Synthesis of Isoflavanoid Oligomers Using a Pterocarpan as Inceptive Electrophile

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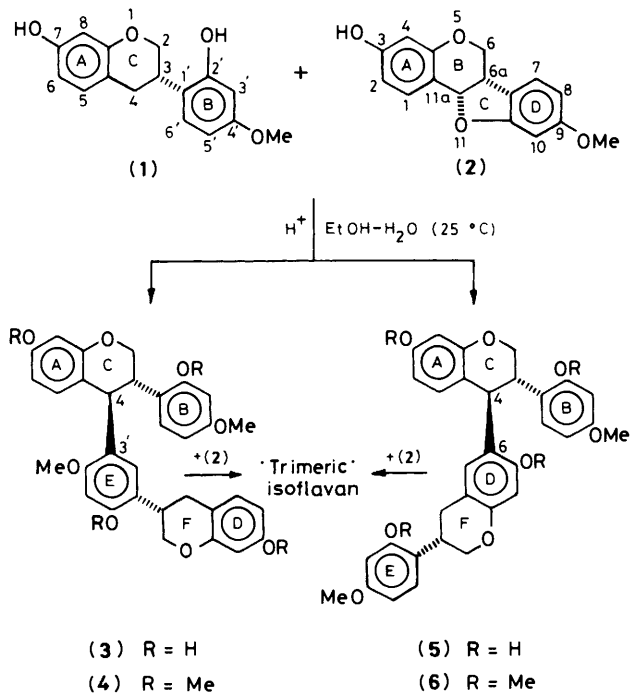
(3*S*)-2',7-Dihydroxy-4'-methoxyisoflavan serves as bifunctional nucleophile at C-5' and C-6, when condensed with the carbocation generated at C-11a of its (6a*S*,11a*S*)-3-hydroxy-9-methoxypterocarpan analogue under mild acid conditions or by photolysis, to form isomeric (3*S*,4*S*)-[4,3']- and -[4,6]-3,4-*trans*-bi-isoflavanoids, and hence the [4,3':4,6]-tri-isoflavanoid homologue. Structural assignments are supported by an analogous series of condensations. Self-condensation of the pterocarpan generates both isoflavan–pterocarpan and isoflavan–isoflavene analogues in low yields. The [4,3']-bi-isoflavanoid is identical with the first natural oligomer from *Dalbergia nitidula*.

Re-examination of the phenolic content of the heartwood of *Dalbergia nitidula* Welw. *ex* Bak.[1] has provided the first indication of the natural existence of oligomers among the isoflavonoid metabolites.[2] Isolation of one of these in low yield (0.05%) from the MeOH extract led to its characterization as the dimeric (3*S*,4*S*)-3,4-*trans*-4-[(3*S*)-6',7-dihydroxy-4'-methoxyisoflavan-3'-yl]-2',7-dihydroxy-4'-methoxy-isoflavan (**3**). Structural confirmation was by synthesis from the concomitant (3*S*)-2',7-dihydroxy-4'-methoxyisoflavan [(+)-vestitol][3] (**1**) and (6a*S*,11a*S*)-3-hydroxy-9-methoxypterocarpan [(+)-medicarpin][4] (**2**) (Scheme 1).



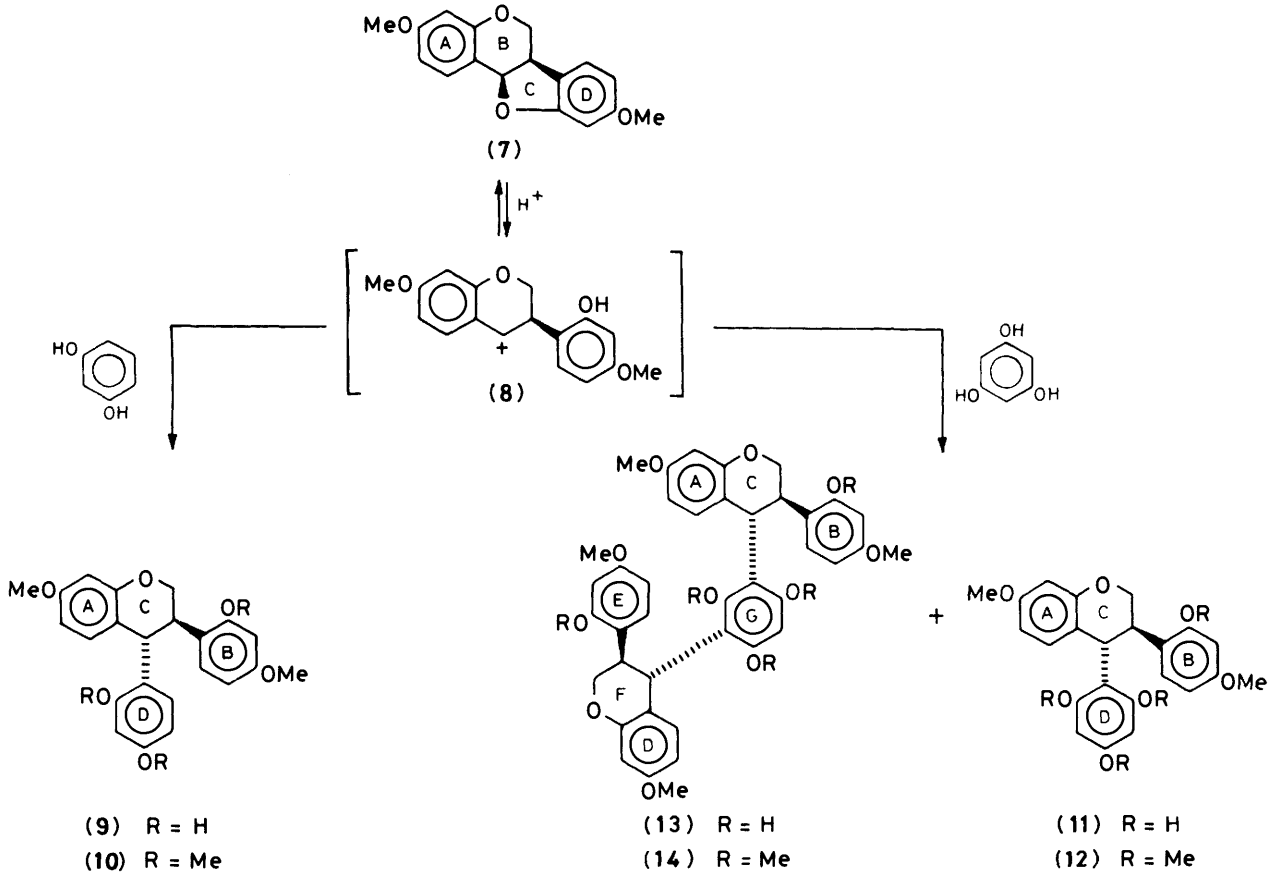
Scheme 1.

Thus, under conditions similar to those used for the synthesis of condensed tannins (2M HCl; 25 °C)[5] the pterocarpan (**2**), as prospective electrophile, and the nucleophilic isoflavan (**1**) condense to give the natural [4,3']-bi-isoflavan (**3**) and its [4,6]-positional isomer (**5**) in 20 and 15% yield respectively.† The ^{1}H n.m.r. spectra of these isomeric ($C_{32}H_{30}O_8$) compounds (**3**) and (**5**) are similar, each displaying 11 aromatic, 9 heterocyclic, and 2 methoxy resonances in agreement with their dimeric nature. This is also in agreement with mass spectrometry [*m/z* 542 (M^+)], with fragmentation dominated in both instances by flavanyl ions representing the constituent units [*m/z* 272 (88%), 270 (100%)], presuming hydrogen transfer. Corresponding results were obtained from the fully methylated ether derivatives (**4**) and (**6**) [*m/z* 598 (M^+)].

The points of bonding of the aforementioned derivatives (**4**) and (**6**) were differentiated by low-power decoupling of the multiplet, δ 2.71, attributed to 4-H_2(F) in the ^{1}H n.m.r. spectrum ($CDCl_3$) of the methyl ether (**4**), resulting in sharpening of an *ortho*-coupled doublet (δ 6.88, *J* 9.0 Hz). This indicates association of the methylene function with the aromatic ABX-system of the D-ring and, by inference, interflavanoid coupling with the 3'-position of the E-ring [B-ring equivalent of the parent isoflavan (**1**)] which exhibits *para*-coupled singlets. By contrast, similar decoupling of the multiplet, δ 2.74 [4-H_2(F)], of the isomeric methyl ether (**6**) results in selective sharpening of the *para*-coupled singlet [δ 6.59, *J* < 1 Hz, 5-H(D)], indicating interflavanoid bonding with the alternative nucleophilic 6-position of the D-ring [A-ring equivalent of the parent isoflavan (**1**)]. These long-range couplings are also evident in the homonuclear 2D shift-correlated spectra of the bi-isoflavanoids (**3**) and (**5**) with distinctive off-diagonal peaks occurring at the appropriate chemical shift co-ordinates [m, δ 2.70, 4-H_2(F) and d, δ 6.77, *J* 8.5 Hz, 5-H(D) for compound (**3**); m, δ 6.67, 4-H_2(F) and s, 6.55, 5-H(D) for compound (**5**)]. Confirmation of such diagnostic evidence was available from similar decoupling of the 3-protons (C- and F-rings) of the methyl ether derivatives (**4**) and (**6**) (m, δ 3.25—3.78 and δ 3.34—3.78), indicating in both instances connectivities with 6'-H(B) and 2'-H(E). These appear respectively as a doublet (δ 6.97, *J* 8.75 Hz) and a *para*-coupled singlet (δ 6.69, *J* < 1 Hz) for the former, (**4**), but as two doublets (δ 6.94 and 6.91, *J* 8.8 Hz) for the latter, (**6**).

With the [4,3']-linkage of the natural bi-isoflavanoid (**3**) and the [4,6]-linkage of its synthetic isomer (**5**) beyond doubt, the 3,4-*trans*-configuration (*J* 9.0 Hz) of substituents on the respective heterocyclic C-rings, assuming half-chair conformations, also define the absolute configurations as (3*S*,4*S*:3*S*) when taken in conjunction with their synthesis from compounds of known absolute configuration. C.d. spectra of both the natural (**3**) and synthetic products (**3**) and (**5**) were identical, the high-amplitude positive Cotton effect at 240 nm confirming the (4*S*)-configuration in terms of the aromatic quadrant rule.[6]

† The same condensation occurs photolytically (λ 300 nm, EtOAc), but is subject to reduced yields.



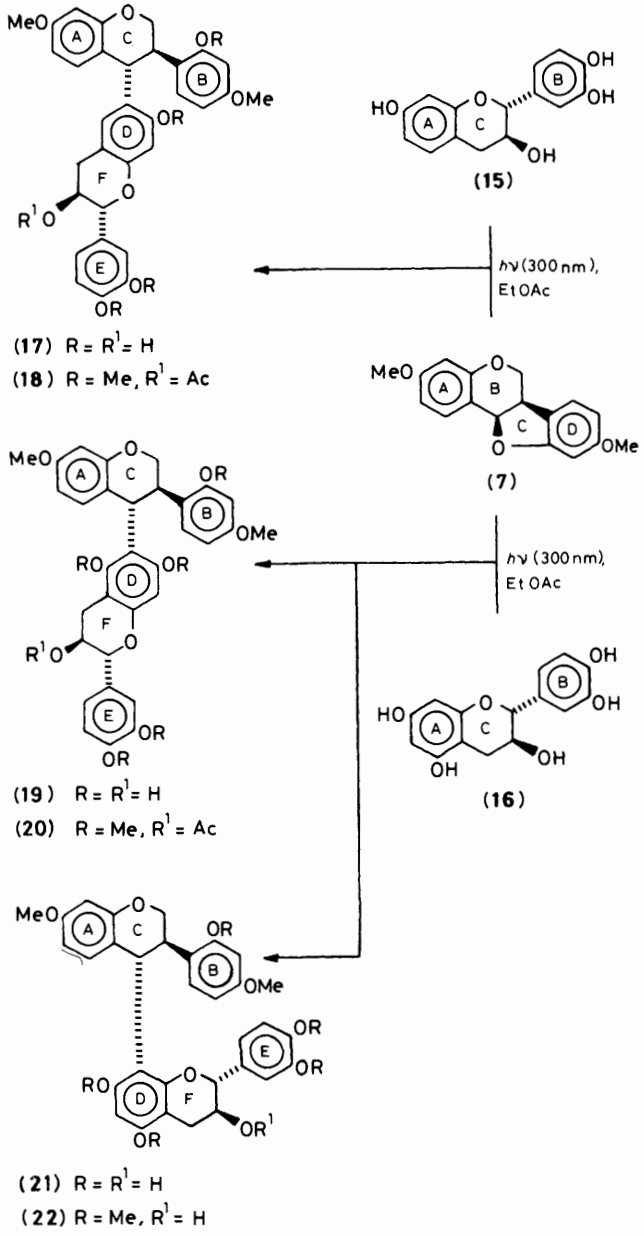
Scheme 2.

Results obtained during the above biomimetic synthesis are consistent with initial evidence illustrating the ability of the (6a*R*,11a*R*)-*cis*-pterocarpan (**7**) to act as prospective electrophile (*cf.* ref. 7) in the presence of 'nucleophilic' resorcinol and phloroglucinol to give the respective 3,4-*trans*-4-arylisoflavans (**9**) and (**11**) in 33 and 70% yield, respectively ($J_{3,4}$ 8.13 and 10.25 Hz), the latter accompanied by the disubstituted bis-(isoflavanyl)trihydroxybenzene (**13**) in low yield (Scheme 2). Preference for ready intermolecular condensation (*vs.* competitive intramolecular recyclization) is undoubtedly dictated by product stability, while reactivity is presumably enhanced by the considerable steric strain resulting from fusion of the heterocyclic B- and C-ring of the pterocarpan,[8,9] and also by the 'nucleophilicity' of the phenol, when applying mild acidic conditions.

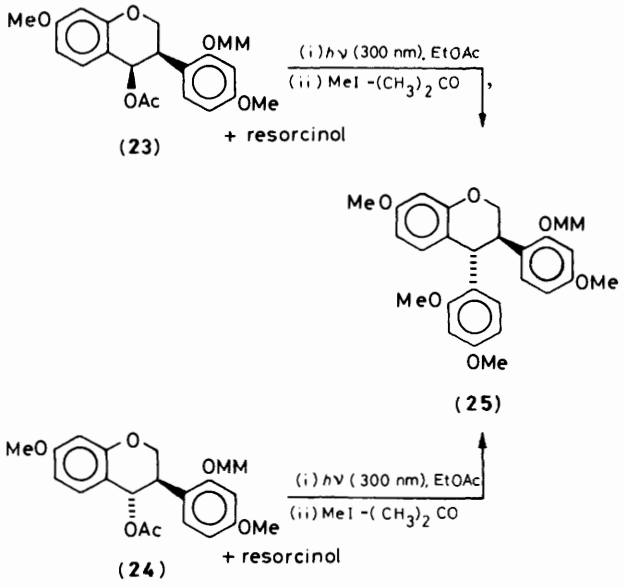
The regioselectivity displayed by the condensation of the pterocarpan (**2**) with the isoflavan (**1**) is in line with both regiospecificity and -selectivity evident from photolytic condensations of the pterocarpan (**7**) with (−)-fisetinidol (**15**) or (+)-catechin (**16**) to yield respectively the [4,6]-coupled dimer (**17**), or the [4,8]-coupled dimer (**21**) accompanied in low yield by its [4,6]-analogue (**19**) (Scheme 3; *cf.* refs. 5 and 10). Isolation of a single product as the methyl ether acetate (**18**) [*m/z* 656 (M^+); 4-H(C), d, δ 4.67, $J_{3,4}$ 8.75 Hz and 5-H(D), s, δ 6.61] from the former regiospecific reaction (**7**) + (**15**)→(**17**) leaves little doubt as to the complete dominance of the C-6 position of the fisetinidol unit as nucleophilic centre. Conversely, for the stereoselective condensation with (+)-catechin (**7**) + (**16**)→(**19**) + (**21**), yielding the respective derivatives (**20**) [*m/z* 686 (M^+); 4-H(C), d, δ 4.86, $J_{3,4}$ 7.50 Hz and 8-H(D), s, δ 6.24] and (**22**) [*m/z* 644 (M^+); 4-H(C), d, δ 4.95, $J_{3,4}$ 10.25 Hz and 6-H(D), s, δ 6.05] in the ratio of 1:3, 8-substitution predominates. Accordingly the sensitivity of electrophilic substitution reactions involving carbenium ions generated from pterocarpans to steric factors (*cf.* ref. 11) is in line with the observation that the nucleophilic sites provided by the bifunctional isoflavan (**1**) are, by analogy with resorcinol-type nucleophilic flavanoids, limited to C-6 and C-5′, the alternatives (C-8 and C-3′) being excluded.

The stereospecificity of condensations involving electrophilic 6a,11a-*cis*-pterocarpans with attendant inversion of configuration are the product of approach by the 'nucleophile' from the least hindered side of the pterocarpan (*cf.* refs. 8 and 9) and steric repulsion between the 3-phenyl group of the isoflavanyl-4-carbenium ion generated and the inserting electrophile. Significance of the latter is emphasised by photolytic condensation of resorcinol with 3,4-*cis*- (**23**) and 3,4-*trans*-4-acetoxyisoflavan (**24**) to yield a single product, the 3,4-*trans*-4-arylisoflavan (**25**) (Scheme 4).

The range of oligomeric isoflavanoids is extended to the 'trimeric' level by condensation of (−)-homopterocarpin (**7**) with (+)-vestitol (**1**), at elevated temperatures (40 °C, 21 h) to yield a single tri-isoflavanoid (**26**) accompanied by the anticipated [4,3′]- and [4,6]-bi-isoflavanoid (**28**) and (**30**), identified as their methyl ethers (**29**) and (**31**) [*m/z* 598 (M^+)] (Scheme 5). Differentiation between the triols (**28**) and (**30**) is confirmed by their respective syntheses *via* condensation of the pterocarpan (**7**) with either the isoflavan (**32**) (A-ring deactivated) or (**33**) (B-ring deactivated), thus leading to either (**29**) or (**31**) respectively, following methylation. The tri-isoflavanoid (**26**) is presumed to originate by elaboration of either or both bi-isoflavanoids (**28**) and (**30**) by further condensation with the pterocarpan unit (**7**), the proposed structure (**26**) being favoured since it allows for a common origin from both bi-isoflavanoid intermediates. Elements of the 500 MHz ^{1}H n.m.r. spectrum of the methyl ether



Scheme 3.



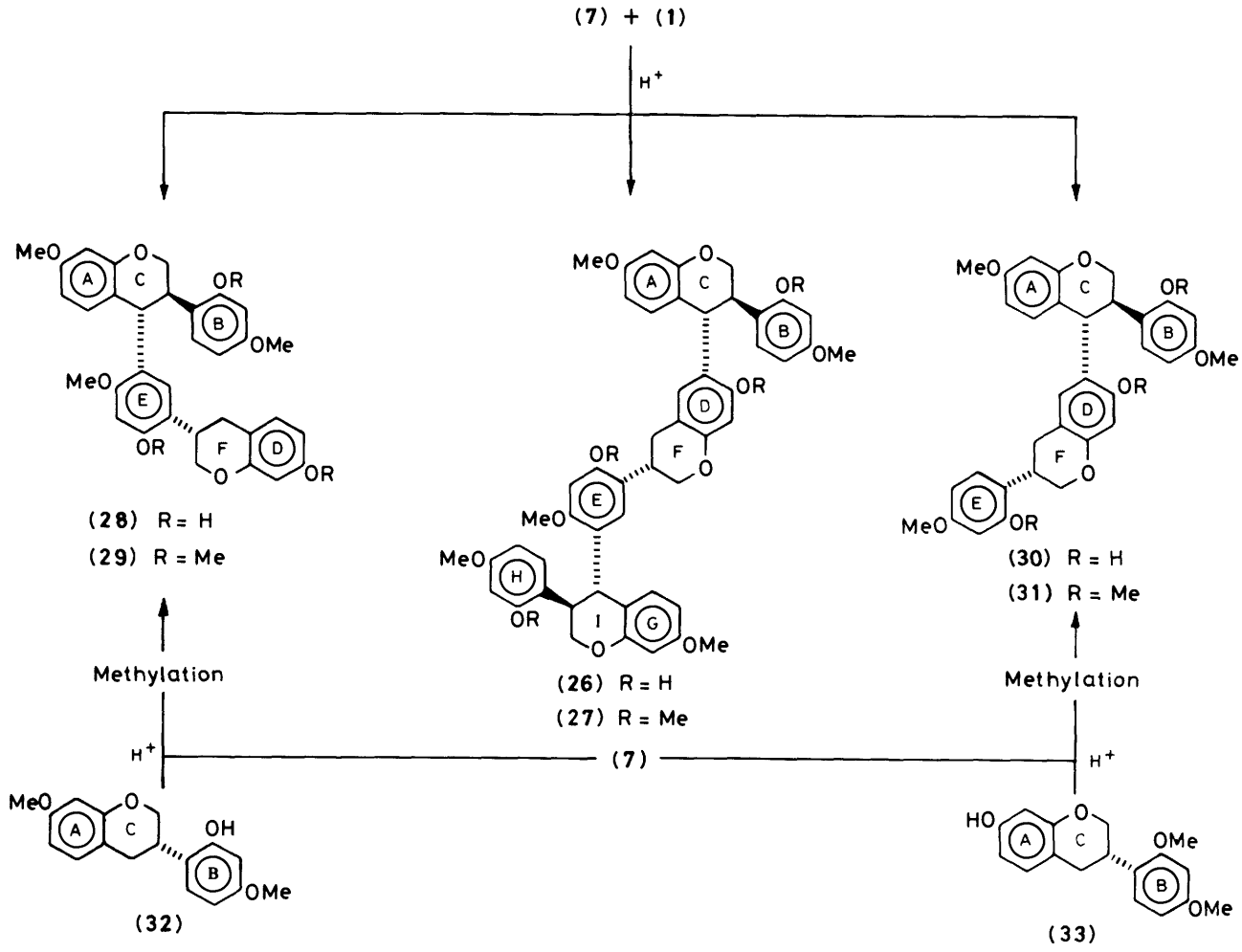
Scheme 4. MM = methoxymethyl

derivative (**27**) [*m/z* 896 (M^+)] are in line with the structure [two doublets, δ 4.89 and 5.01, $J_{3,4}$ 10.0 and 8.75 Hz, 4-H(C) and 4-H(I)]; low-power decoupling of a single methylene resonance (2 dd, δ 2.59 and 2.71, *J* 15.0 and 5.0 Hz and *J* 15.0 and 11.25 Hz) clearly indicating its association with 5-H(D) as the *para*-coupled singlet, δ 6.79, $J < 1$ Hz. Absence, however, of significant long-range benzylic coupling in other aromatic protons precludes determination of the coupling sequence. This was, however, accomplished by the synthesis of the methyl ether derivative of the tri-isoflavanoid, (**27**), by sequential two-step condensations of the pterocarpan (**7**) with selectively deactivated isoflavan and bi-isoflavan units (**34**) and (**36**), thus permitting regiospecific condensations leading to a single product (Scheme 6). This proved to be identical with the derivative (**27**) of the product obtained by direct condensation (Scheme 5). Condensation of (+)-vestitol (**1**) and (+)-medicarpin (**2**) under milder conditions (Scheme 1) similarly provides evidence of the formation of a single tri-isoflavanoid [*m/z* 812 (M^+)], shown to be a diastereoisomer of (**27**) following methylation.

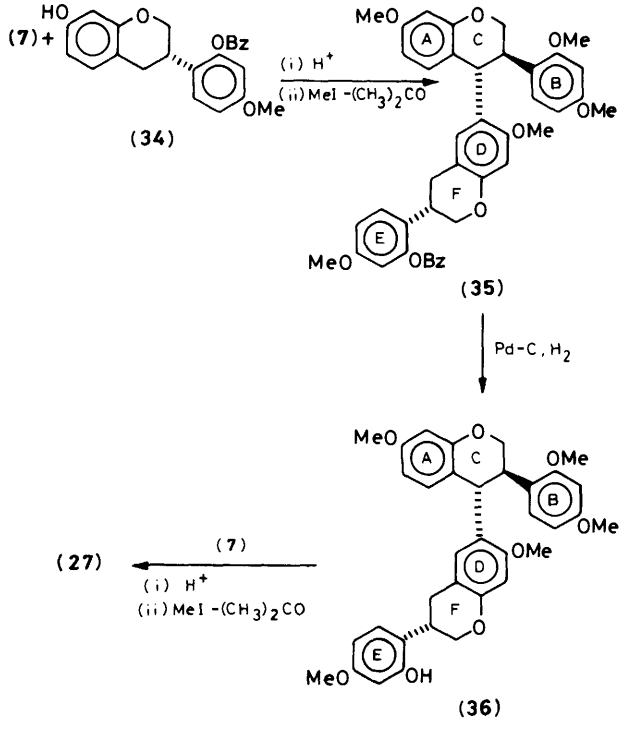
Although the pterocarpans (**2**) and (**7**) employed throughout these condensations possess nucleophilic resorcinol-type A- and D-rings, their inability to compete with the respective isoflavans as nucleophiles is apparent. Inhibition of self-condensation on the part of pterocarpans may be partly attributed to the obvious deactivation of the A rings through inductive electron-withdrawal by the benzylic 11a-oxygen, and the D rings by respective methylation and alkylation of their 9- and 11-oxygen functions. Alternatively the putative isoflavanyl carbenium ion intermediates [*e.g.* (**8**)] originating from the pterocarpans, while also promoting deactivation of their A rings, are presumably too unstable (short lived) to permit propagation of self-condensation *via* attack on the 'liberated' B-ring (pterocarpan D-ring equivalent). Such speculation is apparently confirmed by the excessive time required (168 h) for the self-condensation of (+)-medicarpin (**2**) under similar acid conditions at elevated temperatures (36 °C) to give the novel isoflavanoids (**37**), (**39**), and (**41**) in very low yields (2, 1, and 3% respectively) (Scheme 7). The two isoflavan–isoflav-3-ene products (**37**) and (**39**), characterized * as methyl ether derivatives (**38**) [*m/z* 596 (M^+); 4-H(C), d, δ 4.69, $J_{3,4}$ 8.75 Hz; 5-H(A), d, δ 6.66, $J_{5,6}$ 9.25 Hz; and 2′-H(E) s, δ 6.86] and (**40**) [*m/z* 596 (M^+); 4-H(C), d, δ 4.72, $J_{3,4}$ 8.50 Hz; 5-H(A), d, δ 6.73, $J_{5,6}$ 9.25 Hz; and 5-H(D), s, δ 6.63], are of interest; the former, (**37**), being related to the unique isoflavan–pterocarpan condensate (**41**) and the bi-isoflavan (**3**), and the latter, (**39**), to the bi-isoflavan (**5**). The isoflavan–pterocarpan (**41**) was characterized as its methyl ether (**42**) [*m/z* 582 (M^+); 4-H (C), d, δ 4.63, $J_{3,4}$ 9.00 Hz; 11a-H(E/F), d, δ 5.39, $J_{6a,11a}$ 6.25 Hz; and 7-H(G), s, δ 6.72]. The origin of the isoflavan–pterocarpan product (**41**) is obvious, while the isoflavan–isoflavenes could originate from the direct self-condensation of two isoflavan-4-carbenium ions, [*e.g.* (**37**)], or more likely *via* isoflavan–pterocarpan intermediates, [*e.g.* (**41**)→(**37**), and (**39**)].

Differentiation between the [4,6]- (**39**) and [4,3′]-coupled (**37**) isoflavene analogues was effected by condensation of the

* Sharp narrow doublets δ *ca.* 4.9 [*J* 1.1–1.2 Hz: allylic coupling attributable to to 2-H_2 resonances in their ^{1}H n.m.r. spectra) are highly diagnostic of flav-3-ene units (*cf.* A. J. Liepa, *Austr. J. Chem.*, 1981, **34**, 2647).



Scheme 5.



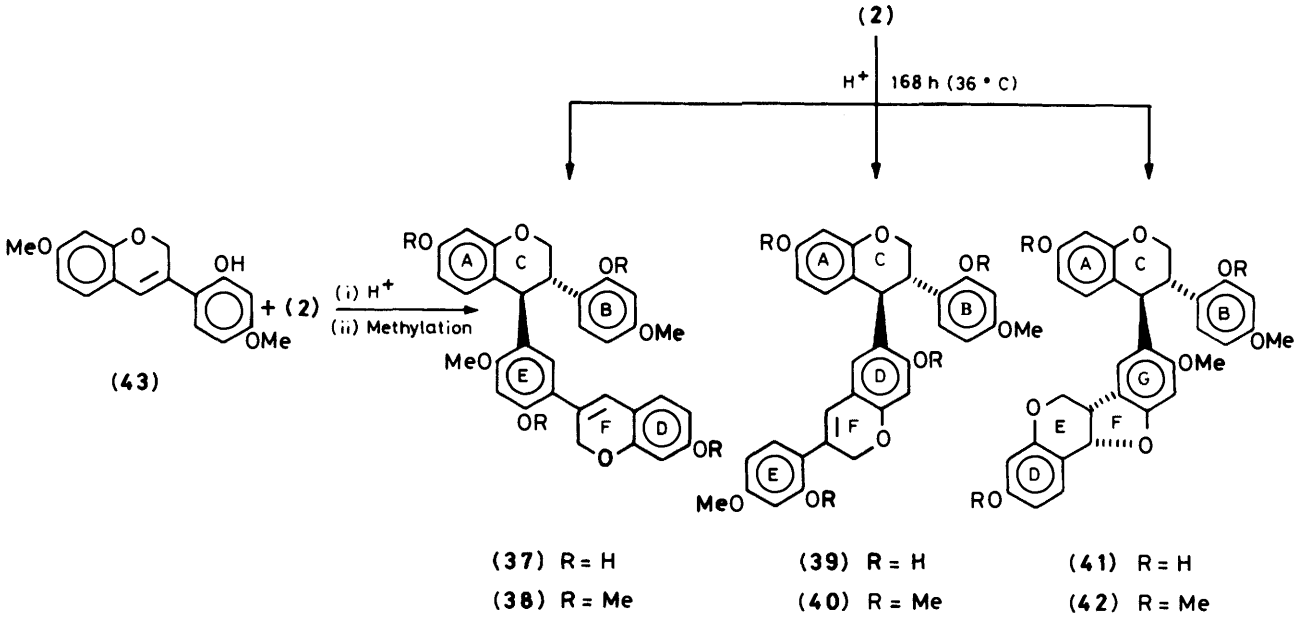
Scheme 6.

pterocarpan, (+)-medicarpin (**2**), with the synthetic isoflavene (**43**) in which the A-ring is deactivated by *O*-methylation (Scheme 7). The B-ring-coupled product after methylation, (**38**), provides proof of the identity of the parent compound (**37**), and hence also of its positional isomer (**39**), both originating from the self-condensation of the pterocarpan (**2**).

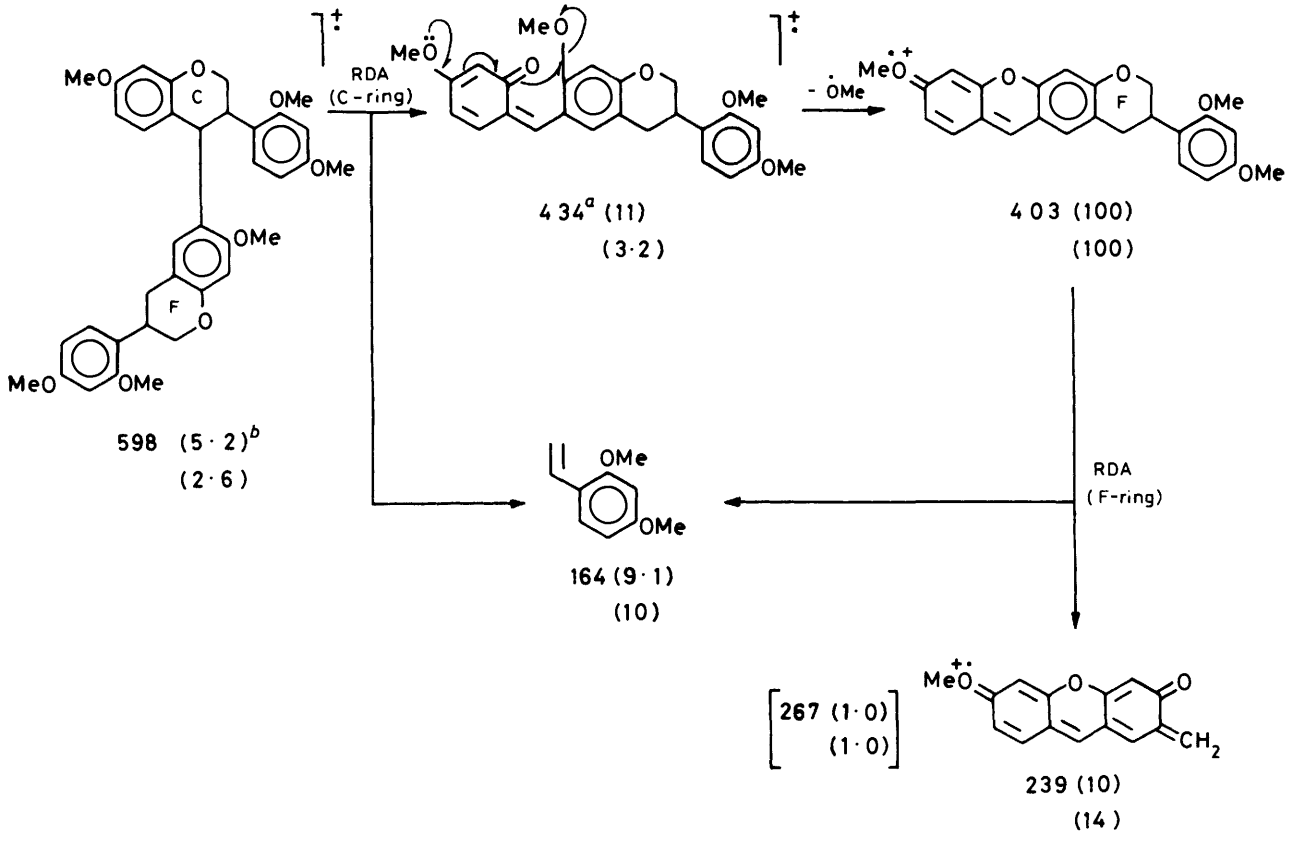
Diagnostic comparisons of the mass fragmentation spectra of the full methyl ether derivatives of the three classes of bi-isoflavanoids permit differentiation not only between [4,6]- and [4,3′]-bi-isoflavans (A- and B-ring-coupled, respectively) of identical mass (*m/z* 598, M^+) (Schemes 8 and 9), but also between analogues comprised of isoflavan, isoflavene, and pterocarpan 'lower' units, thus supplementing the obvious differences between their respective molecular ions (*m/z* 598, 596, and 582) (Scheme 10).

Mass spectra of the bi-isoflavan derivatives (**6**) and (**4**) may be rationalized by invoking preferential retro-Diels–Alder (RDA) fragmentation of the 'upper' heterocyclic C-ring,* followed by recyclization with attendant loss of a methoxyl radical (*cf.* analogous loss for 2′-methoxyisoflavones[12]) to furnish the same base peak (*m/z* 403) for structurally distinct ions in each instance (see m.s. fragmentation Schemes 8 and 9). These ions are accordingly subject to differing RDA fragmentations to give characteristic *m/z* 239 and 267 ions for the A- and B-ring-

* Biflavanoids by contrast are subject to preferential RDA fragmentation of their 'lower', F-rings (J. A. Delcour and G. M. Tuytens, *J. Chem. Soc., Chem. Commun.*, 1983, 1195)



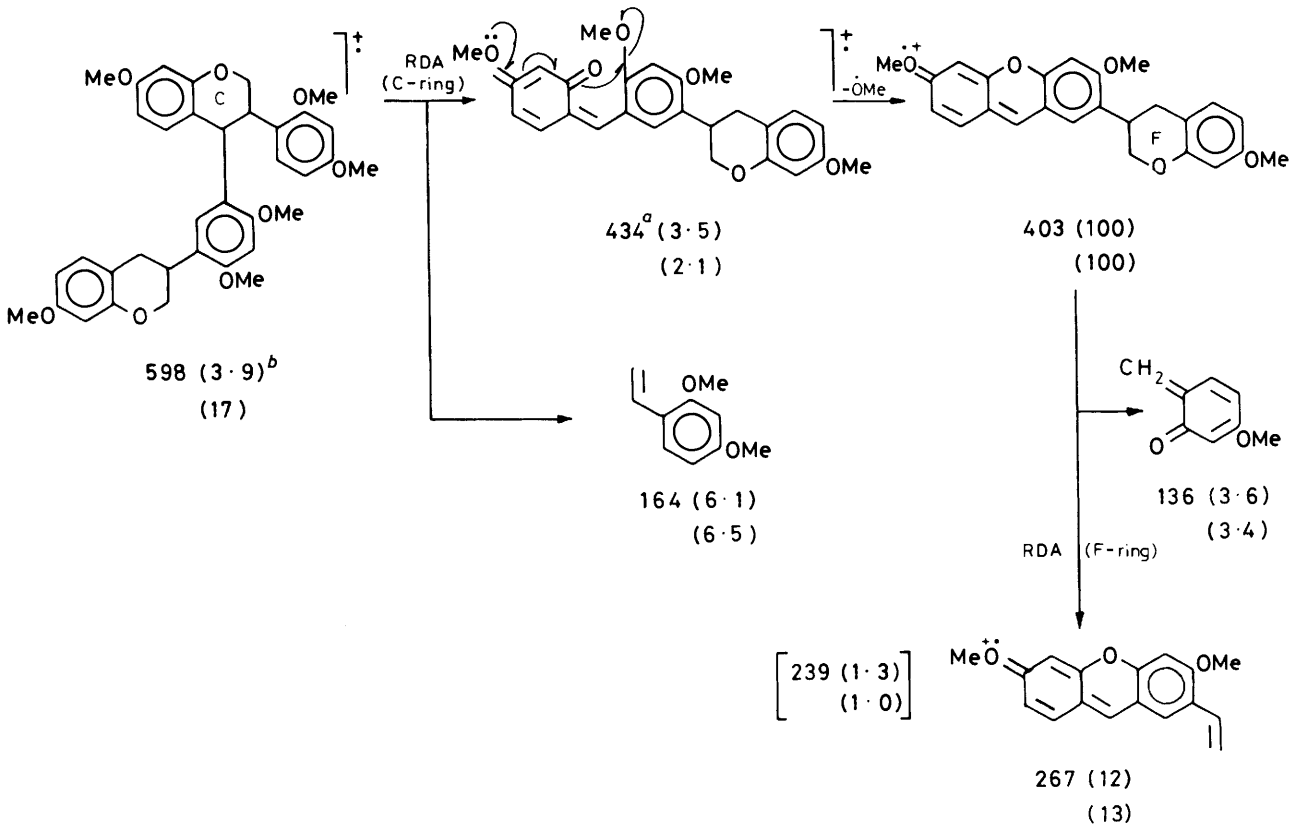
Scheme 7.



Scheme 8. A-Ring-coupled bi-isoflavanoids

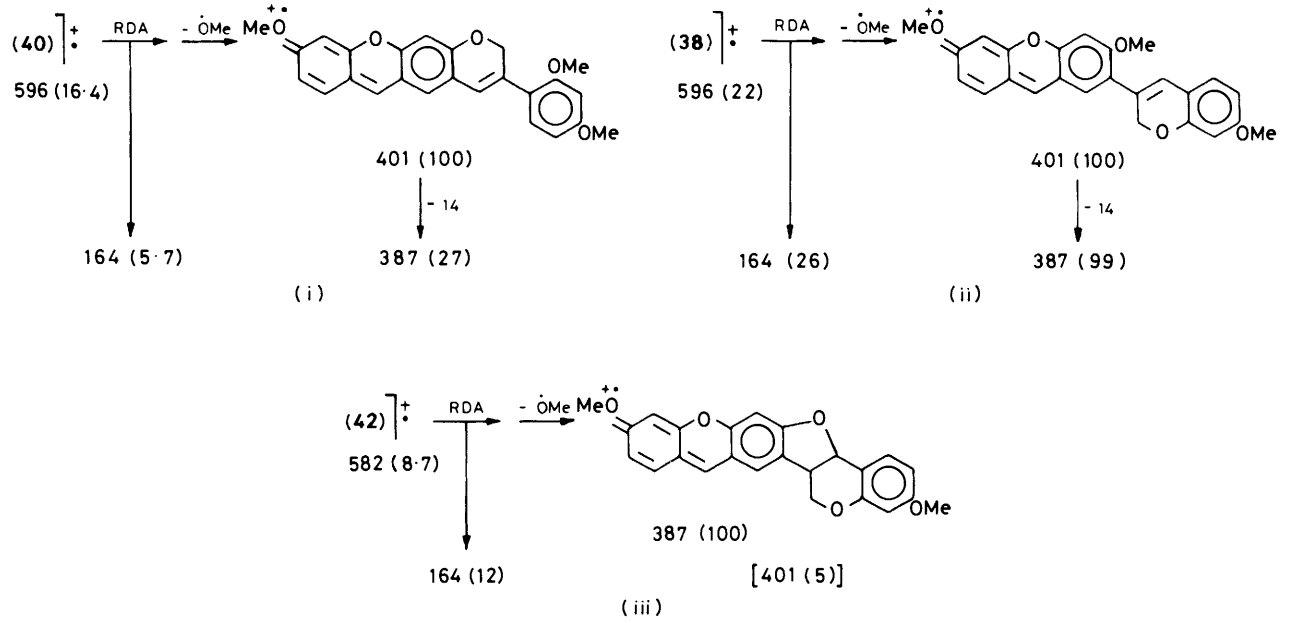
[a] At appearance potential. [b] Relative abundances are successively for the 3*S*, 4*S* and 3*R*, 4*R* series

coupled units (**6**) and (**4**) respectively. Similar initial fragmentation sequences may be postulated for the A- and B-ring-coupled isoflavene analogues (**40**) and (**38**) leading to their respective base peaks *m/z* 401 (Scheme 10). The structurally differing ions cannot be differentiated in this instance as they resist further fragmentation apart from methylene loss, further RDA fission being inhibited. Finally, the D-ring-coupled (B-ring equivalent) pterocarpan analogue (**42**) similarly provides a distinctive base peak at *m/z* 387 which also appears to be stable under the conditions of ionization (Scheme 10).



Scheme 9. B-Ring-coupled bi-isoflavanoids

[a] At appearance potential. [b] Relative abundances are successively for the 3*S*, 4*S* and 3*R*, 4*R* series



Scheme 10.

Base peaks from mass fragmentation spectra of (i) A-ring-coupled isoflavan–isoflavene, methyl ether derivative (**40**); (ii) B-ring-coupled isoflavan–isoflavene, methyl ether derivative (**38**); (iii) D-ring-coupled (B-ring equivalent) isoflavan–pterocarpan, methyl ether derivative (**42**)

Supplementary spectrometric differences between the series of fully *O*-methylated analogues follow from comparison of their c.d. spectra. The maxima of their low-wavelength and high-amplitude Cotton effects are very similar for bi- and tri-isoflavanoids (240 nm) and for the pterocarpan analogue (241.5 nm), but are subject to significant bathochromic shifts for the A- and B-ring-coupled isoflavene analogues (250 and 245 nm, respectively), possibly reflecting the extended conjugation of their stilbene-type chromophores.

In comparison with the bi-isoflavans the aforementioned isoflavene analogues each exhibit additional u.v. absorption at $\lambda_{max.}$ 330 nm in agreement with our observation for the isoflavene (**43**), and also the spectra of polymethoxystilbenes.[13] A selective hypochromic effect at $\lambda_{max.}$ 285 nm (log ε 3.47) of the [4,3′]-isoflavan–isoflavene derivative (**38**) relative to the corresponding absorption (log ε 3.86) of its [4,6]-isomer (**40**) also permits their differentiation.

The biomimetic synthesis of condensed isoflavanoids reported here provides access to hitherto unknown oligomeric isoflavans, their precursors being associated with phytoalexins displaying both antifungal[12-14] and antibacterial activity.[15-17]

Experimental

T.l.c. was performed on DC-Plastikfolin Kieselgel 60 F_{254} (0.25 mm) and compounds were located by H_2SO_4–HCHO (40 : 1) spray reagent. Preparative plates [Kieselgel PF_{254} (1.0 mm)] were not activated prior to use. Methylations were performed either with an excess of diazomethane in MeOH–diethyl ether at −15 °C for 48 h or a slight excess of MeI in dry acetone over K_2CO_3, while acetylations were carried out in acetic anhydride–pyridine. ^{1}H N.m.r. spectra were recorded on Bruker WP-80, WM-250, and WM-500 FT spectrometers with $SiMe_4$ as internal standard, mass spectral data on a Varian CH-5 instrument, and c.d. data on a JASCO J-20 spectropolarimeter. C and H analyses were performed by Analytische Laboratorien, Postfach 1249, D-5250 Engelskirchen, West Germany. In those instances where the available quantities were too low for elemental analysis, purity was assessed by ^{1}H n.mr. spectroscopy.

Extraction of the Heartwood of Dalbergia nitidula *Welw.* ex *Bak.*—Drillings (1 129.4 g) of the heartwood of *D. nitidula* were extracted with diethyl ether (6 × 2 l, 24 h each) followed by MeOH (7 × 2 l, 24 h each) producing, on evaporation of the solvents, a tan coloured resin (23.4 g) and a dark brown resin (150.2 g) respectively.

Isolation of (3S,4S)-3,4-trans-4-[(3S)-6′,7-*Dihydroxy*-4′-*methoxyisoflavan*-3′-*yl*]-2′,7-*Dihydroxy*-4′-*methoxyisoflavan* (**3**).—The methanol extract (20 g) of the heartwood of *D. nitidula* was fractionated by column chromatography [Merck Kieselgel 60; benzene–acetone–MeOH (7:2.5:0.5)] to yield a fraction of R_F 0.36 [t.l.c., benzene–acetone (7:3)] (1.22 g). This fraction was successively rechromatographed by column chromatography (Merck Kieselgel 60) using chloroform–MeOH (95:5), light petroleum (b.p. 60—80 °C)–acetone (55:45), and chloroform–MeOH (9:1) to give the crude [4,3′]-bi-isoflavan (**3**) (27 mg) which was purified by p.l.c. [R_F 0.36; benzene–acetone (7:3)] to give (3*S*,4*S*)]-3,4-*trans*-4-[(3*S*)-6′,7-dihydroxy-4′-methoxyisoflavan-3′-yl]-2′,7-dihydroxy-4′-methoxyisoflavan (**3**) as a solid (11 mg), *m/z* 542 (M^+, 8.1%), 393 (16), 274 (12), 273 (61), 272 (81), 271 (61), 270 (100), 268 (10), 256 (18), 150 (29), and 137 (7); δ (250 MHz; [$^2H_6$] acetone; 297 K) 2.62 [dd, *J* 15.56 and 5.81 Hz, 4-H_{eq}(F)], 2.78 [dd, *J* 15.56 and 12.45 Hz, 4-H_{ax}(F)], 3.36 [m, 3-H(F)], 3.63 and 3.68 (s, 2 OMe), 3.80 [m, 2-H_{ax}(F) and 3-H(C)], 4.14—4.19 [m, 2-H_2(C) and 2-H_{eq}(F)], 4.67 [d, *J* 9.33 Hz, 4-H(C)], 6.23 [d, *J* 2.39 Hz, 8-H(D)], 6.24 [dd, *J* 8.87 and 2.65 Hz, 6-H(A)], 6.26 [br s, 3′-H(B)], 6.28 [dd, *J* 8.51 and 2.74 Hz, 5′-H(B)], 6.32 [dd, *J* 8.42 and 2.39 Hz, 6-H(D)], 6.38 [d, *J* 2.65 Hz, 8-H(A)], 6.50 [d, *J* 8.87 Hz, 5-H(A)], 6.51 [br s, 5′-H(E)], 6.82 [br s, 2′-H(E)], 6.82 [d, *J* 8.42 Hz, 5-H(D)], and 7.01 [d, *J* 8.51 Hz, 6′-H(B)]; 2 D n.m.r. (^{1}H–^{1}H shift correlations) 2 × 4(F)–3(F), 3(F)–2 × 2(F), 2 × 4(F)–2 × 2(F), 4(C)–3(C), 3(C)–2(C), 8(A)–6(A), 6(A)–5(A), 5(A)–8(A), 2′(E)–5′(E), 6(D)–5(D), 6′(B)–5′(B), 4(C)–5(A), and 4(F)–5(D).

(3S,4S)-3,4-trans-2′,4′,7-*Trimethoxy*-4-[(3S)-4′,6′,7-*trimethoxyisoflavan*-3′-*yl*]*isoflavan* (**4**). Methylation (MeI) of compound (**3**) (10 mg) followed by p.l.c. purification [hexane–benzene–acetone (50:45:5), × 3] produced the methyl ether derivative (**4**) (R_F 0.63) as cubes from methanol (8 mg), m.p. 139 °C (Found: C, 72.1; H, 6.4. $C_{36}H_{38}O_8$ requires C, 72.2; H, 6.4%); *m/z* 598 (M^+, 4.0%), 404 (27), 403 (100), 267 (12), 164 (6.1), 151 (4.1), 149 (5.0), and 121 (6.9); δ (80 MHz; $CDCl_3$; 363 K) 2.65—2.98 [m, 4-H_2(F)], 3.25—3.78 [m, 3-H(C + F)], 3.66, 3.67, 3.72 (× 2), 3.75, and 3.78 (each s, together 6 OMe), 3.78—4.50 [m, 2-H_2(C + F)], 4.66 [d, *J* 9.00 Hz, 4-H(C)], 6.25—6.53 [m, 6- and 8-H(A + D), 3′- and 5′-H(B) and 5′-H(E)], 6.63 [d, *J* 8.75 Hz, 5-H(A)], 6.69 [s, 2′-H(E)], 6.88 [d, *J* 8.75 Hz, 5-H(D)], and 6.97 [d, *J* 8.75 Hz, 6′-H(B)]; c.d. (*c* 0.3090 in MeOH) $[\theta]_{300}$ 0, $[\theta]_{290}$ − 0.22 × 10^4, $[\theta]_{282}$ −0.10 × 10^4, $[\theta]_{275}$ −0.14 × 10^4, $[\theta]_{264}$ 0, $[\theta]_{240}$ 1.16 × 10^4, $[\theta]_{228}$ 0, $[\theta]_{224}$ −0.14 × 10^4, $[\theta]_{220}$ − 0.08 × 10^4, and $[\theta]_{215}$ −0.16 × 10^4; $\lambda_{max.}$(MeOH) 210, 220sh, and 282 nm.

General Condensation and Work-up Procedures for Acid-catalysed Condensations.—The pterocarpan (6a*S*,11a*S*)-3-hydroxy-9-methoxypterocarpan [(+)-medicarpin][4] (**2**) or (6a*R*,11a*R*)-3,9-dimethoxypterocarpan [(−)-homopterocarpin][18] (**7**) and an appropriate nucleophile were dissolved in acidic (3M HCl) aqueous ethanol and the solution was stirred at constant temperature within the range 20—50 °C for 12—168 h. The solution was extracted with EtOAc (4 × 50 ml) and the combined extracts were dried (Na_2SO_4) after treatment with a minimum of aqueous sodium hydrogen carbonate. Evaporation of the solvent followed by p.l.c. afforded the condensed products.

Photolytic Condensations.—The pterocarpan [(**2**) or (**7**)] and a nucleophile were dissolved in a minimum volume of dry ($MgSO_4$) EtOAc and irradiated at 300 nm for *ca.* 20 h under N_2. The products were isolated by p.l.c. following evaporation of the solvent.

Condensations.

(i) *Condensation of* (—)-*Homopterocarpin* (**7**) *with Resorcinol.*—A solution of (—)-homopterocarpin (**7**) (200 mg) and resorcinol (200 mg) in 50% aqueous EtOH (50 ml) and 0.5M HCl (2.5 ml) was stirred at 50 °C for 12 h. A single product (**9**) (104 mg) was obtained by p.l.c. [R_F 0.41; hexane–chloroform–MeOH (2:7:1)].

(3R,4R)-3,4-trans-4-(2,4-*Dimethoxyphenyl*)-2′,4′,7-*trimethoxyisoflavan* (**10**). Purification of the product, following methylation of crude (**9**) with MeI, by p.l.c. [R_F 0.49; hexane–benzene–acetone (5:4:1)] gave the methyl ether (**10**) as *small cubes* (90 mg), m.p. 66 °C (Found: C, 71.3; H, 6.5. $C_{26}H_{28}O_6$ requires C, 71.5; H, 6.5%); *m/z* 436 (M^+, 2.6%), 271 (4.4), 242 (28), 241 (100), 164 (14), 149 (12), and 121 (12); δ (80 MHz; $CDCl_3$; 363 K) 3.51, 3.54, 3.59 (× 2), and 3.61 (each s, together 5 OMe), 3.42—3.73 [m, 3-H(C)], 3.92—4.20 [m, 2-H_2(C)], 4.53 [d, *J* 8.13 Hz, 4-H(C)], 6.05—6.27 [m, 6-and 8-H(A) and 3′,- and 5′-H(B + D)], 6.41 [d, *J* 7.50 Hz, 5-H(A)], 6.61 [d, *J* 8.75 Hz, 6-H(D)], and 6.77 [d, *J* 8.75 Hz, 6′-H(B)]; c.d. (*c* 0.2260 in MeOH) $[\theta]_{300}$ 0, $[\theta]_{270}$ 0.39 × 10^4, $[\theta]_{250}$ 0, $[\theta]_{240}$ −1.06 × 10^4, $[\theta]_{230}$ − 0.26 × 10^4, $[\theta]_{225}$ −0.44 × 10^4, and $[\theta]_{215}$ 0.

Photolytic condensation of (—)-homopterocarpin (**7**) (100 mg) with resorcinol (100 mg) in dry EtOAc (16 ml) for 20 h gave the identical product (**10**) (93 mg) following methylation with MeI.

(ii) *Condensation of* (−)-*Homopterocarpin* (**7**) *with Phloroglucinol.*—The pterocarpan (**7**) (500 mg) and phloroglucinol (500 mg) were dissolved in 50% aqueous EtOH (100 ml) and 0.5M HCl (5 ml) and the solution was stirred at 50 °C for 12 h. Two products, (**11**) (R_F 0.30; 693 mg) and (**13**) (R_F 0.46; 141 mg), were obtained by p.l.c. [hexane–chloroform–MeOH (2:7:1)].

(3R,4S)-3,4-trans-2′,4′,7-*Trimethoxy*-4-(2,4,6-*trimethoxyphenyl*)*isoflavan* (**12**). The product (**11**) was methylated (MeI) and the product was purified by p.l.c. [R_F 0.49; hexane–benzene–acetone (5:4:1)] to yield compound (**12**) as *small cubes* (510 mg), m.p. 64 °C (Found: C, 69.3; H, 6.4. $C_{27}H_{30}O_7$ requires C, 69.5; H 6.5%); *m/z* 466 (M^+, 3.6%), 272 (18), 271 (100), 164 (8.0), 121 (5.1), and 59 (10); δ (80 MHz; $CDCl_3$; 363 K) 3.39 (×2), 3.51, 3.57 (×2), and 3.59 (each s, together 6 OMe), 3.95—4.23 [m, 2-H_2(C) and 3-H(C)], 4.83 [br d, *J* 10.25 Hz, 4-H(C)], 5.83 [s, 3- and 5-H(D)], 6.02—6.24 [m, 6-and 8-H(A) and 3′- and 5′-*H*[B)], 6.36 [d, *J* 8.00 Hz, 5-H(A)], and 6.83 [d, *J* 8.50 Hz, 6′-H(B)]; c.d. (*c* 0.2480 in MeOH) $[\theta]_{290}$ 0, $[\theta]_{265}$ 0.68 × 10^4, $[\theta]_{250}$ 0, $[\theta]_{240}$ −1.09 × 10^4, $[\theta]_{230}$ −0.01 × 10^4, $[\theta]_{225}$ −0.27 × 10^4, and $[\theta]_{215}$ 0.

1,3,5-*Trimethoxy*-2,4-*bis*-[(3R,4S)-3,4-trans-2′,4′,7-*trimethoxyisoflavan*-4-*yl*]*benzene* (**14**). Methylation (MeI) of (**13**) followed by p.l.c. [hexane–benzene–acetone (5:4:1)] gave the methyl ether (**14**) (R_F 0.34) as a solid (80 mg) (Found: C, 70.5; H, 6.4. $C_{45}H_{48}O_{11}$ requires C, 70.6; H, 6.3%); *M/z* 764 (M^+, 5.8%) 571 (13), 570 (64), 569 (100), 431 (3.5), 375 (15), 359 (20), 164 (13), 151 (16), and 121 (13); δ [80 MHz; $(CD_3)_2SO_4$]; 423 K 3.03, 3.44 (×2), 3.63 (×2), 3.67 (×2), and 3.70 (each s, together 9 OMe), 4.03—4.31 [m, 2-H_2(C + F) and 3-H(C + F)], 4.64 [br d, *J* 10.00 Hz, 4-H(C + F)], 6.15—6.53 [m, 5-, 6-, and 8-H(A + D), 3′-and 5′-H(B + C) and 6-H(G)], and 6.94 [d, *J* 8.13 Hz, 6′-*H*[B + E)]; c.d. (*c*) 0.2120 in MeOH) $[\theta]_{300}$ 0, $[\theta]_{275}$ −1.00 × 10^4, $[\theta]_{255}$ −0.30 × 10^4, $[\theta]_{240}$ 3.68 × 10^4, $[\theta]_{225}$ −0.06 × 10^4, $[\theta]_{220}$ −0.46 × 10^4, and $[\theta]_{215}$ 0.

Both products, (**12**) (83 mg) and (**14**) (21 mg), were also obtained by photolysis of the pterocarpan (**7**) (100 mg) with phloroglucinol (100 mg) in dry EtOAc (16 ml) for 20 h followed by methylation (MeI).

(iii) *Condensation of* (−)-*Homopterocarpin* (**7**) *with* (−)-*Fisetinidol* (**15**).—Photolytic condensation of (−)-homopterocarpin (**7**) (100 mg) with (−)-fisetinidol (**15**) (150 mg) in dry EtOAc (10 ml) for 40 h yielded a single product (**17**) (40 mg) which was isolated by p.l.c. [R_F 0.34; hexane–chloroform–MeOH (2:7:1)].

(3R,4R)-3,4-trans-4-[(2R,3S)-2,3-trans-3-*Acetoxy*-3′,4′,7-*trimethoxyflavan*-6-*yl*]-2′,4′,7-*trimethoxyisoflavan* (**18**). The product (**17**) was methylated (diazomethane) and the product was purified by p.l.c. [R_F 0.47; hexane–chloroform–MeOH (20:79:1), ×2] and acetylated to give the methyl ether acetate (**18**) as a solid (19 mg) (Found: C, 69.6; H, 6.3. $C_{38}H_{40}O_{10}$ requires C, 69.5; H, 6.1%); *m/z* 656 (M^+, 17%), 462 (43), 461 (96), 419 (24), 317 (13), 302 (31), 298 (13), 287 (18), 281 (13), 273 (13), 272 (47), 239 (10), 180 (31), 168 (34), 165 (11), 164 (14), 154 (14), 153 (24), *152* (100), 151 (33), 149 (18), 136 (13), 124 (60), 123 (14), 122 (31), and 121 (17); δ (80 MHz; $CDCl_3$; 363 K) 1.85 [s, 3-OAc(F)], 2.63 [dd, *J* 15.63 and 6.88 Hz, 4-H_{ax}(F)], 2.90 [dd, *J* 15.63 and 5.00 Hz, 4-H_{eq}(F)], 3.41—3.75 [m, 3-H(C)], 3.61, 3.65, 3.70, 3.71, 3.75, and 3.81 (each s, together 6 OMe), 4.01—4.55 [m, 2-H_2(C)], 4.67 [d, *J* 8.75 Hz, 4-H(C)], 4.89 [d, *J* 6.88 Hz, 2-H(F)], 5.11—5.36 [m, 3-H(F)], 6.24—6.46 [m, 6- and 8-H(A), 3′- and 5′-H(B), and 8-H(D)], 6.61 [s, 5-H(D)], 6.65 [d, *J* 8.13 Hz, 5-H(A)], 6.80—6.93 [m, 2′-, 5′-, and 6′-H(E)], and 6.96 [d, *J* 8.75 Hz, 6′-*H*(B)]; c.d. (*c* 0.2250 in MeOH) $[\theta]_{300}$ 0.030 × 10^4, $[\theta]_{290}$ 0.10 × 10^4, $[\theta]_{283}$ 0.03 × 10^4, $[\theta]_{270}$ 0.17 × 10^4, $[\theta]_{247}$ 0, $[\theta]_{235}$ −0.62 × 10^4, $[\theta]_{225}$ −0.06 × 10^4, $[\theta]_{220}$ −0.16 × 10^4, and $[\theta]_{215}$ −0.06 × 10^4.

(iv) *Condensation of* (−)-*Homopterocarpin* (**7**) *with* (+)-*Catechin* (**16**).—Photolysis of the pterocarpan (**7**) (100 mg) and (+)-catechin (**16**) (200 mg) in dry EtOAc (10 ml) for 25 h produced two products, (**21**) (R_F 0.37; 81 mg) and (**19**) (R_F 0.54; 36 mg) following p.l.c. separation [chloroform–MeOH (85:15)].

(3R,4S)-3,4-trans-4-[(2R,3S)-2,3-trans-3-*Hydroxy*-3′,4′,5,7-*tetramethoxyflavan*-8-*yl*]-2,′4′,7-*trimethoxyisoflavan* (**22**). The product (**21**) was methylated (MeI) and purified by p.l.c. [R_F 0.41; hexane–benzene–acetone (4:4:2), ×2] to yield the methyl ether (**22**) as a solid (40 mg) (Found: C, 68.1; H, 6.3. $C_{37}H_{40}O_{10}$ requires C, 68.2; H, 6.2%); *m/z* 644 (M^+, 43%), 626 (3.6), 506 (3.9), 464 (27), 463 (38), 451 (35), 450 (53), 449 (100), 431 (8.0), 314 (17), 313 (36), 301 (13), 299 (13), 297 (15), 285 (14), 284 (13), 283 (35), 272 (34), 271 (47), 270 (40), 269 (69), 255 (12), 254 (12), 253 (17), 241 (31), 239 (10), 232 (16), 226 (11), 180 (28), 179 (19), 165 (30), 164 (49), 163 (37), 152 (16), 151 (40), 149 (29), 137 (20), and 121 (36); δ (80 MHz; $CDCl_3$; 373 K) 2.51 [dd, *J* 16.25 and 8.13 Hz, 4-H_{ax}(F)], 2.95 [dd, *J* 16.25 and 5.63 Hz, 4-H_{eq}(F)], 3.57, 3.61, 3.73 (×2), 3.76 (×2) and 3.86 (each s, together 7 OMe), 4.01—4.42 [m, 2-H_2(C) and 3-H(C + F)], 4.58 [d, *J* 7.75 Hz, 2-H(F)], 4.95 [d, *J* 10.25 Hz, 4-H(C)], 6.05 [s, 6-H(D)], 6.24—6.49 [m, 3′-and 5′-H(B) and 6- and 8-H(A)], 6.65 [d, *J* 8.13 Hz, 5-H(A)], 6.66—6.71 [m, 2′- and 5′-H(E)], 6.77 [d, *J* 8.13 Hz, 6′-H (E)], and 7.05 [d, *J* 8.75 Hz, 6′-H(B)]; c.d. (*c* 0.2220 in MeOH) $[\theta]_{290}$ 0, $[\theta]_{283}$ −0.10 × 10^4, $[\theta]_{279}$ 0, $[\theta]_{270}$ 0.35 × 10^4, $[\theta]_{255}$ 0, $[\theta]_{237}$ −2.90 × 10^4, and $[\theta]_{210}$ 0.

(3R,4S)-3,4-trans-4-[(2R,3S)-2,3-trans-3-*Acetoxy*-3′,4′,5,7-*tetramethoxyflavan*-6-*yl*]-2′,3′,7-*trimethoxyisoflavan* (**20**). Impure (**19**) was separated by p.l.c. [R_F 0.35; hexane–chloroform–MeOH (2:7:1), ×2] and methylated with diazomethane. P.l.c. purification [hexane–chloroform–MeOH (40:55:5)] of the product gave the methyl ether (R_F 0.56; 14 mg) which was acetylated and the product purified by p.l.c [hexane–benzene–acetone (4:4:2), ×2] to yield the monoacetate (**20**) (R_F 0.41) as a solid (13 mg) (Found: C, 68.2; H, 6.3. $C_{39}H_{42}O_{11}$ requires C, 68.2; H, 6.2%); *m/z* 686 (M^+, 3.5%), 505 (14), 492 (40), 491 (100), 449 (19), 270 (13), 269 (64), 164 (14), 151 (26), and 121 (11); δ (80 MHz; $CDCl_3$; 365 K) 1.85 [s, 3-OAc(F)], 2.63 [dd, *J* 16.00 and 7.75 Hz, 4-H_{ax}(F)], 3.01 [dd, *J* 16.00 and 5.50 Hz, 4-H_{eq}(F)], 3.26, 3.51, 3.64, 3.73, 3.75, 3.82, and 3.86 (each s, together 7 OMe), 4.14—4.37 [m, 2-H_2(C) and 3-H(C)], 4.86 [2 d, *J* 7.50 Hz, 2-H(F) and 4-H(C)], 5.11—5.36 [m, 3-H(F)], 6.24 [s, 8-H(D)], 6.25—6.45 [m, 3′, and 5′-H(B) and 6- and 8-H(A)], 6.65 [d, *J* 8.75 Hz, 5-H(A)], 6.87—6.93 [m, 2′-, 5′-, and 6′-H(E)], and 7.05 [d, *J* 8.75 Hz, 6′-H(B)]; c.d. (*c* 0.2420 in MeOH) $[\theta]_{290}$ 0, $[\theta]_{280}$ −0.30 × 10^4, $[\theta]_{260}$ 0, $[\theta]_{240}$ −1.10 × 10^4, and $[\theta]_{215}$ 0.

(v) *Condensation of* (−)-*Homopterocarpin* (**7**) *with* (+)-*Vestitol* (**1**).—(3*S*)-2′,7-Dihydroxy-4′-methoxyisoflavan [(+)-vestitol][3] (**1**) (200 mg), $\lambda_{max.}$(MeOH) (log ε) 206 (4.44) and 282 nm (3.70), [obtained by catalytic hydrogenation (10% Pd–C in EtOH) of (+)-medicarpin (**2**)[4]], and (−)-homopterocarpin (**7**) (200 mg) were dissolved in a mixture of EtOH (10 ml) and 3M HCl (5 ml) and the mixture was stirred for 21 h at 40 °C. Separation of the products by p.l.c. [hexane–chloroform–MeOH (30:67:3)] gave two fractions, R_F 0.35 (146 mg) and R_F 0.28 (120 mg).

(3R,4R)-3,4-trans-2′,4′,7-*Trimethoxy*-4-[(3S)-2′,4′,7-*trimethoxyisoflavan*-6-*yl*]*isoflavan* (**31**). The fraction with R_F 0.35 was methylated (MeI) and the product was purified by p.l.c. [hexane–benzene–MeOH (5:4:1)] to yield compound (**31**) (R_F 0.59) as *cubes* from methanol (42 mg), m.p. 102 °C (Found: C, 72.1; H, 6.4. $C_{36}H_{38}O_8$ requires C, 72.2; H, 6.4%); *m/z* 598 (M^+,

2.6%), 404 (37), 403 (100), 239 (14), 164 (11), 151 (21), and 121 (18); δ (80 MHz; $CDCl_3$; 303 K) 2.79 [m, 4-H_2(F)], 3.34—3.68 [m, 3-H(C + F)], 3.70, 3.75, 3.76, 3.78, and 3.79 (×2) (each s, together 6 OMe), 3.86—4.51 [m, 2-H_2(C + F)], 4.75 [d, *J* 8.13 Hz, 4-H(C)], 6.33—6.50 [m, 6- and 8-H(A), 3'- and 5'-H(B + E), and 8-H(D)], 6.65 [s, 5-H(D)], 6.77 [d, *J* 8.75 Hz, 5-H(A)], 6.96 [d, *J* 8.75 Hz, 6'-H(E)], and 7.04 [d, *J* 8.13 Hz, 6'-H(B)]; c.d. (*c* 0.1972 in MeOH) $[\theta]_{300}$ 0, $[\theta]_{299}$ 0.42 × 10^4, $[\theta]_{275}$ 0.04 × 10^4, $[\theta]_{260}$ 0, $[\theta]_{240}$ −1.68 × 10^4, $[\theta]_{230}$ −0.56 × 10^4, $[\theta]_{220}$ −1.62 × 10^4, and $[\theta]_{210}$ −0.16 × 10^4; $\lambda_{max.}$(MeOH) (log ε) 209 (4.71) and 285 nm (3.98).

(3R,4R)-3,4-trans-2',4',7-*Trimethoxy*-4-[(3S)-4',6',7-*trimethoxyisoflavan*-3'-yl]*isoflavan* (**29**). Following methylation (MeI) of the fraction R_F 0.28 the product was separated by p.l.c. [hexane–benzene–acetone (5:4:1)] into two compounds, (**27**) and (**29**). The latter, (**29**), (R_F 0.44) was obtained as *cubes* from methanol–acetone (27 mg), m.p. 89 °C (Found: C, 72.1; H, 6.5. $C_{36}H_{38}O_8$ requires C, 72.2; H, 6.4%); *m/z* 598 (M^+, 2.3%), 404 (29), 403 (100), 267 (13), 164 (6.5), 151 (5.4), and 121 (8.5); δ (80 MHz; $CDCl_3$; 303 K) 2.70—3.07 [m, 4-H_2(F)], 3.26—3.61 [m, 3-H(C + F)], 3.73 (×2), 3.76, 3.77 (×2), and 3.82 (each s, together 6 OMe), 3.83—4.25 [m, 2-H_2(C + F)], 4.70 [d, *J* 8.75 Hz, 4-H(C)], 6.32—6.54 [m, 6- and 8-H(A + D), 3'- and 5'-H(B), and 5'-H(E)], 6.66 [d, *J* 8.13 Hz, 5-H(A)], 6.69 [s, 2'-H(E)], 6.96 [d, *J* 8.13 Hz, 5-H(D)], and 7.01 [d, *J* 8.75 Hz, 6'-H(B)]; c.d. (*c* 0.2404 in MeOH) $[\theta]_{300}$ 0, $[\theta]_{290}$ 0.36 × 10^4, $[\theta]_{278}$ 0, $[\theta]_{250}$ −0.08 × 10^4, $[\theta]_{240}$ −0.68 × 10^4, $[\theta]_{235}$ −0.46 × 10^4, $[\theta]_{230}$ −1.30 × 10^4, $[\theta]_{223}$ −0.42 × 10^4, $[\theta]_{215}$ −0.66 × 10^4, and $[\theta]_{210}$ −0.04 × 10^4.

(3S)-2',4',7-*Trimethoxy*-5',6-*bis*-[(3R,4R)-3,4-trans-2',4',7-*trimethoxyisoflavan*-4-yl]*isoflavan* (**27**). The trimer (**27**), obtained from the methylated (MeI) fraction with R_F 0.28 by p.l.c. (R_F 0.32) as indicated above, was purified by h.p.l.c. [waters μ-porasil (300 × 4 mm) in hexane–dichloroethane–MeOH (45:54.95:0.05); retention time 16 min at a flow rate of 2 ml min^{-1}] to yield a *solid* (30 mg) (Found: C, 72.2; H, 6.4. $C_{54}H_{56}O_{12}$ requires C, 72.3; H, 6.3%); *m/z* 896 (M^+, 7.7%), 731 (13), 703 (16), 702 (52), 701 (100), 596 (5.0), 568 (20), 537 (15), 460 (13), 433 (22), 404 (29), 403 (96), 297 (9.0), 271 (22), 269 (11), 268 (14), 267 (69), 239 (20), 164 (35), 151 (55), 149 (25), 137 (18), and 121 (28); δ (500 MHz; C_6D_6; 353 K) 2.50 [dd, *J* 15.00 and 5.00 Hz, 4-H_{eq}(F)], 2.71 [dd, *J* 15.00 and 11.25 Hz, 4-H_{ax}(F)], 3.22, 3.27, 3.31, 3.32 (×2), 3.34, 3.36, 3.37, and 3.39 (each s, together 9 OMe), 3.45—3.54 [m, 3-H(F)], 3.68 [dd, *J* 10.63 and 10.00 Hz, 2-H_{ax}(F)], 4.06—4.19 [m, 3-H(C + I) and 2-H_{eq}(F)], 4.28—4.48 [m, 2-H_2(C + I)], 4.89 and 5.01 [2 d, *J* 10.00 and 8.75 Hz, 4-H(C) and 4-H(I)], 6.11, 6.45, and 6.83 [3 s, 8-H(D), 3'-H(E), and 6'-H(E)], 6.79 [s, 5-H(D)], 6.27 and 6.49 [2 dd, *J* 9.38 and 1.89 Hz and *J* 9.38 and 1.89 Hz, 6-H(A), 5'-H(B), 6-H(G), and 5'-H(H)], 6.28, 6.33, 6.71, and 6.73 [4 d, each *J* 1.89 Hz, 8-H(A), 3'-H(B), 8-H(G), and 3'-H(H)], and 6.82, 6.93, 7.04, and 7.19 [4 d, *J* 9.38, 8.75, and 8.75 Hz, 5-H(A), 6'-H(B), 5-H(G), and 6'-H(H)]; c.d. (*c* 0.3450 in MeOH) $[\theta]_{300}$ 0, $[\theta]_{291}$ 0.4 × 10^4, $[\theta]_{270}$ 0, $[\theta]_{245}$ −1.35 × 10^4, $[\theta]_{230}$ −0.48 × 10^4, $[\theta]_{225}$ −0.86 × 10^4, $[\theta]_{210}$ −0.12 × 10^4.

Photolysis of (−)-homopterocarpin (**7**) (200 mg) and (+)-vestitol (**1**) (200 mg) in dry EtOAc (8 ml) for 6 h gave only the dimers (**29**) (15 mg) and (**31**) (30 mg) after methylation (MeI) and separation of the products.

(vi) *Condensation of* (−)-*Homopterocarpin* (**7**) *with* (3S)-7-*Hydroxy*-2',4'-*dimethoxyisoflavan* (**33**).—7-*O*-Methoxymethylmedicarpan (700 mg), derived by methoxymethylation (CH_3OCH_2Cl–Adogen 464)[19] of (+)-medicarpin (**2**) (1.2 g),[4] was hydrogenated (10% Pd–C in EtOH) and hydrolysed (3M HCl–EtOH; 80 °C for 1 h) to the isoflavan (**33**) (350 mg) following methylation (MeI). The isoflavan (**33**) (200 mg) and (−)-homopterocarpin (**7**) (100 mg) were dissolved in 67% aqueous EtOH (15 ml) and 3M HCl (5 ml) and the solution was stirred for 24 h at 40 °C. The product (23 mg) was obtained by successive p.l.c. separations in hexane–chloroform–MeOH (30:67:3) (R_F 0.43) and hexane–benzene–acetone (4:4:2) (R_F 0.41). Methylation (MeI) followed by p.l.c. purification [hexane–benzene–acetone (5:4:1)] gave the methyl ether (**31**) (R_F 0.46) as cubes (21 mg), m.p. 102 °C, identical in all respects with product (**31**) from condensation (v).

(vii) *Condensation of* (−)-*Homopterocarpin* (**7**) *with* (3S)-2'-*Hydroxy*-4',7-*dimethoxyisoflavan* (**32**).—The isoflavan (**32**) (200 mg), prepared by methylation (MeI) followed by hydrogenation (10% Pd–C in EtOH) of (+)-medicarpin (**2**),[4] was condensed with the pterocarpan (**7**) (100 mg) under identical conditions as outlined above (vi). The product (31 mg) was separated by p.l.c. [hexane–chloroform–MeOH (30:67:3); R_F 0.30], methylated (MeI), and the product purified by p.l.c. [hexane–benzene–acetone (50:45:5), ×3] to yield the methyl ether (**29**) (R_F 0.54) as cubes (30 mg), m.p. 89 °C, identical in all respects with product (**29**) from condensation (v).

(viii) *Condensation of* (+)-*Medicarpin* (**3**) *with* (+)-*Vestitol* (**1**).—(+)-Medicarpin (**2**) (100 mg) and (+)-vestitol (**1**) (200 mg)[3] were dissolved in 70% aqueous EtOH (11 ml), 3M HCl (5 ml) was added, and the mixture was stirred for 20 h at 30 °C. The condensation produced two products, (**3**) (R_F 0.36) and (**5**) (R_F 0.46), after separation by p.l.c. [benzene–acetone (7:3)].

(3S,4S)-3,4-trans-4-[(3S)-6',7-*Dihydroxy*-4'-*methoxyflavan*-3'-*yl*]-2',7-*dihydroxy*-4'-*methoxyisoflavan* (**3**). The [4,3']-bi-isoflavan (**3**) was obtained as a solid (40 mg), identical in all respects with the natural product (**3**) isolated from *D. nitidula*.

(3S,4S)-3,4-trans-2',4'7-*Trimethoxy*-4-[(3S)-4',6',7-*trimethoxyisoflavan*-3'-*yl*]*isoflavan* (**4**). Methylation (MeI) of compound (**3**) (38 mg) followed by p.l.c. purification [hexane–benzene–acetone (50:45:5), ×3] gave the hexamethyl ether (**4**) (R_F 0.63) as *cubes* (34 mg), m.p. 139 °C, identical in all respects with the methyl ether derivative (**4**) of the natural product (**3**) from *D. nitidula*.

(3S,4S)-3,4-trans-4-[(3S)-2',7-*Dihydroxy*-4'-*methoxyisoflavan*-6-*yl*]-2',7-*dihydroxy*-4'-*methoxyisoflavan* (**5**). The second product (**5**) from condensation (viii) was obtained as a solid (30 mg), *m/z* 542 (M^+, 1.2%), 272 (32), 270 (45), 269 (21), 255 (19), 151 (15), 150 (100), 149 (17), 148 (13), 138 (16), 137 (41), 135 (22), 134 (10), 123 (11), and 121 (10); δ (250 MHz; [$^2H_6$]acetone; 297 K) 2.66 [dd, *J* 16.20 and 5.54 Hz, 4-H_{eq}(F)], 2.84 [dd, *J* 16.20 and 11.51 Hz, 4-H_{ax}: (F)], 3.40 [m, 3-H (F)], 3.64 [m, 3-H(C) and OMe], 3.69 (s, OMe), 3.90 [dd, *J* 10.23 and 10.23 Hz, 2-H_{ax}(F)], 4.10—4.29 [m, 2-H_2 (C) and 2-H_{eq} (F)], 4.70 [d, *J* 7.67 Hz, 4-H (C)], 6.28 [dd, *J* 8.55 and 2.85 Hz, 5'-H(B)], 6.30 [d, *J* 2.28 Hz, 8-H(A)], 6.31 [dd, *J* 8.83 and 2.28 Hz, 6-H(A)], 6.33 [br s, 8-H(D)], 6.38 [dd, *J* 8.50 and 2.75 Hz, 5'-H(E)], 6.40 [d, *J* 2.85 Hz, 3-H(B)], 6.46 [d, *J* 2.75 Hz, 3'-H(E)], 6.56 [br s, 5-H(D)], 6.64 [d, *J* 8.83 Hz, 5-H(A)], 7.00 [d, *J* 8.50 Hz, 6'-H(E)], and 7.20 [d, *J* 8.55 Hz, 6'-H(B)]; 2D n.m.r. (^1H–^1H shift correlations (2 × 4(F)–3(F), 3(F)–2 × 2(F), 2 × 4(F)–2 × 2(F), 4(C)–3(C), 3(C)–2 × 2(C), 3'(B)–5'(B), 5'(B)–6'(B), 5(A)–6(A), 3'(E)–5'(E), and 5'(E)–6'(E).

(3S,4S)-3,4-trans-2',4',7-*Trimethoxy*-4-[(3S)-3',4',7-*trimethoxyisoflavan*-6-*yl*]*isoflavan* (**6**). Methylation (MeI) of the [4,6]-bi-isoflavan (**5**) (26 mg) gave the methyl ether (**6**) which was purified by p.l.c. [hexane–benzene–acetone (50:45:5), ×3; R_F 0.67] to yield *cubes* from methanol–acetone (23 mg), m.p. 143 °C (Found: C, 72.1; H, 6.5. $C_{36}H_{38}O_8$ requires C, 72.2; H, 6.4%); *m/z* 598 (M^+, 5.2%), 404 (29), 403 (100), 239 (10), 164 (9.1), 151 (16), and 121 (13); δ (80 MHz; $CDCl_3$; 363 K) 2.63—2.84 [m, 4-H_2(F)], 3.34—3.78 [m, 3-H(C + F)], 3.61, 3.70, 3.73, 3.76, 3.78, and 3.79 (each s, together 6 OMe), 3.76—4.56 [m, 2-H_2(C + F)],4.66 [d, *J* 8.75 Hz, 4-H(C)], 6.25—6.50 [m, 6- and 8-H(A), 3'- and 5'-H(B + E) and 8-H(D)], 6.59 [s, 5-H(D)], 6.66

[d, *J* 9.00 Hz, 5-H(A)], 6.91 [d, *J* 8.75 Hz, 6'-H(E)], and 6.94 [d, *J* 8.75 Hz 6'-H(B)]; c.d. (*c* 0.2730 in MeOH) $[\theta]_{300}$ 0, $[\theta]_{290}$ -0.25×10^4, $[\theta]_{280}$ -0.14×10^4, $[\theta]_{258}$ 0, $[\theta]_{240}$ 1.85×10^4, $[\theta]_{224}$ 0, $[\theta]_{220}$ -0.22×10^4, and $[\theta]_{215}$ 0.

An identical pair of bi-isoflavans, (**3**) (12 mg) and (**5**) (11 mg), were obtained by photolysis of (+)-medicarpin (**2**) (100 mg) and (+)-vestitol (**1**) (200 mg) in dry EtOAc (6 ml) for 60 h.

(ix) *Self-condensation of* (+)-*Medicarpin* (**2**).—(+)-Medicarpin was stirred in 50% aqueous EtOH (10 ml) with 3 M HCl (0.1 ml) for 168 h at 36 °C to yield a mixture of three self-condensed products, (**37**), (**39**), and (**41**), obtained as a mixture (R_F *ca.* 0.13; 52 mg) by p.l.c. [hexane–chloroform–MeOH (30:65:5)]. This mixture was separated into three components, (**38**) (R_F 0.44), (**40**) (R_F 0.51), and (**42**) (R_F 0.58), by p.l.c. [hexane–benzene–acetone (5:4:1), ×2] after methylation (MeI).

(3S,4S)-3,4-trans-2',4',7-*Trimethoxy*-4-(4',6',7-*trimethoxyisoflav*-3-*en*-3'-*yl*)*isoflavan* (**38**). Isolated as a solid (4 mg) (Found: C, 72.3; H, 6.3. $C_{36}H_{36}O_8$ requires C, 72.5; H, 6.1%); *m/z* 596 (M^+, 22%), 582 (22), 463 (4.7), 421 (18), 418 (11), 417 (15), 415 (11), 403 (11), 402 (26), 401 (100), 389 (6), 388 (28), 387 (99), 372 (6.8), 371 (5.9), 357 (6.4), 299 (11), 298 (5.5), 297 (21), 286 (4.4), 285 (19), 283 (6.5), 271 (6.9), 165 (6.6), 164 (27), 161 (5.4), 151 (21), 149 (16), 137 (6.2), and 121 (27); δ (80 MHz; $CDCl_3$; 303 K) 3.56—4.00 [m, 3-H(C)], 3.69 (×2), 3.72, 3.75 (×2), and 3.78 (each s, together 6 OMe), 4.13—4.41 [m, 2-H_2(C)], 4.69 [d, *J* 8.75 Hz, 4-H(C)], 4.89 [d, *J* 1.1 Hz, 2-H_2(F)], 6.28—6.53 [m, 6- and 8-H(A + D), 3'- and 5'-H(B), 5'-H(E), and 4-H(F)], 6.66 [d, *J* 9.25 Hz, 5-H(A)], 6.86 [s, 2'-H(E)], 6.89 [d, *J* 9.00 Hz, 5-H(D)], and 6.98 [d, *J* 9.00 Hz, 6'-H(B)]; c.d. (*c* 0.2590 in MeOH) $[\theta]_{300}$ 0, $[\theta]_{290}$ 0.20×10^4, $[\theta]_{280}$ 0, $[\theta]_{275}$ -0.08×10^4, $[\theta]_{270}$ 0, $[\theta]_{245}$ 1.20×10^4, $[\theta]_{232}$ 0, $[\theta]_{225}$ -0.5×10^4, and $[\theta]_{220}$ 0; $\lambda_{max.}$(MeOH) (log ε) 205 (4.51), 285 (3.47), and 330 nm (3.78).

(3S,4S)-3,4-trans-2',4',7-*Trimethoxy*-4-(2',4',7-*trimethoxyisoflav*-3-*en*-6-*yl*)*isoflavan* (**40**). Isolated as a solid (2 mg) (Found: C, 72.2; H, 6.2. $C_{36}H_{36}O_8$ requires C, 72.5; H, 6.1%); *m/z* 596 (M^+, 16.4%), 582 (3.9), 403 (8.2), 402 (30), 401 (100), 388 (7.4), 387 (27), 229 (3.4), 164 (5.7), 151 (4.1), 149 (5.3), and 121 (7.5); δ (80 MHz; $CDCl_3$; 303 K) 3.52—3.95 [m, 3-H(C)], 3.69, 3.72, 3.75, 3.77, 3.78, and 3.81 (each s, together 6 OMe), 4.13—4.34 [m, 2-H_2(C)], 4.72 [d, *J* 8.50 Hz, 4-H(C)], 4.93 [d, *J* 1.1 Hz, 2-H_2(F)], 6.27—6.59 [m, 6- and 8-H(A), 3'- and 5'-H(B + E), 8-H(D), and 4-H(F)], 6.63 [s, 5-H(D)], 6.73 [d, *J* 9.25 Hz, 5-H(A)], 7.00 [d, *J* 8.75 Hz, 6'-H(E)], and 7.19 [d, *J* 9.00 Hz, 6'-H(B)]; c.d. (*c* 0.2590 in MeOH) $[\theta]_{290}$ 0, $[\theta]_{285}$ -0.12×10^4, $[\theta]_{280}$ 0, $[\theta]_{250}$ 0.96×10^4, $[\theta]_{235}$ 0, and $[\theta]_{215}$ -0.60×10^4; $\lambda_{max.}$(MeOH) (log ε) 203 (4.55), 283 (3.86), and 330 nm (3.84).

(3S,4S)-3,4-trans-4-[(6aS,11aS)-3,9-*Dimethoxypterocarpan*-8-*yl*]-2',4',7-*trimethoxyisoflavan* (**42**). Compound (**42**) was obtained as a solid (6 mg) (Found: C, 71.7; H, 6.1. $C_{35}H_{34}O_8$ requires C, 72.1; H, 5.9%); *m/z* 582 (M^+, 8.7%), 580 (3.1), 421 (5.9), 401 (5.0), 389 (11), 388 (57), 387 (100), 385 (11), 297 (7.5), 164 (12), 151 (9.0), 149 (13), and 121 (12); δ (80 MHz; $CDCl_3$; 363 K) 3.25—3.56 [m, 6a-H(E/F), 6-H_{ax}(E)], 3.59, 3.66, 3.72, and 3.75 (×2) (each s, together 5 OMe), 3.69—3.88 [m, 3-H(C)], 3.95—4.09 [m, 6-H_{eq}(E)], 4.17—4.47 [m, 2-H_2(C)], 4.63 [d, *J* 9.00 Hz, 4-H(C)], 5.39 [d, *J* 6.25 Hz, 11a-H(E/F)], 6.25—6.44 [m, 6- and 8-H(A), 3'- and 5'-H(B), 4-H(D), and 10-H(G)], 6.56 [dd, *J* 8.50 and 2.50 Hz, 2-H(D)], 6.63 [d, *J* 8.00 Hz, 5-H(A)], 6.72 [s, 7-H(G)], 6.94 [d, *J* 9.25 Hz, 6'-H(B)], and 7.34 [d, *J* 8.50 Hz, 1-H(D)]; c.d. (*c* 0.1960 in MeOH) $[\theta]_{300}$ -0.48×10^4, $[\theta]_{290}$ -1.36×10^4, $[\theta]_{265}$ 0, $[\theta]_{240}$ 4.12×10^4, and $[\theta]_{210}$ 0.

Photolysis of (+)-medicarpin (**2**) (150 mg) in dry EtOAc (4 ml) for 80 h produced only compound (**42**) (4 mg) following separation and methylation of the products as indicated above.

(x) *Condensation of* (+)-*Medicarpin* (**2**) *with* 2'-*Hydroxy*-4',7-*dimethoxyisoflav*-3-ene (**43**).—2'-*Hydroxy*-4',7-*dimethoxyisoflav*-3-*ene* (**43**). (−)-Homopterocarpin (7) (500 mg) and toluene-*p*-sulphonic acid (10 mg) in benzene (200 ml) were refluxed for 2 h and the solvent was evaporated. P.l.c. separation [hexane–benzene–acetone (5:4:1)] gave the isoflavene (**43**) (R_F 0.33) as a solid (130 mg), *m/z* 284 (M^+, 100%), 283 (45), 269 (28), 161 (16), 148 (27), and 133 (14); δ (80 MHz; $CDCl_3$; 303 K) 3.72 and 3.75 (each s, together 2 OMe), 4.97 (d, *J* 1.1 Hz, 2-H_2), 5.75 (s, 2'-OH), 6.36—6.64 (m, 3'-,4-,5'-,6-, and 8-H), 6.95 (d, *J* 9.38 Hz, 6'-H), and 7.09 (d, *J* 8.13 Hz, 5-H); $\lambda_{max.}$(MeOH) (log ε) 203 (4.49), 280 (3.98), and 322 nm (3.93).

(3S,4S)-3,4-trans-2',4',7-*Trimethoxy*-4-(4',6',7-*trimethoxyisoflav*-3-*en*-3'-*yl*)*isoflavan* (**38**). (+)-Medicarpin (**2**) (130 mg) and the isoflavene (**43**) (120 mg) were dissolved in 80% aqueous EtOH (15 ml) and 3M HCl (3 ml), and the solution was stirred for 60 h at 28 °C. Separation by p.l.c. [R_F 0.37; benzene–acetone (8:2)] followed by methylation (MeI) and subsequent purification by p.l.c. [hexane–benzene–acetone (5:4:1)] produced the methyl ether (**38**) (R_F 0.41) as a solid (3 mg), identical with the product (**38**) obtained by condensation (ix).

Synthesis of 3,4-cis-(**23**) *and* 3,4-trans-4-*Acetoxy*-4',7-*dimethoxy*-2'-*methoxymethoxyisoflavan* (**24**) *and their respective Condensations with Resorcinol.*—(3R)-4',7-*Dimethoxy*-2'-*methoxymethoxyisoflavanone.* (6a*R*,11a*R*)-3,9-Dimethoxypterocarpan [(−)-homopterocarpin] (**7**) (500 mg) was hydrogenated (10% Pd–C in EtOH) to the corresponding (3*R*)-2'-hydroxy-4',7-dimethoxyisoflavan (480 mg) which was purified by p.l.c. [R_F 0.18; hexane–dichloroethane (2:8)]. Methoxymethylation (CH_3OCH_2Cl–Adogen 464)[19] of a portion of this product (375 mg) yielded the 4'-*O*-methoxymethyl analogue (250 mg) [R_F 0.59; hexane–benzene–acetone (5:4:1)] which was subsequently oxidized on being stirred with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (400 mg) in MeOH (AR, 40 ml) for 36 h at *ca.* 25 °C. Evaporation of the solvent followed by p.l.c. purification [hexane–benzene–acetone (5:4:1)] gave the 4',7-dimethoxy-2'-methoxymethoxyisoflavanone (R_F 0.39) as a solid (150 mg), *m/z* 344 (M^+, 35%), 315 (22), 299 (24), 283 (35), 195 (23), 194 (100), 177 (14), 165 (12), 163 (17), 162 (35), 161 (36), 151 (27), 150 (18), 149 (64), and 121 (28); δ (80 MHz; $CDCl_3$; 304 K) 3.41 (s, OCH_2OCH_3), 3.75 and 3.84 (each s, together 2 OMe), 4.22 (dd, *J* 10.63 and 5.63 Hz, 2-H_{ax}), 4.34—4.78 (m, 2-H_{eq} and 3-H), 5.13 (s, OCH_2OCH_3), 6.38—6.75 (m, 3'-,5'-,6-, and 8-H), 7.03 (d, *J* 8.13 Hz, 6'-H), and 7.91 (d, *J* 8.75 Hz, 5-H).

3,4-cis-4-*Acetoxy*-4',7-*dimethoxy*-2'-*methoxymethoxyisoflavan* (**23**). 4',7-Dimethoxy-2'-methoxymethoxyisoflavanone (150 mg) was dissolved in dry THF–EtOH (1:1) (20 ml) and the solution was stirred with $NaBH_4$ (200 mg) for 12 h at *ca.* 25 °C. Acetone (100 ml) was added, and following evaporation of the solvent, water (50 ml) was added and the mixture extracted with EtOAc (3 × 20 ml). The combined extracts were washed with water (10 × 20 ml), dried (Na_2SO_4), and the solvent was evaporated. Two products, (R_F 0.38; 57 mg) and (R_F 0.28; 49 mg), were obtained by p.l.c. separation [hexane–benzene–acetone (5:4:1), ×2]. Acetylation of the former (R_F 0.38) product gave compound (**23**) as cubes from ethanol-acetone (61 mg), m.p. 120 °C; *m/z* 388 (M^+, 6.3%), 328 (32), 284 (44), 283 (100), 269 (12), 194 (36), 161 (20), and 149 (16); δ (80 MHz; $CDCl_3$; 304 K) 1.81 (s, 4-OAc), 3.47 (s, OCH_2OCH_3), 3.78 (s, 2 OMe), 3.66—3.91 (m, 3-H), 4.28 (dd, *J* 10.00 and 3.75 Hz, 2-H_{eq}), 4.58 (dd, *J* 10.00 and 12.50 Hz, 2-H_{ax}), 5.19 (s, OCH_2OCH_3), 6.13 (d, *J* 3.10 Hz, 4-H), 6.41—6.59 (m, 5'-,6-, and 8-H), 6.72 (d, *J* 2.50 Hz, 3'-H), 6.92 (d, *J*, 8.75 Hz, 6'-H), and 7.27 (d, *J* 8.75 Hz, 5-H).

3,4-trans-4-*Acetoxy*-4',7-*dimethoxy*-2'-*methoxymethoxyisoflavan* (**24**). Acetylation of the second product (R_F 0.28) from the above reduction yielded compound (**24**) as a solid (52 mg), *m/z* 388 (M^+, 46%), 328 (47), 285 (51), 284 (100), 283 (72), 270 (22), 269 (45), 268 (16), 195 (41), 194 (71), 181 (31), 179 (30), 162 (49),

161 (59), 152 (41), 151 (50), 150 (45), 149 (56), and 121 (44); δ (80 MHz; $CDCl_3$; 304 K) 2.03 (s, 4-OAc), 3.50 (s, OCH_2OCH_3), 3.41—3.66 (m, 3-H), 3.72 and 3.75 each (s, together 2 OMe), 4.41 (m, 2-H_2), 5.19 (s, OCH_2OCH_3), 6.19 (d, *J* 4.75 Hz, 4-H), 6.31—6.56 (m, 5'-,6-, and 8-H), 6.69 (, *J* 2.50 Hz, 3'-H), 6.97 (d, *J* 8.75 Hz, 6'-H), and 7.19 (d, *J* 8.75 Hz, 5-H).

(3R,4R)-3,4-trans-4-(2,4-*Dimethoxyphenyl*)-4',7-*dimethoxy*-2'-*methoxymethoxyisoflavan* (**25**). Photolytic condensation of compound (**24**) (50 mg) with resorcinol (50 ml) in dry EtOAc (5 ml) for 32 h gave a single product (30 mg) (R_F 0.46) following isolation by p.l.c. [hexane–chloroform–MeOH (2:7:1)]. Methylation (MeI) and purification by p.l.c. [hexane–benzene–acetone (5:4:1)] afforded the methyl ether derivative (**25**) (R_F 0.44) as *cubes* from ethanol–acetone (25 mg), m.p. 132 °C (Found: C, 69.5; H, 6.5. $C_{27}H_{30}O_7$ requires C, 69.5; H, 6.5%); *m/z* 466 (M^+, 6.7%), 273 (3.8), 272 (3.4), 271 (3.4), 242 (21), 241 (100), 161 (3.1), 151 (6.0), 149 (3.5), 137 (6.7), and 121 (5.5); δ (80 MHz; $CDCl_3$; 303 K) 3.41 (s, OCH_2OCH_3), 3.66, 3.70, 3.72, and 3.75 (each s, together 4 OMe), 3.59—3.88 (m, 3-H(C)], 4.13—4.34 [m, 2-H_2(C)], 4.72 [d, *J* 8.75 Hz, 4-H(C)], 5.00—5.13 [m, OCH_2OCH_3], 6.25—6.50 [m, 6- and 8-H(A), 3- and 5-H(D), and 5'-H(B)], 6.64 [d, *J* 2.50 Hz, 3'-H(B)], 6.72 [d, *J* 8.13 Hz, 5-H(A)], 6.86 [d, *J* 8.75 Hz, 6-H(D)], and 7.03 [d, *J* 8.75 Hz, 6'-H(B)].

Repetition of the photolysis outlined above with the 3,4-*cis*-isoflavan (**23**) (35 mg) and resorcinol (35 mg) in dry EtOAc (5 ml) for 15 h yielded the identical product (**25**) (27 mg) following isolation, methylation, and purification.

Synthesis of (3S)-2',4',7-*Trimethoxy*-5',6-*bis*-[(3R,4R)-3,4-trans-2',4',7-*trimethoxyisoflavan*-4-*yl*]*isoflavan* (**27**).—(3S)-2'-*Benzyloxy*-7-*hydroxy*-4'-*methoxyisoflavan* (**34**). (3*S*)-2'-Hydroxy-4'-methoxy-7-methoxymethoxyisoflavan (1.2 g), obtained by methoxymethylation (CH_3OCH_2Cl–Adogen 464)[19] followed by catalytic hydrogenation (10% Pd–C in EtOH) of (+)-medicarpin (**2**), was refluxed for 10 h in dry acetone (100 ml) with α-chlorotoluene (4 ml), KI (*ca.* 10 mg), and K_2CO_3 (2 g). The mixture was filtered and the solvent was evaporated to yield (3*S*)-2'-benzyloxy-4'-methoxy-7-methoxymethoxyisoflavan (1.07 g) after purification by p.l.c. [R_F 0.57; hexane–benzene–acetone (5:4:1)]. The latter (900 mg) was refluxed with 3M HCl (5 ml) dissolved in MeOH (100 ml) for 1 h, the major portion of the MeOH was evaporated off, water (*ca.* 70 ml) was added, and the mixture was extracted with EtOAc (3 × 50 ml). The extract was washed free of acid with water, dried (Na_2SO_4), and the solvent was evaporated. P.l.c. separation [hexane–benzene–acetone (5:4:1)] of the product produced the isoflavan (**34**) (R_F 0.28) as cubes from ethanol (886 mg), m.p. 155 °C; *m/z* 362 (M^+, 1.2%), 298 (6.0), 270 (97), 256 (18), 255 (100), 151 (14), and 135 (20); δ (80 MHz; [$^2H_6$]acetone; 303 K) 2.86 (m, 4-H_2), 3.34—3.75 (m, 3-H), 3.72 (s, OMe), 3.92 (dd, *J* 9.38 and 8.13 Hz, 2-H_{ax}), 4.22 (dd, *J* 9.38 and 3.75 Hz, 2-H_{eq}), 5.16 (s, OCH_2Ph), 6.27 (d, *J* 2.50 Hz, 8-H), 6.33 (dd, *J* 8.13 and 2.50 Hz, 6-H), 6.50 (dd, *J* 8.13 and 2.50 Hz, 5'-H), 6.66 (d, *J* 2.50 Hz, 3'-H), 6.86 (d, *J* 8.13 Hz, 5-H), 7.09 (d, *J* 8.13 Hz, 6'-H), 7.20—7.58 (m, OCH_2Ph), and 8.03 (s, 7-OH).

(3R,4R)-3,4-trans-4-[(3S)-2'-*Benzyloxy*-4',7-*dimethoxyisoflavan*-6-*yl*]-2',4',7-*trimethoxyisoflavan* (**35**). (−)-Homopterocarpin (**7**) (400 mg) and the isoflavan (**34**) (800 mg) were dissolved in EtOH (40 ml), 3M HCl (15 ml) was added, and the solution was stirred at 40 °C for 72 h. The crude condensed product (107 mg) was isolated by p.l.c. [R_F 0.40; hexane–benzene–acetone (4:4:2)], methylated (MeI), and purified by p.l.c. [hexane–benzene–acetone (5:4:1)] to yield the methyl ether (**35**) (R_F 0.41) as a solid (100 mg) *m/z* 674 (M^+, 38%), 673 (36), 672 (39), 510 (11), 481 (37), 480 (57), 479 (100), 420 (35), 419 (41), 390 (17), 389 (36), 388 (14), 387 (26), 373 (24), 299 (11), 297 (30), 283 (21), 281 (14), 270 (22), 269 (29), 257 (11), 256 (16), 255 (23), 253 (11), 252 (16), 251 (37), 241 (30), 240 (42), 239 (32), 227 (18), 225 (11), 178 (31), 165 (22), 164 (36), 163 (20), 161 (26), 152 (14), 151 (39), 150 (28), 149 (43), 148 (12), 143 (10), 138 (17), 137 (43), 135 (11), 133 (13), 122 (14), and 121 (41); δ (80 MHz; $CDCl_3$; 303 K) 2.77 [m, 4-H_2(F)], 3.13—3.66 [m, 3-H(F)], 3.66, 3.70, 3.72, and 3.73 (× 2) (each s, together 5 OMe), 3.66—4.41 [m, 3-H(C) and 2-H_2(C + F)], 4.69 [d, *J* 7.50 Hz, 4-H(C)], 5.03 (s, OCH_2Ph), 6.25—6.56 [m, 6- and 8-H(A), 3'- and 5'-H(B + E), and 8-H(D)], 6.59 [s, 5-H(D)], 6.72 [d, *J* 8.75 Hz, 5-H(A)], 6.91 [d, *J* 8.13 Hz, 6'-H(E)], 6.97 [d, *J* 8.13 Hz, 6'-H(B)], and 7.31 (s, OCH_2Ph).

(3R,4R)-3,4-trans-4-[(3S)-2'-*Hydroxy*-4',7-*dimethoxyisoflavan*-6-*yl*)-2',4',7-*trimethoxyisoflavan* (**36**). Debenzylation of compound (**35**) (100 mg) was effected by catalytic hydrogenation with 10% Pd–C (50 mg) in acetone (40 ml) for 1 h. Filtration and evaporation of the solvent produced the dimer (**36**) which was purified by p.l.c. [R_F 0.16: hexane–benzene–acetone (5:4:1)] to yield a solid (75 mg), *m/z* 584 (M^+, 42%), 583 (12), 582 (38), 421 (15), 420 (31), 419 (13), 403 (18), 391 (27), 390 (67), 389 (100), 387 (29), 297 (13), 283 (12), 272 (27), 270 (11), 269 (15), 257 (22), 255 (22), 254 (16), 253 (25), 251 (11), 241 (14), 240 (22), 239 (47), 223 (24), 178 (25), 165 (17), 164 (54), 163 (17), 151 (44), 150 (34), 149 (62), 137 (61), 135 (10), 133 (12), and 121 (58); δ (80 MHz, $CDCl_3$; 373 K) 2.77 [m, 4-H_2(F)], 3.09—3.56 [m, 3-H(F)], 3.59, 3.66, 3.68, 3.69, and 3.70 (each s, together 5 OMe), 3.70—4.38 [m, 2-H_2(C + F) and 3-H(C)], 4.67 [d, *J* 8.50 Hz, 4-H(C)], 6.23—6.53 [m, 6- and 8-H(A), 3', and 5'-H(B + E), and 8-H(D)], 6.59 [s, 5-H(D)], 6.66 [d, *J* 9.00 Hz, 5'-H(A)], 6.88 [d, *J* 8.25 Hz, 6'-H(E)], and 6.97 [d, *J* 9.00 Hz, 6'-H(B)].

(3S)-2',4',7-*Trimethoxy*-5',6-*bis*-[(3R,4R)-3,4-trans-2',4',7-*trimethoxyisoflavan*-4-*yl*]*isoflavan* (**27**). Condensation of the dimer (**36**) (75 mg) with (−)-homopterocarpin (**7**) (50 mg) in EtOH (10 ml) and 3M HCl (2.5 ml) at 40 °C for 24 h produced a single trimer (13 mg) following separation by p.l.c. [R_F 0.28; benzene–acetone (9:1), × 2]. Methylation (MeI) and subsequent purification of the product (R_F 0.50) by p.l.c. [hexane–benzene–acetone (5:4:1), × 3] yielded the methyl ether (**27**) as a solid (4 mg), identical with the trimer (**27**) obtained from the condensation (v).

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