# New Pterocarpenes from *Brya ebenus*

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Five pterocarpenes (bryacarpenes 1—5) and an isoflavan (bryaflavan) have been isolated from the heartwood of *Brya ebenus* and identified as 4,10-dihydroxy-3,8,9-trimethoxy-, 10-hydroxy-3,8,9-trimethoxy-, 3,8,9,10-tetramethoxy-, 4-hydroxy-3,9,10-trimethoxy-, and 3,9,10-trimethoxy-6*H*-benzofuro[3,2-*c*][1]benzopyran, and (3*S*)-3',6,7-trihydroxy-2',4'-dimethoxyisoflavan.

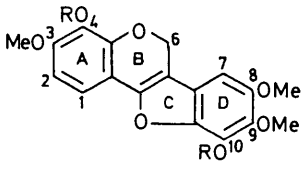
Pterocarpenes and pterocarpans can be oxidised to coumestones, and chromans to coumarins, by using dichlorodicyanobenzoquinone.

THE dense, dark heartwood of *Brya ebenus* DC. (Leguminosae) (cocus wood, West Indian ebony) is used in turnery and inlay work, and for musical instruments including the bagpipe. It has been suspected [1] of causing dermatitis in woodworkers, and facial eczema in flautists. It was of interest therefore to examine the extractives and compare them with those from true ebony (*Diospyros* spp., Ebenaceae) which include numerous naphthols and naphthoquinones.[2] Phenolics and related quinones are also present in *B. ebenus* but they are isoflavanoid in type. The chloroform extract of the heartwood contains a large number of compounds, some of which have been separated by extensive column and thin layer chromatography. We report here on the principal colourless compounds, five pterocarpenes and an isoflavan.

*Bryacarpene*-1.—This compound, $C_{18}H_{16}O_7$, is the principal pterocarpene, and was first isolated by Hausen [1] but the structure was not investigated. The n.m.r. spectrum includes signals from two hydroxy- and three methoxy-groups, a 2-proton singlet at δ 5·59, and in the aromatic region an AB system (2H) and a singlet (1H) at δ 6·38. In the absence of carbonyl absorption (i.r.) the two remaining oxygens must be in ether linkages, and the chromophore was recognised as a pterocarpene by comparison with known compounds.[3,4]

[1] B. M. Hausen, Thesis, University of Hamburg, 1970.
[2] R. H. Thomson, 'Naturally Occurring Quinones,' 2nd edn., Academic Press, London, 1971.
[3] D. R. Perrin and W. Bottomley, *J. Amer. Chem. Soc.*, 1962, **84**, 1919.
[4] S. H. Harper, A. D. Kemp, W. G. E. Underwood, and R. V. M. Campbell, *J. Chem. Soc.* (*C*), 1969, 1109.

The 2-proton singlet could then be assigned to the methylene group at C-6 and the arrangement of the



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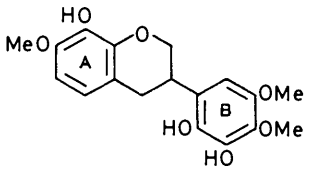

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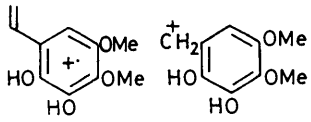

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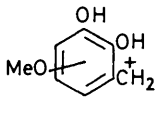

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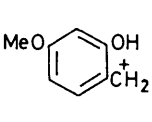

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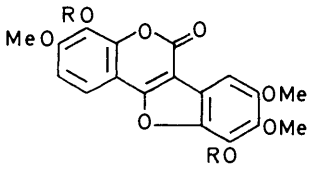


(3)

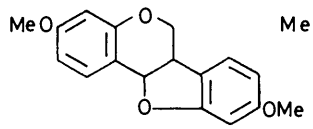
substituents as in (1; R = H) was determined as follows.

Hydrogenolysis of bryacarpene-1 over palladium gave the isoflavan (2), the five ring C protons showing the characteristic ABMXX' signals in the n.m.r. spectrum.[5,6] The mass spectrum displayed a typical isoflavan fragmentation pattern [6] with major peaks at *m/e* 348 (98%; $M^+$), 196 (98; *a*), 195 (92), 184 (96), 183 (96; *b*), and 153 (100; *c*). The ion (*c*) is presumably formed mainly from (*b*) by loss of formaldehyde but may include a contribution arising from ring A by retro-Diels–Alder fission and hydrogen transfer. The formation of (*a*) and (*b*) shows that ring B contains two hydroxy- and two methoxy-groups, and hence there must be one hydroxy- and one methoxy-group in ring A. The substituents in bryacarpene-1 can be assigned correspondingly to rings D and A of (1).

Oxidation of bryacarpene-1 dimethyl ether with 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) gave the lactone, bryacarpenone-1 dimethyl ether (3; R = Me), showing $\nu_{CO}$ 1738 $cm^{-1}$. In the n.m.r. spectrum of this compound the 2-proton singlet had disappeared while the AB quartet had shifted 0·47, and the aromatic singlet 0·77 p.p.m. downfield. This latter shift is attributable to the deshielding effect of the carbonyl group, and the proton responsible for the aromatic singlet is therefore H-7. It follows that ring D of bryacarpene-1 dimethyl ether can be represented as in (1; R = Me).

Similar oxidations of 2*H*-chromens to lactones have been effected in high yield with chromium trioxide in pyridine [7] and autoxidation of pterocarpenes to coumestones is also efficient:[8] indeed we found it virtually impossible to obtain our pterocarpenes completely free from the corresponding lactones. DDQ, however, can oxidise pterocarpans and chromans, as well as pterocarpenes, directly to αβ-unsaturated lactones. Thus homopterocarpin (4) gave the coumestone (5), and the coumarin (12) was obtained from the corresponding isoflavan (see below). The pterocarpan (4) was unaffected by manganese dioxide or *o*-chloranil.[4]

The protons in ring A of bryacarpene-1 form an AB system. On phytochemical grounds the substituents are most probably located at C-3 and C-4, and it was noted that the chemical shift of the AB system in bryacarpene-1 dimethyl ether was in good agreement with that of 3,4,8,9-tetramethoxypterocarpene.[8] Structure (1; R = Me) was confirmed by synthesis. Oxidative coupling of 7,8-dimethoxy-4-hydroxycoumarin with 3-methoxycatechol using potassium iodate,[9] followed by methylation gave bryacarpenone-1 dimethyl ether in low yield. Reduction of bryacarpenone-1 dimethyl ether with lithium aluminium hydride afforded the alcohol (6) which was cyclised in hot diglyme [10] to give bryacarpene-1 dimethyl ether (1; R = Me). A second compound isolated from the cyclisation reaction



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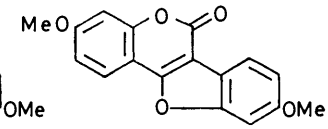

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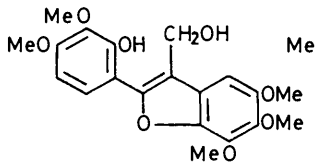

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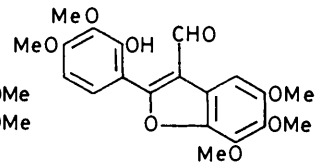


(7)

was the aldehyde (7) which could have been formed either by aerial oxidation of the allylic alcohol (6) or by autoxidation of bryacarpene-1 dimethyl ether.

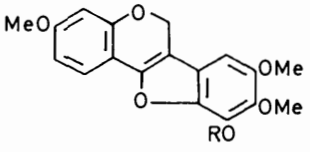
The positions of the hydroxy-groups in bryacarpene-1 remain to be established. A positive Gibb's test indicated that at least one phenolic group had a free *para*-position, and the location of the ring A hydroxy-group at C-4 follows from the observation that the u.v.

[5] K. Kurosawa, W. D. Ollis, B. T. Redman, I. O. Sutherland, A. Braga de Oliveira, O. R. Gottlieb and H. Magalhães, *Chem. Comm.*, 1968, 1263, 1265.
[6] A. Pelter and P. I. Amenechi, *J. Chem. Soc.* (*C*), 1969, 887.
[7] D. M. X. Donnelly, P. J. Kavanagh, G. Kunesch, and J. Polonsky, *J.C.S. Perkin I*, 1973, 965.
[8] D. Ferreira, C. v. d. M. Brink, and D. G. Roux, *Phytochemistry*, 1971, **10**, 1141.
[9] D. M. X. Donnelly and M. A. Fitzgerald, *Phytochemistry*, 1971, **10**, 3147.
[10] W. J. Bowyer, J. N. Chatterjea, S. P. Dhoubhadel, B. O. Handford, and W. B. Whalley, *J. Chem. Soc.*, 1964, 4212.

spectrum of bryacarpenone-1 (3; R = H) (prepared by oxidation of bryacarpene-1 diacetate with DDQ, and hydrolysis) was not affected by the addition of sodium acetate. Convincing evidence for the presence of hydroxy-groups at C-4 and C-8 or C-10 was obtained by deuteriation with deuterium oxide, in trimethylamine–dimethylformamide.[11] After heating for 6 h the signal for H-1 in the n.m.r. spectrum had disappeared together with the hydroxy-signals, and that for H-7 had diminished by *ca.* 70%. To distinguish between (1; R = H) and the 4,8-dihydroxy-isomer we examined the solvent-induced shifts of the methoxy-protons. In fully methylated compounds the signals from methoxy-groups *ortho* to hydrogen should move upfield by >0·3 p.p.m. on changing from chloroform to benzene solution.[6] In agreement with structure (1; R = Me) two methoxy-signals shifted upfield 0·45 and 0·53 p.p.m., the other shifts being much smaller (0·03, 0·07, and 0·24 p.p.m.). Similarly in the diacetate (1; R = Ac) two methoxy-signals shifted upfield 0·50 and 0·59 p.p.m. but the third moved only 0·02 p.p.m. Although esters are less satisfactory than ethers [6] these shifts provide strong support for structure (1; R = Ac) as the shifts of other protons, although substantial, were smaller than those of the methoxy-protons. Further evidence in support of structure (1; R = H) was sought by observing the upfield shift of the aromatic protons on converting bryacarpene-1 into its anion in dimethyl sulphoxide solution. A shift of 0·94 p.p.m. for H-7 suggests that it is *para* to a hydroxy-group, the value being above the usual range (0·71—0·79 p.p.m.) for simple phenols [12] (*cf.* also bryacarpene-2, below). It should be noted however, that the shift for H-1 (0·56 p.p.m.) was less than normal.

*Bryacarpenes-2 and -3.*—On spectroscopic evidence bryacarpene-2 is a hydroxytrimethoxypterocarpene. It formed an acetate, and a methyl ether identical with bryacarpene-3 from which a hydroxytetramethoxyisoflavan was obtained by hydrogenolysis. The mass spectrum of this compound had only two major peaks, the molecular ion at *m/e* 346 (93%), and the base peak at 210 ($C_{11}H_{14}O_4$, monomethyl ether of (*a*) arising from ring B by retro-Diels–Alder cleavage. The other ion from this fragmentation (*d*) ($C_8H_9O_2$) appeared at *m/e* 137 (13%). Hence ring A of the isoflavan and of bryacarpene-3 contains one methoxy-group, and the B ring of the isoflavan and the D ring of bryacarpene-3 each possess three methoxy-groups. The orientation of the methoxy-groups as shown in (8; R = Me) was deduced from the n.m.r. spectrum of the lactone, bryacarpenone-3, obtained by DDQ oxidation of bryacarpene-3. H-7 had the same chemical shift as H-7 in the spectrum of (3; R = Me), and the ABX signals from ring A were similar to those of (5). Structure (8; R = Me) was confirmed by synthesis of bryacarpenone-3 from 3-methoxycatechol and 4-hydroxy-7-methoxycoumarin. Bryacarpene-3 is therefore (8; R = Me) and the derived isoflavan has structure (9).

In bryacarpene-2 the hydroxy-group is assigned to C-10 (8; R = H) by comparison of the chemical shift of H-7 with that of H-7 in bryacarpene-1 (1; R = H), and in the corresponding acetates and lactone acetates. Further, the signal for H-7 shifts upfield 0·79 p.p.m.

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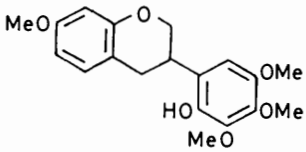


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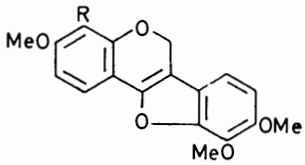



(10)

when bryacarpene-2 is converted into its anion in dimethyl sulphoxide solution, in agreement with its position *para* to a phenolic group.[12]

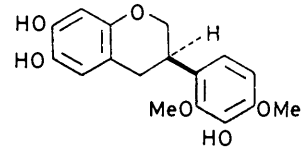
*Bryacarpene-4.*—Spectroscopic data show that this minor component is a hydroxytrimethoxypterocarpene. Hydrogenolysis gave an isoflavan whose mass spectrum included major peaks (all >90% intensity) at *m/e* 180, 167, 153, 137, 122, and 121. The isoflavan has therefore two methoxy-groups in ring B, and one hydroxy- and one methoxy-group in ring A, the charge being shared almost equally between the two fragments on retro-Diels–Alder fission. The allocation of substituents to rings A and D in bryacarpene-4 follows, and the arrangement shown in (10; R = OH) was deduced from the following evidence. In the n.m.r. spectrum of bryacarpene-4 the four aromatic protons comprise two AB systems (best seen in $C_6D_6$ solution), one of which corresponds closely to that of bryacarpene-1 (1; R = H); moreover the signal at lowest field disappeared on deuteriation in triethylamine–dimethylformamide. We conclude that ring A has the same structure in bryacarpenes-1 and -4. On oxidation of bryacarpene-4 acetate with DDQ to a lactone, the signal for one proton (H-7) moved downfield by 0·58 p.p.m. This proton is part of the second AB system which therefore comprises H-7 and H-8, and accordingly bryacarpene-4 has structure (10; R = OH).

*Bryacarpene-5.*—Less information was obtained on this minor constituent of *B. ebenus* but on spectroscopic evidence it is clearly a trimethoxypterocarpene. As the n.m.r. signals for two of the aromatic protons are identical with those for H-7 and H-8 in the spectrum of bryacarpene-4 (10; R = OH), and the signals for the other three aromatic protons are virtually the same as those for H-1, H-2, and H-4 in the spectrum of bryacarpene-3 (8; R = Me) we conclude that bryacarpene-5

[11] G. W. Kirby and L. Ogunkoya, *J. Chem. Soc.*, 1965, 6914.
[12] R. J. Highet and P. J. Highet, *J. Org. Chem.*, 1965, **30**, 902.

has structure (10; R = H). The n.m.r. spectrum of the lactone obtained by DDQ oxidation is consistent with this structure.

*Bryaflavan.*—This optically active compound, $C_{15}H_9O(OH)_3(OMe)_2$, was obviously flavanoid but not a pterocarpene. It was recognised as an isoflavan from n.m.r. data, especially the 220 MHz spectrum of the triacetate which clearly revealed the splitting pattern of the ring C protons.[5,6] In the mass spectrum peaks at (*inter alia*) *m/e* 180 (94%), 167 (94), and 139 (16) show that ring B carries a hydroxy- and two methoxy-groups, and ring A has two hydroxy-groups. The orientation of the substituents in ring B is probably as shown in (11) as bryaflavan contains two aromatic protons which form an AB system almost identical in chemical shift with that of one AB pair in duartin (3',7-dihydroxy-2',4',8-trimethoxyisoflavan).[5] The two remaining aromatic

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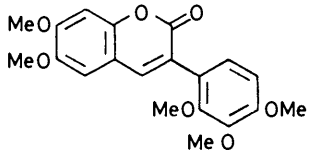


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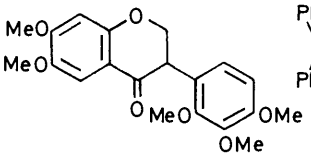


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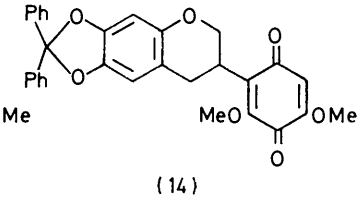


(14)

protons in ring A resonate as singlets and hence the two hydroxy-groups in that ring must be at C-6 and C-7 (11); phenylboronate and diphenylmethylene ether[13] derivatives were prepared.

Structure (11) for bryaflavan was confirmed by a series of oxidations. With DDQ the trimethyl ether gave the 3-arylcoumarin (12), as expected, and treatment with permanganate in aqueous acetone yielded the isoflavanone (13) whose u.v. and n.m.r. spectra were in close agreement with those published[14] for the racemic compound, but the m.p. and i.r. spectra (KBr) were different. Further oxidation of the isoflavanone (13) gave the corresponding pentamethoxyisoflavone identical with an authentic sample isolated[14] from *Pterodon pubescens*. Finally the position of the hydroxy-group in ring B of (11) was established by oxidising the diphenylmethylene ether of bryaflavan with Fremy's salt which afforded an orange quinone (14) whose structure was consistent with its spectroscopic properties.

The absolute configuration of (−)-duartin and related isoflavans has been established[5] as 3*S*, and the o.r.d. curves of these compounds all show a negative Cotton effect in the region 260—300 nm. (−)-Bryaflavan shows a negative Cotton effect of similar form in its c.d. curve [$\lambda_{max.}$ 299 nm ($\Delta\varepsilon$ −0·74)] and evidently has the same 3*S* configuration (*cf.* ref. 15).

## EXPERIMENTAL

Spectra were measured for solutions in EtOH (u.v.) and $CDCl_3$ (n.m.r.), and for KBr discs (i.r.) unless otherwise stated. Petrol refers to light petroleum (b.p. 60—80°).

*Extraction of* Brya ebenus.—Ground heartwood (1300 g) was extracted (Soxhlet) successively with petrol, ether, and chloroform. The ether extract (45 g) was chromatographed on a column of silica gel eluting with benzene containing increasing amounts of ether, then ether containing increasing proportions of chloroform. The fractions eluted with benzene–ether (20—80%), and with ether alone, were combined (1·35 g) and run on silica gel p.l.c. plates in chloroform. Four bands (A—D) were separated. Further chromatography of band D (lowest $R_F$) on silica plates in chloroform–ethyl acetate (3 : 1 and 4 : 1) eventually gave bryacarpenes-1 (140 mg), -2 (70 mg), and -4 (34 mg). Further chromatography of band B in chloroform–benzene (1 : 1) yielded bryacarpenes-3 (129 mg) and -5 (10 mg).

Part of the chloroform extract (20 g) was chromatographed on a column of silica gel eluting successively with benzene, ether, chloroform, and ethanol. The combined fractions obtained with chloroform–ethanol (<50%) were put down a second column in benzene containing increasing amounts of chloroform. The fraction obtained with neat chloroform (2·58 g) was transferred to a third column from which ether–chloroform (8 : 2 and 1 : 1) eluted bryaflavan (1·03 g).

*Bryacarpene*-1 (1; R = H).—*4,10-Dihydroxy-3,8,9-trimethoxy-6H-benzofuro*[3,2-c][1]*benzopyran* was crystallised from chloroform as needles, m.p. 204—205° (Found: C, 62·5; H, 4·7%; $M^+$, 344·0887. $C_{18}H_{16}O_7$ requires C, 62·8; H, 4·7%; *M*, 344·0895), $\lambda_{max.}$ 228, 318, 332, and 348 nm (log ε 4·24, 4·20, 4·26, and 4·14), $\nu_{max.}$ 3360, 1655, 1627, and 1607 $cm^{-1}$, δ 7·10 and 6·53 (each 1H, d, *J* 9 Hz, H-1 and -2), 6·38 (1H, s, H-7), 5·59 (2H, s, $-OCH_2C=$), 5·89 and 5·47 (each 1H, s, OH), and 3·91, 3·88, and 3·87 (each 3H, s, OMe); after heating bryacarpene-1 (20 mg) with deuterium oxide (1 ml), triethylamine (5 ml), and dimethylformamide (0·5 ml) in a sealed tube under nitrogen at 100° for 6 h, on removal of solvents and crystallisation, the n.m.r. spectrum showed δ 6·53 (1H, s, H-2), 6·38 (*ca.* 0·3H, s, H-7), 5·59 (2H, s, $-OCH_2C=$), and signals for 3 OMe; *diacetate* (1; R = Ac), needles, m.p. 204—205° (from dichloromethane–petrol) (Found: C, 61·5; H, 4·7. $C_{22}H_{20}O_9$ requires C, 61·7; H, 4·7%), $\lambda_{max.}$ ($CHCl_3$) 293sh, 339, and 356 nm (log ε 4·14, 4·41, and 4·33), $\nu_{max.}$ 1775, 1750, 1655, 1638, 1620, 1600, and 1190 $cm^{-1}$, δ 7·30 and 6·53 (each 1H, d, *J* 9 Hz, H-1 and -2), 6·68 (1H, s, H-7), 5·53 (2H, s, $-OCH_2C=$), 3·89, 3·86, and 3·82 (each 3H, s, OMe), and 2·45 and 2·35 (each 3H, s, OAc); *dimethyl ether* (1; R = Me), prepared with $Me_2SO_4$–$K_2CO_3$–$Me_2CO$, needles, m.p. 124—125° (from dichloromethane–petrol) (Found: C, 64·6; H, 5·6. $C_{22}H_{20}O_9$ requires C, 64·5; H, 5·4%), $\nu_{max.}$ 1665, 1610, and 1595 $cm^{-1}$, δ 7·22 and 6·53 (each 1H, d, *J* 8 Hz, H-1 and -2), 6·51 (1H, s, H-7), 5·58 (2H, s, $-OCH_2C=$), 4·23 (3H, s, OMe), and 3·89 (12H, s, OMe).

[13] L. Jurd, *J. Org. Chem.*, 1962, **27**, 872.
[14] R. Braz Filho, O. R. Gottlieb, and R. M. Viegas Assumptção, *Phytochemistry*, 1971, **10**, 2835.
[15] D. M. X. Donnelly, P. J. Keenan, and J. P. Prendergast, *Phytochemistry*, 1973, **12**, 1157.

*Bryacarpenone*-1 (3; R = H).—The foregoing diacetate (100 mg) and 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) (200 mg) were kept in dioxan (20 ml) at room temperature for 10 h. After removal of solvent the residue was chromatographed on a short column of alumina in chloroform to give the *lactone diacetate* (3; R = Ac) as plates, m.p. 249—251° (from acetone) (60 mg) (Found: C, 60·0; H, 4·3%; $M^+$, 442·0886. $C_{22}H_{18}O_{10}$ requires C, 59·7; H, 4·1%; *M*, 442·0889), $\nu_{max.}$ 1777, 1785, 1760, and 1745sh $cm^{-1}$, δ 7·85 and 7·02 (each 1H, d, *J* 9 Hz, H-1 and -2), 7·43 (1H, s, H-7), 3·98, 3·94, and 3·91 (each 3H, s, OMe), and 2·48 and 2·44 (each 3H, s, OAc). The diacetate (40 mg) in 0·1N-ethanolic potassium hydroxide (5 ml) was heated under reflux for 1 h, cooled, and acidified to precipitate 4,10-*dihydroxy*-3,8,9-*trimethoxybenzofuro*[3,2-c][1]*benzopyran*-6-*one* (3; R = H), needles, m.p. 279—280° (from dioxan) (25 mg) (Found: C, 59·9; H, 4·1%; $M^+$, 358·0679. $C_{18}H_{14}O_8$ requires C, 60·3; H, 3·9%; *M*, 358·0689), $\lambda_{max.}$ 261, 342, and 350sh nm (log ε 4·50, 4·42, and 4·39), $\nu_{max.}$ 3400, 1760, 1644, and 1610 $cm^{-1}$, δ [$(CD_3)_2SO$] 7·48 and 7·18 (each 1H, d, *J* 9 Hz, H-1 and -2), 6·95 (1H, s, H-7), and 3·93, 3·89, and 3·77 (each 3H, s, OMe).

*Bryacarpenone*-1 *Dimethyl Ether* (3; R = Me).—Bryacarpene-1 dimethyl ether (1; R = Me) (40 mg) and DDQ (100 mg) were kept in dioxan (4 ml) at room temperature for 5 h and worked up as above. The *lactone* (3; R = Me) crystallised from dichloromethane–petrol in needles, m.p. 197—198° (25 mg) (Found: C, 62·2; H, 5·7%; $M^+$, 386·0960. $C_{20}H_{18}O_8$ requires C, 62·2; H, 6·2%; *M*, 386·1001), $\lambda_{max.}$ 253·5, 314sh, 341·5, and 356 nm (log ε 3·27, 2·95, 3·31, and 3·24), $\nu_{max.}$ 1738, 1642, and 1610 $cm^{-1}$, δ 7·70 and 6·98 (each 1H, d, *J* 9 Hz, H-1 and -2), 7·28 (1H, s, H-7), and 4·23, 4·03, 3·97, 3·95, and 3·92 (each 3H, s, OMe).

A similar oxidation of homopterocarpin (4) (200 mg) with DDQ (600 mg) in dioxan (30 ml) left overnight, gave coumestrol dimethyl ether (5), m.p. 198—200° (lit.,[4] 196—198°) (198 mg), $\nu_{max.}$ 1740, 1630, and 1608 $cm^{-1}$, δ 8·0—7·7 and 7·2—6·8 (6H, m, ArH), and 3·88 (6H, s, OMe).

*Hydrogenolysis of Bryacarpene*-1.—Bryacarpene-1 (20 mg) in acetic acid (5 ml) was shaken with hydrogen and palladised charcoal (20 mg; 10%) overnight at room temperature. Work-up gave 2′,3′,8-*trihydroxy*-4′,5′,7-*trimethoxyisoflavan* (2) which crystallised from ether in needles, m.p. 140—142° (10 mg) (Found: $M^+$, 348·1207. $C_{18}H_{20}O_7$ requires *M*, 348·1259), $\lambda_{max.}$ 238 and 284 nm (log ε 3·96 and 3·56), $\nu_{max.}$ 3410, 1632, and 1610 $cm^{-1}$, δ 6·57 and 6·44 (each 1H, d, *J* 9 Hz, H-5 and -6), 6·22 (1H, s, H-6′), 5·52br (3H, OH), 4·48 (1H, q, *J* 10 and 3 Hz, H-2), 4·13 (1H, t, *J* 10 Hz, H-2), 3·6br (1H, m, H-3), 3·00 (2H, m, H-4), and 3·90, 3·85, and 3·76 (each 3H, s, OMe), *m/e* 349 (18%), 348 (98), 197 (45), 196 (98), 195 (92), 184 (96), 183 (96), 182 (18), 181 (10), 169 (13), 162 (22), 154 (10), 153 (100), 149 (22), 133 (14).

*Synthesis of Bryacarpene*-1 *Dimethyl Ether* (1; R = Me).—To 4-hydroxy-7,8-dimethoxycoumarin (2·2 g), and 3-methoxycatechol (1·54 g) in acetone (30 ml) and water (30 ml) was added rapidly a solution of potassium iodate (1·4 g) and sodium acetate (3 g) in water (60 ml). After 24 h the acetone was removed *in vacuo*, and the black solid was collected, dried, and then heated under reflux for 6 h with methyl iodide (2 ml) and anhydrous potassium carbonate (2 g) in acetone (100 ml). After work-up, the crude product was chromatographed on a column of silica gel. Elution with benzene gave a yellow-brown product (not identified) followed by a bright blue fluorescent band (in benzene–chloroform, 1 : 4) which yielded bryacarpenone-1 dimethyl ether, m.p. 199° (from dichloromethane–petrol) (400 mg) identical with that described above. This compound (300 mg) in ether (100 ml) was heated under reflux for 2 h with lithium aluminium hydride (210 mg). Work-up gave the phenolic alcohol (6) as an unstable white solid, δ 7·28 and 6·61 (each 1H, d, *J* 9 Hz, ArH), 6·88 (1H, s, ArH), 4·72 (2H, s, $CH_2OH$), and 5 MeO signals. It was cyclised by heating in boiling diglyme (5 ml) for 10 min, and on cooling, water was added, and the mixture was extracted with ether. The crude product was separated by t.l.c. on silica gel in chloroform–ethyl acetate (3 : 1) to give the alcohol (6), the aldehyde (7) (22 mg), bryacarpenone-1 dimethyl ether (30 mg), and bryacarpene-1 dimethyl ether, m.p. 123—125° (from dichloromethane–petrol) (15 mg) identical with that described above. 2-(2-*Hydroxy*-3,4-*dimethoxyphenyl*)-5,6,7-*trimethoxybenzofuran*-3-*carbaldehyde* (7) showed $\lambda_{max.}$ 217, 253, and 342 nm, $\nu_{max.}$ 3400sh, 3170br, 1664, and 1612 $cm^{-1}$, δ 10·13 (1H, s, CHO), 7·43 (1H, s, ArH), 7·32 and 6·64 (each 1H, d, *J* 8 Hz, ArH), 6·43br (1H, OH), and signals for 5 MeO (Found: $M^+$, 388·1154. $C_{20}H_{20}O_8$ requires *M*, 388·1157).

*Bryacarpene*-2 (8; R = H).—10-*Hydroxy*-3,8,9-*trimethoxy*-6H-*benzofuro*[3,2-c][1]*benzopyran* was crystallised from ether as needles, m.p. 188—189° (Found: $M^+$, 328·0946. $C_{18}H_{16}O_6$ requires *M*, 328·0945), $\lambda_{max.}$ 217, 244sh, 338, and 353 nm (log ε 4·53, 4·17, 4·39, and 4·33), $\nu_{max.}$ 3390, 1650, 1615, and 1602 $cm^{-1}$, δ 7·48 (1H, d, *J* 9 Hz, H-1), 6·53 (1H, dd, *J* 9 and 3 Hz, H-2), 6·48 (1H, d, *J* 3 Hz, H-4), 6·37 (1H, s, H-7), 5·90 (1H, s, OH), 5·53 (2H, s, $-OCH_2C=$), and 3·93, 3·89, and 3·79 (each 3H, s, OMe); the *acetate* had m.p. 160° (from ether) (Found: $M^+$, 370·1050. $C_{20}H_{18}O_7$ requires *M*, 370·1052), $\lambda_{max.}$ 215, 246sh, 253sh, 339, and 356 nm (log ε 4·52, 4·25, 4·22, 4·49, and 4·41), $\nu_{max.}$ 1770, 1655, 1620, and 1595 $cm^{-1}$, δ 7·43 (1H, d, *J* 9 Hz, H-1), 6·53 (1H, dd, *J* 9 and 3 Hz, H-2), 6·48 (1H, d, *J* 2 Hz, H-4), 6·69 (1H, s, H-7), 5·53 (2H, s, $-OCH_2C=$), and 3·89, 3·86, and 3·79 (each 3H, s, OMe); methylation with $Me_2SO_4$–$K_2CO_3$–$Me_2CO$ gave the methyl ether, m.p. 122°, identical (i.r.) with bryacarpene-3 described below.

Oxidation of bryacarpene-2 acetate with DDQ in dioxan overnight gave 10-*acetoxy*-3,8,9-*trimethoxybenzofuro*[3,2-c]-[1]*benzopyran*-6-*one*, m.p. 197° (subl.) (from ether) (Found: $M^+$, 384·0842. $C_{20}H_{16}O_8$ requires *M*, 384·0844), $\lambda_{max.}$ 218, 248, 304, 343, and 358sh (log ε 4·48, 4·27, 3·95, 4·41, and 4·37), $\nu_{max.}$ 1777 and 1735 $cm^{-1}$, δ 7·89 (1H, d, *J* 9 Hz, H-1), 7·45 (1H, s, H-7), 6·98 (1H, dd, *J* 9 and 3 Hz, H-2), 7·00 (1H, d, *J* 3 Hz, H-4), 3·99 (3H, s, OMe), and 3·91 (6H, s, OMe).

*Bryacarpene*-3 (8; R = Me).—3,8,9,10-*Tetramethoxy*-6H-*benzofuro*[3,2-c][1]*benzopyran* gave needles, m.p. 122° (from ether) (Found: C, 66·3; H, 5·4%; $M^+$, 342·1100. $C_{19}H_{18}O_6$ requires C, 66·6; H, 5·3%; *M*, 342·1103), $\lambda_{max.}$ 215, 245sh, 254sh, 388, and 355 nm (log ε 4·53, 4·24, 4·18, 4·50, and 4·41), $\nu_{max.}$ 1648, 1610, 1585, and 1560 $cm^{-1}$, δ 7·43 (1H, d, *J* 9 Hz, H-1), 6·50 (1H, dd, *J* 9 and 3 Hz, H-2), 6·49 (1H, d, *J* 3 Hz, H-4), 5·53 (2H, s, $-OCH_2=C$), 4·23 (3H, s, OMe), 3·88 (6H, s, OMe), and 3·80 (3H, s, OMe), δ ($C_6D_6$) 7·41 (1H, d, *J* 9 Hz, H-1), 6·46 (1H, d, *J* 3 Hz, H-4), 6·40 (1H, dd, *J* 9 and 3 Hz, H-2), 6·19 (1H, s, H-7), 5·19 (2H, s, $-OCH_2C=$), 3·96, 3·82, 3·44, and 3·22 (each 3H, s, OMe). Oxidation of this compound (50 mg) with DDQ (100 mg) in cold dioxan (20 ml), and work-up as before gave 3,8,9,10-*tetramethoxybenzofuro*[3,2-c][1]*benzopyran*-6-*one* (48 mg) as needles,

m.p. 191—192° (from ether) (Found: $M^+$, 356·0893. $C_{19}H_{16}O_7$ requires $M$, 356·0995), $\lambda_{max.}$ 220, 253, 303, 343, and 357sh (log ε 4·50, 4·34, 4·02, 4·47, and 4·41), $\nu_{max.}$ 1730, 1632, and 1602 $cm^{-1}$, δ 7·88 (1H, d, $J$ 9 Hz, H-1), 7·27 (1H, s, H-7) (obscured by $CHCl_3$ signal), 6·92 (2H, m, H-2 and -4), and 4·24, 3·94, 3·92, and 3·88 (each 3H, s, OMe). This compound was synthesised by oxidative coupling of 4-hydroxy-7-methoxycoumarin (192 mg) with 3-methoxycatechol (154 mg) by potassium iodate, followed by methylation, as described above; yield 5 mg, m.p. 190—192°, identical i.r. spectrum and $R_F$.

*Hydrogenolysis of Bryacarpene*-3.—The pterocarpene (8; R = Me) (34 mg) in ethyl acetate (10 ml) was shaken with hydrogen and palladised charcoal (10 mg; 10%) for 1 h. The mixture was filtered, evaporated, and purified by p.l.c. and crystallisation from ether to give *2′-hydroxy-3′,4′,5′,7-tetramethoxyisoflavan* (9), m.p. 112° (Found: $M^+$, 346·1414. $C_{19}H_{22}O_6$ requires $M$, 346·1416), $\lambda_{max.}$ 213, 285, and 291 nm (log ε 4·51, 3·90, and 3·91), $\nu_{max.}$ 3480, 1638, and 1605 $cm^{-1}$, δ 6·99 (1H, d, $J$ 9 Hz, H-5), 6·48 (1H, dd, $J$ 9 and 3 Hz, H-6), 6·42 (2H, s, H-6′ and -8) (resolved into d + s in $C_6D_6$ soln.), 5·59 (1H, s, OH), 4·38 (1H, q, $J$ 10 and 3 Hz, H-2), 4·12 (1H, t, $J$ 10 Hz, H-2), 3·6br (1H, m, H-3), 3·04br (1H, H-4), 2·96br (1H, H-4), and 3·97, 3·88, 3·76, and 3·75 (each 3H, s, OMe), *m/e* 347 (8%), 346 (93), 211 (8), 210 (100), 209 (16), 198 (13), 197 (9), 183 (6), and 137 (13).

*Bryacarpene*-4 (10; R = OH).—*4-Hydroxy-3,9,10-trimethoxy-6H-benzofuro*[3,2-c][1]*benzopyran* gave crystals, m.p. 154—155° (from ether) (34 mg) (Found: $M^+$, 328·0946. $C_{18}H_{16}O_6$ requires $M$, 328·0946), $\lambda_{max.}$ 232, 255sh, 315, 333, and 350 nm (log ε 4·41, 4·20, 4·20, 4·38, 4·44, and 4·32), $\nu_{max.}$ 3325, 1650, and 1623 $cm^{-1}$, δ 7·06 and 6·52 (each 1H, d, $J$ 9 Hz, H-1 and -2), 6·90 (2H, s, H-7 and -8) (resolved into a narrow dd in $C_6D_6$ soln.), 5·48 (2H, s, $-OCH_2C=$), 5·02 (1H, s, OH), and 4·18, 3·90, and 3·88 (each 3H, s, OMe); after deuteriation in $D_2O$–$Et_3N$–$Me_2N{\cdot}CHO$ for 24 h at 95° the n.m.r. spectrum changed to δ 6·91 (2H, s, H-7 and -8), 6·53 (1H, s, H-2), 5·60 (2H, s, $-OCH_2C=$), 6·18 (3H, s, OMe), and 3·90 (6H, s, OMe); *acetate*, m.p. 143° (from ether) (10 mg) (Found: $M^+$, 370·1050. $C_{20}H_{18}O_7$ requires $M$, 370·1052), $\lambda_{max.}$ 217, 244, 253, 334, and 352 (log ε 4·40, 4·21, 4·19, 4·35, and 4·25), $\nu_{max.}$ 1765 and 1615 $cm^{-1}$, δ 7·36 and 6·57 (each 1H, d, $J$ 9 Hz, H-1 and -2), 6·90 (2H, s, H-7 and -8), 5·56 (2H, s, $-OCH_2C=$), 4·19, 3·91, and 3·84 (each 3H, s, OMe), and 2·56 (3H, s, OAc). Oxidation of the acetate (10 mg) with DDQ in dioxan as above gave *4-acetoxy-3,9,10-trimethoxybenzofuro*[3,2-c][1]*benzopyran-6-one*, m.p. 220—225° (from ether) (7 mg) (Found: $M^+$, 384·0846. $C_{20}H_{16}O_8$ requires $M$, 384·0844), $\lambda_{max.}$ 256, 304sh, and 344 nm (log ε 4·19, 3·77, and 3·59), $\nu_{max.}$ 1770, 1730, 1640, 1620, and 1600 $cm^{-1}$, δ 7·88 and 7·02 (each 1H, d, $J$ 9 Hz, H-1 and -2), 7·48 and 7·04 (each 1H, d, $J$ 10 Hz, H-7 and -8), 4·20 (3H, s, OMe), 3·96 (6H, s, OMe), and 2·45 (3H, s, OAc).

*Hydrogenolysis of Bryacarpene*-4.—Bryacarpene-4 (10 mg) in ethyl acetate (5 ml) was shaken with hydrogen and palladised charcoal (10 mg; 10%) for 3 h. Work-up gave *2′,8-dihydroxy-3′,4′,7-trimethoxyisoflavan* as needles, m.p. 143—145° (Found: $M^+$, 332·1261. $C_{18}H_{20}O_6$ requires $M$, 332·1259), $\lambda_{max.}$ 235 and 275 nm (log ε 4·33 and 3·74), $\nu_{max.}$ 3440, 3350, and 1625 $cm^{-1}$, δ 6·78 and 6·42 (each 1H, d, $J$ 9 Hz, H-5 and -6), 6·59 and 6·46 (each 1H, d, $J$ 10 Hz, H-5′ and -6′), 5·98 and 5·43 (each 1H, s, OH), 4·46 (1H, q, $J$ 10 and 3 Hz, H-2), 5·89 (1H, t, $J$ 10 Hz, H-2), 3·6br (1H, m, H-3), 2·99 (2H, m, H-4), and 3·89, 3·86, and 3·82 (each 3H, s, OMe), *m/e* 332 (20%), 180 (94), 179 (13), 168 (22), 167 (100), 165 (28), 164 (16), 153 (90), 152 (14), 151 (18), 149 (11), 138 (32), 137 (92), 134 (11), 133 (92), 123 (11), 122 (92), 121 (97), 109 (18), 107 (22), 106 (25), and 105 (33).

*Bryacarpene*-5 (10; R = H).—*3,9,10-Trimethoxy-6H-benzofuro*[3,2-c][1]*benzopyran* gave needles, m.p. 96—100° (from ether) (Found: $M^+$, 312·0996. $C_{18}H_{16}O_5$ requires $M$, 312·0997), $\lambda_{max.}$ 217, 243, 252sh, 323sh, 337, and 354 nm (log ε 4·45, 4·27, 4·24, 4·34, 4·45, and 4·34), $\nu_{max.}$ 1658, 1615, 1593, and 1570 $cm^{-1}$, δ 7·44 (1H, d, $J$ 9 Hz, H-1), 6·49 (1H, dd, $J$ 9 and 3 Hz, H-2), 6·48 (1H, d, $J$ 3 Hz, H-4), 6·89 (2H, s, H-7 and -8) (resolved into a narrow dd in $C_6D_6$ soln.), 5·53 (2H, s, $-OCH_2C=$), and 4·19, 3·90, and 3·78 (each 3H, s, OMe). Oxidation of (10; R = H) (5 mg) with DDQ in cold dioxan overnight gave *3,9,10-trimethoxybenzofuro*[3,2-c][1]*benzopyran-6-one*, m.p. 194—197° (from ether) (Found: $M^+$, 326·0788. $C_{18}H_{14}O_6$ requires $M$, 326·0790), δ 7·92 and 6·96 (each 1H, d, $J$ 9 Hz, H-1 and -2), 7·47 and 7·07 (each 1H, d, $J$ 9 Hz, H-7 and -8), 6·99 (1H, d, $J$ 2 Hz, H-4), and 4·20, 3·96, and 3·90 (each 3H, s, OMe).

*Bryaflavan* (11).—(3S)-*3′,6,7-Trihydroxy-2′,4′-dimethoxyisoflavan* gave pale yellow prisms or needles, m.p. 188—189° (from ether) (Found: C, 63·9; H, 5·9%; $M^+$, 318·1103. $C_{17}H_{18}O_6$ requires C, 64·1; H, 5·7%; $M$, 318·1103), $[\alpha]_D^{25}$ −17·3° (MeOH), $\lambda_{max.}$ 216, 283sh, and 300 nm (log ε 4·37, 3·63, and 3·78), c.d. $\lambda_{max.}$ (MeOH) 228 (Δε + 4·23), 235 (+3·17), and 299 nm (−0·74), $\nu_{max.}$ 3400 and 1617 $cm^{-1}$, δ [$(CD_3)_2SO$] 6·70 and 6·55 (each 1H, d, $J$ 9 Hz, H-5′ and -6′), 6·44 (1H, s, H-5), 6·18 (1H, s, H-8), and 3·73 (6H, s, OMe), ring c proton signals partly obscured by solvent peaks, *m/e* 369 (16%), 318 (100), 180 (94), 168 (95), 167 (94), 165 (28), 151 (90), 139 (16), 137 (16), 133 (90), 123 (13), 107 (20), 91 (10), and 77 (13); *triacetate*, plates, m.p. 160—161° (from dichloromethane–petrol) (Found: $M^+$, 444·1420. $C_{23}H_{24}O_9$ requires $M$, 444·1420), $\lambda_{max.}$ 281 nm (log ε 3·69), $\nu_{max.}$ 1769, 1761sh, 1755sh, 1610, and 1500 $cm^{-1}$, δ (220 MHz) 6·93 and 6·71 (each 1H, d, $J$ 9 Hz, H-5′ and -6′), 6·89 (1H, s, H-5), 6·69 (1H, s, H-8), 3·82 (6H, s, OMe), 2·37 (3H, s, OAc), 8·28 (3H, s, OAc), 8·27 (3H, s, OAc), 4·29 (1H, q, $J$ 10 and 3 Hz, H-2), 3·97 (1H, t, $J$ 10 Hz, H-2), 3·54 (1H, m, H-3), 2·94 (1H, d, $J$ 4 Hz, H-4), and 2·91br (1H, H-4); *trimethyl ether*, needles, m.p. 186—187° (from chloroform–petrol) (Found: C, 66·8; H, 7·0%; $M^+$, 360·1572. $C_{20}H_{24}O_6$ requires C, 66·65; H, 6·7%; $M$, 360·1573); heating with benzeneboronic anhydride in benzene gave the *phenylboronate*, m.p. 206—207° (from chloroform–petrol) (Found: $M^+$, 393·1337. $C_{23}H_{21}BO_6$ requires $M$, 393·1337). Heating the isoflavan (160 mg) with dichlorodiphenylmethane (130 mg) at 230° for 5 min gave, after t.l.c. on silica gel in chloroform, and crystallisation from ether–petrol, the *diphenylmethylene ether*, m.p. 78° (Found: $M^+$, 482·1729. $C_{30}H_{26}O_6$ requires $M$, 482·1729), $\lambda_{max.}$ 306 nm (log ε 4·18), *m/e* 483 (28%), 482 (100), 315 (10), 180 (20), 168 (18), 167 (18), 165 (92), 133 (89), and 105 (89).

*6,7-Dimethoxy-3-(2′,3′,4′-trimethoxyphenyl)coumarin* (12).—Bryaflavan trimethyl ether (50 mg) and DDQ (100 mg) were heated under reflux in benzene (50 ml) for 24 h. After cooling, the suspension was transferred to a column of alumina, eluted with benzene, and the product crystallised from chloroform–petrol to give the *coumarin* (12) as needles, m.p. 148—150° (30 mg) (Found: $M^+$, 356·1258. $C_{20}H_{20}O_7$ requires $M$, 356·1259), $\lambda_{max.}$ 260sh and 355 nm (log ε 4·35 and 4·52), $\nu_{max.}$ 1715, 1622, and 1580 $cm^{-1}$,

δ 7·66 (1H, s, H-4), 7·12 and 6·63 (each 1H, d, *J* 9 Hz, H-6′ and -5′), 6·88 (2H, s, H-5 and -8), and 3·96, 3·91, 3·89, 3·88, and 3·86 (each 3H, s, OMe).

2′,3′,4′,6,7-*Pentamethoxyisoflavan*-4-*one* (13).—To bryaflavan trimethyl ether (200 mg) in acetone (25 ml), aqueous potassium permanganate (7%; 10 ml) was added dropwise, with stirring, in 3 h. Stirring was continued for 10 h, then water (50 ml) was added, the excess of permanganate was destroyed with sodium dithionite, and the acetone was removed. The mixture was extracted with ether, and the extract was washed with sodium hydrogen carbonate solution, and dried. As t.l.c. showed that much of the starting material was unchanged, the oxidation was repeated. The crude product was purified by t.l.c. on silica gel in chloroform–ethyl acetate (4 : 1), and crystallised from benzene to give the flavanone as needles, m.p. 110—112° (Found: $M^+$, 374·1361. Calc. for $C_{20}H_{22}O_7$: *M*, 374·1364), $\lambda_{max.}$ 235, 275, and 340 nm (log ε 4·34, 4·08, and 3·86), $\nu_{max.}$ 1680 and 1615 $cm^{-1}$, δ 7·39 (1H, s, H-5), 6·82 and 6·62 (each 1H, d, *J* 8 Hz, H-6′ and -5′), 6·48 (1H, s, H-8), 4·54 (2H, m, H-2), 4·18 (1H, m, H-3), and 3·93 (3H), 3·90 (3H), 3·88 (6H), and 3·84 (3H) (all s, OMe), *m/e* 374 (91%), 195 (16), 194 (100), 181 (16), 180 (18), 151 (9), and 137 (6).

2′,3′,4′,6,7-*Pentamethoxyisoflavone*.—The above isoflavanone (75 mg) in dry benzene (10 ml) was heated under reflux with DDQ (200 mg) for 48 h, cooled, and filtered. Chromatography on silica gel in chloroform gave the isoflavone as needles, m.p. 171—172° (lit.,[14] 170—172°) (from ethanol) (37 mg) identical (t.l.c., mixed m.p., and mass spectrum) with an authentic sample.

2-(6,7-*Diphenylmethylenedioxychroman*-3-*yl*)-3,5-*dimethoxy*-p-*benzoquinone* (14).—To 6,7-diphenylmethylenedioxy-3′-hydroxy-2′,5′-dimethoxyisoflavan (50 mg) in methanol (20 ml) was added a solution of Fremy's salt (100 mg) and M/6-potassium dihydrogen phosphate (5 ml) in water (50 ml). After shaking for 30 min, the methanol was removed *in vacuo*, and the mixture was extracted with ether, dried, and evaporated. The residual *quinone* (14) was obtained as orange crystals (from ether–petrol) (35 mg) (Found: $M^+$, 496·1517. $C_{30}H_{24}O_7$ requires *M*, 496·1491), $\lambda_{max.}$ ($CHCl_3$) 297 and 425 nm (log ε 4·22 and 2·07), $\nu_{max.}$ 1680, 1640, 1595, and 1580 $cm^{-1}$, δ 7·60—7·28 (10H, m, ArH), 7·50 (1H, s, H-5), 6·42 (1H, s, H-8), 5·82 (1H, s, Q-H), 3·92 and 3·78 (each 3H, s, OMe), 4·37 (1H, t, *J* 10 Hz, H-2), 4·08 (1H, m, H-2), 3·60 (1H, m, 3-H), 3·07br (1H, H-4), and 2·97 (1H, d, *J* 2 Hz, H-4).

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