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OXIDATIVE TRANSFORMATIONS OF LIGNANS - REACTIONS OF DIHYDROCUBEBIN AND A DERIVATIVE WITH DDQ

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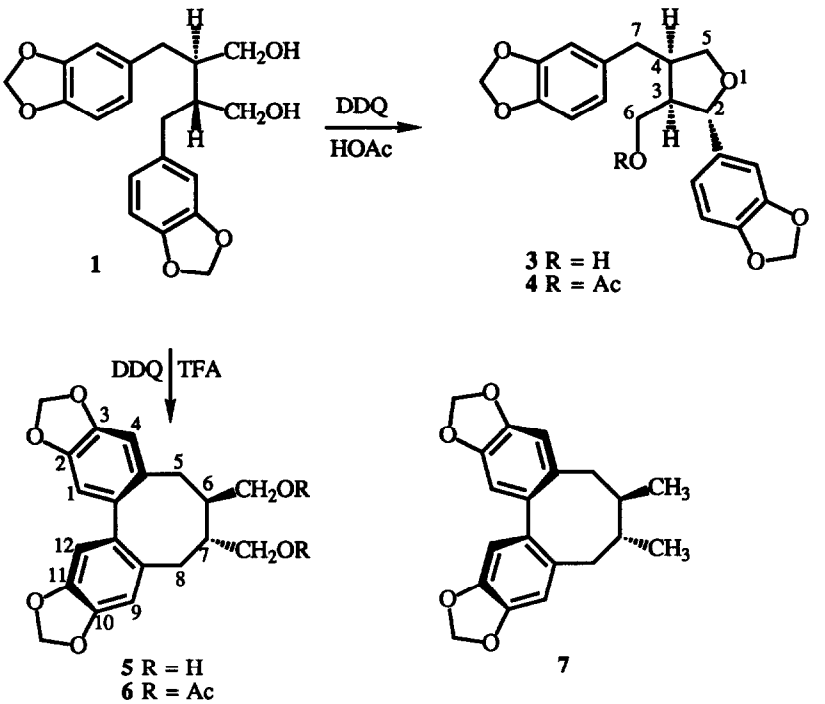
Summary Treatment of dihydrocubebin (**1**) with DDQ in acetic acid gives the 2-aryltetrahydrofuran (**3**) while with DDQ in trifluoroacetic acid it affords the isomeric dibenzocyclooctadiene (**5**) Treatment of the 3,4-dibenzyltetrahydrofuran (**2**), obtained by cyclisation of (**1**), with DDQ in acetic acid gives a mixture of the acetoxy compound (**8**) and the aryl tetralin (**9**), while with DDQ in trifluoroacetic acid it gives the dibenzocyclooctadiene (**10**) The structural elucidation of these products is described and mechanisms for their formation are presented

In continuation of our studies of the oxidation[1,2] and rearrangement[3,4] reactions of lignans we now report the reaction of dihydrocubebin (**1**)[5,6] and the derived tetrahydrofuran (**2**)[6] with DDQ (2,3-dichloro-5,6-dicyano-1,4-benzoquinone) in acetic acid and in trifluoroacetic acid

When (-)-dihydrocubebin (**1**) was treated with 1 6 equivalents of DDQ in acetic acid dehydrogenation occurred to give an alcohol $C_{20}H_{20}O_6$, which formed a monoacetate on treatment with acetic anhydride and pyridine Examination of the ^{1}H n m r spectrum of the alcohol indicated that it contained a primary alcohol group since the two protons at δ 3 73 and 3 87 p p m which formed part of an ABX system were both moved downfield to δ 4 15 and 4 31 p p m in the spectrum of the acetate Two further ABX systems were also evident suggesting the presence of two further CH_2 groups, but these were unaffected by acetylation Furthermore, the low field doublet at δ 4 78 p p m was also unaffected by acetylation, suggesting that it was due to the benzylic proton of a benzylic ether ArC<u>H</u>OR These deductions pointed to the 2-aryl tetrahydrofuran structure (**3**) for this product but gave no indication of the relative stereochemistry However, comparison of the ^{1}H and ^{13}C n m r spectra with those in the literature[7,8] confirmed that the product was dihydrosesamin (**3**) having the 2,3 *trans* 3,4 *cis* configuration (Scheme 1) The direct oxidative conversion of (**1**) to (**3**) could be regarded as a possible model for the biosynthesis of such compounds



Scheme 1

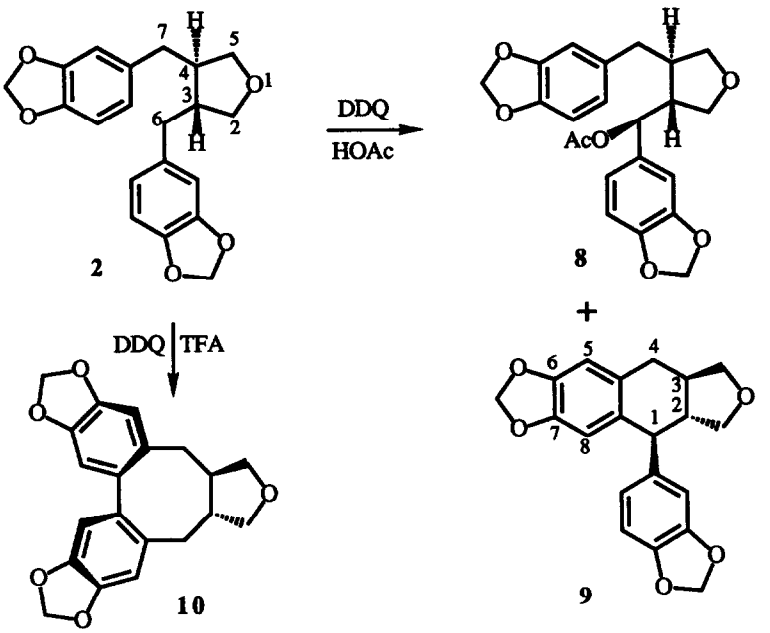
When (-)-dihydrocubebin (**1**) was treated with 2 3 equivalents of DDQ in trifluoroacetic acid dehydrogenation afforded a diol $C_{20}H_{20}O_6$, m p 272°C, which was isomeric with (**3**) and formed a diacetate m p 276°C on acetylation The ^{1}H n m r spectrum of the diol indicated clearly that in this case the two CH_2OH groups present in the starting material had been retained in the product since the signals at δ 3 66 and 3.25 p p m , which both integrated for two protons, were moved to 4 25 and 3 93 p.p.m. in the spectrum of the diacetate The ^{1}H and ^{13}C n.m r spectra also indicated that the rest of the aliphatic system, including the two benzylic CH_2 groups, was also intact These assignments were also fully supported by spin decoupling experiments However the diol and its diacetate each gave only two singlets in the aromatic region of the ^{1}H n m r spectrum, each integrating for two protons Furthermore, the ^{13}C n m r spectra indicated that both the diol and its diacetate had a very symmetrical structure since only ten signals were present in the spectrum of the diol and only 12 in that of the diacetate These observations suggested that oxidative coupling of the

aromatic rings had occurred leading to the dibenzocyclooctadiene (**5**). These conclusions were supported by comparison with the work of Chattopadhyay and Rao[9] and in particular by comparison of the above spectra with those of the related compound (**7**) previously reported.[9,10] Both (**5**) and (**6**) showed positive Cotton effects at 257 and 300 nm thus indicating that the biphenyl unit of the dibenzoocyclooctadiene system possesses the absolute configuration shown.[9,11,12]

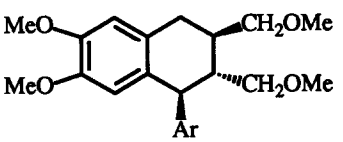
When the *trans* 3,4-dibenzyltetrahydrofuran (**2**)[6] was treated with 1.5 equivalents of DDQ in acetic acid two products were obtained. The first had a molecular formula $C_{22}H_{22}O_7$ which corresponded to the introduction of an acetoxy group. This was confirmed by the i r and n m.r. spectra which in the latter case further indicated that substitution had taken place at one of the benzylic positions. Thus the ABX systems of the tetrahydrofuran ring were largely unchanged (although no longer equivalent), while one of the benzylic protons had been moved downfield to 5.41 p.p.m. due to the introduction of the acetoxy substituent. This effect was also seen in the ^{13}C n.m.r spectrum in which one of the benzylic carbon atoms of the starting material had been moved downfield by ~40 p.p m , the rest of the spectrum being virtually unchanged. This information therefore lead to structure (**8**) for this product (Scheme 2) and in view of the large coupling constant (9 7 Hz) associated with the benzylic proton it was assigned the *erythro* configuration.[13,14]

The second product from the reaction of (**2**) with DDQ in acetic acid had a molecular formula $C_{20}H_{18}O_5$ corresponding to dehydrogenation Analysis of the n m r spectra of this compound and comparison with data in the literature[15,16] lead to the conclusion that it was an aryltetralin In particular, the loss of one benzylic proton and one aromatic proton leaving a doublet at δ 3.70 (H-1) and two singlets at 6.29 and 6.60 p p m (H-5 and H-8) suggested the formation of a 6,7-dioxygenated 1-aryltetralin (**9**) Furthermore, the large coupling constant (10.0Hz) between H-1 and H-2 indicated the *trans* configuration shown, as in phyltetralin (**11**)[15] and lintetralin (**12**).[16] The aryltetralin (**9**) was also the major product obtained when (**2**) was treated with DDQ in acetic anhydride.

When (**2**) was treated with 2.3 equivalents of DDQ in trifluoroacetic acid a single product, m p 280°C, isomeric with (**9**), was obtained As in the case of the diol (**5**) it was evident from the ^1H and ^{13}C n.m r spectra that the aliphatic part of the molecule had been retained intact in thisproduct but that the aromatic region had been greatly simplified, showing only two singlets atδ 6 64 and 6 67 p.p.m. The ^{13}C n.m r spectrum also suggested that the product had a verysymmetrical structure and lead to the conclusion that oxidative coupling had taken place leading to the dibenzocyclooctadiene (**10**). This conclusion was fully supported by spin decoupling experiments on the ^1H n m r. spectrum and by comparison of the spectral data with those of compounds (**5**) and (**6**) prepared earlier and compound (**7**) obtained from austrobailignan under



2 8 9 10

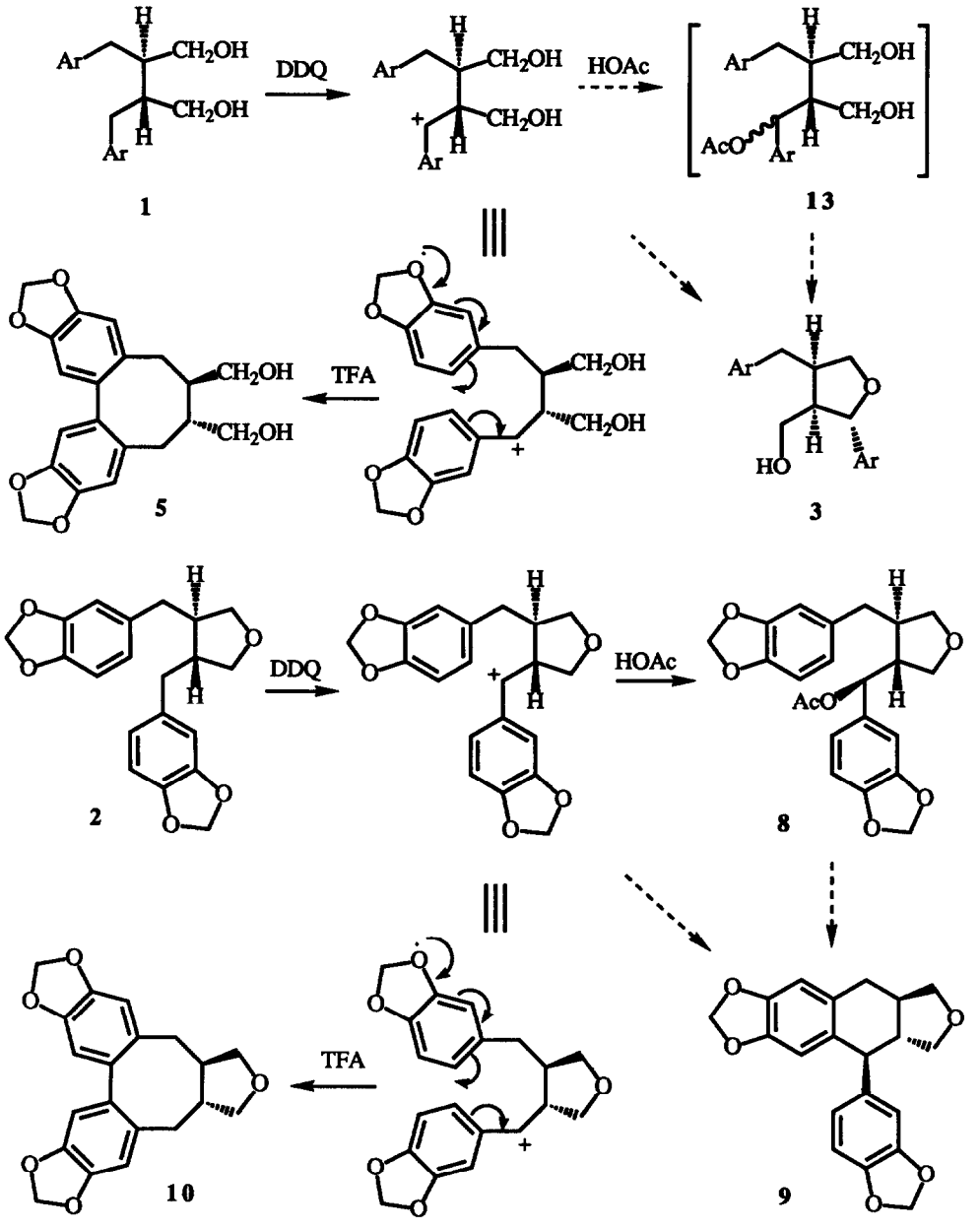


11 Ar = veratryl
12 Ar = piperonyl

Scheme 2

similar reaction conditions[9] Compound (**10**) showed positive Cotton effects at 252 and 297 nm, confirming the configuration of the biaryl system[9,11,12]

The ability of DDQ to bring about benzylic and allylic oxidation is well documented[17,18] and its use leading to tetrahydrofuran formation has also been reported[19,20] Possible mechanisms for the various reactions reported here are shown in Scheme 3 It is clear that the divergent reaction paths in acetic as opposed to trifluoroacetic acid must be associated with the use of a more acidic, less nucleophilic reaction medium in the latter case. It is possible that the isolation of the acetoxy compound (**8**) in the reaction of (**2**) with DDQ in acetic acid may, at least in this case, offer a clue to the different mechanisms operating Thus, in the presence of the more nucleophilic solvent it is likely that the initially formed carbocation is trapped or at least preferentially solvated in such a way that biaryl coupling is precluded By analogy it would be tempting to suggest that a similar intermediate (**13**) might be involved in the production of (**3**) from (**1**)



Scheme 3

Acknowledgement

We are grateful to Dr. Jurgen Schulte and Prof. R. D. Gillard for providing facilities and assistance in obtaining the CD data We also acknowledge financial assistance from the UGC and CSIR New Delhi

Experimental:

^{1}H and ^{13}C n.m r. spectra were recorded on Varian HA-100 and XL-100 instruments, with high field ^{1}H n.m.r. spectra being recorded on Bruker 250 and 360-MHz instruments. Mass spectra were recorded on a VG 12-253 quadropole instrument and on a double focussing VG ZAB-E instrument. Silica gel-G was used for column chromatography and for tlc. Melting points are uncorrected CD spectra were obtained on a Jobin Yvon Dichrographe III and u.v. spectra on a Perkin Elmer Lambda 5 spectrophotometer

Reaction of dihydrocubebin (1) with DDQ in acetic acid: Isolation of dihydrosesamin (3).

To a solution of dihydrocubebin (**1**) (0.17g, 0.47 mmoles) in glacial acetic acid (6 ml) was added DDQ (0.17g, 0.74 mmoles, 1.6 equivalents) and the mixture stirred for 4h. The reaction mixture was poured onto crushed ice (50g) and extracted with ether (3 x 20ml). The organic layer was washed with aq. $NaHSO_3$ (3 x 20ml), H_2O (3 x 20 ml), aq. $NaHCO_3$ (3 x 20 ml), brine (3 x 20ml) and dried ($MgSO_4$). After removal of the solvent a pale brown gum (0 19g) was obtained, which showed four new spots on tlc (eluent CH_2Cl_2-EtOAc 4·1) Column chromatography of the residue on Silica gel (eluent CH_2Cl_2-EtOAc 95·5) yielded fraction -1 (30mg), fraction-2 (80mg) and fraction-3 (unreacted dihydrocubebin (**1**), 60mg). Further chromatography of fraction-2 (eluent CH_2Cl_2-EtOAc 95:5) yielded dihydrosesamin (**3**) as a colourless gum (60mg, 35%). m/z 356 (60% M^+), 217 (10%), 192 (12%), 178 (14%), 149 (34%), 135 (100%), 77 (34%) ^{1}H n.m.r. δ($CDCl_3$) 4 78d (J6.2,H-2), 2.33m (H-3), 2.67m (H-4), 3.71dd (J6 3,8 5,H-5a), 4.03dd (J6.5,8.5,H-5b), 3 73dd (J6.6,10.8, H-6a), 3 87dd (J6.9,10 7,H-6b), 2.52dd (J10.3,13 1,H-7a), 2.86dd (J4.9,13.1,H-7b) 1 72br (OH), 6.6-6 8m (arom),5.92s and 5.93s (OCH_2O). ^{13}C n.m r. δ($CDCl_3$) 82.99 (C-2), 52.73 (C-3), 42.47 (C-4), 73.02 (C-5), 60.97 (C-6), 33 38 (C-7), 134.31, 137 22 (C-1', C-1"), 106.43, 108 19, 108 42, 109 08 (C-2', C-2", C-5', C-5"), 146.07, 147.01, 147 91, 147.98 (C-3', C-3", C-4', C-4"), 119 18, 121 55 (C-6', C-6"), 101 01, 101 11 (OCH_2O)

Preparation of dihydrosesamin acetate (4).

Dihydrosesamin (**3**) (40mg) in dry pyridine (1ml) was treated with acetic anhydride (1ml) at $0^{o}C$ and allowed to stand at room temperature for 0.5h. The reaction mixture was poured onto crushed ice (50g) and extracted with chloroform (3 x 10ml). The organic layer was washed with 1% HCl (3 x 10ml), brine (3 x 10ml) and dried ($MgSO_4$). After removal of the organic solvent a pale brown gum (40mg) was obtained, which was purified by column chromatography on silica gel (eluent CH_2Cl_2) to yield dihydrosesamin acetate (**4**) (30mg)

m/z 398 (52% M^+), 338 (14%), 202 (30%), 173 (20%), 135 (100%), 77 (42%). ^{1}H n.m.r. δ($CDCl_3$) 4.75d(J6.1,H-2), 2.50m(H-3), 2.68m(H-4), 3.71dd(J6.6,8.6,H-5a), 4.05dd (J6.5,8.7,H-5b), 4.15dd (J7.4,11.2, H-6a), 4.31dd (J6.9,11.2,H-6b), 2.50m (H-7a), 2.80dd (J4.9,12.9,H-7b), 2.04s (OAc), 6.5-6.8m (arom.), 5.93s and 5.94s (OCH_2O). ^{13}C n.m.r. δ($CDCl_3$) 83.24 (C-2), 49.31 (C-3), 42.54 (C-4), 72.87 (C-5), 62.77 (C-6), 33.37 (C-7) 133.91, 136.45 (C-1',C-1"), 106.41, 108.24, 108.49, 109.00 (C-2',C-2",C-5',C-5"),147.74 (C-3', C-3",C-4',C-4"), 119.29, 121.58 (C-6',C-6"), 101.06, 101.18 (OCH_2O), 21.01, 170.80 (OAc).

Reaction of dihydrocubebin (1) with DDQ in trifluoroacetic acid: Isolation of the dibenzocyclooctadiene diol (5)

To a mixture of dihydrocubebin (0.12g, 0.34 mmoles) and DDQ (0 18g, 0.79 mmoles, 2.3 equivalents) was added freshly distilled TFA (4ml) and the mixture stirred for 2h The reaction mixture was poured onto crushed ice (50g) and extracted successively with benzene (3 x 20ml) and ethyl acetate (3 x 20ml). The combined benzene extract was washed successively with aq $NaHSO_3$ (3 x 20ml), H_2O (3 x 20ml), aq NaOH (3 x 20ml), brine (3 x 20ml) and dried ($MgSO_4$). After removal of the solvent a brown residue (60mg) was obtained, which resisted crystallisation from benzene, chloroform and methanol Column chromatography of the residue on silica gel (eluent CH_2Cl_2-EtOAc 1:1) yielded a colourless solid (20mg), which on crystallisation from $CHCl_3$-MeOH gave colourless crystals of the dibenzocyclooctadiene diol (5) (18mg, total yield ≥50%, see below) m.p. 272°C. m/z 356 (100% M^+), 267 (32%), 254 (20%), 237 (18%), 209 (28%), 200 (12%), 151 (30%). λ_{max}(CH_3CN) 290 (ε = 6,410), 259sh (ε = 4,505) and 232sh (ε = 7,717)nm CD data (CH_3CN) 256 6nm (Δε = 9.36) and 300.6nm (Δε = 3.81). ^{1}H n m.r. δ($CDCl_3$/20% d_6-DMSO) 2.73d (J13 0,H-5a, H-8a), 2.05dd (J10 2,13.0,H-5b,H-8b), 1.43m (H-6,H-7), 3 66d (J 9.2) and 3.25dd (J6.0,9.2, (CH_2OH), 4 4br (OH), 5.95d (J1.0) and 5.97d (J1.0,OCH_2O), 6 67s and 6.77s (arom.) ^{13}C n.m.r. δ($CDCl_3$/20% d_6-DMSO) 146 74, 145.18 (C-2,C-3,C-10,C-11), 134 97, 133.15 (C-1a,C-4a,C-8a,C-12a), 108.92, 107.96 (C-1,C-4,C-9, C-12), 43.90 (C-6,C-7), 34.82 (C-5,C-8), 65.19 (CH_2OH), 100 63 (OCH_2O) The combined ethyl acetate extract from the above reaction was also washed successively with aq $NaHSO_3$ (3 x 20ml), H_2O (3.20ml) aq NaOH (3 x 20ml), brine (3 x 20ml) and dried ($MgSO_4$) After removal of the solvent, a reddish brown residue (70mg) was obtained, which resisted crystallisation from benzene, chloroform and methanol and showed a streak on tlc (CH_2Cl_2 - EtOAc 1:1)

Preparation of the dibenzocyclooctadiene diacetate (6).

Compound (5) (8mg) in pyridine (0.5ml) was treated with acetic anhydride (0 5ml) at 0°C and the solution left at room temperature overnight The reaction mixture was poured into ice-water (5ml) and extracted was $CHCl_3$ (3 x 5ml) The organic layer was washed with 1% HCl (3 x 10ml), brine (3 x 10ml) and dried

($MgSO_4$). After removal of the solvent a brown residue (8mg) was obtained which showed a single spot on tlc (CH_2Cl_2 - EtOAc 9:1). See below for spectral data.

Acetylation of ethyl acetate soluble fraction: Isolation of dibenzocyclooctadiene diacetate (6)

To the ethyl acetate soluble fraction from the above experiment (70mg) dissolved in pyridine (3ml) was added acetic anhydride (3ml) and the mixture left at room temperature overnight The reaction mixture was poured onto crushed ice (50g) and extracted with $CHCl_3$ (3 x 20ml). The organic layer was washed with 1% HCl (3 x 20ml), brine (3 x 20ml) and dried ($MgSO_4$) After removal of the solvent, a reddish brown residue (80mg) was obtained, which was identical on tlc (CH_2Cl_2 - EtOAc 9·1) with the diacetate (6) prepared above Column chromatography of the residue on silica gel (eluent CH_2Cl_2 - EtOAc 9·1) yielded an amorphous powder (60mg), which crystallised from $CHCl_3$-MeOH to give dibenzocyclooctadiene acetate (6) (50mg) m p. 276°C m/z 440 (100% M^+), 381 (12%), 320 (22%), 267 (32%), 237 (14%), 209 (16%), 151 (20%) λ_{max}(CH_3CN) 290 (ε = 12,430), 258sh (ε = 11,054) and 236sh (ε = 13,634)nm. CD data(CH_3CN) 257.6nm (Δε = 11.78) and 300.6nm (Δε = 6.06) ^{1}H n.m.r. δ($CDCl_3$) 2.60d (J13 7,H-5a,H-8a), 2.20dd (J9.5,13.7,H-5b,H-8b), 1.73m(H-6,H-7), 4.25d(J9.6) and 3 93dd (J5 9,9.6,C$\underline{H}_2$OAc), 2 09s (OAc), 5.98s (OCH_2O), 6 72s and 6.73s (arom.) ^{13}C n m.r. δ($CDCl_3$) 147.36, 146 06 (C-2,C-3,C-10,C-11), 133 74, 133 59 (C-1a,C-4a,C-8a,C-12a), 109 13, 108 68 (C-1,C-4,C-9,C-12), 41.35 (C-6,C-7), 35 43 (C-5,C-8), 68.01 (C$\underline{H}_2$OAc), 101.18 (OCH_2O), 21 05, 171 29 (OAc)

Reaction of *trans* 3,4-di(3,4-methylenedioxybenzyl)tetrahydrofuran (2) with DDQ in acetic acid: Isolation of compounds (8) and (9)

To a mixture of the *trans* 3,4-dibenzyltetrahydrofuran (2) (0 14g, 0.41 mmoles) and DDQ (0 14g, 0 62 mmoles, 1.5 equivalents) was added acetic acid (6ml) and the mixture stirred at room temperature for 2h The reaction mixture was poured onto crushed ice (50g) and extracted with ether (3 x 20ml) The organic layer was washed with aq. $NaHSO_3$ (3 x 20ml), H_2O (3 x 20ml), aq $NaHCO_3$ (3 x 20ml), brine (3 x 20ml) and dried ($MgSO_4$) After removal of the solvent, a pale yellow residue (0.12g) was obtained, which showed 6 close running spots on tlc (hexane-EtOAc 7 3) Column chromatography of the residue on silicagel (eluent hexane-EtOAc 7:3) gave 4 fractions Chromatography of fraction-4 (eluent hexane-EtOAc 9·1) yielded compound (8) (50mg, 34%) m/z 398 (14% M^+) 338 (20%), 151 (80%) and 135 (100%). ^{1}H n.m.r δ($CDCl_3$) 3 48dd (J5 3,8 9) and 3 72dd (J5.2,9 3 H-2a,H-5a), 3 83dd(J7 0,8 9) and 3.97dd(J7.2,9 2,H-2b and H-5b), 2.31m and 2.04m (H-3 and H-4), 5.41d (J9 7, H-6) and 2 31m (H-7), 5 89d(J1 4), 5 91d(J1 4), 5.93d(J1.4) and 5.95d(J1 4,OCH_2O), 6.3-6 7m (arom), 2 01s (OAc) ^{13}C n m r δ($CDCl_3$) 70 69, 73 25 (C-2,C-5), 43 65, 49 77 (C-3,C-4), 77 37(C-6), 39 38 (C-7), 133.01, 133 56 (C-1', C-1"), 145 86, 147.39, 147.53, 147.77 (C-3',C-3",C-4',C-4"), 107 13, 107 98(x 2), 108 86

(C-2',C-2",C-5',C-5"), 121.01, 121.45 (C-6',C-6"), 100.81, 101.16 (OCH_2O), 21.22, 169.94 (OAc).

Chromatography of fraction-2 on silica gel (eluent hexane-EtOAc 9:1) yielded compound (9) (10mg, 8%). m/z 338 (42% M^+), 135 (14%), 84 (50%) and 49 (100%). ^1H n.m.r. δ($CDCl_3$) 3.70d (J10.0,H-1), 2.21m (H-2,H-3), 2.71dd (J9.6,15.0,H-4a), 2.96dd (J4.0,15.6,H-4b), 6.29s and 6.60s (H-5,H-8), 4.19t (J7.3) 3.81t (J7.4) and 3.50m (4H,CH_2O), 6.55d (J1.5), 6.66dd (J1.7,8.0) and 6.74d (J7.9,arom), 5 87s and 5.95s (OCH_2O). ^{13}C n.m.r.δ($CDCl_3$) 50.88 (C-1), 42.23 (C-2), 49.99 (C-3), 32.83 (C-4), 129 50 (C-4a), 108 63 (C-5), 148 00 (C-6) 109.30 (C-8), 138.58 (C-8a), 72.22, 73.09 (CH_2O), 133.06 (C-1'), 108.28 (C-2'), 146.12 (C-3'), 146.38 (C-4'), 108.16 (C-5'), 121.63 (C-6'), 100.85, 100.95 (OCH_2O). Chromatography of fraction-1 on silica gel (eluent, hexane-EtOAc 9:1) yielded the unreacted *trans* 3,4-dibenzyl tetrahydrofuran (2) (15mg)

Reaction of *trans* 3,4-di(3,4-methylenedioxybenzyl)tetrahydrofuran (2) with DDQ in TFA: Isolation of the dibenzocyclooctadiene (10)

To a mixture of the *trans* 3,4-dibenzyltetrahydrofuran (2) (0 1g 0 3 mmoles) and DDQ (0.13g), 0.6 mmoles, 2 equivalents) was added freshly distilled TFA (4ml) and the mixture stirred at room temperature for 2h. The reaction mixture was poured onto crushed ice (50g) and extracted with benzene (3 x 20ml). The organic layer was washed with aq. $NaHSO_3$ (3 x 20ml), H_2O (3 x 20ml), aq. NaOH (3 x 20ml), brine (3 x 20ml) and dried ($MgSO_4$) After removal of the solvent, a reddish brown residue (80mg) was obtained, which resisted crystallisation from benzene, chloroform and methanol. Column chromatography of the residue on silica gel (eluent hexane-EtOAc 4·1) yielded a colourless solid (40mg) which on crystallisation from chloroform-methanol gave colourless crystals of the dibenzocyclooctadiene tetrahydrofuran (10) (20mg, 20%), m p 280°C. m/z 338 (100% M^+), 267 (12%), 209 (10%) and 152 (12%). λ_{max}(CH_3CN) 287 (ε = 10,485), 253sh = 7,813) and 230 (ε = 11,385)nm. CD data (CH_3CN) 252 6nm (Δε = 26.91) and 297.6nm (Δε = 11 32). n m r δ($CDCl_3$) 2 54d (J13.1,H-5a,H-8a), 2.23dd (J9.2,13.1,H-5b,H-8b), 1.81m (H-6,H-7), 4.03t (J7 5) and 3 40dd (J7 5,11.0,CH_2O), 5 97d (J1.0) and 5.98d (J1.0, OCH_2O), 6.64s and 6.67s (arom) ^{13}C n m.r δ($CDCl_3$) 147.33, 145 74 (C-2,C-3,C-10,C-11), 134 18, 133 30 (C-1a,C-4a,C-8a,C-12a), 110 54, 108.89 (C-1,C-4,C-9,C-12), 49.08 (C-6,C-7), 32 73 (C-5,C-8), 72 78 (CH_2O), 101.07 (OCH_2O)

Reaction of *trans* 3,4-dibenzyl tetrahydrofuran (2) with DDQ in acetic anhydride: Isolation of the aryl tetralin (9).

To a mixture of the *trans* 3,4-dibenzyltetrahydrofuran (2) (0 12g, 0 35 mmoles) and DDQ (0 12g 0.53 mmoles, 1 5 equivalents) was added acetic anhydride (6ml) and the mixture stirred at room temperature for 2h The reaction mixture was poured onto crushed ice (50g) and extracted with ether (3 x 20ml) The organic layer was washed successively with aq $NaHSO_3$ (3 x 20ml), H_2O (3 x 20ml), aq. $NaHCO_3$ (3 x 20ml), brine

(3 x 20ml) and dried ($MgSO_4$). After removal of the solvent a pale brown residue (140mg) was obtain Crystallisation of the residue from $CHCl_3$ followed by recrystallisation from methanol yielded a colourl crystalline solid (30mg) m.p. 182°C, which was identified as 2,3-dichloro-5,6-dicyano-1,4-dihydroxybe diacetate. Evaporation of the mother liquor followed by column chromatography of the residue (90mg) silica gel (eluent, hexane-EtOAc 4:1) yielded aryltetralin (**9**) (40mg) and compound (**8**) (5mg).

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