

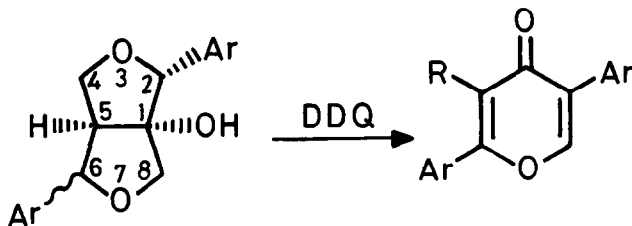
REACTIONS OF PAULOWNIN, GMELINOL AND GUMMADIOL WITH
2,3-DICHLORO-5,6-DICYANO BENZOQUINONE.

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Summary. Paulownin and gmelinol react with DDQ to give 4-pyrone derivatives. Gummadiol reacts under the same conditions to give a pyrone aldehyde and an unsaturated γ -lactone.

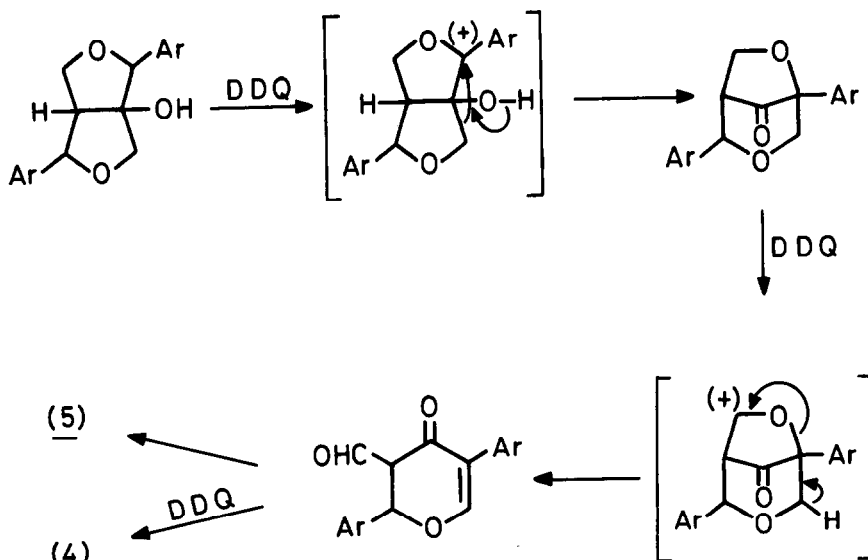
2,3-Dichloro-5,6-dicyanobenzoquinone (DDQ) has been previously shown to react with lignans of the monoarylidene-butyrolactone and aryl-tetralin series.^{1,2} We have now studied the reactions of this reagent with paulownin (1),³⁻⁵ gmelinol (2)⁵⁻⁷ and gummadiol (3),^{8,9} three lignans belonging to the 2,6-diaryl-3,7-dioxabicyclo[3.3.0]octane series.¹⁰



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|----------------------------------|--|
| 1. Ar = 3,4-methylenedioxyphenyl | 4a. R = CHO, Ar = 3,4-methylenedioxyphenyl |
| 2. Ar = 3,4-dimethoxyphenyl | 4b. R = CHO, Ar = 3,4-dimethoxyphenyl |
| | 5. R = CH ₂ OH, Ar = 3,4-dimethoxyphenyl |
| | 6. R = CH ₂ OAc, Ar = 3,4-dimethoxyphenyl |

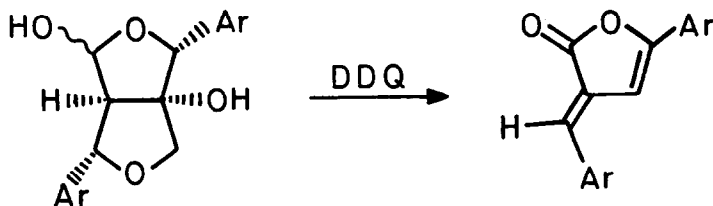
When paulownin (1) was heated under reflux with three equivalents of DDQ in dry benzene a yellow crystalline solid, m.p. 138-142^o was obtained (yield 25%), M⁺ 364.0584 (C₂₀H₁₂O₇); ν_{\max}^{KBr} 1605, 1635, 1690, 1730 cm⁻¹, $\lambda_{\max}^{\text{EtOH}}$ 248(4.00), 282(3.97), 322(4.19)nm,

which formed a yellow 2,4-dinitrophenylhydrazone m.p. 258-260° (M^+ 544). The ^1H n.m.r. spectrum contained a sharp singlet at 10.20 p.p.m. due to an aldehyde proton and another sharp singlet at 7.70 p.p.m. due to a vinylic proton, but contained none of the aliphatic signals characteristic of the parent lignan skeleton. By comparing the n.m.r. and u.v. spectra with those of 4-pyrone derivatives¹¹⁻¹² and by considering its likely mode of formation (Scheme 1) structure (4a) is proposed for this product. It therefore represents the first example of a new class of lignan having a rearranged carbon skeleton.



When gmelinol (2) was treated with DDQ under exactly the same conditions two products were obtained, one of which was readily identified as the pyrone aldehyde (4b) by comparison with the product obtained from the paulownin reaction. The second product was obtained as a yellow solid, m.p. 122-4°, (yield 27%), M^+ 398.1367 ($\text{C}_{22}\text{H}_{20}\text{O}_7$); $\nu_{\text{max}}^{\text{KBr}}$ 1650, 3500 cm^{-1} ; $\lambda_{\text{max}}^{\text{EtOH}}$ 252(4.03), 279(3.96), 304(4.19)nm. The ^1H n.m.r. spectrum contained a sharp singlet at 7.84 p.p.m. and a broad singlet at 4.77 p.p.m. which sharpened after D_2O exchange, showing the presence of a CH_2OH group. This was confirmed by the preparation of a monoacetate (M^+ 440) in which this signal was shifted downfield to 5.38 p.p.m. and structure (5) is therefore assigned to this product.

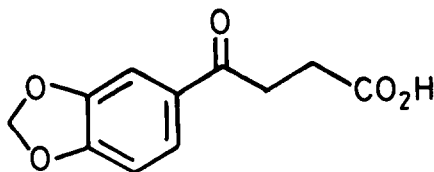
The reaction of gummadiol (3) with DDQ gave once again two products, one of which was identified as the pyrone aldehyde (4a) previously obtained from paulownin. The second product was obtained as a yellow crystalline solid m.p. 240-245^o (yield 29%) and gave a molecular ion at m/e 336.0634 ($C_{19}H_{12}O_6$). It showed a carbonyl absorption at 1760 cm^{-1} which suggested the presence of a γ -lactone or five-membered ketone, and had u.v. maxima at 240(3.97), 280(3.62) and 400(4.20)nm. The u.v. and i.r. spectra strongly resembled those of the known γ -lactone (8)¹³ and the compound was therefore assigned structure (7). This was confirmed by carrying out an independent synthesis of (7) from 3-(3',4'-methylenedioxybenzoyl) propanoic acid (9)¹⁴.



3. Ar = 3,4-methylenedioxyphenyl

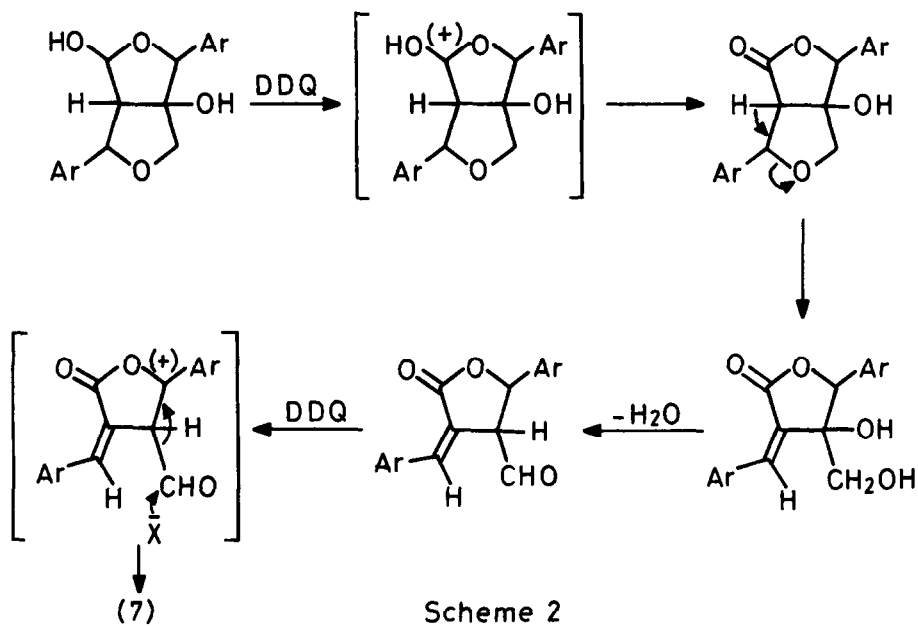
7. Ar = 3,4-methylenedioxyphenyl

8. Ar = phenyl



9.

A possible mechanism to account for the formation of (7) from gummadiol is shown in Scheme 2. The deviation from the pathway leading to pyrones arises due to the possibility of oxidation to the lactone, in turn leading to activation of the α -hydrogen (H-5).



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(Received in UK 24 July 1981)