Some Photochemical and Oxidative Conversions of Pterocarpans and Isoflavans: Functional Requirements for Cyclization of Isoflavans to Pterocarpans

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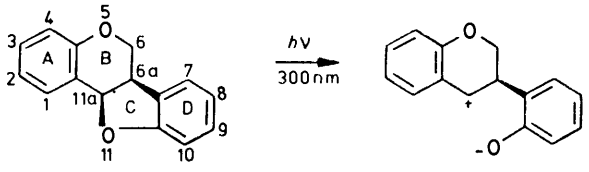
Photolysis of pterocarpans in methanol or acetic acid provides the first general and also direct method of access to 4-functionalized 2'-hydroxy-3,4-*trans*-isoflavans by C-ring fission and solvolysis. Spontaneous recyclization to the pterocarpan is governed by functional-dependent factors such as the effective delocalization of the transient 4-carbocation and formation of quinone-methide intermediates. In isolated instances there is also photoreduction to isoflavans, or formation of an 8-hydroxy-9-methoxymethoxypterocarpan by solvolysis following fission of the 8,9-methylenedioxy-ring system. Oxidative conversions of 2',7-dihydroxyisoflavans to pterocarpans with 2,3-dichloro-5,6-dicyanobenzoquinone in methanol may proceed *via* unstable quinone methides, or *via* 4-carbocation intermediates after hydride abstraction. However, appropriate 2'-hydroxy-4'-methoxy-disubstitution provides the first example of selective aromatic methoxylation of the B-ring under oxidative conditions.

DEWICK and MARTIN [1] have recently shown by means of feeding experiments that isoflavones and isoflavanones are efficient precursors of both isoflavans and pterocarpans, and obtained some evidence of a restricted degree of interconversion of these metabolic end-products. Their studies further indicate that subsequent to 2'-hydroxylation of an isoflavone, the biogenetic pathway to pterocarpans follows a stereospecific reduction sequence *via* isoflavanone, isoflavan-4-ol, and 4-carbocation species.

These aspects of the suggested terminal steps in pterocarpan biosynthesis are in accord with our earlier chemical evidence [2] regarding functional requirements for the spontaneous cyclization of 4-substituted 2'-hydroxyisoflavans, and also with our demonstration [3] of what is still the only stable natural example, (+)-ambanol, amongst the unstable 2'-oxygenated isoflavan-4-ols. Our present work examines the effect of functionality on the isoflavan ⟶ pterocarpan cyclization, providing evidence of side-chain reactivity and of limited photoreduction of pterocarpans during photolytic C-ring fission.[2] Indirect evidence of hydride-ion abstraction and of B-ring aromatic methoxylation of isoflavans during oxidation with 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) in methanolic solution is also obtained, the former supplementing knowledge regarding the oxidative isoflavan ⟶ pterocarpan conversion.[4]

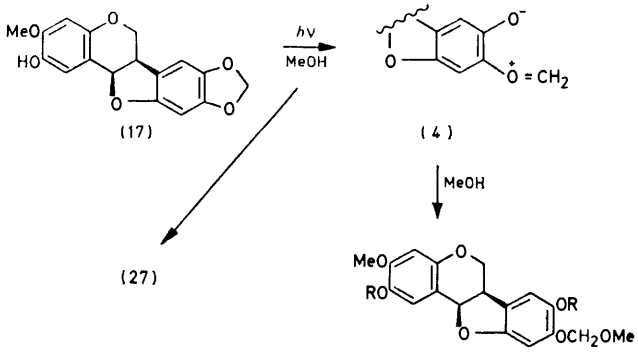
The route to 4-functionalized 2'-hydroxy-3,4-*trans*-isoflavans is based on photolysis of pterocarpans (1) at 300 nm in methanol and in acetic solutions.[2] The predominant photochemical reaction involves scission of the O-11–C-11a bond to produce a carbonium phenoxide zwitterion [5] (2) as in the heterocyclic ring fission of flavonoids.[6] The photolytic intermediate undergoes solvolysis to yield the thermodynamically less stable 4-substituted 3,4-*trans*-isoflavan isomers (3) (*cf.* ref. 2) in which the 3- and 4-substituents both occupy equatorial positions on the assumption of a half-chair conformation. A 3,4-*cis*-isomer is also formed in low yield in only one instance [*cf.* (16) $\xrightarrow{\text{HOAc, } h\nu}$ (26a) + (26b)].

In one case a novel photolytic opening of the 8,9-methylenedioxy-bridge (1,3-benzodioxole D-ring) of 2-hydroxypterocarpin (17) also occurs [as an alternative to



(3) R = Me or Ac

photolytic C-ring fission (17) ⟶ (27)] under the foremention conditions to form the 8-hydroxy-9-methoxymethoxy-derivative (5); a reaction which presumably proceeds *via* a stabilized oxonium–phenoxide inter-



(5) R = H
(6) R = Ac

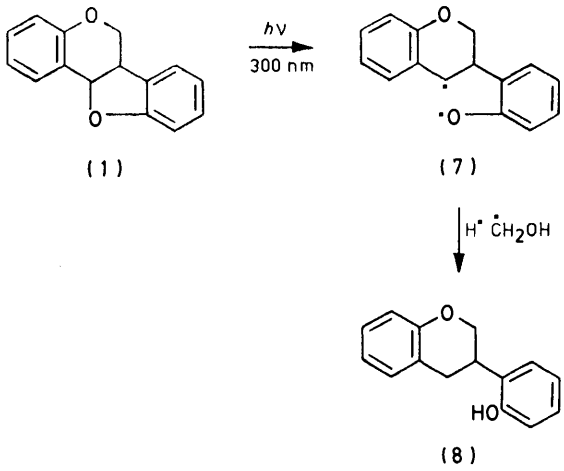
mediate (4) followed by addition of methanol. Proof of structure of the methoxymethoxy-derivative (5) is obtained by its conversion into the diacetate (6) when aromatic protons placed *ortho* to the hydroxy-function undergo greater deshielding than those located in *meta*-positions (*cf.* Table 1).

TABLE 1

Chemical shifts of aromatic protons of 2,8-dihydroxy-3-methoxy-9-methoxymethoxypterocarpan (5) and its diacetate (6)

	Chemical shifts (δ) of aromatic protons			
Compound	H-1	H-7	H-4	H-10
(5)	6.97	6.94	6.45	6.41
(6)	7.11	7.09	6.52	6.48
Δδ	+0.14	+0.15	+0.07	+0.07

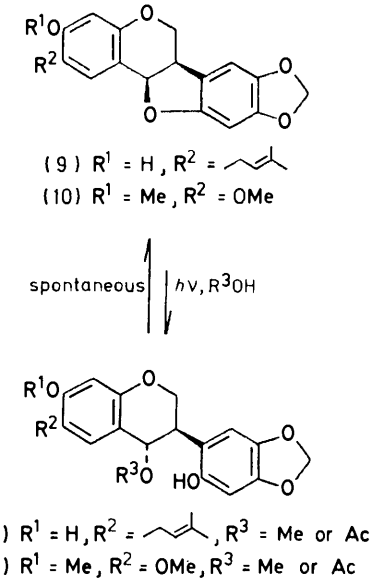
Another notable phenomenon is the direct photoreduction of the unsubstituted pterocarpan (1) in both methanol and acetic acid solutions to 2′-hydroxyisoflavan (8) as one of two products; a reaction which plausibly involves solvents as reducing agents of the biradical (7).



(1) (7) (8)

Photolyses at 300 nm of the natural pterocarpans (9) and (10) were carried out in methanol or acetic acid solution. The formation of products (11) and (12) could only be inferred from qualitative thin layer chromatography owing to their rapid reversion to starting material during preparative separations. All isolation attempts thus result in the recovery of the pterocarpans (9) and (10). Similar results were obtained upon irradiation of (13) and (14) in acetic acid solution with the result that products (20) and (22) could not be isolated. This rapid reversion is attributed to the acidic medium which catalyses cyclization. The products (19), (21), and (23)—(28) are reasonably stable and may be isolated after photolysis of the corresponding pterocarpans (13)—(18) in the appropriate solvents.

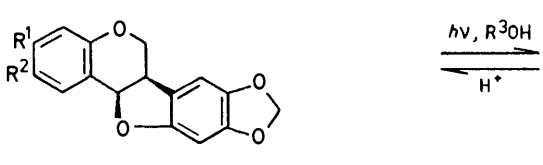
Since a 2′-hydroxy- and 4′,5′-methylenedioxy-substituted B-ring is common to all isoflavan products (11), (12), and (19)—(28), the factors which permit their recyclization to pterocarpans centre mainly around A-ring substitution. Rapid recyclization to pterocarpans appears to require (*cf.* Table 2) a combination of 7-hydroxy plus 6-isopentenyl function (9) or 6,7-dimethoxylation (10) coupled with 4-methoxy or 4-acetoxy as leaving groups. Similar results are observed with 3,4-*trans*-2′,4-dihydroxyisoflavans with A-ring substitution represented by a 7-methoxy plus a 6-isopentenyl function, or a



furan ring occupying these positions.[2] As expected, acetylation neutralizes the promoting effect of the 7-hydroxy-group (in the presence of a 6-isopentenyl group) irrespective of 4-methoxy- or 4-acetoxy-substitution. The same is true where the 6- and 7-positions accommodate a furanoid ring. Methoxylation at C-7 coupled with hydroxy- or acetoxy-substitution at C-6 exercises a retarding effect on cyclization. However, reversion to pterocarpans is dramatically enhanced in the presence of acid. The effect, therefore, of A-ring functionality on the 4-hydroxy-(or 4-alkoxy-) isoflavan ⟶ pterocarpan conversion indicates that cyclization is most likely carbocation-mediated.

Confirmation of the carbonium-ion hypothesis is obtained by the synthesis of pterocarpans (1), (29), and (30), which are deficient in A-ring functionality, *via* 2*H*-chromen and *o*-chloromercuriphenols according to the method of Horino and Inoue.[7] Pterocarpans (1) and (29) are smoothly converted into the corresponding 4-functionalized isoflavans (31), (32), (33), and (34) in almost quantitative yield upon photolysis. No spontaneous reversion was apparent and cyclization is detectable only after 8 h in the presence of hydrochloric acid. These phenomena are probably due to lack of resonance stabilization of the incipient 4-carbocation in the absence of the 7-oxygen function.

The effect of B-ring substitution on the cyclization of isoflavans is reflected in the photolysis of 7-hydroxypterocarpan (30) to isoflavan-4-ol derivatives which are distinguishable by thin layer chromatography, but which revert to the starting materials during isolation procedures. Rapid reversion of such 2′,6′-dihydroxy-



(13) R^1R^2 = 

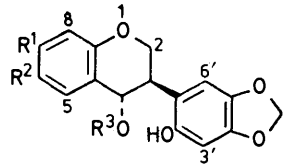
(14) R^1 = OMe, R^2 = 

(15) R^1 = OAc, R^2 = 

(16) R^1R^2 = 

(17) R^1 = OMe, R^2 = OH

(18) R^1 = OMe, R^2 = OAc



(19) R^1R^2 = , R^3 = Me

(20) R^1R^2 = , R^3 = Ac

(21) R^1 = OMe, R^2 = , R^3 = Me

(22) R^1 = OMe, R^2 = , R^3 = Ac

(23) R^1 = OAc, R^2 = , R^3 = Me

(24) R^1 = OAc, R^2 = , R^3 = Ac

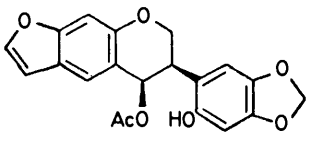
(25) R^1R^2 = , R^3 = Me

(26a) R^1R^2 =  , R^3 = Ac

(27) R^1 = OMe, R^2 = OH, R^3 = Me

(28) R^1 = OMe, R^2 = OAc, R^3 = Me

isoflavan-4-ol derivatives (35) in the absence of 7-hydroxylation is attributed to the added 6′-hydroxy-function which in the presence of 2′-hydroxylation enhances the



(26b)

nucleophilicity of the resultant resorcinol-type B-ring, and hence of the 2′-functionality.[8] Conformational analysis indicates that 6a,11a-*cis*-pterocarpan formation could arise *via* either twisted boat, inverted half-chair (S_N2 mechanisms) or inverted sofa conformation (S_N1 or S_N2) of the 4-oxygenated 3,4-*trans*-2′-hydroxyisoflavans in which the substituents adopt $3_{ax},4_{ax}$ orientations.

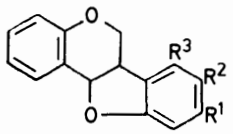
In order to assess the possible role of oxidation in the isoflavan ⟶ pterocarpan conversion, the 2′,7-dihydroxyisoflavans (36) and (37) were oxidized with DDQ in benzene or methanol solutions under nitrogen to yield the pterocarpans (38) and (39), respectively, in agreement with the recent findings by Cornia and Merlini.[4] Quinone methides were proposed as intermediates in the forementioned oxidative conversion, and in order to examine this hypothesis several isoflavans with modified substituents were subjected to the same conditions. Thus,

TABLE 2

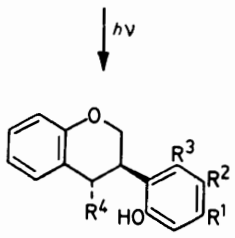
Relative speed of isoflavan ⟶ pterocarpan conversions. Time needed for (A) first signs of cyclization, (B) *ca.* 50% cyclization, and (C) 100% cyclization

	Functional group: Position					Acetone			1% H+ at 20 °C			1% H+ at 42 °C			10% H+ at 20 °C		
Compound	4	6	7	4′ 5′	6′	A	B	C	A	B	C	A	B	C	A	B	C
(11)	OMe/OAc		OH	OCH_2O	H			<5 min			<5 min			<5 min			<5 min
(12)	OMe/OAc	OMe	OMe	OCH_2O	H			<5 min			<5 min			<5 min			<5 min
(19)	OMe			OCH_2O	H	1 h	8 h	>24 h		<5 min	5 min			<5 min			<¼ h
(20)	OAc			OCH_2O	H						<5 min			<5 min			<¼ h
(21)	OMe		OMe	OCH_2O	H	24 h				<5 min	5 min			<5 min			<¼ h
(22)	OAc		OMe	OCH_2O	H						<5 min			<5 min			<5 min
(23)	OMe		OAc	OCH_2O	H	>24 h			7 h		>24 h	½ h*	1 h	5 h		½ h	1½ h
(24)	OAc		OAc	OCH_2O	H	24 h			5 h		24 h	½ h				5 min	1 h
(25)	OMe			OCH_2O	H	>24 h			<5 min	4 h		<5 min	½ h	1 h			<¼ h
(26a)	OAc			OCH_2O	H	24 h			<5 min	1 h		<5 min	½ h	½ h			<¼ h
(27)	OMe	OH	OMe	OCH_2O	H	24 h				<5 min	½ h			<5 min			½ h
(28)	OMe	OAc	OMe	OCH_2O	H	24 h				5 min	¼ h			<5 min			5 min
(31)	OMe	H	H	H H	H	>24 h			8 h	>24 h		2 h	>5 h		5 h	>8 h	
(32)	OAc	H	H	H H	H	>24 h			8 h	>24 h		2 h	>5 h		5 h	>8 h	
(34)	OMe	H	H	OCH_2O	H	>24 h			8 h	24 h		1 h	5 h	>5 h	3 h	5 h	>8 h
(35)	OAc	H	H	OCH_2O	H	>24 h			8 h	24 h		1 h	5 h	>5 h	3 h	5 h	>8 h
(36)	OMe/OAc	H	H	H H	OH			<5 min			<5 min			<5 min			<5 min

isoflavans with the 2′- and 7-hydroxy-groups blocked by methyl and methoxymethyl groups respectively (40)—(42), or possessing a 7-hydroxy-function but lacking substitution at C-2′ (43), all undergo benzylic oxidation to isoflavanones (44)—(47) of which (45) and (46) are obtained almost quantitatively and (47) in high yield.



(1) $R^1 = R^2 = R^3 = H$
(29) $R^1R^2 = OCH_2O, R^3 = H$
(30) $R^1 = R^2 = H, R^3 = OH$



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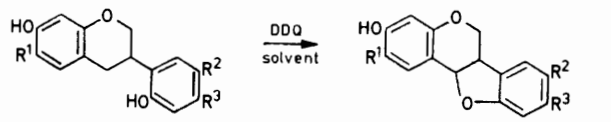
(31) $R^1 = R^2 = R^3 = H, R^4 = OMe$
(32) $R^1 = R^2 = R^3 = H, R^4 = OAc$
(8) $R^1 = R^2 = R^3 = R^4 = H$
(33) $R^1R^2 = OCH_2O, R^3 = H, R^4 = OMe$
(34) $R^1R^2 = OCH_2O, R^3 = H, R^4 = OAc$
(35) $R^1 = R^2 = H, R^3 = OH, R^4 = OMe$ or OAc

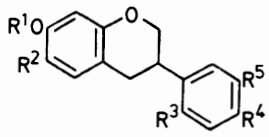
The reaction is analogous to the oxidation of 6-hydroxytetralin to 6-hydroxytetralin-1-one with DDQ,[9] and no products of side-reactions were observed. In the conversion (40) ⟶ (44) a methoxy-group is introduced simultaneously into the 6-isopentyl side-chain; a reaction which presumably proceeds *via* a benzylcarbocation followed by solvolysis with methanol.



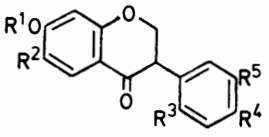
(36) $R^1 = R^2 = R^3 = H$
(37) $R^1 =$  , $R^2R^3 = OCH_2O$

(38) $R^1 = R^2 = R^3 = H$
(39) $R^1 =$  , $R^2R^3 = OCH_2O$

A further interesting example is the oxidation of 7-hydroxy-2′-methoxyisoflavan (48) in methanol with two mol of DDQ, giving 3,4-*trans*-4-methoxyisoflavan (49) and isoflavanone (50) analogues in almost equally poor yields (6 and 8% respectively). Benzylic methoxylation could in this instance proceed by 1,6-addition of methanol to an intermediate quinone methide (*cf.* ref. 4), or alternatively, as judged from the foregoing [(40) ⟶ (44)] side-chain methoxylation, by hydride abstraction as initial step (*cf.* ref. 9) followed by solvolysis of the resultant carbocation. Oxidation of the 4-methoxy-3,4-*trans*-isoflavan (49) by a second mol of DDQ followed by further addition of solvent could result in an acetal, capable of hydrolysis to the isoflavanone (50).

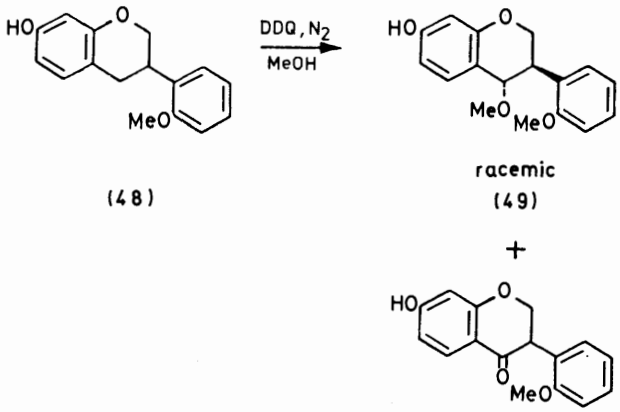


(40) $R^1 = Me, R^2 =$  , $R^3 = OCH_2OCH_3, R^4R^5 = OCH_2O$
(41) $R^1 = Me, R^2 = R^5 = H, R^3 = OCH_2OCH_3, R^4 = OMe$
(42) $R^1 = Me, R^2 = R^4 = R^5 = H, R^3 = OCH_2OCH_3$
(43) $R^1 = R^2 = R^3 = R^5 = H, R^4 = OMe$



(44) $R^1 = Me, R^2 =$  , $R^3 = OCH_2OCH_3, R^4R^5 = OCH_2O$
(45) $R^1 = Me, R^2 = R^5 = H, R^3 = OCH_2OCH_3, R^4 = OMe$
(46) $R^1 = Me, R^2 = R^4 = R^5 = H, R^3 = OCH_2OCH_3$
(47) $R^1 = R^2 = R^3 = R^5 = H, R^4 = OMe$

The latter mechanism would appear applicable in all the forementioned cases of isoflavan ⟶ isoflavanone conversions where the 7-hydroxy-function is blocked by alkylation. However, in those isoflavan ⟶ pterocarpan or isoflavan ⟶ isoflavanone conversions where



(48)

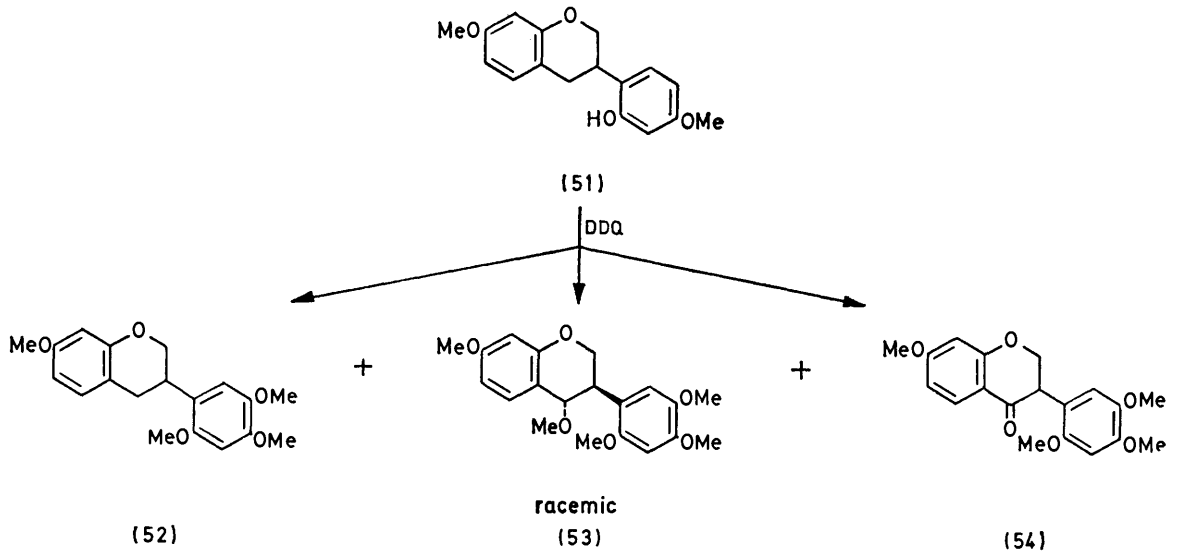
racemic
(49)

+

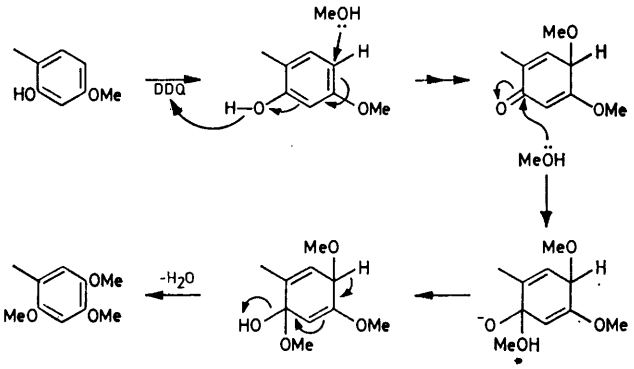
(50)

the 7-hydroxy-function is free, highly unstable quinone methide intermediates are equally feasible.

Further elaboration of the theme is reflected in the remarkable aromatic methoxylations which accompany the oxidation of 2′-hydroxy-4′,7-dimethoxyisoflavan (51) in methanol with DDQ. Thus, although benzylic



methoxylation and oxidation occur as in the previous instance, these appear to be preceded by aromatic methoxylation of the B-ring as illustrated by the formation of three products (52)—(54). A reasonable mechanism for this novel aromatic methoxylation is outlined (*cf.* Scheme). Obvious prerequisites for the reaction are 2′-hydroxylation and 4′-methoxylation



SCHEME

which combine to promote aromatic 2′,5′-dimethoxylation thus inhibiting the expected cyclization to pterocarpans following hydride abstraction by the oxidant.

The foregoing series of oxidative reactions illustrate the relative ease of *in vitro* 2′-hydroxyisoflavan–pterocarpan interconversions involving carbocation (*via* hydride abstraction) or unstable quinone methide (only in the presence of a 7-hydroxy-function) intermediates.

EXPERIMENTAL

M.p.s were determined with a Reichert Thermopan microscope. Mass spectra and accurate mass values were measured with a Varian CH-5 double-focusing mass spectrometer, while ^{1}H n.m.r. spectra were recorded on a Bruker WP-80 instrument for solutions in deuteriochloroform, unless otherwise stated, using $SiMe_4$ as internal standard. C.d. measurements were performed on a JASCO J-20 polarimeter for solutions in spectroscopically pure methanol. Merck silica gel 60 was used for column chromatography and Merck silica gel PF_{254} for preparative t.l.c. R_F Values refer to chromatography on precoated Merck t.l.c. plastic sheets (silica gel 60 PF_{254}) and colour reactions to $HClO_4$–$FeCl_3$ spray reagent. Irradiations were carried out in a Rayonet photochemical reactor (New England Ultra Violet Company) at 300 nm [except for (15) where 254 nm was used] in a quartz flask and under nitrogen.

Photolysis of Pterocarpans. General Procedure.—The optically active (6a*R*,11a*R*)-pterocarpans (9), (10), and (13)—(18) were isolated from *Neorautanenia amboensis* Schinz,[10] while pterocarpans (1), (29), and (30) were obtained synthetically.[7] A solution of the pterocarpan (100 mg) in the solvent (100 cm^3 methanol or 10 cm^3 acetone to which 90 cm^3 glacial acetic acid was added) was irradiated for 6—16 h, the reaction being monitored by t.l.c. In cases where methanol was used, the solvent was evaporated off under diminished pressure, while the acetic acid was neutralised ($NaHCO_3$), extracted with ether, dried (Na_2SO_4), and evaporated. The final products were obtained by thin layer or column chromatography of the residues.

Upon irradiation of edunol (9) in methanol for 12 h the formation of a product (R_F 0.12 *vs.* R_F edunol 0.22 in benzene–n-hexane–acetone, 5 : 4 : 0.5 v/v) was observed, but could not be isolated. Similar results were obtained upon photolysis of 2-methoxypterocarpin (10) in methanol (R_F product 0.36 *vs.* R_F pterocarpin 0.57 in benzene–n-hexane–acetone, 5 : 4 : 1 v/v) or in acetic acid and with neorautane (13) and 3-*O*-methyledunol (14) in acetic acid.

trans-(3R,4S)-3,4,6,7-*Tetrahydro*-3-(6-*hydroxy*-1,3-*benzodioxol*-5-*yl*)-4-*methoxy*-8,8-*dimethyl*-2H,8H-*benzo*[1,2-b;5,4-b′]*dipyran* (19) (30.3%), a yellow glass, had R_F 0.65 (benzene–n-hexane–acetone, 5 : 4 : 1 v/v) (Found: M^+, 384.1886. $C_{22}H_{24}O_6$ requires M, 384.1877); *m/e* 384 (M^+, 8.5%); δ_H 4.25 (d, J 5.0 Hz, H-2 and H-4), 3.47 (q, J 5.0 Hz, H-3), 6.84 (s, H-5), 6.25 (s, H-8), 6.16 (s, H-3′), 6.44 (s, H-6′), 6.09 (s, OH), 3.44 (s, OMe), 5.72 (s, OCH_2O), 1.72 (t, J 7.0 Hz, H-3″), 2.66 (t, J 7.0 Hz, H-4″), and 1.25 and 1.28 (2 s, 2 × Me); $[\theta]_{210}$ 0, $[\theta]_{230}$ −18 432, $[\theta]_{265}$ −960, $[\theta]_{278}$ 0, $[\theta]_{300}$ +3 840, $[\theta]_{335}$ 0 (*c* 0.11).

trans-(3R,4S)-3,4-*Dihydro*-3-(6-*hydroxy*-1,3-*benzodioxol*-5-*yl*)-4,7-*dimethoxy*-6-(3-*methylbut*-2-*enyl*)-2H-1-*benzopyran* (21) (22.1%), a yellow glass, had R_F 0.74 (benzene–n-

hexane–acetone, 5 : 4 : 1 v/v) (Found: *m/e*, 366.1454. $C_{22}H_{22}O_5$ requires 366.1467); *m/e* 398 (M^+, 4.1%); δ_H ([$^2H_6$]acetone) 4.47 (d, *J* 5.0 Hz, H-2 and H-4), 3.58 (q, *J* 5.0 Hz, H-3), 6.91 (s, H-5), 6.82 (s, H-3′), 6.33 (s, H-6′), 8.33 (s, OH), 3.38, 3.77 (2 s, 2 × OMe), 5.75 (OCH_2O), 3.18 (d, *J* 6.5 Hz, H-1″), 5.22 (t, *J* 6.5 Hz, H-2″), and 1.67 (2 s, 2 × Me); $[\theta]_{215}$ 0, $[\theta]_{227}$ −8 106, $[\theta]_{263}$ 0, $[\theta]_{290}$ +2 510, $[\theta]_{305}$ 0, $[\theta]_{315}$ −965, $[\theta]_{330}$ 0 (*c* 0.10).

trans-(3R,4S)-7-*Acetoxy*-3,4-*dihydro*-3-(6-*hydroxy*-1,3-*benzodioxol*-5-*yl*)-4-*methoxy*-6-(3-*methylbut*-2-*enyl*)-2H-1-*benzopyran* (23) (63.5%), a yellow glass, had R_F 0.61 (benzene–n-hexane–acetone, 5 : 4 : 1 v/v) (Found: M^+, 426.1669. $C_{24}H_{26}O_7$ requires *M*, 426.1678); *m/e* 426 (M^+, 9.4%); δ_H ([$^2H_6$]acetone) 4.42 (d, *J* 5.0 Hz, H-2), 3.59 (q, *J* 5.0 Hz, H-3), 4.34 (d, *J* 5.0 Hz, H-4), 7.09 (s, H-5), 6.53 (s, H-8), 6.45 (s, H-3′), 6.64 (s, H-6′), 8.45 (s, OH), 3.38 (s, OMe), 5.75 (s, OCH_2O), 3.13 (d, *J* 6.5 Hz, H-1″), 5.16 (t, *J* 6.5 Hz, H-2″), and 1.67 (2 s, 2 × Me); $[\theta]_{224}$ 0, $[\theta]_{235}$ −11 833, $[\theta]_{262}$ −2 130, $[\theta]_{278}$ −3 550, $[\theta]_{286}$ 0, $[\theta]_{292}$ +3 787, $[\theta]_{300}$ 0, $[\theta]_{309}$ −1 657, $[\theta]_{330}$ 0 (*c* 0.18).

trans-(3R,4S)-4,7-*Diacetoxy*-3,4-*dihydro*-3-(6-*hydroxy*-1,3-*benzodioxol*-5-*yl*)-6-(3-*methylbut*-2-*enyl*)-2H-1-*benzopyran* (24) (19.5%), a yellow glass, had R_F 0.49 (benzene–n-hexane–acetone, 5 : 4 : 1 v/v), (Found: M^+, 454.1639. $C_{25}H_{26}O_8$ requires *M*, 454.1628); *m/e* 454 (M^+, 5.7%); δ_H 4.41 (d, *J* 5.0 Hz, H-2), 3.27 (q, *J* 5.0 Hz, H-3), 5.43 (d, *J* 5.0 Hz, H-4), 6.78 (s, H-5), 6.47 (s, H-8), 6.31 (s, H-3′), 6.78 (s, H-6′), 7.00 (s, OH), 2.28, 2.13 (2 s, 2 × OAc), 5.70 (dd, *J* 3.0 and 1.2 Hz, OCH_2O), 3.06 (d, *J* 6.5 Hz, H-1″), 5.09 (t, *J* 6.5 Hz, H-2″), and 1.63 and 1.69 (2 s, 2 × Me).

trans-(5S,6R)-6,7-*Dihydro*-6-(6-*hydroxy*-1,3-*benzodioxol*-5-*yl*)-5-*methoxy*-5H-*furo*[3,2-g][1]*benzopyran* (25) (26.6%), light yellow needles (from acetone), had m.p. 144—145 °C, R_F 0.62 (benzene–n-hexane–acetone, 5 : 4 : 1 v/v) (Found: C, 66.9; H, 4.7. $C_{19}H_{16}O_6$ requires C, 67.1; H, 4.7%); *m/e* 340 (M^+, 2.0%); δ_H 4.44 (d, *J* 5.0 Hz, H-2 and H-4), 3.59 (q, *J* 5.0 Hz, H-3), 7.42 (s, H-5), 6.95 (s, H-8), 6.34 (s, H-3′), 6.50 (s, H-6′), 5.95 (s, OH), 3.48 (s, OMe), 5.78 (s, OCH_2O), 7.42 (d, *J* 2.2 Hz, H-2″), and 6.59 (dd, *J* 2.2 and 1.0 Hz, H-3″).

trans-(5S,6R)-5-*Acetoxy*-6,7-*dihydro*-6-(6-*hydroxy*-1,3-*benzodioxol*-5-*yl*)-5H-*furo*[3,2-g][1]*benzopyran* (26a) (15.6%), an oil, had R_F 0.47 (chloroform) (Found: *m/e* 308.0704. $C_{18}H_{12}O_5$ requires 308.0685); *m/e* 368 (M^+, 2.1%); δ_H ([$^2H_6$]acetone) 4.44 (d, *J* 5.0, H-2), 3.61 (q, *J* 5.0, H-3), 6.23 (d, *J* 5.0, H-4), 7.48 (s, H-5), 6.94 (s, H-8), 6.44 (s, H-3′), 6.56 (s, H-6′), 8.41 (s, OH), 2.06 (s, OAc), 5.75 (s, OCH_2O), 7.64 (d, *J* 2.2 Hz, H-2″), and 6.72 (dd, *J* 2.2 and 1.0 Hz, H-3″); $[\theta]_{225}$ 0, $[\theta]_{243}$ +10 016, $[\theta]_{255}$ 0, $[\theta]_{283}$ −4 293, $[\theta]_{292}$ 0, $[\theta]_{303}$ +7 154, $[\theta]_{320}$ 0 (*c* 0.123).

cis-(5R,6R)-5-*Acetoxy*-6,7-*dihydro*-6-(6-*hydroxy*-1,3-*benzodioxol*-5-*yl*)-5H-*furo*[3,2-g][1]*benzopyran* (26b) (1.7%), a glass, had m.p. 65—70 °C, R_F 0.22 (chloroform) (Found: *m/e* 308.0711. $C_{18}H_{12}O_5$ requires 308.0685); *m/e* 368 (M^+, 2.2%); δ_H ([$^2H_6$]acetone) 4.63 (q, *J* 12.5 and 10.5 Hz, H-2_{ax}), 4.28 (octet, *J* 10.5, 4.0, and 1.5 Hz, H-2_{eq}), 3.80 (m, *J* 10.5 and 4.0 Hz, H-3), 6.23br (q, *J* 4.0 and 1.5 Hz, H-4), 7.50 (s, H-5), 6.95 (s, H-8), 6.47 (s, H-3′), 6.61 (s, H-6′), 8.41 (s, OH), 1.86 (s, OAc), 5.75 (s, OCH_2O), 7.66 (d, *J* 2.2 Hz, H-2″), 6.44 (dd, *J* 2.2 and 1.0 Hz, H-3″); $[\theta]_{215}$ 0, $[\theta]_{235}$ +9 051, $[\theta]_{260}$ +838, $[\theta]_{290}$ +4 190, $[\theta]_{320}$ 0 (*c* 0.21).

trans-(3R,4S)-3,4-*Dihydro*-3-(6-*hydroxy*-1,3-*benzodioxol*-5-*yl*)-4,7-*dimethoxy*-2H-1-*benzopyran*-6-*ol* (27) (9.1%), a yellow glass, had R_F 0.30 (chloroform–acetone, 9 : 1 v/v) (Found: *m/e* 314.0814. $C_{17}H_{14}O_6$ requires 314.0790); *m/e* 346 (M^+, 8.5), δ_H 4.18 (d, *J* 5.0 Hz, H-2 and H-4), 3.50 (q, *J* 5.0, H-3), 6.76 (s, H-5), 6.38 (s, H-8), 6.34 (s, H-3′), 6.47 (s, H-6′), 1.66 and 5.19 (2 s, 2 × OH), 3.44 and 3.75 (2 s, 2 × OMe), and 5.80 (s, OCH_2O).

trans-(3R,4S)-6-*Acetoxy*-3,4-*dihydro*-3-(6-*hydroxy*-1,3-*benzodioxol*-5-*yl*)-4,7-*dimethoxy*-2H-1-*benzopyran* (28) (42.3%), yellow *rosettes* (from acetone), had m.p. 158—160 °C, R_F 0.31 (chloroform–acetone, 9 : 1 v/v) (Found: C, 61.8; H, 5.2. $C_{20}H_{20}O_8$ requires C, 61.9; H, 5.2%); *m/e* 388 (M^+, 6.1%); δ_H ([$^2H_6$]acetone) 4.38 (d, *J* 5.0 Hz, H-2), 3.59 (q, *J* 5.0 Hz, H-3), 4.31 (d, *J* 5.0 Hz, H-4), 6.89 (s, H-5), 6.47 (s, H-8), 6.44 (s, H-3′), 6.61 (s, H-6′), 3.36 and 3.73 (2 s, 2 × OMe), 2.17 (s, OAc), and 5.77 (dd, *J* 3.0 and 1.2 Hz, OCH_2O); $[\theta]_{210}$ 0, $[\theta]_{225}$ −8 614, $[\theta]_{255}$ 0, $[\theta]_{293}$ +6 596, $[\theta]_{320}$ 0 (*c* 0.10).

(6aR,11aR)-6a,11a-*Dihydro*-2,8-*dihydroxy*-3-*methoxy*-9-*methoxymethoxy*-6H-*benzofuro*[3,2-c][1]*benzopyran* (*photocarpin*) (5) (10.2%), needles (from ethanol), had m.p. 210—211 °C, R_F 0.60 (chloroform–methanol, 49 : 1 v/v) (Found: C, 62.2; H, 5.1. $C_{18}H_{18}O_7$ requires C, 62.4; H, 5.2%); *m/e* 346 (M^+, 88.7%); δ_H 6.97 (s, H-1), 6.94 (s, H-7), 6.45 (s, H-4), 6.41 (s, H-10), 5.38 (d, *J* 6.5 Hz, H-11a), 3.45 (m, H-6a), 4.16 (m, H-6_{eq}), 3.59 (m, H-6_{ax}), 5.06 (s, OCH_2), 3.81 (s, 3-OMe), 3.52 (s, OMe), 6.03 (s, OH), and 5.28 (s, OH).

trans-3,4-*Dihydro*-3-(2-*hydroxyphenyl*)-4-*methoxy*-2H-1-*benzopyran* (31) (33.3%), needles (from acetone), had m.p. 185—186 °C (decomp.), R_F 0.42 (benzene–n-hexane–acetone, 5 : 4 : 1 v/v) (Found: C, 74.9; H, 6.3. $C_{16}H_{16}O_3$ requires C, 75.0; H, 6.3%); *m/e* 256 (M^+, 9.9%); δ_H 4.31 (d, *J* 5.0 Hz, H-2), 3.66 (q, *J* 5.0 Hz, H-3), 4.47 (d, *J* 5.0 Hz, H-4), 7.18—6.41 (m, aromatic H), 8.38 (s, OH), and 3.31 (s, OMe).

trans-4-*Acetoxy*-3,4-*dihydro*-3-(2-*hydroxyphenyl*)-2H-1-*benzopyran* (32) (33.4%), a glass, had R_F 0.40 (benzene–n-hexane–acetone, 5 : 4 : 1 v/v) (Found: M^+, 284.1244. $C_{17}H_{16}O_4$ requires *M*, 284.1251); *m/e* 284 (M^+, 9.7%); δ_H 4.48 (d, *J* 5.0 Hz, H-2), 3.44 (q, *J* 5.0 Hz, H-3), 5.75 (d, *J* 5.0 Hz, H-4), 7.28—6.50 (m, aromatic H), and 2.13 (s, OAc).

3,4-*Dihydro*-3-(2-*hydroxyphenyl*)-2H-1-*benzopyran* (8) (33.7%), white needles (from benzene), had m.p. 137—138 °C, R_F 0.52 (benzene–n-hexane–acetone, 5 : 4 : 1 v/v (Found: C, 79.6; H, 6.4. $C_{15}H_{14}O_2$ requires C, 79.6; H, 6.2%); *m/e* 226 (M^+, 83.5%); δ_H 4.09 (dd, *J* 10.0 and 9.5 Hz, H-2_{ax}), 4.31 (octet, *J* 10.0, 3.5, and 1.5 Hz, H-2_{eq}), 3.50 (m, ΣJ 24.0 Hz, H-3), 7.06—6.53 (m, aromatic H), and 5.00 (s, OH).

trans-3,4-*Dihydro*-3-(6-*hydroxy*-1,3-*benzodioxol*-5-*yl*)-4-*methoxy*-2H-1-*benzopyran* (33) (87.5%), cubes (from carbon tetrachloride–chloroform), had m.p. 138—139 °C, R_F 0.53 (chloroform–acetone, 19 : 1 v/v) (Found: M^+, 300.1227. $C_{17}H_{16}O_5$ requires *M*, 300.1245); *m/e* 300 (M^+, 15.7%); δ_H 4.31 (d, *J* 5.0 Hz, H-2 and H-4), 3.52 (q, *J* 5.0 Hz, H-3), 7.25—6.66 (m, aromatic H), 6.28 (s, H-3′), 6.44 (s, H-6′), 5.89 (s, OH), 3.44 (s, OMe), and 5.72 (s, OCH_2O).

trans-4-*Acetoxy*-3,4-*dihydro*-3-(6-*hydroxy*-1,3-*benzodioxol*-5-*yl*)-2H-1-*benzopyran* (34) (53.3%), a white amorphous solid, had R_F 0.31 (benzene–acetone, 19 : 1 v/v) (Found: M^+, 328.1218. $C_{18}H_{16}O_6$ requires *M*, 328.1239); *m/e* 328 (M^+, 10.2%); δ_H 4.41 (d, *J* 5.0 Hz, H-2), 3.34 (*q*, *J* 5.0 Hz, H-3), 5.53 (d, *J* 5.0 Hz, H-4), 7.25—6.66 (m, aromatic H), 6.31 (s, H-3′), 4.53 (s, OH), 2.13 (s, OAc), and 5.69 (dd, *J* 3.0 and 1.2 Hz, OCH_2O).

Cyclization of Isoflavan-4-ol Derivatives.—Cyclization of the isoflavan-4-ols was carried out in acetone containing the

percentages of concentrated hydrochloric acid and at the temperatures indicated in Table 2. The reaction was followed by qualitative t.l.c. and in three cases, (19), (31), and (34), the products were isolated and identified (n.m.r. and mass spectra) as the pterocarpans (13), (1), and (29).

Synthesis of Isoflavans.—The isoflavan (37) was obtained by catalytic hydrogenation [11] of edunol (9), while all other isoflavans were synthesized [12] *via* the corresponding isoflavones.

3,4-*Dihydro*-7-*hydroxy*-3-(6-*hydroxy*-1,3-*benzodioxol*-5-*yl*)-6-(3-*methylbutyl*)-2H-1-*benzopyran* (37) (81%), a white solid, had R_F 0.55 (n-hexane–benzene–acetone, 4 : 3 : 2 v/v) (Found: M^+, 356.1613. $C_{21}H_{24}O_5$ requires M, 356.1617); *m/e* 356 (M^+, 47.0%); δ_H ([$^2H_6$]acetone) 7.72 and 8.0 (2 s, 2 × OH), 6.68 (s, H-5), 6.57 (s, H-6′), 6.41 (s, H-8), 6.21 (s, H-3′), 5.76 (s, OCH_2O), 4.14 (octet, J 10.0, 3.5, and 1.5 Hz, H-2$_{eq}$), 3.89 (dd, J 10.0 and 9.5 Hz, H-2$_{ax}$), 3.47 (m, ΣJ 24 Hz, H-3), 2.82 (m, H-4), 2.52 (t, J 7.0 Hz, H-1″), 1.69—1.30 (m, H-2″ and H-3″), and 0.88 and 0.94 (2 d, J 7.0 Hz, 2 × Me).

3,4-*Dihydro*-7-*hydroxy*-3-(2-*hydroxyphenyl*)-2H-1-*benzopyran* (36) (89%), a white solid, had R_F 0.38 (benzene–acetone, 9 : 1 v/v) (Found: M^+, 242.0937. $C_{15}H_{14}O_3$ requires M, 242.0939); *m/e* 242 (M^+, 43.7%); δ_H ([$^2H_6$]-acetone) 3.97 (dd, J 10.0 and 9.5 Hz, H-2$_{ax}$), 4.24 (octet, J 10.0, 3.5, and 1.5 Hz, H-2$_{eq}$), 3.53 (m, ΣJ 24 Hz, H-3), 2.88 (m, H-4), 6.22—7.09 (m, aromatic H), and 8.30 and 7.95 (2 × s, 2 × OH).

3,4-*Dihydro*-7-*methoxy*-3-(6-*methoxymethoxy*-1,3-*benzodioxol*-5-*yl*)-6-(3-*methylbutyl*)-2H-1-*benzopyran* (40) (64%), a light yellow oil, had R_F 0.42 (benzene) (Found: M^+, 414.2038. $C_{24}H_{30}O_6$ requires M, 414.2034); *m/e* 414 (M^+, 72.7%); δ_H ([$^2H_6$]acetone) 3.88 (dd, J 10.0 and 9.5 Hz, H-2$_{ax}$), 4.15 (octet, J 10.0, 3.5, and 1.5 Hz, H-2$_{eq}$), 3.53 (m, ΣJ 24 Hz, H-3), 2.78 (m, H-4), 6.70 (s, H-5), 6.61 (s, H-8), 6.25 (s, H-3′), 6.68 (s, H-6′), 3.67—3.37 (2 s, 2 × OMe), 5.05 (s, OCH_2), 5.80 (s, OCH_2O), 2.52 (t, J 7.0 Hz, H-1″), 1.63—1.25 (m, H-2″ and H-3″), and 0.89, (2 d, J 7.0 Hz, 2 × Me).

3,4-*Dihydro*-7-*methoxy*-3-(4-*methoxy*-2-*methoxymethoxyphenyl*)-2H-1-*benzopyran* (41) (84%), white needles (from ethanol), had m.p. 83—84 °C, R_F 0.46 (n-hexane–acetone, 4 : 1 v/v) (Found: C, 69.3; H, 6.7. $C_{19}H_{22}O_5$ requires C, 69.1; H, 6.7%); *m/e* 330 (M^+, 35.7%); δ_H 3.96 (dd, J 10.0 and 9.5 Hz, H-2$_{ax}$), 4.28 (octet, J 10.0, 3.5, and 1.5 Hz, H-2$_{eq}$), 3.51 (m, ΣJ 24 Hz, H-3), 2.90 (m, H-4), 7.00—6.34 (m, aromatic H), 3.71, 3.69, and 3.41 (3 s, 3 × OMe), and 5.12 (s, OCH_2).

3,4-*Dihydro*-7-*methoxy*-3-(2-*methoxymethoxyphenyl*)-2H-1-*benzopyran* (42) (90%), a light yellow oil, had R_F 0.62 (n-hexane–acetone, 4 : 1 v/v) (Found: M^+, 300.1367. $C_{18}H_{20}O_4$ requires M, 300.1356); *m/e* 300 (M^+, 43.9%), δ_H 4.01 (dd, J 10.0 and 9.5 Hz, H-2$_{ax}$), 4.31 (octet, J 10.0, 3.5, and 1.5 Hz, H-2$_{eq}$), 3.66 (m, J 24 Hz, H-3), 2.93 (m, H-4), 6.36 (dd, J 8.5 and 2.5 Hz, H-6), 6.32 (d, J 2.5 Hz, H-8), 7.16—6.72 (m, H-5, -3′, -4′, -5′, and -6′), 3.71 and 3.43 (2 s, 2 × OMe), and 5.15 (s, OCH_2).

3,4-*Dihydro*-7-*hydroxy*-3-(4-*methoxyphenyl*)-2H-1-*benzopyran* (43) (93%), white needles (from ethanol), had m.p. 158—160 °C, R_F 0.42 (benzene–ethyl acetate, 9 : 1 v/v) (Found: C, 74.9; H, 6.3. $C_{16}H_{16}O_3$ requires C, 75.0; H, 6.3%); *m/e* 256 (M^+, 60.2%), δ_H ([$^2H_6$]acetone) 3.85 (dd, J 10.0 and 9.5 Hz, H-2$_{ax}$), 4.12 (octet, J 10.0, 3.5, and 1.5 Hz, H-2$_{eq}$), 3.06 (m, ΣJ 24 Hz, H-3), 2.78 (m, H-4), 6.74 (d, J 8.5 Hz, H-5), 6.24 (dd, J 8.5 and 2.5 Hz, H-6), 6.16 (d, J 2.6 Hz, H-8), 6.74 (d, J 8.5 Hz, H-3′ and -5′), 7.08 (d, J 8.5 Hz, H-2′ and -6′), 7.89 (s, OH), and 3.67 (s, OMe).

3,4-*Dihydro*-7-*hydroxy*-3-(2-*methoxyphenyl*)-2H-1-*benzopyran* (48) (89%), white needles (from ethanol–acetone), had m.p. 131—132 °C, R_F 0.40 (benzene–ethyl acetate, 19 : 1 v/v) (Found: M^+, 256.1109. $C_{16}H_{16}O_3$ requires M, 256.1095); *m/e* 256 (M^+, 53.1%); δ_H 3.96 (dd, J 10.0 and 9.5 Hz, H-2$_{ax}$), 4.26 (octet, J 10.0, 3.5, and 1.5 Hz, H-2$_{eq}$), 3.57 (m, ΣJ 24 Hz, H-3), 2.90 (m, H-4), 6.25 (dd, J 8.5 and 2.5 Hz, H-6), 6.19 (d, J 2.5 Hz, H-8), 7.18—6.62 (m, H-5, -3′, -4′, -5′, and -6′), 4.75 (s, OH), and 3.76 (s, OMe).

3,4-*Dihydro*-3-(2-*hydroxy*-4-*methoxyphenyl*)-7-*methoxy*-2H-1-*benzopyran* (51) (97%), needles (from ethanol), had m.p. 131—133 °C, R_F 0.32 (benzene–acetone, 9 : 1 v/v) (Found: C, 71.2; H, 6.4. $C_{17}H_{18}O_4$ requires C, 71.3; H, 6.3%); *m/e* 286 (M^+, 38.8%); δ_H 3.94 (dd, J 10.0 and 9.5 Hz, H-2$_{ax}$), 4.26 (octet, J 10.0, 3.5, and 1.5 Hz, H-2$_{eq}$), 3.44 (m, ΣJ 24 Hz, H-3), 2.87 (m, H-4), 6.87—6.19 (m, aromatic H), 5.43 (s, OH), and 3.65 and 3.62 (2 s, 2 × OMe).

Oxidation of Isoflavans. General Procedure.—DDQ (2—3 mmol) was added to a solution of the isoflavan (1 mmol) in the appropriate solvent (15 cm^3) [(37) in dry benzene or in dry methanol; (38) in dry benzene, and all others in dry methanol] under nitrogen and the mixture was stirred at room temperature for 15 min [(37) and (38)] or 12 h (all other isoflavans), the reaction being followed by t.l.c. The excess of DDQ was removed by filtration through alumina and subsequent thin layer or column chromatography delivered the products.

6a,11a-*Dihydro*-3-*hydroxy*-6H-*benzofuro*[3,2-c][1]*benzopyran* (38) (65.0%), needles (from ethanol), had m.p. 147—150 °C, R_F 0.52 (benzene–acetone, 9 : 1 v/v) (Found: C, 75.1; H, 5.0. $C_{15}H_{12}O_3$ requires C, 75.0; H, 5.0%); *m/e* 240 (M^+, 100%); δ_H 6.25—7.29 (m, aromatic H), 5.52br (s, OH), 5.37 (d, J 6.5 Hz, H-11a), 4.12 (m, H-6$_{eq}$), and 3.59 (m, H-6$_{ax}$ and H-6a).

2,3-*Dihydro*-7-*methoxy*-3-(6-*methoxymethoxy*-1,3-*benzodioxol*-5-*yl*)-6-(1-*methoxy*-3-*methylbutyl*)-1-*benzopyran*-4-*one* (44) (9%), a yellow-red oil, had R_F 0.68 (benzene–ethyl acetate, 19 : 1 v/v) (Found: M^+, 458.1918. $C_{25}H_{30}O_8$ requires M, 458.1932); *m/e* 458 (M^+, 55.9%), δ_H 7.86 (s, H-5), 6.71 (s, H-6′), 6.51 (s, H-8), 6.34 (s, H-3′), 4.53—4.06 (m, H-2 and H-3), 3.82, 3.39, and 3.13 (3 s, 3 × OMe), 4.98 (s, OCH_2), 5.82 (s, OCH_2O), 1.83—1.24 (m, H-1″, H-2″, and H-3″), and 0.93 and 0.90 (2 d, J 6.5 Hz, 2 × Me).

2,3-*Dihydro*-7-*methoxy*-3-(4-*methoxy*-2-*methoxymethoxyphenyl*)-1-*benzopyran*-4-*one* (45) (86.3%), white cubes (from ethanol), had m.p. 129 °C, R_F 0.40 (benzene–ethyl acetate, 9 : 1 v/v) (Found: C, 66.1; H, 5.8. $C_{19}H_{20}O_6$ requires C, 66.3; H, 5.9%); *m/e* 344 (M^+, 60.3%); δ_H 7.83 (d, J 8.75 Hz, H-5), 6.94 (d, J 8.75 Hz, H-6′), 6.36—6.66 (m, H-3′, -5′, -6, and -8), 5.05 (s, OCH_2), and 3.71, 3.77, and 3.37 (3 s, 3 × OMe).

2,3-*Dihydro*-7-*methoxy*-3-(2-*methoxymethoxyphenyl*)-1-*benzopyran*-4-*one* (46) (91.0%), white needles (from ethanol), had m.p. 91 °C, R_F 0.40 (benzene–ethyl acetate, 19 : 1 v/v) (Found: C, 68.9; H, 5.8. $C_{18}H_{18}O_5$ requires C, 68.8; H, 5.8%); *m/e* 314 (M^+, 65.2%); δ_H 4.59—4.12 (m, H-2 and H-3), 7.85 (d, J 8.5 Hz, H-5), 6.54 (dd, J 8.5 and 2.5 Hz, H-6), 6.37 (d, J 2.5 Hz, H-8), 7.21—6.88 (m, H-3′, -4′, -5′, and -6′), 3.37 and 3.76 (2 s, 2 × OMe), and 5.06 (s, OCH_2).

2,3-*Dihydro*-7-*hydroxy*-3-(4-*methoxyphenyl*)-1-*benzopyran*-4-*one* (47) (61.1%), white needles (from ethanol), had m.p. 197—199 °C, R_F 0.39 (benzene–ethyl acetate, 4 : 1 v/v) (Found: C, 70.6; H, 5.2. $C_{16}H_{14}O_4$ requires C, 71.1; H,

5.2%); *m/e* 270 (M^+, 12.2%); δ_H ([$^2H_6$]acetone) 4.55—3.82 (m, H-2 and H-3), 7.62 (d, *J* 8.5 Hz, H-5), 6.47 (dd, *J* 8.5 and 2.5 Hz, H-6), 6.29 (d, *J* 2.5 Hz, H-8), 6.75 (d, *J* 8.5 Hz, H-3′ and H-5′), 7.10 (d, *J* 8.5 Hz, H-2′ and H-6′), 9.20 (s, OH), and 3.69 (s, OMe).

3,4-*Dihydro*-7-*hydroxy*-4-*methoxy*-3-(2-*methoxyphenyl*)-2H-1-*benzopyran*(49) (6.2%), a yellow oil, had R_F 0.24 (n-hexane–benzene–acetone, 5 : 4 : 1 v/v) (Found: M^+, 286.1188. $C_{17}H_{18}O_4$ requires *M*, 286.1200); *m/e* 286 (M^+, 27.3%); δ_H 4.34 (d, *J* 5.0 Hz, H-2 and H-4), 3.67 (q, *J* 5.0 Hz, H-3), 6.28 (dd, *J* 8.5 and 2.5 Hz, H-6),6.21 (d, *J* 2.5 Hz, H-8), 7.03—6.53 (m, H-3′, -4′, -5′, and -6′), 5.01 (s, OH), and 3.80 and 3.37 (2 s, 2 × OMe).

2,3-*Dihydro*-7-*hydroxy*-3-(2-*methoxyphenyl*)-1-*benzopyran*-4-*one* (50) (8.5%), a white amorphous solid, had R_F 0.20 (n-hexane–benzene–acetone, 5 : 4 : 1 v/v) (Found: M^+, 270.0877. $C_{16}H_{14}O_4$ requires *M*, 270.0888); *m/e* 270 (M^+, 35.5%); δ_H ([$^2H_6$]acetone) 4.67—4.06 (m, H-2 and H-3), 7.66 (d, *J* 8.5 Hz, H-5), 6.49 (dd, *J* 8.5 and 2.5 Hz, H-6), 6.30 (d, *J* 2.5 Hz, H-8), 7.23—6.69 (m, H-3′, -4′, -5′, and -6′), 2.78 (s, OH), and 3.73 (s, OMe).

3,4-*Dihydro*-7-*methoxy*-3-(2,4,5-*trimethoxyphenyl*)-2H-1-*benzopyran* (52) (16.5%), light yellow needles (from ethanol), had m.p. 85—86 °C, R_F 0.41 (chloroform–ethyl acetate 19 : 1 v/v) (Found: C, 69.0; H, 6.8. $C_{19}H_{22}O_5$ requires C, 69.1; H, 6.7%); *m/e* 315 (M^+ − 15, 50.7%); δ_H 4.09 (m, H-2), 3.35 (m, Σ *J* 24 Hz, H-3), 2.75 (m, *J* 15.0, 5.0, and 3.5 Hz, H-4), 6.82 (d, *J* 8.5 Hz, H-5), 6.33 (dd, *J* 8.5 and 2.5 Hz, H-6), 6.25 (d, *J* 2.5 Hz, H-8), 5.58 (s, H-3′), 6.17 (s, H-6′), 3.72, 3.66, 3.12, and 3.11 (4 s, 4 × OMe).

trans-3,4-*Dihydro*-4,7-*dimethoxy*-3-(2,4,5-*trimethoxyphenyl*)-2H-1-*benzopyran* (53) (31.7%), a yellow oil, had R_F 0.30 (chloroform–ethyl acetate, 19 : 1 v/v) (Found: M^+ − 15, 345.1342. $C_{19}H_{21}O_6$ requires M − 15, 345.1338); *m/e* 360 (M^+, 7.5%); δ_H 4.36 (m, H-2), 3.23 (m, H-3), 4.04 (m, H-4), 6.97 (d, *J* 8.5 Hz, H-5), 6.37 (dd, *J* 8.5 and 2.5 Hz, H-6), 6.25 (d, *J* 2.5 Hz, H-8), 6.22 (s, H-6′), 5.54 (s, H-3′), and 3.71, 3.67, 3.41, 3.10, and 2.87 (5 s, 5 × OMe).

2,3-*Dihydro*-7-*methoxy*-3-(2,4,5-*trimethoxyphenyl*)-1-*benzopyran*-4-*one* (54) (18.1%), a yellow solid, had R_F 0.21 (chloroform–ethyl acetate, 19 : 1 v/v) (Found: M^+, 344.1246. $C_{19}H_{20}O_6$ requires *M*, 344.1254); *m/e* 345 (M^+ + 1, 100%); δ_H 4.44 (m, H-2 and H-3), 7.74 (d, *J* 8.5 Hz, H-5), 6.49 (dd, *J* 8.5 and 2.5 Hz, H-6), 6.30 (d, *J* 2.5 Hz, H-8), 6.24 (s, H-6′), 5.59 (s, H-3′), and 3.77, 3.75, 3.26, and 3.23 (4 s, 4 × OMe).

Support by the Sentrale Navorsingsfonds of this University and the South African Council of Scientific and Industrial Research, Pretoria, is acknowledged. We thank Professor D. Ferreira for discussions.

[0/1955 *Received*, 19*th December*, 1980]

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