Dalbergia Species. Part IX.[1] Phytochemical Examination of *Dalbergia stevensonii* Standl

By **Dervilla M. X. Donnelly** * and **John C. Thompson,** Department of Chemistry, University College, Belfield Dublin 4, Ireland
W. B. Whalley and **Saboor Ahmad,** The School of Pharmacy, 29/39 Brunswick Square, London WC1N 1AX

The bark and heartwood of *Dalbergia stevensonii* have yielded twenty-three natural products of which one, stevenin, is a new neoflavanoid [6-hydroxy-4-(3-hydroxyphenyl)-7-methoxycoumarin], and two are new racemic isoflavanones. The structures of the extractives have been examined by physical methods and in addition the new compounds have been synthesised. The oxygenation pattern relating the structures of isoflavones, isoflavanones, pterocarpans, and coumestones suggests a common biosynthetic origin.

Dalbergia stevensonii Standl (Leguminosae-Lotoideae) is a small tree indigenous to British Honduras and is the source of Honduras rosewood. On the basis of the phylogenetic classification,[2] it belongs to the specific series *Dalbergia brasilianae*.

A chromatographic examination of the n-hexane extract of the bark yielded only glut-5-en-3β-ol (XI). Extracts of the heartwood afforded twenty-three natural products of which one is a new neoflavanoid and two are new racemic isoflavanones. We report here on the isolates and discuss the methods of identification and the syntheses of the new compounds.

Neoflavanoids.—Four neoflavanoids have been isolated from the heartwood, (*S*)-4-methoxydalbergione [3,4] (Ia), (*S*)-4′-hydroxy-4-methoxydalbergione [3] (Ib), dalbergin [5] (IIa), and a new phenol, $C_{16}H_{12}O_5$, stevenin.[1] The spectral data identified compounds (Ia), (Ib), and (IIa) and confirmation was obtained by comparison with authentic samples. The spectroscopic data for stevenin and the 4-phenylcoumarins dalbergin and melannein [6] were similar. The formation of a dimethyl and a diethyl ether confirmed the presence of two phenolic hydroxy-groups. The aromatic proton regions of the n.m.r. spectra of stevenin and its derivatives furnished no conclusive

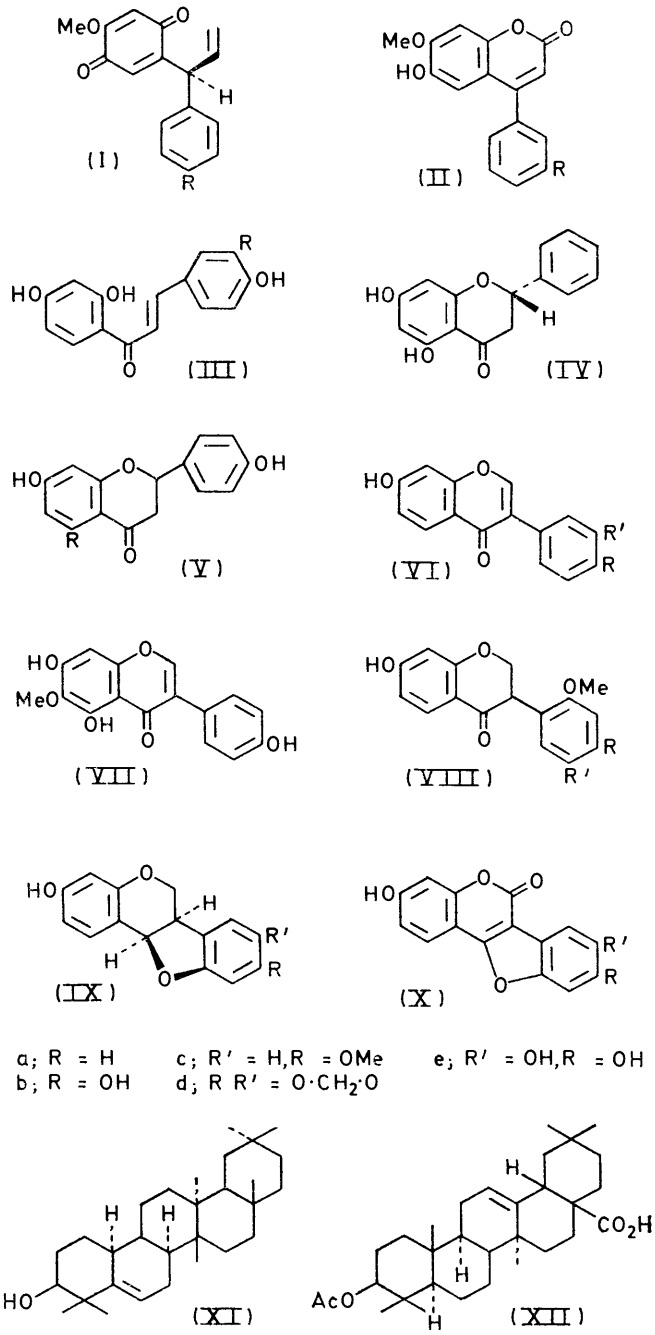
[1] Part VIII, D. M. X. Donnelly, J. O'Reilly, and J. C. Thompson, *Phytochemistry*, 1972, **11**, 823.
[2] A. Braga de Oliveira, O. R. Gottlieb, W. D. Ollis, and C. T. Rizzini, *Phytochemistry*, 1971, **10**, 1863.
[3] W. B. Eyton, W. D. Ollis, I. O. Sutherland, O. R. Gottlieb, M. Taveira Magalhães, and L. M. Jackman, *Tetrahedron*, 1965, **21**, 2683.
[4] B. J. Donnelly, D. M. X. Donnelly, and C. B. Sharkey, *Phytochemistry*, 1965, **4**, 337.
[5] V. K. Ahluwalia, P. L. Sawhney, and T. R. Seshadri, *J. Sci. Ind. Res. India*, 1956, **15***B*, 66.
[6] B. J. Donnelly, D. M. X. Donnelly, and A. M. O'Sullivan, *Tetrahedron*, 1968, **24**, 2617.

evidence for the orientation of the substituent in ring B, except to exclude it from position 4', as the A_2B_2 system was absent. The two singlets characteristic of 5- and 8-protons in 6,7-disubstituted neoflavanoids were present. The mass spectrum of stevenin showed the ion *m/e* 241, which could arise by loss of C_2H_3O from the molecular ion or by loss of a methyl radical from *m/e* 256. The lower mass ions were not abundant and no metastable peaks were apparent.

Insufficient material was available for degradative studies and a synthesis of the dimethyl ethers corresponding to the two likely structures, [6,7-dimethoxy-4-(3-methoxyphenyl)coumarin and 6,7-dimethoxy-4-(2-methoxyphenyl)coumarin] was undertaken. Thus acylation of 1,2,4-trimethoxybenzene by *m*-methoxybenzoyl chloride gave 2-hydroxy-3',4,5-trimethoxybenzophenone, which on fusion with sodium acetate and acetic anhydride formed di-*o*-methylstevenin, identical (m.p.; i.r., u.v., and n.m.r. spectra) with that obtained from natural material. 6,7-Dimethoxy-4-(2-methoxyphenyl)-coumarin was synthesised similarly. The synthesis of 6-ethoxy-7-methoxy-4-(3-ethoxyphenyl)coumarin indicated the positions of the free phenolic groups and that stevenin had structure (IIb). This was confirmed by synthesis by a route involving a modified Pechmann reaction and selective methylation of the 7-position.[7] The yields from these syntheses were unsatisfactory and an improved route to coumarins by oxidation of the corresponding neoflavene with chromium trioxide and pyridine has been elaborated.[8]

A low ν_{CO} value was recorded in the solid state spectra of stevenin. A similar observation[6] was made for dalbergin, melannein, and some 4-unsubstituted coumarins.[9] However, the methylated derivatives of each 4-phenylcoumarin exhibited the expected lactone-type frequency. In an attempt to account for the low ν_{CO} values, i.r. spectra in the solid state and in solution were measured for a series of 4-phenylcoumarins (see Table 1).* The magnitude of the difference in solid state ν_{CO} value between methyl ether and phenolic coumarin was independent of the position of the hydroxy-group. The effect is probably due to intermolecular hydrogen bonding and may well depend on the crystal structure rather than on the molecular structure.

Flavonoids.—The flavanones obtained from the heartwood of *D. stevensonii* were (−)-pinocembrin (IV), (±)-liquiritigenin (Va), and (±)-naringenin (Vb). An analysis of their u.v., i.r., and n.m.r. spectra facilitated the assignment of structures and confirmation was obtained by mixed m.p. determinations with authentic samples. The isomeric chalcone isoliquiritigenin was also isolated. Flavanones are uncommon in the Leguminosae, especially in species of *Dalbergia* and *Macherium*. This constituted the first recorded example of the isolation of (−)-pinocembrin and naringenin from these genera. Liquiritigenin has been reported to occur in *D. latifolia*[10] and butin in *Macherium villosum*.[11]



Isoflavonoids.—Isoflavonoids are widely distributed in the subfamily *Lotoideae* and *D. stevensonii* contains isoflavones, isoflavanones, pterocarpans, and coumestones. With respect to oxygenation pattern, two distinct series are present: (*a*) compounds with a 4'-OMe group (9-OMe in pterocarpan nomenclature) and (*b*) a 4',5'-methylene-

* We thank Dr. H. E. Rubalcava for these measurements.

[7] S. K. Mukerjee, T. Saroja, and T. R. Seshadri, *Indian J. Chem.*, 1969, **7**, 844.

[8] D. M. X. Donnelly, P. J. Kavanagh, G. Kunesch, and J. Polonsky, *J.C.S. Perkin I*, 1973, 965.

[9] B. K. Sabata and M. K. Rout, *J. Indian Chem. Soc.*, 1964, **41**, 74.

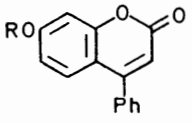
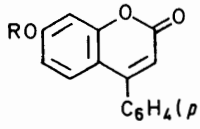
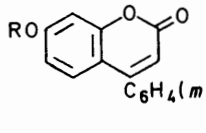
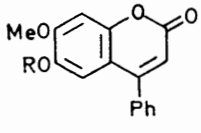
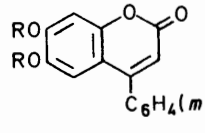
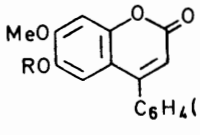
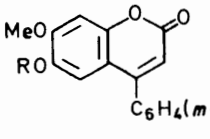
[10] G. D. Bhatia, S. K. Mukerjee, and T. R. Seshadri, *Indian J. Chem.*, 1965, **3**, 422.

[11] A. Braga de Oliveira, O. R. Gottlieb, and W. D. Ollis, *Anais Acad. brasil. Ciênc.*, 1968, **40**, 147.

dioxy-group (8,9- in pterocarpan nomenclature). The isoflavonoids presumably arise biosynthetically from a chalcone precursor by an enzyme mediated aryl migration. Isoliquiritigenin (IIIa) and butein (IIIb), the

TABLE 1

I.r. data for 4-arylcoumarins

Compound	ν_{CO}/cm^{-1} In KBr R = H	In KBr R = Me	In $CHCl_3$ R = H	In $CHCl_3$ R = Me
	1696	1732	1712	1712
	1707	1737	1706	1711
	1702	1718	1715	
	1692	1727	1710	1709
	1660	1728		1711
	1669	1728	1707	1711
	1664	1708		1710

two chalcones with the oxygenation pattern equivalent to that of the isoflavanoid series in *D. stevensonii* heartwood, were found in the extractives. The twin series of similar substitution pattern exhibited by the four isoflavonoid types suggests a common biosynthetic pathway.[12]

Isoflavones. The isoflavones present were daidzein (VIe), formononetin (VIc), ψ-baptigenin (VId), and tectorigenin (VII), identified from examination of their spectra (i.r., n.m.r., and mass) and the corresponding spectra of their *O*-acetates. Tectorigenin is the only example, among the isoflavonoids isolated, having a 5-hydroxy-group. Tectorigenin and its 7-methyl ether have previously been isolated from the leaves of *Dalbergia sissoo*.[13]

Isoflavanones.[14] The racemic isoflavanones 7-hydroxy-2′,4′-dimethoxyisoflavanone (VIIIc) and 7-hydroxy-2′-methoxy-4′,5′-methylenedioxyisoflavanone (VIIId) were isolated as a mixture which was acetylated and then separated (t.l.c.). The predominant mass spectral fragmentation pattern of the isoflavanones was of the retro-Diels–Alder type; accordingly it was possible to distinguish peaks due to dimethoxy- (*m/e* **164**) and methoxymethylenedioxy- (*m/e* **178**) B-rings. The u.v. spectra of the isoflavanones exhibited bathochromic shifts on addition of sodium acetate, characteristic of the 7-hydroxy-substituent. The i.r. spectra [$\nu_{max.}$ 3300 (OH) and 1662 cm^{-1} (CO)] supported the isoflavanone structures. Detailed examination of the n.m.r. spectra identified low-field 5-proton signal in each case. The 2′-substituent in isoflavanones results in non-equivalence of the 2-protons in the heterocyclic ring. The protons at position 2 each give rise to a quartet of which two peaks only were detectable, and these in turn were overlapped. The 3-proton signal appeared in each case as a quartet. The complexity of the spectrum is analogous to that of flavanones. A simple pattern is observed [a doublet (2-H) and triplet (3-H)] for isoflavanones without a 2′-substituent [15] and this is a useful guide to the substitution pattern of ring B.

7-Acetoxy-2′,4′-dimethoxyisoflavanone and 7-acetoxy-2′-methoxy-4′,5′-methylenedioxyisoflavanone were synthesised. The syntheses involved the rearrangement [16] of the corresponding chalcones with thallium(III) acetate, and subsequent debenzylation and cyclisation of the acetals to the known 7-hydroxy-2′,4′-dimethoxyisoflavone [17] and 7-hydroxy-2′-methoxy-4′,5′-methylenedioxyisoflavone.[18] Because of low solubility, the

[12] P. M. Dewick, W. Barz, and H. Grisebach, *Biochim. Biophys. Acta*, 1970, **215**, 203; A. Pelter and P. Stainton, *J. Chem. Soc.* (*C*), 1966, 701; C. P. Falshaw, R. A. Harmer, W. D. Ollis, R. E. Wheeler, V. R. Lalitha, and N. V. Subba Rao, *ibid.* 1969, 374; N. T. Keen, A. I. Zaki, and J. J. Sims, *Phytochemistry*, 1972, **11**, 1031.

[13] A. Banerji, V. V. S. Murti, T. R. Seshadri, and R. S. Thakur, *Indian J. Chem.*, 1963, **1**, 25.

[14] (*a*) F. E. King, M. F. Grundon, and K. G. Neill, *J. Chem. Soc.*, 1952, 4580; (*b*) L. Crombie and D. A. Whiting, *ibid.*, 1963, 1569; (*c*) H. Suginome, *J. Org. Chem.*, 1959, **24**, 1655; (*d*) S. Balakrishna, J. D. Ramsnathan, T. R. Seshadri, and B. Venkataraman, *J. Sci. Ind. Res., India*, 1961, **20B**, 134; *Proc. Roy. Soc.* (*A*), 1962, 268; (*e*) W. D. Ollis, *Experientia*, 1966, **22**, 777; (*f*) R. S. Burden, J. A. Bailey, and G. W. Dawson, *Tetrahedron Letters*, 1972, 4175.

[15] R. V. Campbell, S. H. Harper, A. D. Kemp, *J. Chem. Soc.*, 1969, 1787; M. FitzGerald, Ph.D. Thesis, National University of Ireland, 1972. (*S*)-4′,7-dihydroxyisoflavanone was isolated from *Pericopsis mooniana*.

[16] W. D. Ollis, K. L. Ormond, B. T. Redman, R. J. Roberts, and I. O. Sutherland, *J. Chem. Soc.* (*C*), 1970, 125.

[17] W. Cocker, T. B. H. McMurry, and P. A. Staniland, *J. Chem. Soc.*, 1965, 1034.

[18] C. S. Rangaswami and B. V. Rama Shastry, *Arch. Pharm.*, 1959, **292**, 170; K. Fukui, M. Nakayama, and K. Okazaki, *Nippon Kagaku Zasshi*, 1965, **86**, 960.

isoflavones were acetylated prior to hydrogenation to the isoflavanones.

The isolation of compounds (VIIIc and d) from the heartwood of *D. stevensonii* brings to fourteen the number of known naturally occurring isoflavanones. However the existence of padmakastein (4′,5-dihydroxy-7-methoxyisoflavanone), one of the first reported, is in doubt.[19]

The genus Dalbergia is the source of the isoflavanone violanone [14e] (3′,7-dihydroxy-2′,4′-dimethoxyisoflavanone). The isoflavanones occur most widely in heartwoods but have also been obtained from roots,[14b] seeds,[20] and leaves.[21]

Pterocarpans.[22] (6a*R*,11a*R*)-3-Hydroxy-9-methoxypterocarpan (IXc) and (6a*R*,11a*R*)-3-hydroxy-8,9-methylenedioxypterocarpan (IXd) co-occur, together with their racemates, in the heartwood extract. The optically active compounds were separated from the racemates by fractional crystallisation, and the optically active mixture was separated after acetylation. Hydrogenolysis of the mixed acetates and subsequent acetylation gave the isoflavans (3*R*)-2′,7-diacetoxy-4′,5′-methylenedioxyisoflavan and (3*R*)-2′,7-diacetoxy-4′-methoxyisoflavan (vestitol diacetate).[23]

The mass spectral fragmentation patterns of the isoflavans confirmed the substitution pattern of the parent pterocarpans. Some discrepancies in i.r. spectra of a similar pterocarpan mixture from *Andira inermis* [24] and *Swartzia madagascariensis* [25] have been reported.

Coumestones. Medicagol (Xd) and 12-*O*-methylcoumesterol (Xc) were the components in the mixture of coumestones isolated from the methanol extract (see Scheme 2). The compounds were identified by their fragmentation patterns on electron impact and by their u.v. and i.r. spectra. Authentic samples of the acetates (Xc and d) were available. There are now twenty-one known naturally occurring coumestones.[25,26] Coumestones are restricted to the *Leguminosae* except for wedelolactone and demethylwedelolactone, which occur in the leaves of *Wedelia alba* (Compositae).[26]

The isolation of the triterpene 3β-acetoxyolean-12-en-28-oic acid (XII) is not unexpected and has been reported in *D. spruceana*,[14e] *D. barretoana*,[27] *D. villosa*,[27] *D. latifolia*,[28] and *M. incorruptibile*.[29] Glut-5-en-3β-ol is recorded for the first time in the Dalbergia genus.

EXPERIMENTAL

Unless otherwise stated, the following generalisations apply. M.p.s were determined on a Kofler hot-stage apparatus. I.r. spectra were measured for KBr discs; u.v. spectra were determined for solutions in methanol; 60 MHz n.m.r. spectra were determined for solutions in deuteriochloroform (tetramethylsilane as internal reference). Mass spectra were obtained with an A.E.I. MS902 (direct inlet) instrument. Optical rotations were measured on a Perkin-Elmer model 141 Polarimeter.

Separations by column chromatography were carried out with Merck silica gel. Merck Kieselgel HF_{254} and $H_{254+366}$ were used for thick- and thin-layer chromatography (t.l.c.), respectively. During isolation processes the appropriate combination of fractions was determined by t.l.c. Thin-layer chromatograms were examined with u.v. illumination and by spraying with chlorosulphonic acid in acetic acid. Solvent systems for development were (*A*) chloroform–acetone (9 : 1); (*B*) light petroleum (b.p. 60—80°)–ethyl acetate (7 : 3); (*C*) benzene–ethyl acetate (9 : 1); (*D*) chloroform–acetone (8·5 : 1·5); (*E*) benzene–ethyl acetate (7 : 3); (*F*) chloroform–benzene (1 : 1).

Identification of the Extractives of Dalbergia stevensonii *Standl.*—The elemental analysis and spectroscopic data used in the identification of the extractives are summarised in Table 2.

Extraction of the Bark.—Isolation of glut-5-en-3β-ol (XI). Powdered bark (8·5 kg) was continuously extracted with hot light petroleum (b.p. 60—80°) for 48 h. The extract was concentrated and the dark brown gum (12·4 g) which separated on cooling was chromatographed on alumina (300 g). Elution with benzene–diethyl ether (19 : 1) gave a solid, which crystallised from methanol in needles of glut-5-en-3β-ol (300 mg), m.p. 211—213° (lit.,[30] 211°), $[\alpha]_D^{21}$ +65° ($CHCl_3$) (lit.,[31] +62°) (Found: C, 84·9; H, 12·1%; M^+, 426. Calc. for $C_{30}H_{50}O$: C, 84·4; H, 11·8%; *M*, 426); $\nu_{max.}$ 3425 cm^{-1}; τ 4·32 (m, C$\underline{H}$=CH) and 6·5 (m, C$\underline{H}$·OH). The acetate had m.p. 189—191° (lit.,[31] 192—194°), $[\alpha]_D^{21}$ +80·3° ($CHCl_3$) (lit.,[30] +80°).

Oxidation of glut-5-en-3β-ol (50 mg) with Jones reagent yielded glut-5-en-3-one, m.p. 244·5—245° (lit.,[32] 243°), $[\alpha]_D^{23}$ +27·9° ($CHCl_3$) (lit.,[32] +30°), $\nu_{max.}$ 1710 cm^{-1}.

Extraction of the Heartwood.—Powdered heartwood (3 kg) was extracted with hot n-hexane (4 days) giving fraction A (5·5 g) and subsequently with hot benzene (4 days) and

[19] L. Farkas, N. Nógrádi, S. Antus, and A. Gottsegen, *Tetrahedron*, 1969, **25**, 1013.
[20] M. Krishnamurti, Y. R. Sambhy, and T. R. Seshadri, *Tetrahedron*, 1970, **26**, 3023.
[21] V. K. Ahluwalia, G. P. Sachdev, and T. R. Seshadri, *Indian J. Chem.*, 1966, **4**, 250.
[22] T. B. H. McMurry, E. Martin, D. M. X. Donnelly, and J. C. Thompson, *Phytochemistry*, 1972, **11**, 3283.
[23] K. Kurosawa, W. D. Ollis, B. T. Redman, I. O. Sutherland, A. Braga de Oliveira, O. R. Gottlieb, and H. Magalhães Alves, *Chem. Comm.*, 1968, 1263.
[24] W. Cocker, T. Dahl, C. Dempsey, and T. B. H. McMurry, *J. Chem. Soc.*, 1962, 4906.
[25] S. H. Harper, A. D. Kemp, W. G. E. Underwood, and R. V. M. Campbell, *J. Chem. Soc.* (*C*), 1969, 1109.
[26] (*a*) T. R. Govindachari, K. Nagaraja, B. R. Pai, and P. C. Parthasarathy, *J. Chem. Soc.*, 1956, 629; 1957, 545; (*b*) N. R. Krishnawami, T. R. Seshadri, 'Chemistry of Natural and Synthetic Colouring Matters,' Academic Press, New York, 1962; (*c*) H. N. Khastgir, P. C. Duttagupta, and P. Sengupta, *Tetrahedron*, 1961, **14**, 275; (*d*) J. Eisenbeiss and H. Schmid, *Helv. Chim. Acta*, 1959, **42**, 61; (*e*) L. B. Norton and R. Hansberry, *J. Amer. Chem. Soc.*, 1945, **67**, 1609; (*f*) E. M. Bickoff, G. M. Loper, C. H. Hanson, J. H. Graham, S. C. Witt, and R. R. Spencer, *Crop Science*, 1967, **7**, 259, and references therein; (*g*) D. M. X. Donnelly and M. A. FitzGerald, *Phytochemistry*, 1971, **10**, 3147; (*h*) T. Saitoh and S. Shibata, *Chem. and Pharm. Bull.* (*Japan*), 1969, **17**, 729; (*i*) N. Adityachaudhury and P. K. Gupta, *Chem. and Ind.*, 1970, 1113; (*j*) E. Wong and G. C. M. Leitch, *Phytochemistry*, 1971, **10**, 466; (*k*) H. Zilg and H. Grisebach, *ibid.*, 1968, **7**, 1765.
[27] A. da Silva Braga, V. H. Arndt, H. Magalhães Alves, O. R. Gottlieb, M. Taveira Magalhães, and W. D. Ollis, *Anais Acad. brasil. Ciênc.*, 1967, **39**, 249.
[28] V. K. Dhingra, S. K. Mukerjee, T. Saroja, and T. R. Seshadri, *Phytochemistry*, 1971, **10**, 2551.
[29] H. Magalhães Alves, V. H. Arndt, W. D. Ollis, W. B. Eyton, O. R. Gottlieb, and M. Taveira Magalhães, *Phytochemistry*, 1966, 1327.
[30] F. G. Fisher and N. Seiler, *Annalen*, 1961, **644**, 162.
[31] A. C. Paton, F. S. Spring, and R. Stevenson, *J. Chem. Soc.*, 1958, 2640.
[32] D. A. H. Taylor, *J. Chem. Soc.* (*C*), 1967, 490.

TABLE 2

Identification of extractives of *Dalbergia stevensonii*, Standl. Compounds in fraction B

Compound	Crystal type (solvent) m.p. (°C) (lit.)	$[\alpha]_D$ (°) (solvent)	Analysis: Required (Calc.) (%) Found (%) Mass spectrum	(KBr) $\nu_{max.}$/cm^{-1}	$\lambda_{max.}$(MeOH)/nm (log ϵ)	τ (Solvent)
Neoflavanoids						
(*S*)-4-Methoxydalbergione (Ia)	Yellow needles (di-isopropyl ether), 108—110 (118—119) [2,4]	−15·4 ($CHCl_3$) +76·8 (C_6H_6)		1666, 1646 1625	206 (4·26), 260 (4·16)	2·78 (s, B-ring), 3·58 (s, 6-H), 4·15 (s, 3-H), 6·19 (s, OMe), 3·6—3·73 (1H, m), and 4·6—5·17 (3H, m) (C_3H_4 residue) ($CDCl_3$)
(*S*)-4′-Hydroxy-4-methoxydalbergione (Ib)	Orange rosettes (methanol), 180—185 * (172—178 *) [3]	−69·9 (acetone)		3460, 1669 1645		
Dalbergin (IIa)	Prisms (methanol), 214—216 (209—210) [5]			3236, 1695 1631 1710 ($CHCl_3$)	237 (4·23), 260 (4·05), 301 (3·85), 355 (4·0)	0·5 (s, 6-OH), 2·44 (s, B-ring), 2·87 (s, 5-H), 3·12 (s, 8-H), 3·8 (s, 3-H), 6·08 (s, OMe), [$(CD_3)_2SO$]
Stevenin (IIb)	Needles (methanol) 254		$C_{16}H_{12}O_5$ C, 67·4; H, 4·4 C, 67·6; H, 4·3 M^+ 284 (100%)	3289, 1667 1621 1707 ($CHCl_3$)	222infl (4·74), 284 (4·14), 340 (4·05); in NaOMe 252 (4·49), 312 (3·97), 3·97 (4·08); in NaOAc 301 (4·09), 356 (3·98)	0·48 (s, 6-OH), 3·5 (s, 3-H), 6·08 (s, OMe), 2·47—3·1 (m, aromatic) [$(CD_3)_2SO$]
Flavonoids						
Isoliquiritigenin (IIIa)	Needles (aqueous ethanol) 213 (213—215) [11]					
(−)-Pinocembrin (IV)	Needles (aqueous 50% acetic acid), 198—199 (194—195)	−54·3 (methanol)	$C_{15}H_{12}O_4$ (C, 70·3; H, 4·7) C, 70·6; H, 4·7	3090, 1638sh 1625	210 (4·56), 230sh, 290 (4·31) 325sh; in NaOAc 250 (3·84), 330 (4·53)	−2·15 (s, 5-OH, exchangeable), 2·5 (s, ring B), 3·98 (s, 6- and 8-H), 4·42 (q, J 5·1 and 11·5 Hz, 2-H), 6·91 (d, J 11·5 Hz, 3-H), 7·07 (d, J 5·1 Hz, 3-H) [$(CD_3)_2SO$]
Naringenin (Vb)	Needles (aqueous ethanol), 251 (259)		$C_{15}H_{12}O_5$ (C, 66·3; H, 4·4) C, 66·5; H, 4·3	3250, 1625	203 (4·45), 211 (4·46), 224 (4·43), 289 (4·25), 327 (3·9); in NaOAc 245sh, 325 (4·46); in $AlCl_3$ 224 (4·65), 313 (4·44), 380 (3·68)	−2·16 (s, 5-OH), τ_A 2·6(d) and τ_B 3·1(d) (A_2B_2 system, J_{AB} 8·9 Hz), 4·02 (s, 6- and 8-H), 4·65, 4·45 (q, J 4·3 and 9·2 Hz, 2-H), 6·9 (d, J 4·3 Hz, 3-H) [$(CD_3)_2SO$]
Liquiritigenin	Plates (aqueous ethanol), 203—205 (207) [10]		*m/e* 256 (65%), 137 (100%) $C_{15}H_{12}O_4$ req. *M* 256	3240, 1650	213 (4·4), 230 (4·3), 275 (4·17), 313 (3·87); in NaOMe 248 (4·32), 310sh, 336 (4·36)	0·3—1·24br (s, 4′-OH, 7-OH), 2·6(d) and 3·08(d) (A_2B_2 system, J 8·3 Hz, ring B), τ_A 3·55 (d, 8-H), τ_B 4·5 (q, 6-H), and τ_X 2·26 (d, 5-H) (ABX system, J_{AB} 2·4, J_{BX} 8·3 Hz) [$(CD_3)_2SO$]
Isoflavonoids						
(±)-7-Hydroxy-2′,4′-dimethoxyisoflavanone (VIIIc)	Needles [light petroleum (b.p. 60—80°)–benzene], 184—185					
Monoacetate	Prisms (methanol), 125—127		$C_{19}H_{18}O_6$ C, 66·7; H, 5·3 C, 67·0; H, 5·1	1757 1638		τ_X 1·9 (d) and τ_{AB} 3·2—3·4 (m) (ABX system, J 8·9 Hz, C_6H_5), 6·23 (s, 2 × OMe) 7·78 (s, OAc) (CCl_4)
(±)-7-Hydroxy-2′-methoxy-4′,5′-methylenedioxyisoflavanone (VIIId)	Prisms [light petroleum (b.p. 60—80)–benzene], 189—193		*m/e* 314 (10%), 164 (100%) $C_{17}H_{14}O_6$ req. *M* 314			
Monoacetate	Needles [light petroleum (b.p. 60—80°)–benzene], 150—152					τ_X 1·9 (d) and τ_{AB} 3·0—3·4 (m) (ABX system, J_{AX} 9·1 Hz, s, 6-, 8-H), 4·02 (s, O·CH_2·O), 6·23 (s, OMe), 7·65 (s, OAc) ($CDCl_3$)
Daidzein (VIe)	Plates (acetone), 315—316 * (315—321) [11]		*m/e* 254 $C_{15}H_{10}O_4$ req. *M* 254	3235 1630	209 (4·51), 249 (4·65), 300sh; in NaOAc 253 (4·7), 335 (4·09)	1·56 (s, 2-H), 1·8 (d, $J_{5',6'}$ 7·5 Hz, 5-H), 2·99 (d, 3′- and 5′-H), 2·41 (d, 2′,6′-H) (A_2B_2 system, J 8·5 Hz) [$(CD_3)_2SO$]
Acetate of baptigenin (VId)	Needles (methanol), 166—167 (166)		*m/e* 324 (66%), 282 (100%) $C_{18}H_{12}O_6$ req. *M* 324	1755 1640		1·59 (s, 2-H), 1·65 (d, $J_{5',6'}$ 7·8 Hz), 3·87 (s. O·CH_2·O), 7·61 (s, OAc) [$(CD_3)_2SO$]
Acetate of formononetin (IVc)	Needles (methanol), 169—170 (171) [9,11]		$C_{18}H_{14}O_5$ (C, 69·7; H, 4·55) C, 69·1; H, 4·1	1757 1640		1·56 (s, 2-H), 1·63 (d, J 8·1 Hz, 5-H), τ_A 2·72 and τ_B 3·02 (A_2B_2 system J 9·5 Hz), 6·07 (s, OMe), 7·59 (s, OAc) [$(CD_3)_2CO$]
Tectorigenin (VII)	Needles (benzene–methanol), 226—227 (220—223) [13]		*m/e* 300 $C_{16}H_{12}O_6$ *M* 300		212 (4·42), 267 (4·48), 330sh; in NaOAc, 273 (4·5), 340 (4·09); in $AlCl_3$ 273 (4·46), 375sh, 380 (4·51)	−3·24 (s, 5-OH), 1·95 (s, 2-H), τ_A 2·55 (d) and τ_B 3·15 (d) (A_2B_2 system, J 8·4 Hz) 3·5 (s, 8-H), 6·11 (s, OMe) [$(CD_3)_2CO$]
(−)-3-Acetoxy-9-methoxypterocarpan- (IXc)	Needles (ethyl acetate), 119 (122—123) [22,23]	−182 ($CHCl_3$)	*m/e* 312 (60%), (100%) $C_{18}H_{16}O_5$ req. *M* 312			
(−)-3-Acetoxy-8,9-methylenedioxypterocarpan (IXd)	Needles (ethyl acetate), 176 (176—177) [22,23]	−177 ($CHCl_3$)	*m/e* 326 (55%), 284 (100%) $C_{18}H_{14}O_6$ req. *M* 326			
7-Hydroxy-12-methoxycoumestone [b]	(acetone)		*m/e* 296 (52%), 282 (89%), 267 (100%)	3236 1715 1637		
7-Hydroxy-11,12-methylenedioxycoumestone [b]	320 (*a*) (337) [24e] (*b*) (324—325) [24e]		$C_{16}H_{10}O_5$ and $C_{16}H_8O_6$ req. *M* 282, 296			
Acetates	(acetone), 256—260 (*a*) (240) [24e] (*b*) (263) [24e]		*m/e* 338 (10%), 324 (20), 282 (100) $C_{17}H_{12}O_6$ and $C_{18}H_{16}O_7$ req. *M* 324, 338	1765, 1740		

* Decomp.

methanol (10 days) in the cold. The methanolic extract was re-extracted with diethyl ether. The soluble material (60 g from benzene and 150 g from diethyl ether) constituted fraction B.

Fraction A.—Isolation of (±)-9-*methoxypterocarpan*-3-*ol* (IXc), (±)-8,9-*methylenedioxypterocarpan*-3-*ol* (IXd), *glut*-5-*en*-3β-*ol* (XI), 3β-*acetoxyolean*-12-*en*-28-*oic acid* (XII), *dalbergin* (Ia), *and a series of fatty acids.* A solid (50 mg) deposited from fraction A was collected and washed with benzene. The non-crystalline residue (m.p. 180—181°) contained (±)-9-methoxypterocarpan-3-ol (demethylhomopterocarpin, m.p. 194°) [17] and (±)-8,9-methylenedioxypterocarpan-3-ol (demethylpterocarpin, m.p. 194°).[33] The mass spectrum of the mixture showed *m/e* 284 (18%) and 270 (100%) (Calc. for $C_{16}H_{12}O_5$: 284. Calc. for $C_{16}H_{14}O_4$: 270.) In the n.m.r. spectrum of the mixture, the ratio of intensities of methoxy and methylenedioxy peaks was 1 : 1. The small quantity of material precluded separation of the mixture into its components. The filtrate was chromatographed on silica (450 g), with successively benzene, benzene–chloroform, and acetone, as eluant. Appropriate fractions yielded three combinations, A(i—iii).

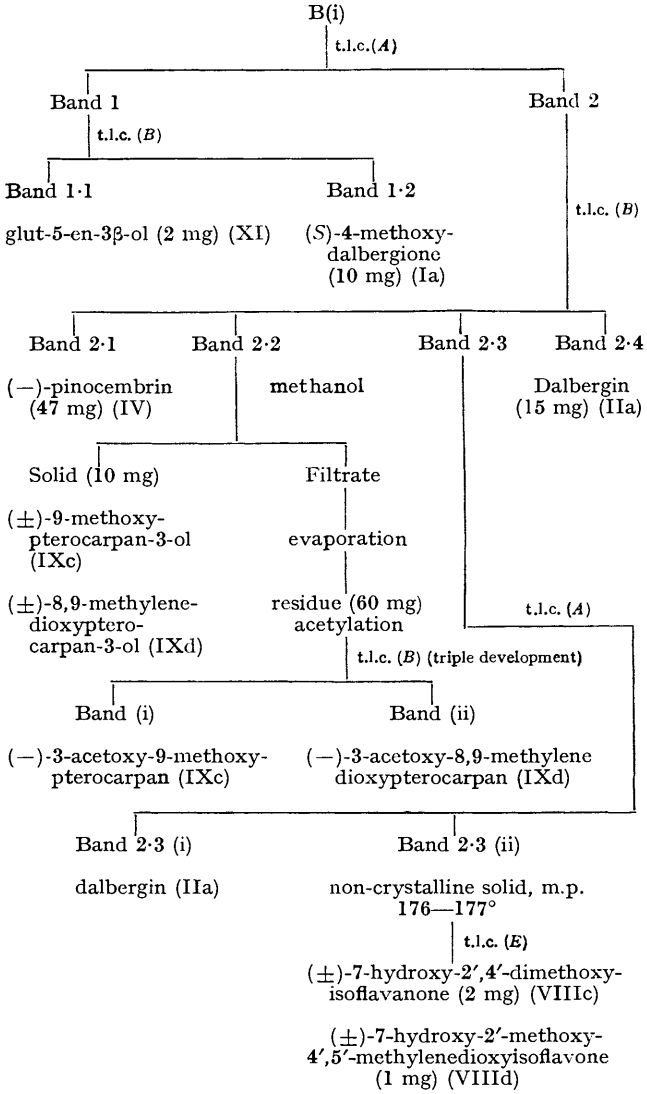
Fraction A(i) (160 mg) was crystallised from di-isopropyl ether giving glut-5-en-3β-ol (150 mg), identified by comparison with a sample obtained from the bark. The mother liquor yielded a residue (10 mg) which was fractionated (t.l.c.). Elution with diethyl ether gave an oil (4 mg), which on addition of methanol afforded needles (3 mg), m.p. 199·5—200°, $[\alpha]_D^{21}$ +39·2° ($CHCl_3$). Insufficient material was available for identification.

Fraction A(ii) (2 g) was a fatty material; g.l.c. analysis of a portion treated with diazomethane showed the presence of a series of unbranched saturated acid esters (C_{19}—C_{27} inclusive). The methyl esters of arachidic, behenic, and lignoceric acids were used as standards.

Fraction A(iii) (2 g) was chromatographed [silica (100 g)]; elution with chloroform–acetone (9 : 1) afforded two main components which were further purified (t.l.c.). 3β-Acetylolean-12-en-28-oic acid (XII) (3 mg), crystallised from methanol, had m.p. 253—254° (lit.,[30] 259—260°), $[\alpha]_D^{21}$ +74° ($CHCl_3$). Dalbergin (IIa) crystallised as prisms from methanol, m.p. and mixed m.p. 215—217°.

Fraction B.—Isolation of glut-5-*en*-3β-*ol* (XI), (S)-4-*methoxydalbergione* (Ia), (−)-5,7-*dihydroxyflavanone* (*pinocembrin*) (IV), (±)- *and* (−)-8,9-*methylenedioxypterocarpan*-3-*ol* (IXd), (±)- *and* (−)-9-*methoxypterocarpan*-3-*ol* (IXc), *dalbergin* (IIa), 7-*hydroxy*-2′,4′-*dimethoxyisoflavanone* (VIIIc), 7-*hydroxy*-2′-*methoxy*-4′,5′-*methylenedioxyisoflavanone* (VIIId), (S)-4′-*hydroxy*-4-*methoxydalbergione* (Ib), 7-*hydroxy*-11,12-*methylenedioxycoumestone* (Xd) (*medicagol*), 7-*hydroxy*-12-*methoxycoumestone* (Xc), *formononetin* (VIc), ψ-*baptigenin* (VId), 6-*hydroxy*-4-(3-*hydroxyphenyl*)-7-*methoxycoumarin* (*stevenin*) (IIb), *tectorigenin* (VII), *naringenin* (Vb), 2′,4,4′-*trihydroxychalcone* (IIIa), 2′,3,4,4′-*tetrahydroxychalcone* (IIIb), *liquiritigenin* (Va), *and daidzein* (VIe). A portion (20 g) of fraction B was chromatographed [silica gel (800 g)] with successively chloroform and chloroform–acetone (9·5 : 0·5; 9 : 1; 4 : 1) as eluant. This procedure was repeated five times. The appropriate combination of fractions B(i—vi) was determined by examination of their n.m.r. spectra and t.l.c. behaviour. The products were purified by preparative t.l.c. The relevant bands on the t.l.c. plates (numbered in order of decreasing R_F value) were eluted with diethyl ether and rechromatographed.

Fraction B(i) [eluant chloroform (1·5 l)] was rechromatographed. The developing solvents (in parentheses) and the compounds isolated are shown in Scheme 1.



SCHEME 1

Fraction B(ii) [eluant chloroform–acetone 9·5 : 0·5 (600 ml)] was an oil purified by t.l.c. giving (S)-4′-hydroxy-4-methoxydalbergione (10 mg) (Ib).

Fraction B(iii) [eluant chloroform–acetone 9·5 : 0·5 (2 l)] was a brown oil, separated into its components as shown in Scheme 2.

Fraction B(iv) [eluant chloroform–acetone 9 : 1 (1·3 l)] was an oil which when treated with acetone gave stevenin (Jb) (66 mg).

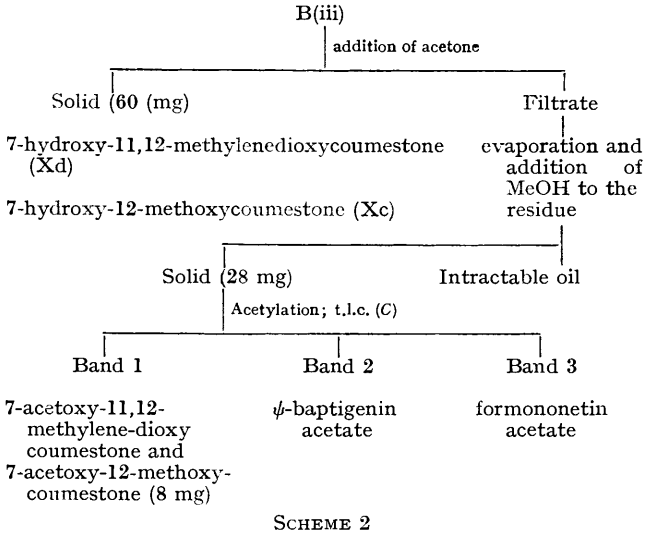
Fraction B(v) [eluant as for B(iv) (600 ml)] was purified by t.l.c. (Scheme 3).

Fraction B(vi), purified by t.l.c. (*D*) gave a major band identified as daidzein (25 mg).

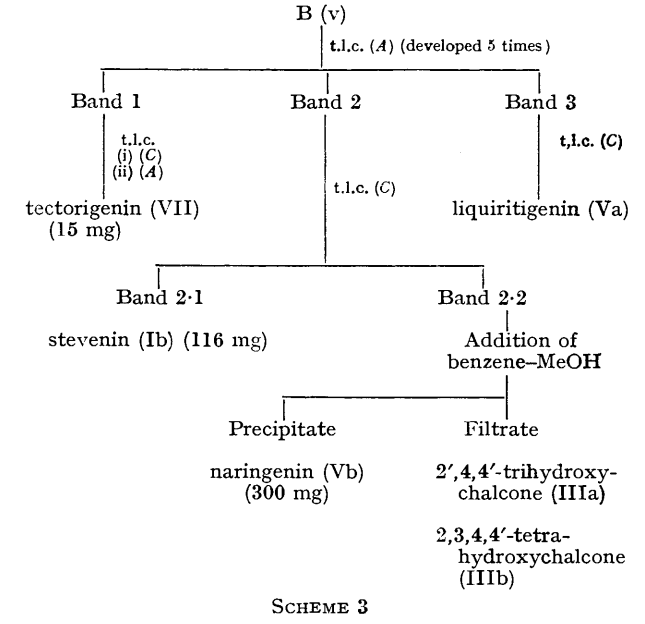
Derivatives of stevenin (IIb).—Methylation of stevenin (50 mg) with anhydrous potassium carbonate (1 g), dimethyl

[33] K. Fukui and M. Nakayama, *Bull. Chem. Soc. Japan*, 1969, **42**, 1408; S. Shibata and Y. Nishikawa, *Chem. and Pharm. Bull. (Japan)*, 1963, **11**, 167; K. Fukui, M. Nakayama, and H. Tsuzuki, *Experientia*, 1968, **24**, 536.

sulphate (0·1 ml), and acetone (10 ml) during 48 h under reflux gave *the dimethyl ether* (30 mg) as needles, m.p. 133·5—135° (from methanol) (Found: C, 69·3; H, 5·2. $C_{18}H_{16}O_5$ requires C, 69·2; H, 5·2%), $\nu_{max.}$ 1723 cm^{-1}, $\nu_{max.}$ ($CHCl_3$) 1711 cm^{-1}.



SCHEME 2



SCHEME 3

Prepared by treatment with diethyl sulphate–potassium carbonate–acetone, the *diethyl ether* formed needles, m.p. 124—125° (from ethanol) (Found: C, 70·8; H, 6·05. $C_{20}H_{20}O_5$ requires C, 70·6; H, 5·0%), $\nu_{max.}$ 1710, 1615, and 1605 cm^{-1}, τ 2·5—3·07 (m, aromatic), 3·8 (s, 3-H), 5·77—6·25 (m, O·CH_2·CH_3), 6·07 (s, OMe), and 8·57 and 8·62 (2 × t, *J* 7·0 Hz, 6- and 3′-O·CH_2·CH_3).

Synthesis of 6,7-*Dimethoxy*-4-(3-*methoxyphenyl*)*coumarin*.—Acylation (catalyst aluminium chloride) of 1,2,4-trimethoxybenzene (10 g) with *m*-methoxybenzoyl chloride (10 g) in anhydrous ether (100 ml) occurred at room temperature during 48 h. The mixture was treated with aqueous hydrochloric acid at 0°. Extraction with ether and benzene, washing the extract with sodium hydrogen carbonate and water, and subsequent evaporation afforded an oil (6 g). Crystallisation from methanol gave 2-*hydroxy*-3′,4,5-*trimethoxybenzophenone* as yellow needles, m.p. 94° (Found: C, 67·1; H, 5·8. $C_{16}H_{16}O_5$ requires C, 66·7; H, 5·6%), τ −2·57 (s, 2-OH), 2·92 (s, 6-H), 3·41 (s, 3-H), and 6·03, 6·11, and 6·27 (3 × s, OMe). The *acetate*, prepared using acetic anhydride–pyridine, was an oil, b.p. 174° at 2·5 mmHg (Found: C, 65·4; H, 5·5. $C_{18}H_{18}O_6$ requires C, 65·8; H, 5·4%).

2-Hydroxy-3′,4,5-trimethoxybenzophenone (4 g), acetic anhydride (10 ml), and fused sodium acetate (2 g) were heated (72 h) under reflux; the product was obtained as a yellow oil (700 mg). Purification of a sample by preparative t.l.c. [multiple development; benzene–ethyl acetate (19 : 1)] yielded 6,7-dimethoxy-4-(3-methoxyphenyl)coumarin (28 mg) as needles from methanol, m.p. and mixed m.p. (with stevenin dimethyl ether) 133—133·5°.

Synthesis of 6-*Ethoxy*-4-(3-*ethoxyphenyl*)-7-*methoxycoumarin*.—Acylation of 1,4-diethoxy-2-methoxybenzene (5 g) with *m*-ethoxybenzoyl chloride (5 g; b.p. 135—40° at 10 mmHg) in dry ether [catalyst aluminium chloride (5 g)] occurred at room temperature during 48 h; the product was isolated in the usual manner. Separation of 2,3′,5-triethoxy-4-methoxybenzophenone and 3′,5-diethoxy-2-hydroxy-4-methoxybenzophenone was achieved with aqueous sodium hydroxide (10%). 2,3′,5-*Triethoxy*-4-*methoxybenzophenone* crystallised from methanol as needles (330 mg), m.p. 103° (Found: C, 69·9; H, 7·1. $C_{20}H_{24}O_5$ requires C, 69·8; H, 7·0%), τ 2·84—3·1 (m, ring B), 3·11 (s, 6-H), 3·64 (s, 3-H), 5·95 (3 × q, *J* 7·0 Hz, O·CH_2·CH_3), 6·1 (s, 4 × OMe), and 8·75 (3 × t, *J* 7·0 Hz, O·CH_2·CH_3). The alkali-soluble 3′,5-*diethoxy*-2-*hydroxy*-4-*methoxybenzophenone* formed yellow needles (124 mg), m.p. 79—80° (from methanol) (Found: C, 68·5; H, 6·3. $C_{18}H_{20}O_5$ requires C, 68·4; H, 6·3%), τ −2·5 (s, 2-OH, exchangeable), 2·54—3·1 (m, B-ring), 2·82 (s, CH), 3·45 (s, 3-H), 6·0 (s, 4-OMe), 5·9 (2 × q, O·CH_2·CH_3), and 8·75 (2 × t, O·CH_2·CH_3).

3′,5-Diethoxy-2-hydroxy-4-methoxybenzophenone (500 mg), acetic anhydride (5 ml), and fused sodium acetate (500 mg) were heated (5 days) under reflux. The mixture was acidified at 0° and extracted with ether. The oily product was purified by t.l.c. [developer (*A*)] to give 6-ethoxy-7-methoxy-4-(3-ethoxyphenyl)coumarin as needles (from methanol), m.p. 123°, identical with stevenin diethyl ether.

Synthesis of Stevenin (IIb).—6,7-*Dihydroxy*-4-(3-*methoxyphenyl*)*coumarin*. A suspension of ethyl (*m*-methoxybenzoyl)acetate (4 g) and 1,2,4-triacetoxybenzene (4 g) in anhydrous ethanol (40 ml) was saturated (72 h) with dry hydrogen chloride. The mixture was poured on ice to give a precipitate (1·8 g) which crystallised from methanol to give 6,7-*dihydroxy*-4-(3-*methoxyphenyl*)*coumarin* as prisms, m.p. 287—288° (Found: C, 68·1; H, 4·2. $C_{16}H_{12}O_5$ requires, C, 67·6; H, 4·3%), $\nu_{max.}$ 1660 cm^{-1}, τ [$(CD_3)_2SO$] 2·3—2·9 (m, B-ring), 3·02 (s, 5- and 8-H), 3·73 (s, 3-H), and 6·02 (s, 3′-OMe). The *diacetate* crystallised from methanol in needles, m.p. 159—160° (Found: C, 65·1; H, 4·25. $C_{20}H_{16}O_7$ requires C, 65·2; H, 4·4%), τ 2·5—3·1 (m, 5-, 8- and ring B protons), 3·6 (s, 3-H), 6·14 (s, OMe), and 7·69 and 7·75 (s, 6- and 7-OAc).

6,7-*Diacetoxy*-4-(3-*acetoxyphenyl*)*coumarin*. Hydriodic acid (57%; 6 ml), 6,7-dihydroxy-4-(3-methoxyphenyl)-coumarin (1·25 g), and acetic anhydride (10 ml) were heated (30 min) under reflux, cooled, and poured into saturated

sodium sulphite solution (100 ml) at 0°. The precipitate crystallised from methanol–ethyl acetate giving 6,7-dihydroxy-4-(3-hydroxyphenyl)coumarin (350 mg) as prisms, m.p. 197°. Acetylation (acetic anhydride–pyridine) gave 6,7-*diacetoxy*-4-(3-*acetoxyphenyl*)*coumarin* (350 mg), which crystallised from methanol as needles, m.p. 122° (Found: C, 64·1; H, 4·4. $C_{21}H_{18}O_8$ requires C, 63·6; H, 4·1%), τ 2·5—2·78 (m, aromatic), 3·54 (s, 3-H), 7·65 (s, 2 × OAc), and 7·73 (s, OAc).

6-*Hydroxy*-4-(3-*hydroxyphenyl*)-7-*methoxycoumarin* (IIb). The preceding triacetate (100 mg), dimethylformamide (25 ml), anhydrous potassium carbonate (1 g), and methyl iodide (0·5 ml) were heated (30 min) under reflux. After 10 min more methyl iodide was added. The solution was cooled, poured into water, and extracted with ether; the extract was evaporated and purified by t.l.c. (*A*). The major fraction was eluted with ether and shown by n.m.r. spectroscopy to be a mixture of the triacetoxy- and diacetoxymethoxy-4-phenylcoumarins. Hydrolysis of the mixture (50 mg) in ethanol (20 ml) and aqueous ammonia (10%; 30 ml) at 90° for 5 min gave an oil. Preparative t.l.c. (*A*) and elution of the less polar yellow band afforded 6-*hydroxy*-4-(3-*hydroxyphenyl*)-7-*methoxycoumarin*, which crystallised from methanol in yellow prisms (3 mg), m.p. 250°, identical with stevenin (Found: M^+, 284. $C_{16}H_{12}O_5$ requires *M*, 284).

Synthesis of 6,7-*Dimethoxy*-4-(2-*methoxyphenyl*)*coumarin*.—Acylation (catalyst aluminium chloride) of 1,2,4-trimethoxybenzene (10 g) by *o*-methoxybenzoylchloride in anhydrous ether (100 ml) occurred at room temperature during 48 h. The oily product deposited 2-*hydroxy*-2′,4,5-*trimethoxybenzophenone*, which formed yellow prisms, m.p. 98° (from methanol) (Found: C, 66·8; H, 5·6. $C_{16}H_{16}O_5$ requires C, 66·7; H, 5·6%), τ −2·6 (s, OH, exchangeable), 2·4—3·0 (m, B-ring), 3·27 (s, 6-H), 3·47 (s, 3-H), and 6·05, 6·19, and 6·35 (3 × s, OMe).

The benzophenone (2 g), acetic anhydride (10 ml), and fused sodium acetate (1 g) were heated (3 days) under reflux to give an oil which was purified by t.l.c. (*F*). Crystallisation from aqueous ethanol of material isolated from the major band gave 6,7-*dimethoxy*-4-(2-*methoxyphenyl*)*coumarin* as prisms (20 g), m.p. 106° (Found: C, 65·6; H, 5·0. $C_{18}H_{16}O_5,H_2O$ requires C, 65·4; H, 5·4%), τ 2·35—3·0 (m, B-ring), 3·11 (s, 5-H), 3·4 (s, 8-H), 3·77 (s, 3-H), and 6·03, 6·21, and 6·27 (each s, 3 × OMe).

Synthesis of 7-*Acetoxy*-2′,4′-*dimethoxyisoflavanone*.—Sodium hydroxide (2 g) in water (5 ml) was added to a solution of di-*O*-benzylresacetophenone (1·1 g) and 2,4-dimethoxybenzaldehyde (0·65 g) in ethanol (20 ml). The mixture was heated (15 min) under reflux, cooled, diluted with water (200 ml), and acidified to pH 3. Extraction with ether gave an oil which crystallised from methanol–acetone (1 : 1) to afford 2′,4′-*bisbenzyloxy*-2,4-*dimethoxychalcone* (1 g) as yellow prisms, m.p. 113—114° (Found: C, 77·6; H, 6·0. $C_{31}H_{28}O_5$ requires C, 77·5; H, 5·9%), $\lambda_{max.}$ 207, 245, and 360 nm (log ε 4·8, 4·2, and 4·14). τ_A 2·0 (d) and τ_B 2·54 (d) (AB system, J_{AB} 16 Hz, CO·CH_A=CH_BAr), τ 2·63 (m, Ph), τ_A 3·5 (q), τ_B 3·55 (d), and τ_X 2·2 (d) (ABX system J_{AB} 2, J_{AX} 9 Hz, 3′-H, 5′-H, and 6′-H), τ 4·9 (s, OCH_2Ph), 6·15, and 6·25 (2, OMe), and τ_{AB} 3·3—3·5 (m) and τ_X 2·7 (d) (ABX system, 3-, 5-, and 6-H).

Thallium(III) acetate (750 mg) was added to the preceding chalcone (480 mg) in methanol (30 ml) and the solution was heated (4 days) under reflux. Purification of the oily product by t.l.c. (*C*) gave 2′,4′-bisbenzyloxy-2,4-dimethoxychalcone (150 mg) and 1-(2,4-bisbenzyloxyphenyl)-2-(2,4-dimethoxyphenyl)-3,3-dimethoxypropan-1-one (200 mg). Further purification of the propan-1-one [t.l.c. (*A*)] afforded an oil, τ (CCl_4) 2·7 (s, Ph), 2·3—2·8 and 3·5—3·8 (m, aromatic H), τ_A 4·5 (d) and τ_B 4·95 (d) [AB system, J_{AB} 8·7 Hz, CO·CH·CH(OMe)$_2$], 6·35 and 6·42 (s, OMe), 6·65 and 6·95 (s, aliphatic OMe), and 5·10 and 4·99 (s, O·CH_2Ph).

Palladised charcoal (10%; 25 mg) was added to the foregoing acetal (200 mg) in ethyl acetate (20 ml). The mixture was stirred in an atmosphere of hydrogen until uptake ceased; the product was purified by t.l.c. (*A*) to give 1-(2,4-*dihydroxyphenyl*)-2-(2,4-*dimethoxyphenyl*)-3,3-*dimethoxypropan*-1-*one*, which formed prisms (64 mg), m.p. 165—166° (from methanol) (Found: C, 62·7; H, 5·8. $C_{19}H_{20}O_7$ requires C, 63·0; H, 6·1%), τ [$(CD_3)_2CO$] −2·75 (s, OH), τ_{AB} 3·4—3·6 (m) and τ_X 2·0 (d) [ABX system, J_{AX} 8·6 Hz, C_6H_3(A)], τ_A 4·65 and τ_B 4·85 [AB system, J_{AB} 9 Hz, CO·CH·CH(OMe)$_2$], τ 6·15 and 6·23 (s, OMe), 6·6 and 6·8 (s, aliphatic OMe), and τ_{AB} 3·4—3·6 (m) and τ_X 2·65 (d) [ABX system, *J* 8·0 Hz, C_6H_3(B)].

Concentrated hydrochloric acid (1 ml) was added to the preceding acetal (80 mg) in ethanol (15 ml) and the solution was warmed (15 min) on a water-bath. Addition of water (100 ml) to the mixture and subsequent extraction with chloroform gave a solid (80 mg) which yielded 7-hydroxy-2′,4′-dimethoxyisoflavone (50 mg) as prisms (from ethanol), m.p. 271° (lit.,[17] 265—267°) (Found: C, 68·9; H, 4·8. Calc. for $C_{17}H_{14}O_5$: C, 68·5; H, 4·7%), $\lambda_{max.}$ (MeOH–NaOAc) 253, 280sh, and 345 nm (log ε 4·5 and 4·13), $\nu_{max.}$ 3200 and 1629 cm^{-1}, τ [$(CD_3)_2SO$] 0·6 (s, OH), 1·74 (s, 2-H), τ_{AB} 2·6—3·2 (m) and τ_X 1·92 (ABX system, J_{AX} 9 Hz, C_6H_3) and 6·02 and 6·11 (s, OMe).

The acetate crystallised from methanol in needles (26 mg), m.p. 143°, τ 7·71 (s, OAc).

7-Acetoxy-2′,4′-dimethoxyisoflavone (26 mg) was hydrogenated in ethyl acetate (10 ml) containing palladium–charcoal (10%; 50 mg) at room temperature (uptake 1 mol. equiv.). The product was purified by t.l.c. (*C*) to yield 7-acetoxy-2′,4′-dimethoxyisoflavanone (15 mg) as prisms (from methanol), m.p. 125—127°.

Dilute ammonia (25%; 10 ml) was added to a solution of 7-acetoxy-2′,4′-dimethoxyisoflavanone (10 mg) in ethanol (5 ml) and the mixture warmed on a steam-bath (20 min). Acidification and extraction of the mixture with diethyl ether yielded an oil. Purification by t.l.c. (*C*) and subsequent crystallisation of the residue from the major band gave prisms (4 mg) of 7-hydroxy-2′,4′-dimethoxyisoflavanone, m.p. 184° (from benzene). This substance was identical (m.p.) with the natural product (VIIIc).

Synthesis of 7-*Acetoxy*-2′-*methoxy*-4′,5′-*methylenedioxyisoflavanone*.—Sodium hydroxide (2 g) in water (5 ml) was added to a solution of di-*O*-benzylresacetophenone (2 g) and 6-methoxypiperonal (1·05 g) in ethanol (15 ml). The mixture was heated (20 min) under reflux; the product was isolated and purified from methanol to afford 2′,4′-*bisbenzyloxy*-2-*methoxy*-4,5-*methylenedioxychalcone* (800 mg) as yellow prisms, m.p. 141—142° (Found: C, 75·3; H, 5·1. $C_{31}H_{26}O_6$ requires C, 75·3; H, 5·3%), $\lambda_{max.}$ 208, 247, 313, and 392 nm (log ε 4·86, 4·2, 4·4, and 4·38), τ_A 1·99 (d) and τ_B 2·68 (d) (AB system, J_{AB} 16 Hz, CO·CH_A=CH_B), τ 4·06 (s, O·CH_2·O), 4·9 (s, 2 × O·CH_2Ph), 6·25 (s, OMe), τ_A 3·45 (d), τ_B 3·45 (q), and τ_X 2·2 (d) (ABX system, J_{AB} 2·0, J_{AX} 8·7 Hz, C_6H_3), and τ 3·5 and 3·2 (s, 3- and 6-H).

Thallium(III) acetate (1·45 g) was added to the preceding chalcone (725 mg) in methanol (50 ml) and the solution was heated (4 days) under reflux. Fractionation of the oily

product [t.l.c. (*C*)] gave 2′,4′-bisbenzyloxy-2-methoxy-4,5-methylenedioxychalcone and 1-(2,4-bisbenzyloxyphenyl)-3,3-dimethoxy-2-(2-methoxy-4,5-methylenedioxyphenyl)-propan-1-one, which was further purified [t.l.c. (*A*)] to afford an oil, τ 6·85 and 6·6 (s, aliphatic OMe), 6·35 (s, OMe), and 4·85 and 4·95 (s, O·CH_2Ph). Palladised charcoal (10%; 25 mg) was added to this acetal dissolved in ethyl acetate (15 ml) and the suspension was stirred in hydrogen (12 h) to yield 1-(2,4-dihydroxyphenyl)-3,3-dimethoxy-2-(2-methoxy-4,5-methylenedioxyphenyl)propan-1-one (50 mg) as prisms from methanol, τ −2·76 (s, OH), 6·53 and 6·7 (s, aliphatic OMe), 6·1 (s, OMe), 4·1 (s, O·CH_2·O), τ_A 4·6 (d) and τ_B 4·85 (d) [AB system, J_{AB} 8·9 Hz, CO·CH–CH(OMe)$_2$], τ_{AB} 3·65 (m) and τ_X 2·1 (d) (ABX system, J_{AX} 9·1 Hz, C_6H_3), and τ 3·05 (s) and 3·45 (s) (6- and 3-H).

Concentrated hydrochloric acid (0·5 ml) was added to this acetal (50 ml) dissolved in ethanol (15 ml) and the mixture was warmed (15 min) on a steam-bath to yield 7-hydroxy-2′-methoxy-4′,5′-methylenedioxyisoflavone (40 mg) as needles, m.p. 299—301° (from ethanol) (lit.,[18] 298—301°). The acetate had m.p. 173° (lit.,[18] 175—176°).

A solution of 7-acetoxy-2′-methoxy-4′,5′-methylenedioxyisoflavone (40 mg) in ethyl acetate (5 ml) containing palladium–charcoal (10%; 25 mg) was hydrogenated to give an oil which was chromatographed [t.l.c. (*C*)]. 7-Acetoxy-2′-methoxy-4′,5′-methylenedioxyisoflavanone (2 mg) was obtained as needles, m.p. 150—152° [from benzene–light petroleum (b.p. 60—80°)], identical (mass spectra) with the natural product (VIIId).

Hydrogenolysis of the Mixture of (−)-3-*Acetoxy*-8,9-*methylenedioxypterocarpan and* (−)-3-*Acetoxy*-9-*methoxypterocarpan.*—The experimental details have been published elsewhere.[22] The separation of the mixture from hydrogenolysis [t.l.c. multiple development; benzene–ethyl acetate (32 : 1)] gave (3*R*)-2′,7-diacetoxy-4′-methoxyisoflavan (1 mg), m.p. 115—118° [needles from benzene–light petroleum (b.p. 60—80°) (1 : 1)], *m/e* 356 (*M*, 30%) and 150 (100%) (Calc. for $C_{20}H_{20}O_6$: *M*, 356); and (3*R*)-2′,7-diacetoxy-4′,5′-methylenedioxyisoflavan (3 mg), m.p. 160—161° [needles from benzene–light petroleum (b.p. 60—80°) (1 : 1)], *m/e* 370 (M^+, 14%) and 164 (100%) (Calc. for $C_{20}H_{18}O_7$: *M*, 370).

We thank the Minister for Education, Republic of Ireland, for a maintenance grant (to J. C. T.), and CIBA (Basle) for the support of one of us (S. A.). We also thank Professor H. Erdtman for a sample of (−)-pinocembrin, Dr. E. M. Bickoff for samples of the coumestone acetates, and Professor T. R. Seshadri, for a sample of ψ-baptigenin.

[3/409 *Received*, 22*nd February*, 1973]