"	132.9	132.8	} 133.9
C-6'	120.4	120.3	
C-6"	121.8	122.5	} 121.3
C-2'	111.2	111.0	
C-2"	111.3	111.3	} 107.9
C-5'	111.9	111.7	
C-5"	113.1	113.6	} 108.8
C-2	79.5	76.7	73.2
C-3	80.3	88.4	46.5
C-4	49.1	48.3	46.5
C-5	73.3	72.7	--
C-6	32.2	33.0	39.2
C-7	42.8	40.1	--
ArOMe	55.8	55.8	--
	55.9	55.9	--
OAc	--	22.0	--
		170.6	
OCH_2O	--	--	100.7

449($M+H^+$, 4), 432(15), 353(50), 151(100). Acc. Mass 448.2103. $C_{24}H_{32}O_8$ requires 448.2097. ν_{max}(Nujol) 3580(OH), 1735(OAc), 1600(arom.) cm^{-1}, and **15** (0.1 g, 28%) as a pale yellow gum, $[\alpha]_D^{25}$ +2.04 (c 0.22, $CHCl_3$). *m/z*(EI) 490(M^+, 12%), 261(30), 151(100). *m/z*(CI) 508($M+NH_4^+$, 50%), 473(50), 353(20), 261(20), 151(100). Acc. Mass 490.2201. $C_{26}H_{34}O_9$ requires 490.2203. ν_{max}(Nujol) 3580(OH), 1735(OAc), 1600(arom.) cm^{-1}. For NMR spectra see Tables 1 and 2.

Preparation of diacetate 15

To a solution of **9** (0.2 g, 0.49 mmol) in pyridine (3 ml) was added freshly distilled acetic anhydride (3 ml) and the mixture allowed to stand overnight. The reaction mixture was then poured into ice-water and extracted with EtOAc (3x30 ml). The combined ethyl acetate extracts were washed successively with dil.HCl (3x20 ml) and brine (3x20 ml), then dried ($MgSO_4$) and filtered. Removal of the solvent under reduced pressure gave a reddish brown residue (0.2 g). Column chromatography (eluent, hexane - EtOAc 7:3) yielded **15** (0.18 g, 75%) as a pale yellow gum. See above for spectral data.

Table 5 : ^{1}H NMR spectra of aryltetralin derivatives

	18	22	19	30	31	5
H-1	3.96 d (11.6)	4.32 d (11.9)	4.08 d (11.6)	4.12 d (11.4)	4.12 d (11.4)	3.70 d (10.0)
H-2	2.40 q (10.2)	2.03 d (11.9)	2.45 q (10.2)	2.54 m	2.66 m	2.21 m
H-4a	3.13 d (16.2)	2.68 d (16.6)	3.90 d (17.1)	3.61 s	3.71 s	2.71 dd (9.6, 15.0)
H-4b	3.05 d (16.2)	3.27 d (16.6)	3.05 d (17.1)	--	--	2.96 dd (4.0, 15.6)
Arom.	6.35 s	6.22 s	6.33 s	6.23 s	6.13 s	6.29 s
	6.65 s	6.59 s	6.59 s	6.33 s	6.31 s	6.60 s
	6.61 s	6.64 d (1.8)	6.62 s	6.68 s	6.78 s	6.55 d
	6.82 d (8.2)	6.83 d (8.2)	6.83 d (8.2)	6.82 d (8.2)	6.83 d (8.2)	6.66 dd (1.7, 8.0)
	6.74 m	6.77 m	6.76 dd (1.6, 8.2)	6.72 m	6.73 m	6.74 d (7.9)
2-CH_2O	3.76 m	3.62 dd	3.75 d (9.6)	3.78 t (7.9)	3.71 s	--
	3.81 m	(2.5, 9.6)	3.92 m	3.90 m	3.89 m	3.50 m
		3.18 dd (1.9, 9.6)				
3-CH_2O	3.79 m	3.57 m	3.88 d (10.5)	3.94 d (9.5)	4.05 d (11.1)	4.19 t (7.3)
	4.05 d (9.0)		4.69 d (10.5)	4.01 d (9.5)	5.17 d (11.1)	3.81 t (7.3)
ArOMe	3.61 s	3.57 s	3.62 s	3.62 s	3.63 s	--
	3.80 s	3.81 s	3.82 s	3.80 s	3.82 s	--
	3.87 s	3.83 s	3.86 s	3.86 s	3.88 s	--
	3.89 s	3.89 s	3.90 s	3.89 s	2.90 s	--
ROMe	--	3.30 s				
		3.41 s				
OCH_2O	--	--	--	--	--	5.87 s
						5.95 s
OH	2.12 s		--	--	--	--
OAc	--	--	1.99 s	2.30 s	2.04 s	--
	--		--	--	2.20 s	--

Preparation of methyl ethers 10 and 11

To a solution of **9** (0.5 g, 1.23 mmol) in freshly distilled THF (50 ml) was added NaH (about 1 g washed free from paraffin wax with hexane) and the mixture was stirred for ½ h at room temperature. Methyl iodide (1 ml) was added and the mixture left stirring overnight. The excess NaH was then decomposed by addition of aqueous methanol. The organic solvents were distilled off from the reaction mixture, which was then neutralised with dil.HCl and extracted with EtOAc (3x30 ml). The combined ethyl acetate extracts were washed successively with $NaHCO_3$ (3x20 ml) and brine (3x20 ml), then dried ($MgSO_4$) and filtered. Removal of the solvent under reduced pressure gave a brown residue (0.5 g). Column chromatography (eluent, hexane - EtOAc 4:1) followed by crystallisation from methanol yielded **10** (0.15 g, 28%) as colourless shining crystals, m.p.88-90°C, $[\alpha]_D^{25}$ +10.76 (c 0.13, $CHCl_3$). *m/z*(EI) 434(M^+, 13%), 371(12), 282(70), 265(55), 233(100), 201(40), 189(75), 177

Table 6 : ^{13}C NMR spectra of aryltetralin derivatives

	18	22	28	19	30	31	5
C-6	147.6	146.9	147.1	147.3	148.0	148.0	148.0x2
C-7	147.8	147.4	147.3	147.6	148.7	148.2	--
C-3'	147.9	147.5	147.6	147.9	149.2	148.6	146.12
C-4'	149.1	148.9	147.8	149.2	--	149.4	146.38
C-4a	125.7	125.6	125.6	125.6	125.6	125.5	129.5
C-8a	130.8	131.1	131.1	130.4	133.0	132.3	133.01
C-1'	136.4	138.3	138.3	136.2	135.8	135.4	133.06
C-6'	120.9	121.8	121.8	120.9	120.9	121.0	121.63
C-5	111.1	111.0	110.3	111.2	109.3	109.4	} 108.63x2
C-8	112.3	111.8	111.0	111.9	111.2	111.3	
C-2'	--	112.3	112.3	112.0	111.8	111.5	} 108.16x2
C-5'	--	112.8	112.8	--	--	--	
C-1	52.2	45.2	47.7	53.1	51.6	52.1	50.88
C-2	44.3	43.5	45.2	44.0	43.9	43.8	42.23
C-3	77.3	72.7	78.1	85.5	78.4	86.1	49.99
C-4	38.4	39.2	33.5	34.7	74.2	72.9	32.88
2-CH_2O	70.4	70.8	70.8	70.1	70.2	69.0	73.09
3-CH_2O	78.5	79.0	76.8	75.2	78.4	73.8	72.22
ArOMe	55.8	55.7	55.7	55.8	55.8	55.8	--
	55.9	55.8	55.8	55.8	55.8	55.9	--
	55.9	55.9	55.9	55.9	55.9	55.9	--
	--	55.9	58.2	--	--	60.0	--
ROMe		59.1	58.5				
		59.3	58.8				
			58.9				
OCH_2O	--	--	--	--	--	--	100.95
							100.85
OAc	--			22.1	21.1	21.2	--
	--			170.9	171.0	170.0	--
OAc	--			--	--	22.2	--
	--			--	--	171.7	--

(65). *m/z*(CI) 452($M+NH_4^+$, 15%), 435($M+H^+$, 6), 402(6), 385(33), 353(65), 265(25), 235(25), 177(30), 151(100). Acc. Mass 434.23096. $C_{24}H_{34}O_7$ requires 434.23045. ν_{max}(Nujol) 3580(OH), 1600(arom.), 1100(CH_2OMe) cm^{-1}, and **11** (0.3 g, 54%) as a pale yellow gum, $[\alpha]_D^{25}$ +2.5 (c 0.04, $CHCl_3$). *m/z*(EI) 448(M^+, 5%), 418(100), 386(47), 371(22). *m/z*(CI) 466($M+NH_4^+$, 20%), 436(22), 419(8), 402(7), 385(42), 353(75), 265(25), 235(28), 177(25), 151(100), 115(8). Acc. Mass 448.2445. $C_{25}H_{36}O_7$ requires 448.2461. ν_{max}(Nujol) 1600(arom.), 1100(CH_2OMe) cm^{-1}. For NMR spectra see Tables 1 and 2.

Preparation of 3,4-dibenzyl-3-hydroxy-tetrahydrofuran 12

To a solution of **9** (0.3 g, 0.74 mmol) in pyridine (4 ml) was added p-toluenesulfonyl chloride (0.6 g, 3.2 mmol, 4.5 equiv.) and the mixture left at room temperature overnight. The reaction mixture was then poured

Table 7 : ^{1}H NMR spectra of dibenzocyclooctadiene derivatives

	20	21	24	25	6	7
H-1	6.70 s	6.70 s	6.77 s	6.75 s	6.67 s	6.40 s
H-4	6.71 s	6.72 s [2H]	6.78 s	6.82 s [2H]	6.77 s	6.70 s
H-9	6.76 s	6.86 s	6.81 s	6.91 s	--	--
H-12	6.77 s		6.82 s		--	--
H-5a	2.83 d (13.3)	2.6 m	2.84 d (13.9)	3.75 d (14.3)	2.73 d (13.0)	2.54 d (13.1)
H-5b	2.62 d (13.3)	2.8 m	2.47 d (13.9)	3.88 m	2.05 dd (10.2, 13.0)	2.23 dd (9.2, 13.1)
H-6	--	--		--	1.43 m	1.81 m
H-7	2.07 m	2.1 m	1.86 m	2.20 m	--	--
H-8a	2.31 m [2H]	2.4 m	2.50 m	2.23 dd	2.05 dd (10.2, 13.0)	2.54 d (13.1)
H-8b		2.8 m		2.43 dd (13.6, 10.0)	2.73 d (13.0)	2.23 dd (9.2, 13.1)
H-13a	3.68 d (8.4)	3.7 m	3.47 d (9.0)	4.18 d (9.2)	3.66 d (9.2)	4.03 d (7.5)
H-13b	3.87 m	4.15 m	3.37 m	3.81 d (9.2)	--	--
H-14a	3.71 dd (7.3, 12.2)	3.7 m	3.52 dd (6.0, 9.3)		3.25 dd (6.0, 9.2)	3.40 dd (7.5, 11.0)
H-14b	4.06 t (7.5)	4.8 m	3.66 dd (3.4, 9.6)		--	--
ArOMe	3.88 s	3.90 s	3.87 s	3.87 s	--	--
	3.89 s	3.91 s	3.88 s	3.88 s	--	--
	3.94 s	3.92 s	3.90 s	3.91 s	--	--
	3.95 s	3.98 s	3.91 s	3.93 s	--	--
ROMe	--	--	3.36 s	3.32 s	--	--
			3.38 s	3.44 s		
OH	1.70 br.s	--	1.86 m	--	4.4 br.	--
OCH_2O	--	--	--	--	5.95 d (1.0)	5.97 d (1.0)
					5.97 d (1.0)	5.98 d (1.0)
OAc	--	1.90 s		1.96 s	--	--

into ice-water and extracted with EtOAc (3x30 ml). The combined extracts were washed successively with dil. HCl (3x20 ml) and brine (3x20 ml), then dried ($MgSO_4$) and filtered. Removal of the solvent under reduced pressure gave a brown residue (0.3 g). Column chromatography (eluent, CH_2Cl_2 - EtOAc 9:1) yielded **12**, which crystallised from methanol as colourless crystals (0.21 g, 73%), m.p.130-132°, $[\alpha]_D^{25}$ –33.14 (c 0.175, $CHCl_3$). *m/z*(EI) 388(M^+, 40%), 219(15), 191(5), 151(100), 137(15). *m/z*(CI) 406($M+NH_4^+$, 100%), 388(M^+, 20), 151(35). Acc. Mass 388.1896. $C_{22}H_{28}O_6$ requires 388.1886. ν_{max}(Nujol) 3580(OH), 1600(arom.) cm^{-1}. For NMR spectra see Tables 3 and 4.

Preparation of 3,4-dibenzyl-3-acetoxy-tetrahydrofuran 13 and diacetate 15

To a solution of **9** (0.2 g, 0.49 mmol) in glacial acetic acid (10 ml) cooled to 0°C was added conc. H_2SO_4

Table 8 : ^{13}C NMR spectra of dibenzocyclooctadiene derivatives

	20	21	24	25	6	7
C-2	147.0	147.0	147.1	147.0	146.74	
C-3	147.8	147.5	147.4	147.3	145.18	147.33x2
C-10	148.1	148.7	147.7	147.6	--	
C-11	148.7	--	148.5	148.7		146.06x2
C-1a	125.8	126.8	128.2	127.7	134.97	
C-4a	131.9	132.3	132.5	132.0	133.15	133.74x2
C-8a	133.8	133.7	133.7	134.0	--	
C-12a	134.4	133.8	133.9		--	133.59x2
C-1	111.8	113.5	111.6	111.6	108.92	
C-4	114.0	113.9	111.9	111.9	107.96	109.13x2
C-9	114.6	114.0	112.0	112.0	--	
C-12	115.0	114.2	115.0	114.0	--	108.68x2
C-6	75.1	85.1	71.7	82.6	43.90	
C-7	52.9	53.7	46.2	46.8	--	49.08x2
C-5	38.6	35.7	41.0	39.5	34.82	32.78
C-8	26.9	26.4	31.6	29.9	--	72.78
C-13	78.4	73.4	75.8	73.4	65.19	--
C-14	71.2	71.1	80.1	77.5	--	--
OMe	56.0	55.8	56.0	55.8		--
	56.1	55.9	56.1	55.9	--	--
	--	56.0	58.9	56.0	--	--
	--	56.1	59.1	56.0	--	--
	--	--	59.4	58.7		--
				59.3		
OCH_2O	--	--			100.63	100.59x2
OAc	--	22.3		22.2	--	--
		171.5		171.4		

(6 drops) dropwise with gentle shaking. The mixture was left at room temperature for 3 h, during which time the yellow colour of the solution slowly changed to red. The reaction mixture was then poured into ice-water and extracted with EtOAc (3x30 ml). The combined ethyl acetate extracts were washed successively with $NaHCO_3$ (3x20 ml) and brine (3x20 ml), then dried ($MgSO_4$) and filtered. Removal of the solvent under reduced pressure gave a pale yellow residue (0.2 g). Column chromatography (eluent, CH_2Cl_2 - EtOAc 9:1) yielded **13** (0.15 g, 71%) as a colourless gum, $[\alpha]_D^{25}$ –29.84 (c 0.5, $CHCl_3$). *m/z*(EI) 430(M^+, 10%), 370(8), 219(28), 191(10), 151(100), 137(5). *m/z*(CI) 448($M+NH_4^+$, 25%), 430(M^+, 10), 388(20), 371(30), 233(10), 219(15), 151(100). Acc. Mass 430.1994. $C_{24}H_{30}O_7$ requires 430.1992. ν_{max}(Nujol) 1735(OAc), 1600(arom.) cm^{-1}, and **15** (0.03 g, 12%) as a pale yellow gum. For NMR spectra of **13** see Tables 3 and 4.

Preparation of 1-aryltetralin 18

To a mixture of 3,4-dibenzyl-3-hydroxy-tetrahydrofuran **12** (0.2 g, 0.51 mmol) and DDQ (0.4 g, 1.76

mmol, 3.5 equiv.) was added glacial acetic acid (8 ml) and the mixture stirred for 5 h. The reaction mixture was then poured into ice cold water and extracted with EtOAc (3x30 ml). The combined ethyl acetate extracts were washed successively with $NaHCO_3$ (3x20 ml), sodium metabisulphite (3x20 ml), and brine (3x20 ml), then dried ($MgSO_4$) and filtered. Removal of the solvent under reduced pressure gave a brown residue (0.2 g). Column chromatography (eluent, hexane - EtOAc 1:1) followed by crystallisation from methanol yielded aryltetralin **18** (0.165 g, 83%) as an amorphous powder, m.p.245°. $[\alpha]_D^{25}$ –38.84 (c 0.095, $CHCl_3$). *m/z*(EI) 386(M^+, 95%), 368(75), 337(85), 327(78), 307(81), 275(61), 165(71), 151(100), 131(34), 115(46), 91(25). *m/z*(CI) 404($M+NH_4^+$, 100%). Acc. Mass 386.1739. $C_{22}H_{26}O_6$ requires 386.1729. ν_{max}(Nujol) 3580(OH), 1600(arom.) cm^{-1}. For NMR spectra see Tables 5 and 6.

Preparation of acetate 19

To a solution of 1-aryltetralin **18** (0.07 g, 0.18 mmol) in dry pyridine (2 ml) was added acetic anhydride (2 ml) and the mixture was refluxed for 6 h. The reaction mixture was then poured into ice-water and extracted with EtOAc (3x30 ml). The combined ethyl acetate extracts were washed successively with dil.HCl (3x10 ml) and brine (3x10 ml), then dried ($MgSO_4$) and filtered. Removal of the solvent gave a reddish brown residue (0.07 g). Column chromatography (eluent, hexane - EtOAc 7:3) followed by crystallisation from methanol yielded colourless shining crystals of **19** (0.07 g, 90%), m.p.178°C. $[\alpha]_D^{25}$ +4.14 (c 0.14, $CHCl_3$). *m/z*(EI) 428(M^+, 5%), 368(100), 337(75), 327(42), 307(95), 275(35), 230(55), 217(37), 201(50), 189(40), 165(52), 151(97), 115(34). *m/z*(CI) 446($M+NH_4^+$, 22%), 429($M+H^+$, 6), 386(15), 369(100). Acc. Mass 428.1831. $C_{24}H_{28}O_7$ requires 428.1835. ν_{max}(Nujol) 1735(OAc), 1600(arom.) cm^{-1}. For NMR spectra see Tables 5 and 6.

Preparation of dibenzocyclooctadiene 20

To a mixture of 3,4-dibenzyl-3-hydroxy-tetrahydrofuran **12** (0.1 g, 0.3 mmol) and DDQ (0.13 g, 0.6 mmol, 2 equiv.) was added freshly distilled trifluoroacetic acid (5 ml) and the mixture stirred at room temperature for 3 h. The reaction mixture was then poured into ice-water and extracted with EtOAc(3x30 ml). The combined ethyl acetate extracts were washed successively with sodium metabisulphite (3x20 ml), $NaHCO_3$ (3x20 ml), and brine (3x20 ml), then dried ($MgSO_4$) and filtered. Removal of the solvent under reduced pressure gave a reddish brown residue (0.1 g), which was purified by column chromatography (eluent, CH_2Cl_2 - EtOAc 4:1), followed by crystallisation from methanol, to give the dibenzocyclooctadiene **20** (0.07 g, 70%) as colourless crystals, m.p.110-12°. *m/z*(EI) 386(M^+, 100%), 368(11), 301(15), 286(10), 270(30), 241(2), 151(4).

m/z(CI) 404($M+NH_4^+$, 100%), 386(M^+, 33), 369(77). Acc. Mass 386.1742. $C_{22}H_{26}O_6$ requires 386.1729. ν_{max}(Nujol) 3580(OH), 1600(arom.) cm^{-1}. For NMR spectra see Tables 7 and 8.

Preparation of acetate 21

To a solution of dibenzocyclooctadiene **20** (0.025 g, 0.065 mmol) in dry pyridine (2 ml) was added acetic anhydride (2 ml) and the mixture refluxed for 9 h. The reaction mixture was poured into ice-water and extracted with EtOAc (3x30 ml). The combined ethyl acetate extracts were washed successively with dil.HCl (3x10 ml) and brine (3x10 ml), then dried ($MgSO_4$) and filtered. Removal of the solvent under reduced pressure gave a reddish brown residue (0.025 g). Column chromatography (eluent, hexane - EtOAc 7:3) yielded **21** (0.02 g, 72%) as a pale yellow gum, *m/z*(EI) 428(M^+, 12%), 402(6), 369(10), 368(42), 353(8), 337(15). *m/z*(CI) 446($M+NH_4^+$, 10%), 388(8), 386(20), 369(100), 370(22), 339(25), 167(22). Acc. Mass 428.1835. $C_{24}H_{28}O_7$ requires 428.1835. ν_{max}(Nujol) 1735(OAc), 1600(arom.) cm^{-1}. For NMR spectra see Tables 7 and 8.

Preparation of the 1-aryltetralin 22, dibenzocyclooctadiene 24 and spirodienone 26

To a mixture of **10** (0.2 g, 0.3 mmol) and DDQ (0.15 g, 0.6 mmol, 2 equiv.) was added freshly distilled TFA (3 ml) and the mixture was stirred for 3 h at room temperature. The reaction mixture was then poured onto crushed ice and extracted with EtOAc (3x30 ml). The combined ethyl acetate extracts were successively washed with sodium metabisulphite (3x20 ml), $NaHCO_3$ (3x20 ml), and brine (3x20 ml), then dried ($MgSO_4$) and filtered. Removal of the solvent under reduced pressure gave a reddish brown residue (0.2 g). Column chromatography (eluent, hexane - EtOAc 4:1) yielded the 1-aryltetralin **22** (0.05 g, 25%) as a pale yellow gum, $[\alpha]_D^{25}$ +39.76 (0.05, $CHCl_3$). *m/z*(EI) 432(M^+, 20%), 414(5), 400(5), 369(30), 337(68), 305(15), 269(10), 217(32), 151(53). *m/z*(CI) 450($M+NH_4^+$, 6%), 433($M+H^+$, 10), 415(35), 383(100). Acc. Mass 432.2150. $C_{24}H_{32}O_7$ requires 432.2148. ν_{max}(Nujol), 3580(OH), 1600(arom.), 1100(CH_2OMe) cm^{-1}, the dibenzocyclooctadiene **24** (0.08 g, 40%) as a pale yellow gum, $[\alpha]_D^{25}$ +196.39 (0.071, $CHCl_3$). *m/z*(EI) 432(M^+, 50%), 337(20), 301(18), 299(20), 286(22), 270(45). *m/z*(CI) 450($M+NH_4^+$, 5%), 449(10), 433($M+H^+$, 7), 432(M^+, 10), 417(20), 415(30), 384(25), 383(100), 369(10). Acc. Mass 432.2156. $C_{24}H_{32}O_7$ requires 432.2148, and the spirodienone **26** (0.03 g, 16%), which crystallised from benzene to give colourless shining crystals, m.p. 160°C, $[\alpha]_D^{25}$ –267.52 (0.025, $CHCl_3$). ^1H NMR (δ) 6.74s, 6.63s, 5.77s, 5.65s (H-1,H-4,H-10,H-13), 3.83s (2xOMe), 3.78s (OMe), 3.47s (OMe), 3.31s (OMe), 3.64d (J9.5,H-14a), 3.55d (J9.5,H-14b), 3.48d (H-15a), 3.41d (H-15b), 3.50dd (H-5a), 3.22t (J8.7,H-5b), 2.53m (H-7), 2.66dd(J9.6,13.9,H-8a)2.21dd (J2.4,13.9,H-8b). ^{13}C

NMR (δ) 182.5 (C-11), 176.5 (C-9), 149.9 (C-2), 148.3 (C-3), 146.8 (C-12), 133.0 (C-4a), 127.2 (C-1a), 114.7 (C-4), 113.8 (C-1), 109.6 (C-13), 104.5 (C-10), 80.9 (C-6), 76.5 (CH_2), 72.5 (CH_2), 59.6, 58.9, 56.0, 55.9, 55.3 (5xOMe), 42.9 (C-8a), 42.3 (C-8), 37.6 (C-7), 36.8 (C-5). *m/z*(EI) 416(M^+, 25%), 384(5), 339(10), 301(10), 285(12), 201(15), 152(12). *m/z*(CI) 417($M+H^+$, 100%). Acc. Mass 416.1807. $C_{23}H_{28}O_7$ requires 416.1835. ν_{max}(Nujol) 1659(C=O), 1637(C=O), 1604(arom.) cm^{-1}. For NMR spectra of **22** see Tables 5 and 6, and for **24** see Tables 7 and 8.

Preparation of acetate 23

To a solution of 1-aryltetralin **22** (0.05 g, 0.12 mmol) in dry pyridine (2 ml) was added acetic anhydride (2 ml) and the mixture refluxed for 18 h. The reaction mixture was poured onto crushed ice and extracted with EtOAc (3x20 ml). The combined ethyl acetate extracts were washed successively with dil.HCl (3 x 10 ml) and brine (3x10 ml), then dried ($MgSO_4$) and filtered. Removal of the solvent under reduced pressure gave a reddish brown residue (0.05 g). Column chromatography (eluent, Hexane - EtOAc 4:1) yielded **23** (0.02 g, 30%) as a pale yellow gum, *m/z*(EI) 474(M^+, 1%), 442(5), 414(20), 382(10), 337(100). *m/z*(CI) 492($M+NH_4^+$, 1%), 475($M+H^+$, 1), 432(5), 415(40), 383(100). For NMR spectra see Tables 5 and 6.

Preparation of acetate 25

To a solution of dibenzocyclooctadiene **24** (0.07 g, 0.16 mmol) in dry pyridine (2 ml) was added acetic anhydride (2 ml) and the mixture refluxed for 18 h. The reaction mixture was poured onto crushed ice and extracted with EtOAc (3x20 ml). The combined ethyl acetate extracts were washed successively with dil.HCl (3 x 10 ml) and brine (3x10 ml), then dried ($MgSO_4$) and filtered. Removal of the solvent under reduced pressure gave a reddish brown residue (0.07 g). Column chromatography (eluent, Hexane - EtOAc 4:1) yielded **25** (0.02 g, 26%) as a pale yellow gum. *m/z*(EI) 474(M^+, 10%), 414(25), 369 (15), 342(15), 337(45), 319(18), 299(20). *m/z*(CI) 415(45%), 383(100). Acc. Mass 474.2248. $C_{26}H_{34}O_8$ requires 474.2254. For NMR spectra see Tables 7 and 8.

Preparation of 1-aryltetralin 22 and arylnaphthalene 27

To a mixture of **10** (0.2 g, 0.46 mmol) and DDQ (0.35 g, 1.5 mmol, 3 equiv.) was added glacial acetic acid (4 ml) and the mixture stirred for 3 h at room temperature. The reaction mixture was then poured onto crushed ice and extracted with EtOAc (3x30 ml). The combined ethyl acetate extracts were washed successively

with sodium metabisulphite (3x20 ml), $NaHCO_3$ (3x20 ml), and brine (3x20 ml), then dried ($MgSO_4$) and filtered. Removal of the solvent under reduced pressure gave a reddish brown residue (0.2 g). Column Chromatography (eluent, hexane - EtOAc 1:1) yielded 1-aryltetralin **22** (0.09 g, 45%) as a pale yellow gum, and arylnaphthalene **27** (0.05 g, 27%), which crystallised from methanol as colourless crystals, m.p.151°C, $[\alpha]_D^{25}$ – 5.2 (c 0.05, $CHCl_3$). ^1H NMR (δ) 3.31s (ROMe), 3.76s, 3.88s, 4.01s, 4.02s (ArOMe), 4.54d (J10.6) and 4.65d (J10.6,CH_2), 6.82s (H-8), 6.90m (H-6'), 7.03d (J8.6,H-5'), 7.27s (H-5), 8.32s (H-4a and 4b), 10.40s (CHO). ^{13}C NMR (δ) 55.8, 55.9, 56.0, 56.1 (ArOMe), 58.2 (ROMe), 68.4 (CH_2), 106.0, 107.7, 110.9, 113.5 (C-5,8,2',5'), 122.6 (C-6'), 128.2, 130.3, 130.4, 131.0, 131.2, 131.7 (C-4a,8a,1,2,3,4), 139.7 (C-1'), 148.4, 148.7, 150.1, 151.7 (C-6,7,3',4'), 192.4 (CO). *m/z*(EI) 396(M^+, 18%), 381(10), 364(100), 349(32), 305(32), 261(38), 189(33), 151(23). Acc. Mass 396.1561. $C_{23}H_{24}O_6$ requires 396.1573. ν_{max}(Nujol) 1710(CHO), 1600(arom.), 1100(CH_2OMe) cm^{-1}.

Preparation of 1-aryltetralin 28

To a mixture of **11** (0.17 g, 0.3 mmol) and DDQ (0.15 g, 0.6 mmol, 2 equiv.) was added freshly distilled TFA (3 ml) and the mixture stirred for 2 h at room temperature. The reaction mixture was then poured onto crushed ice and extracted with EtOAc (3x30 ml). The combined extracts were washed successively with sodium metabisulphite (3x20 ml) and $NaHCO_3$ (3x20 ml), then dried ($MgSO_4$) and filtered. Removal of the solvent under reduced pressure gave a brown residue (0.17 g). Column chromatography (eluent, hexane - EtOAc 4:1) yielded **28** (0.1 g, 59%) as a pale yellow gum, *m/z*(EI) 446(M^+, 18%), 416(12), 369(25), 337(55), 306(11), 231(15), 151(25). *m/z*(CI) 446(M^+, 6%), 415(95), 383(100). Acc. Mass 446.2275. $C_{25}H_{34}O_7$ requires 446.2304. ν_{max}(Nujol) 1600(arom.), 1100(CH_2OMe) cm^{-1}. For NMR spectra see Tables 5 and 6.

Preparation of arylnaphthalene 27

To a mixture of **11** (0.1 g, 0.3 mmol) and DDQ (0.25 g, 1.5 mmol, 5 equiv.) was added glacial acetic acid (4 ml) and the mixture stirred for 3 h at room temperature. The reaction mixture was then poured onto crushed ice and extracted with EtOAc (3x30 ml). The combined ethyl acetate extracts were washed successively with sodium metabisulphite (3x20 ml), $NaHCO_3$ (3x20 ml), and brine (3x20 ml), then dried ($MgSO_4$) and filtered. Removal of the solvent under reduced pressure gave a reddish brown residue (0.1 g). Column chromatography (eluent, hexane - EtOAc 4:1) yielded **27** (0.085 g, 96%), which crystallised from methanol as colourless crystals, m.p.151°C. See above for spectral data.

Preparation of 1-aryltetralins 19 and 30

To a mixture of 3,4-dibenzyl-3-acetoxy-tetrahydrofuran **13** (0.295 g, 0.3 mmol) and DDQ (0.3 g, 0.6 mmol, 2 equiv.) was added glacial acetic acid (8 ml) and the mixture was stirred for 8 h at room temperature. The reaction mixture was then poured onto crushed ice and extracted with EtOAc (3x30 ml). The combined ethyl acetate extracts were washed successively with sodium metabisulphite (3x20 ml), $NaHCO_3$ (3x20 ml), and brine (3x20 ml), then dried ($MgSO_4$) and filtered. Removal of the solvent under reduced pressure gave a reddish brown residue (0.28 g). Column chromatography (eluent, hexane - EtOAc 4:1) yielded **19** (0.195 g, 66%), which crystallised from methanol as colourless crystals, m.p.178°, and **30** (0.05 g, 16%), which crystallised from methanol as colourless crystals, m.p.191°C, $[\alpha]_D^{25}$ –3.57 (c 0.14, $CHCl_3$). *m/z*(EI) 444(M^+, 25%), 384(95), 366(22), 352(51), 337(57), 325(88), 307(34), 189(33), 165(54), 151(100), 115(34). *m/z*(CI) 462($M+NH_4^+$, 15%), 427(5), 404(45), 386(95), 385(100), 369(85). Acc. Mass 444.1752. $C_{24}H_{28}O_8$ requires 444.1784. ν_{max}(Nujol) 3580(OH), 1735(OAc), 1600(arom.) cm^{-1}. For NMR spectra see Tables 5 and 6.

Preparation of 1-aryltetralin diacetate 31

To a solution of 1-aryltetralin **30** (0.045 g, 0.1 mmol) in dry pyridine (3 ml) was added acetic anhydride (3 ml) and the mixture was refluxed for 4 h. The reaction mixture was then poured into ice-water and extracted with EtOAc (3x30 ml). The combined ethyl acetate extracts were washed successively with dil.HCl (3x10 ml) and brine (3x10 ml), then dried ($MgSO_4$) and filtered. Removal of the solvent under reduced pressure gave a reddish brown residue (0.045 g). Column chromatography (eluent, hexane - EtOAc 7:3) and crystallisation from methanol yielded **31** (0.04 g, 81%) as colourless shining crystals, m.p.222°C, $[\alpha]_D^{25}$ –2.64 (c 0.06, $CHCl_3$). *m/z*(EI) 486(M^+, 5%), 426(3), 383(41), 366(100), 337(52), 307(22), 189(31), 165(33), 151(55). *m/z*(CI) 487($M+H^+$, 5%), 427(100), 397(10), 386(15), 369(50), 367(55), 339(20), 337(15). Acc. Mass 486.1847. $C_{26}H_{30}O_9$ requires 486.1890. ν_{max}(Nujol) 1735(OAc), 1600(arom.) cm^{-1}. For NMR spectra see Tables 5 and 6.

Preparation of arylnaphthalene lactone 32 and 1-aryltetralin 30

To a mixture of 1-aryltetralin **19** (0.25 g, 0.6 mmol) and DDQ (1.2 g, 5.3 mmol, 9 equiv.) was added glacial acetic acid (8 ml) and the mixture stirred for 20 h at room temperature. The reaction mixture was then poured onto crushed ice and extracted with EtOAc (3x30 ml). The combined ethyl acetate extracts were washed successively with sodium metabisulphite (3x20 ml), $NaHCO_3$ (3x20 ml), and brine (3x20 ml), then dried ($MgSO_4$) and filtered. Removal of the solvent under reduced pressure gave a reddish brown residue (0.25 g).

Column chromatography (eluent, hexane - EtOAc 7:3) yielded **32** (0.06 g, 26%), which crystallised from methanol as colourless crystals, m.p.165°. ^{1}H NMR (δ) 3.84s, 3.90s, 4.00s, 4.06s (ArOMe), 5.20d (J14.9) and 5.26d (J14.9,CH_2), 6.90d J1.9,H-2'), 6.96dd J1.9,8.2,H-6'), 7.05d (J8.2,H-5'), 7.12s (H-8), 7.31s (H-5), 8.31s (H-4a and 4b). ^{13}C NMR (δ) 55.9, 56.0, 56.1 (ArOMe), 69.6 (CH_2), 104.2, 107.7, 111.7, 112.3 (C-5,8,2',5') 124.1 (C-6'), 121.4, 121.6, 128.7, 129.9, 131.7, 132.2 (C-4a,8a,1,2,3,4), 137.9 (C-1'), 149.0, 149.4, 150.2, 152.0 (C-6,7,3',4'), 171.6 (CO). *m/z*(EI) 380(M^+, 100%), 364(17), 351(32), 349(20), 335(10), 261(11), 235(13), 189(19), 163(21), 151(16). *m/z*(CI) 398(M+NH_4^+, 30%), 381(M+H^+, 100), 351(10), 339(15), 309(10), 156(25). Acc. Mass 380.12486. $C_{22}H_{20}O_6$ requires 380.12599. ν_{max}(Nujol) 1760(lactone) cm^{-1}, and **30** (0.12 g, 45%), which crystallised from methanol as colourless crystals, m.p.191°C. See above for spectral data.

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