Photochemical Reactions of Apolignan Precursors

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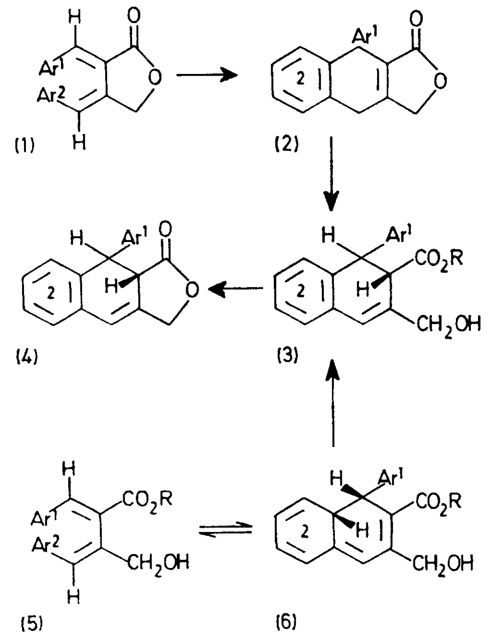
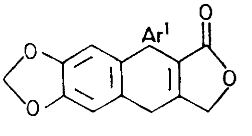
Summary The photochemical rearrangement of (*EE*)-3,4-bisarylmethylenedihydro-2(3*H*)-furanones and related compounds provide a convenient synthesis of apolignans and their derivatives.

FROM our studies on bisarylmethylenesuccinic anhydrides and imides,[1,2,3] we suggest that some naturally occurring apolignans and their derivatives[4] could be formed by the photorearrangement of (*EE*)-3,4-bisarylmethylenedihydro-2(3H)-furanones (**1**) and related compounds.

A photochemical conrotatory ring closure of the furanone (**1**) followed by a hydrogen shift, would provide a convenient synthesis of apolignans, their derivatives, and related model compounds, allowing structure and stereochemistry to be elucidated, verified, or corrected. Such a reaction would also explain the optical activity of apolignans better than processes involving photo-oxidative coupling followed by enzymic reduction of an aromatic ring,[5] suggest the control of photoperiodic processes as the function of the lignan precursor;[6] and permit a direct phytochemical relationship between lignans which would be helpful in plant taxonomy.





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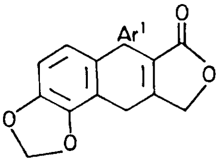

(8)

a; Ar^1 = Ar^2 = Ph.

b; Ar^1 = 3,4,5-trimethoxyphenyl, Ar^2 = 3,4-(methylenedioxy)phenyl.

c; Ar^1 = 3,4-(methylenedioxy)phenyl, Ar^2 = 3,4,5-trimethoxyphenyl

d; Ar^1 = 3,4-(methylenedioxy)phenyl, Ar^2 = phenyl.

e; Ar^1 = Ar^2 = 3,4-(methylenedioxy)phenyl.

Ring 2 contains the substituents of Ar^2.

On irradiation at 366 nm in the absence of oxygen, the furanone (**1a**) in benzene gave the parent compound of the β-apolignans (**2a**)[7] in quantitative yield. Under similar conditions, the furanone (**1b**) gave ($\pm$)-β-apopicropodophyllin (**7b**)[7,8,9] and its isomer (**8b**), while the furanone (**1c**) gave (**2c**) exclusively, illustrating that the initial ring closure to give a 1,8a-dihydronaphthalene (DHN) intermediate occurs only onto the aryl group not in conjugation with the carbonyl group.

Hydrolysis of (**2d**), prepared as described above, gave the *trans*-acid (**3d**, R = H) which can be converted into the lactone (**4d**) related to the α-apolignans.[10] The $J_{1,2}$ value of 15 Hz establishes its configuration [*c.f.* $J_{1,2}$ values of 15·5 and 7·5 Hz observed for *trans*- and *cis*-1,2-dihydro-1-phenylnaphthalene-2,3-dicarboxylic anhydrides].[2,3] Thus the *trans* configuration assigned to α-apopicropodophyllin (**4b**)[8] is correct, though based on an erroneous interpretation of its n.m.r. spectrum.

Irradiation of the ester, (**5d**, R = Me) gave the *cis*-1,2-DHN derivative (**3d**, R = Me) ($J_{1,2}$ 7 Hz). The corresponding *trans*-1,2-DHN derivative (**3d**, R = Me) ($J_{1,2}$ 5 Hz) was obtained by treating the *trans*-acid (**3d**, R = H), from the hydrolysis of the lactone (**2d**),[9] with diazomethane. The marked difference in coupling constants of the *trans*-ester (**3d**, R = Me) and the lactone (**4d**) can be explained as the effect of the lactone ring locking the methine hydrogens at C(1) and C(2) in an *ax–ax* arrangement. In the *trans*-ester (**3d**, R = Me), the sterically less hindered *eq–eq* arrangement is preferred.

Taiwanin A (**1e**),[3] previously assigned an incorrect configuration[5,12,13] does not show observable photochromic properties but when its related ester (**5e**, R = Me) in benzene was irradiated at 366 nm, the solution changed from yellow to orange-red. The colour change, attributed to the formation of the *cis*-1,8a-DHN intermediate (**6e**, R = Me) is reversed thermally or on exposure to white light, establishing photochromism in apolignan precursors.

All compounds were crystalline and gave satisfactory analyses. Structural assignments follow from n.m.r. spectra measured on 100 and 220 MHz Varian spectrometers by PCMU Harwell. We thank the Central Research Laboratories, Ciba-Geigy (UK) Ltd. for financial support and the S.R.C. for a grant for the n.m.r. studies.

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