Phytochemistry, 1971, Vol. 10, pp. 3147 to 3153. Pergamon Press. Printed in England.

PTEROCARPANOID CONSTITUENTS OF *SWARTZIA LEIOCALYCINA**

D. M. X. DONNELLY and M. A. FITZGERALD
Department of Chemistry, University College, Belfield, Dublin 4, Ireland

(*Received* 5 *April* 1971)

Abstract—The proposed structure for leiocalycin from *Swartzia leiocalycina* has been confirmed by degradation and partial synthesis. Co-occurring with the pterocarp-6a-en are two new coumestones, 6-hydroxy-7-methoxy-11,12-methylenedioxycoumestone and 6-hydroxy-5,7-dimethoxy-11,12-methylenedioxycoumestone and the known 6aR,11aR-2-hydroxy-3-methoxy-8,9-methylenedioxypterocarpan.

INTRODUCTION

OUR INTEREST in a phytochemical examination of the West Indian tree *Swartzia leiocalycina* (Leguminosae), commonly called 'Wamara', was aroused by a wish to identify the constituents responsible for its resistance to insect attack. We considered that this genus was possibly a source of pterocarpans such as pisatin and phaseollin, two compounds known to be inhibitory to a wide range of phytopathogenic fungi.[1,2] Furthermore, an examination of this plant could contribute towards a firmer basis for the classification of the Swartzieae which is still disputed. Engler and Melchior[3] place this taxon in the subfamily Caesalpinioideae whilst Hutchinson[4] lists it in the Lotoideae.

RESULTS AND DISCUSSION

The heartwood extractives of *Swartzia leiocalycina* have yielded five oxygen heterocycles. The structures of four were elucidated by use of physical methods in association with syntheses, partial synthesis and degradation.

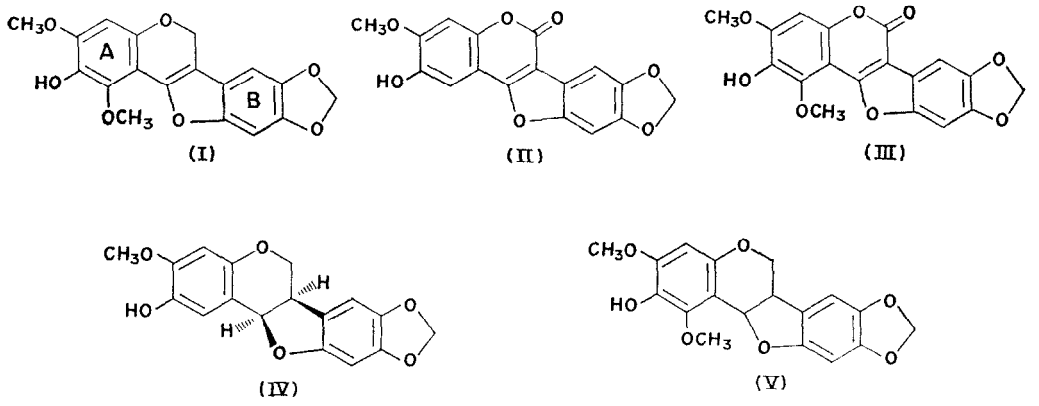
The major constituent, $C_{18}H_{14}O_7$, for which the name leiocalycin is suggested, was isolated from the *n*-hexane extract and is assigned structure (I). Two coumestones† (II) and (III) and 6aR,11aR-2-hydroxy-3-methoxy-8,9-methylenedioxypterocarpan[5] (IV) were obtained from the acetone extract. Insufficient material is available, at present, to permit the assignment of a structure to the fifth compound, $C_{19}H_{14}O_8$.

A feature of the NMR spectrum of leiocalycin is the presence of two methoxyl groups (τ 6·05 and 6·17) and a methylenedioxy group (τ 4·1). A positive Labat test[6] supported the assignment of the latter signal. The aromatic region is characterized by three singlets τ 2·99, 3·33 and 3·7 (in $CDCl_3$). The absorption 3544 cm^{-1} in the IR spectrum indicated

* Reported at the Third Hungarian Bioflavonoid Symposium, Debrecen, Hungary, May 1970.

† The term coumestone, rather than coumestan, was suggested by Professor W. D. OLLIS, "*Recent Advances in the Phytochemistry*", Vol. I, p. 328, Appleton–Century–Crofts, New York to describe coumaranocoumarin.

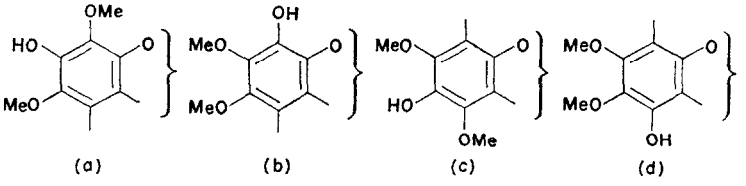
[1] I. A. M. CRUICKSHANK, *Austral. J. Biol. Sci.*, **15**, 147 (1962).
[2] DAWN R. PERRIN and I. A. M. CRUICKSHANK, *Phytochem.* **8**, 971 (1969).
[3] A. ENGLER, *Syllabus der Pflanzenfamilien* (edited by H. MELCHIOR), 12th edn, Vol. II, Borntraeger, Berlin (1964).
[4] J. HUTCHINSON, *The Genera of Flowering Plants*, Vol. I, Oxford University Press (1964).
[5] G. J. H. RALL, J. P. ENGELBRECHT and A. J. BRINK, *Tetrahedron* **26**, 5007 (1970).
[6] J. A. LABAT, *Bull. Soc. Chim. Biol.* **15**, 1344 (1933).



the presence of a free hydroxyl group adjacent to at least one methoxyl substituent.[7] Its phenolic character was confirmed by analysis (IR, NMR) of the monoacetate and monomethyl ether. On the basis of this information a pterocarp-6a-en skeletal structure was assigned. The mass and electronic spectra and the elemental analysis supported this assignment.

The position of the substituents on the two benzene rings was sought by a study of spectra of the products from hydrogenation (V) and subsequent hydrogenolysis (VI) of leiocalycin. The mass spectrum of the pterocarpan (V) cannot be used to assign the various groups to rings A and B as every fragment can reasonably be formulated as arising from either ring.[7,8] However, the mass spectrum of the isoflavan (VI) showed evidence of a typical RDA fragmentation pattern. A further fragmentation was observed due to a homolytic fission of 3,4-bond which gives rise to a diradical in which both electrons would be stabilized by mesomerism over the adjacent benzene ring. The fragments *m/e* 151 and *m/e* 164 could only be rationalized if the methylenedioxy-group was assigned to ring B. A *para*-relationship of two aromatic protons is observed in the NMR spectrum in pyridine ($J_{1,10} < 1{\cdot}0$ c/s) and consequently the methylenedioxy group in ring B of leiocalycin is at the 8,9-position.

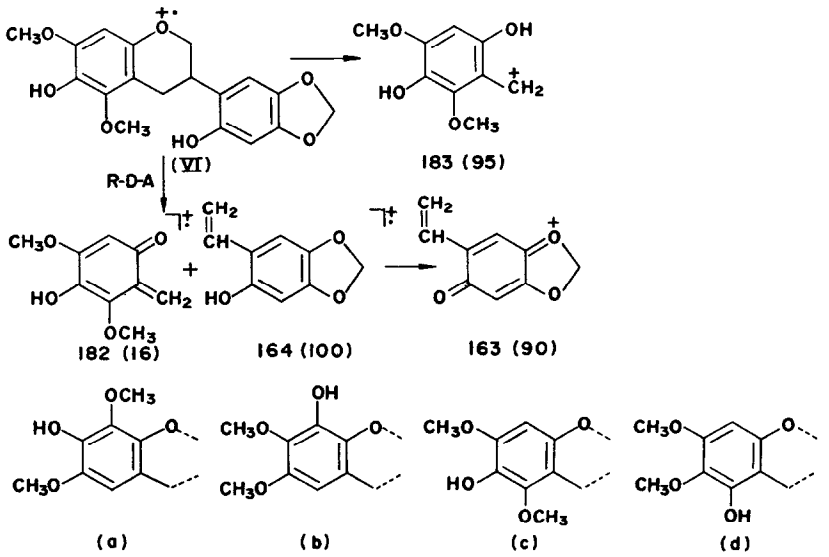
With a view to establishing the substituents on ring A solvent induced methoxyl proton shifts on changing the solvent from $CDCl_3$ to C_6H_6 were studied.[7,9] Leiocalycin monomethyl ether registered shifts of 7, 15 and 57 c/s for the methoxyl groups. A signal of a methoxyl group *ortho* to an aromatic hydrogen would shift upfield by more than 30 c/s on changing solvent. The shifts observed for leiocalycin monomethyl ether suggests a 1,2,3- or 2,3,4-oxygenation pattern.



[7] ANDREW PELTER and P. J. AMENECHI, *J. Chem. Soc.* **C**, 887 (1969).
[8] W. D. OLLIS, *Experientia* **XXII**, 777 (1966).
[9] H. M. FALES and K. S. WARREN, *J. Org. Chem.* **32**, 501 (1967). R. G. WILSON, J. H. BOWIE and D. H. WILLIAMS, *Tetrahedron* **24**, (1968).

In order to site the single hydroxyl group in ring A, the shifts of the methoxyl signals in the monoacetate were studied (3 c/s and 59 c/s). Four possible arrangements (a–d) would account for these results.

A negative Gibbs test excluded arrangements b and d and the isolation of the quinone (VII) as the sole product from the reaction of leiocalycin (I) with Fremy's salt excluded (a). Consequently structure (c) was assigned to the A ring in compound (I). The quinone (VII)

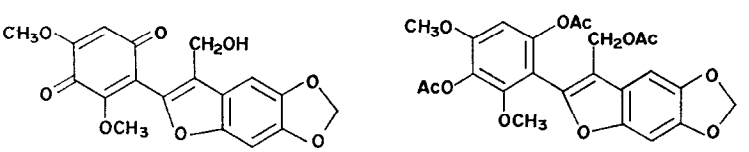


was reduced and acetylated to give 2(2,5-diacetoxy-4,6-dimethoxyphenyl)-3-acetoxymethyl-5,6-methylenedioxybenzofuran (VIII) which structure was confirmed by independent synthesis.

5,7-Dimethoxy-11,12-methylenedioxycoumestone was synthesized by condensation of 4-hydroxy-5,7-dimethoxycoumarin,[10] catechol and sodium acetate in aq. acetone followed by treatment of the product with methylene iodide in DMF. Reductive cleavage of the α-pyrone ring gave 2(2-hydroxy-4,6-dimethoxyphenyl)-3-hydroxymethyl-5,6-methylenedioxybenzofuran, which on treatment with *m*-chloroperbenzoic acid and subsequent reduction and acetylation afforded the benzofuran (VIII).

Leiocalycin (I) is the first example of a pterocarpanoid with a 1,2,3-oxygenation pattern in ring A.

The coumestones II and III were separated as their acetates on TLC. The physical constants and formulae of the two acetates are shown in Table 1.



[10] J. Boyd and A. Robertson, *J. Chem. Soc.* 174 (1948).

TABLE 1

Acetate	formula	M.p.	λ_{max} nm (log ϵ)			ν_{max} cm^{-1}	
II	$C_{19}H_{12}O_8$	256	212(4·6)	246(4·3)	282(3·9)	1755	1726
			310(3·9)	348(4·5)	355sh(4·4)	1630	
III	$C_{20}H_{14}O_9$	243	214(4·7)	246(4·3)	292(3·9)	1750	1740
			349(4·5)			1623	

The UV and IR spectra of the compounds II and III and their acetates resemble those of other coumestones.[11,12] The insolubility in the usual solvents of compound (II) and of its acetate precluded NMR analysis. The mass spectrum of the acetate shows a molecular ion {*m/e* 368 (60)} which on loss of a CH_2CO. gave the base peak {*m/e* 326 (100)}. The subsequent loss of CH_3 {*m/e* 311 (30)} and CO. {*m/e* 283 (10)} radicals is in agreement with the established fragmentation pattern of coumarins.[13]

Metastable peaks were evident for each fragmentation. The spectral data, a positive Labat test[6] and the co-occurrence of 6aR,11aR-2-hydroxy-3-methoxy-8,9-methylenedioxypterocarpan (IV) supports the proposed structure (II). This structure was confirmed by the following synthesis. Condensation of 2-hydroxy-4,5-methylenedioxybenzaldehyde and 2,5-dibenzyloxy-ω,4-dimethoxyacetophenone in acid yielded the corresponding flavylium chloride. Ring contraction, afforded 2(2,5-dibenzyloxy-4-methoxyphenyl)-5,6-methylenedioxybenzofuran-3-carboxylic acid methyl ester, and subsequent debenzylation and cyclization gave 6-hydroxy-7-methoxy-11,12-methylenedioxycoumestone (II).

The structure of coumestone III closely resembled that of compound II. The NMR spectrum of its acetate indicated the presence of two methoxyl groups, and showed three distinct aromatic protons at τ 2·53 (10-H), 2·86 (13-H) and 3·14 (8-H). The co-occurrence of the pterocarp-6a-en (I) was in support of a structure III for the coumestone and this assignment was confirmed by synthesis.

Our analysis of and a structural assignment for 6aR,11aR-(−)-2-hydroxy-3-methoxy-8,9-methylenedioxypterocarpan (IV) was completed prior to the publication[5] of its isolation from *Neorautanenia edulis* (Leguminosae-Lotoideae). The absolute stereochemistry was established by analysis of ORD curve. The absolute configurations in the pterocarpan series are based on the determination of the absolute configuration of C_{11a} of trifolirhizin[14] by its degradation to paraconic acid and on the assumption that the heterocyclic rings are *cis*-fused.[15] The coumestones are biogenetically related to isoflavonoids and not coumarins.[16] Biogenetic proposals infer that coumestones may arise from 3-aryl-4-hydroxycoumarins[17,18] or by allylic oxidation of the pterocarp-6a-ens.[19] A similar skeletal structure but different

[11] S. H. HARPER, A. D. KEMP, W. G. E. UNDERWOOD and R. V. M. CAMPBELL, *J. Chem Soc.* **C**, 1109 (1969).
[12] (a) T. SAITOH and S. SHIBATA, *Chem. Pharm. Bull.* **17**, 729, (1969); (b) H. SILG and H. GRISEBACH, *Phytochem.* **7**, 1765 (1968).
[13] R. H. SHAPIRO and C. DJERASSI, *J. Org Chem.* **30**, 955 (1965).
[14] S. ITO, Y. FUJISE and A. MORI, *Chem. Commun.* 595 (1965).
[15] K. G. R. PACHLER and W. G. E. UNDERWOOD, *Tetrahedron* **23**, 1817 (1967)
[16] H. GRISEBACH and W. BARZ, *Z. Naturforsch.* **18b**, 466 (1963).
[17] H. GRISEBACH and W. BARZ. *Z. Naturforsch* **196**, 569 (1964).
[18] C. P. FALSHAW, R. A. HARMER, W. D. OLLIS, R. E. WHEELER, V. R. LALITHA and N. V. SUBBA RAO, *J Chem. Soc.* (C), 374 (1969).
[19] P. M. DEWICK, W. BARZ and H. GRISEBACK, *Chem. Commun.* 466 (1969).

oxidation state exists between pterocarpans, pterocarp-6a-ens and coumestones. Their co-occurrence in *Swartzia* species[11] would be advantageous in future studies of their biosynthesis.

EXPERIMENTAL

Unless otherwise stated, the following generalizations apply. M.ps were determined on a Kofler hot stage apparatus and are uncorrected. IR spectra were measured in KBr discs and 60 Mc/s NMR spectra in $CDCl_3$ (tetramethylsilane as internal reference). Only significant bands from the IR spectra are quoted. Optical rotations were measured on a Perkin–Elmer Model 141 Polarimeter.

Separations by column chromatography were carried out using Merck silica gel. Merck Kieselgel $PF_{254+366}$ was used for thick- and thin-layer chromatography (TLC). During isolation processes the appropriate combination of fractions was determined by examination of their TLC behaviour. Thin-layer chromatograms were examined with UV illumination.

Isolation of the Constituents of Swartzia leiocalycina

The heartwood shavings (2·5 kg) were exhaustively extracted with hot *n*-hexane (3 days). Evaporation of the solvent afforded a grey solid (2·2 g), which on repeated crystallization from EtOH gave leiocalycin as an amorphous solid (800 mg), m.p. 194–196°. (Found: C, 63·4; H, 4·3. $C_{18}H_{14}O_7$ requires C, 63·2; H, 4·1%); λ_{max}^{MeOH} (nm) (log ϵ) 215 (4·49), 251 (4·23), 259 (4·19), 294 (3·88), 331 (4·34), 347 (4·41), 3·59 (4·42); ν_{max} 3544 cm^{-1}. NMR (DMSO-d_6 τ): 2·73 (s, 7-H), 2·97 (s, 10-H), 3·53 (s, 4-H), 3·94 (s, O.CH_2.O), 4·63 (s, >CH_2), 6·17 (s, OMe), 6·2 (s, OMe).

The mother liquor was further evaporated and yielded a powder which was crystallized repeatedly from EtOH and separated as a solid (70 mg) m.p. 70–72°. ν_{max} 3050 cm^{-1}, 1700 cm^{-1}, 727, 719 cm^{-1}. This mixture (30 mg) was esterified in ether with CH_2N_2 and chromatographed (GLC). Synthetic methyl esters were used as standards. Palmitic (3%), stearic (5%), arachidic (2%), behenic (1%), tricosanoic (2%), liginoceric (27%), pentacosanoic (12%), and cerotic (37%) methyl esters were found to be present (approximate %).

The heartwood shavings were subjected to further extraction with hot benzene and acetone. The acetone extract was evaporated and gave a brown solid (30 g) which was re-extracted with Et_2O (8 × 500 ml). Evaporation of the ether afforded a brown oil (3 g). This oil was fractionated chromatographically on silica (120 g), eluting with $CHCl_3$–acetone (1:1), acetone and acetone–MeOH (4:1 and 1:1). Appropriate fractions were collected yielding three combinations (Ai–Aiii).

Ai (240 mg) was crystallized from MeOH giving 2-hydroxy-3-methoxy-8,9-methylenedioxypterocarpan (140 mg).

Aii (200 mg) was acetylated (Ac_2O-pyridine), was chromatographed (TLC), and eluted (benzene) to give 6-*acetoxy*-7-*methoxy*-11,12-*methylenedioxycoumestone* (40 mg) and 6-*acetoxy*-5,7-*dimethoxy*-11,12-*methylenedioxycoumestone* (20 mg).

Aiii (20 mg) was crystallized from MeOH, giving compound 5 $C_{19}H_{14}O_8$ m.p. 236°.

2-*Acetoxy*-1,3-*dimethoxy*-8,9-*methylenedioxypterocarp*-6*a*-*en*

The acetate was crystallized from acetone and separated as plates m.p. 184–185°. (Found: C, 62·3; H, 4·4. $C_{20}H_{16}O_8$ requires C, 62·5; H, 4·2%); IR 1750 cm^{-1}; UV λ_{max}^{MeOH} (nm) (log ϵ) 211 (4·47), 245 (4·23), 254 (4·24), 289 (3·89), 325 (4·35), 338 (4·47), 356 (4·46); NMR τ 2·96 (s, 7-H), 3·28 (s, 10-H), 3·61 (s, 4-H), 4·1 (s, O.CH_2.O), 4·57 (s, >CH_2), 6·07 and 6·2 (s, 2 × OMe), 7·65 (s, $OCOC\underline{H}_3$); *m/e* 384 (50%) 342 (100), 341 (45).

1,2,3-*Trimethoxy*-8,9-*methylenedioxypterocarp*-6*a*-*en*

A mixture of leiocalycin (100 mg), MeI (60 mg) anhydrous K_2CO_3 and dry acetone was refluxed for 4 hr. The potassium salts were removed and washed with hot acetone. Evaporation of the combined filtrate gave a residue which crystallized from acetone as needles (60 mg), m.p. 174°. (Found: C, 63·6; H, 4·6. $C_{19}H_{16}O_7$ requires C, 64·0; H, 4·5%); UV λ_{max}^{MeOH} (nm) (log ϵ) 213 (4·56), 249 (4·32), 256 (4·32), 292 (4·01), 328 (4·41), 341 (4·6), 356 (4·54); NMR τ 2·98 (s, 7-H), 3·28 (s, 10-H), 3·62 (s, 4-H), 4·0 (s, O.CH_2.O), 4·57 (s, >CH_2), 5·97, 6·1, 6·13 (s, 3 × OMe); *m/e* 352 (40%), 341 (100), 326 (12), 313 (8), 199 (10), 149 (18).

2-*Hydroxy*-1,3-*dimethoxy*-8,9-*methylenedioxypterocarpan* (V)

A mixture of leiocalycin (I) (100 mg), EtOH (50 ml) and Pd-C (10%; 50 mg) was hydrogenated (1 mole absorbed). The catalyst was removed by filtration, and evaporation of the filtrate gave a solid which crystallized from EtOH in needles (60 mg), m.p. 174°. (Found: C, 62·4; H, 4·4. $C_{18}H_{16}O_7$ requires C, 62·8; H, 4·6%); UV λ_{max}^{MeOH} (nm) (log ϵ) 207 (4·9), 231 (4·2), 305 (4·0); NMR τ 3·27 (s, 7-H), 3·54 (s, 10-H), 3·7 (s, 4-H), 4·1 (d, O.CH_2.O J = 2·0 c/s), 4·25 (d, 11a-H, J = 10 c/s), 6·1–6·7 (m, 6,6a-Hs), 5·95, 6·15 (s, 2 × OMe); *m/e* 344 (100%), 329 (12), 176 (10), 175 (10), 162 (28).

6,2′-Dihydroxy-5,7-dimethoxy-4′,5′-methylenedioxyisoflavan (VI)

The pterocarpan (100 mg), EtOH (50 ml) and Pd-C (10%; 50 mg) were hydrogenated for 48 hr at room temp and atmospheric pressure. The catalyst was removed by filtration and the filtrate concentrated to 5 ml. The solid which separated was crystallized from EtOH to give 6,2′-dihydroxy-5,7-dimethoxy-4′,5′-methylenedioxyisoflavan (60 mg) m p 222–224°. (Found: C, 62 6; H, 5·26. $C_{18}H_{18}O_7$ requires C, 62 4; H, 5·24%); IR ($CHCl_3$) 3612, 3540 cm^{-1}, UV λ_{max}^{MeOH} (nm) (log ϵ) 206 (4·8), 297 (3 97); NMR τ (DMSO-d_6), 0·79 (s, OH), 2·08 (s, OH), 3 28 (s, 6′-H), 3·46 (s, 3′-H), 3·75 (s, 8-H), 4 1 (s, O.CH_2.O), 6·23 (s, 2 × OMe), 5 7–7·9 (m, 5Hs); *m/e* 346 (100%), 196 (24), 195 (20), 194 (16), 184 (20), 183 (95), 182 (16), 164 (100), 163 (90), 152 (25), 151 (40), 139 (29). The *diacetate* was crystallized from EtOAc–EtOH (4·1) in needles, m.p. 202–204°. (Found C, 61 5; H, 5 2. $C_{22}H_{22}O_9$ requires C, 61·4; H, 5·2%); ν_{max} 1750 cm^{-1}, NMR, τ 3·31 (s, 6′-H); 3·4 (s, 3′-H), 3·7 (s, 8-H); 4·1 (s, O.CH_2.O), 6 2 (s, 2 × OMe), 7 64, 7·68 (s, 2 × O CO CH_3).

2(2,5-Diacetoxy-4,6-dimethoxyphenyl)-3-acetoxymethyl-5,6-methylenedioxybenzofuran (VIII)

To a solution of leiocalycin (50 mg) in DMF (30 ml) was added, with stirring, a solution of Fremy's salt (200 mg) and KH_2PO_4 (60 mg). The reaction was kept at 25° for 12 hr, then diluted with H_2O and extracted with $CHCl_3$. The $CHCl_3$ extract was washed with dilute HCl, saturated solution of sodium dithionite, H_2O and dried. The residue, obtained on evaporation, was dissolved in dry pyridine (2 ml), Ac_2O (10 ml) and retained at 25° for 12 hr. The solution was then poured into ice-water. The diacetate (VIII) gave prisms (30 mg) m p. 164–165° (from benzene–light petroleum). (Found: C, 59 7, H, 4 7. $C_{24}H_{22}O_{11}$ requires C, 59 3; H, 4·6%) UV λ_{max}^{MeOH} (nm) (log ϵ) 213 (4 71), 259 (4·18), 314 (4·35), IR, 1771, 1733 cm^{-1}; NMR τ 2·95 (s, 4-H), 297 (s, 7-H), 3·36 (s, aromatic H), 3·96 (s, O CH_2 O), 4 87 (s, CH_2 OAc), 6·13, 6·4 (s, 2 × OMe), 7·66, 7·94, 7·96 (s, 3 × OCOCH_3).

2(2-Acetoxy-4,6-dimethoxyphenyl)-3-acetoxymethyl-5,6-methylenedioxybenzofuran

A solution of 4-hydroxy-5,7-dimethoxycoumarin[10] (2·2 g) catechol (1·2 g), NaOAc (6 g) in aq. acetone (1:1) (60 ml) was added rapidly at 25° to a solution of NaOAc (3 g) and potassium iodate (1·4 g) in water (60 ml) and the reaction mixture was kept for 24 hr The crude 11,12-dihydroxy-5,7-dimethoxycoumestone (3 g) was collected and refluxed with CH_2I_2 (3 g) and K_2CO_3 (3 g) in dry DMF (200 ml) for 3 hr. The K salts were removed by filtration. The filtrate was diluted with water and 5,7-dimethoxy-11,12-methylenedioxycoumestone (1 g) was collected. Reduction of the crude product with $LiAlH_4$ (500 mg) in dry ether (100 ml) and subsequent acetylation of the alcohol gave *2(2-acetoxy-4,6-dimethoxyphenyl)-3-acetoxymethyl-5,6-methylenedioxybenzofuran* which was crystallized from benzene–light petroleum (40–60°) and separated in rosettes m p 114–116°. (Found: C, 61·7; H, 4 7. $C_{22}H_{20}O_9$ requires C, 61 7; H, 4 7%.) IR 1763 cm^{-1}, 1722 cm^{-1}. NMR τ 2·9 (s, 4-H), 2·94 (s, 7-H), 3·47, 3·55 (ds, aromatic Hs, J = 3 0 c/s), 3 97 (s, O CH_2.O), 4·86 (s, $-CH_2OAc$), 6·13, 6 19 (s, 2 × OMe), 7 91 (s, 2 × O $COCH_3$).

2(2,5-Diacetoxy-4,6-dimethoxyphenyl)-3-acetoxymethyl-5,6-methylenedioxybenzofuran (VIII) (*synthetic*)

A solution of 2(2-hydroxy-4,6-dimethoxyphenyl)-3-hydroxymethyl-5,6-methylenedioxybenzofuran (400 mg) and *m*-chloroperbenzoic acid[20] (300 mg) in EtOAc (30 ml) was kept at 25° for 6 hr. The excess peracid was removed with sodium sulphite. The residue, obtained by evaporation of the EtOAc, was acetylated (pyridine–Ac_2O). Purification by preparative TLC, (eluant: Et_2O–light petroleum (b p 40–60°)) afforded the benzofuran (VIII) m.p. and mixed m.p. 164–165°

(−)-2-*Hydroxy-3-methoxy-8,9-methylenedioxypterocarpan* (IV) m p. 244–248°, needles from MeOH. (Found· C, 65·2; H, 4·7 Calc for $C_{17}H_{14}O_6$, C, 65·0; H, 4 5%) IR 3450 cm^{-1}, UV λ_{max}^{MeOH} (nm) (log ϵ) 205 (4·8), 231 (4 0), infl. 308 (4 1) NMR, τ (DMSO-d_6) 1 34 (s, OH), 3·02 (s, 7-H), 3·16 (s, 1-H), 3·47 (s, 10-H), 3 52 (s, 4-H), 4·05 (d, OCH_2O, J = 1·0 c/s), 4·49 (d, 11a-H, J = 7 0 c/s), 6 23 (s, OMe), 5·6–6·4 (m, 6 and 6a-Hs). Mixed m.p. with an authentic sample showed no depression.

6-Acetoxy-7-methoxy-11,12-methylenedioxycoumestone. M.p 255–257° from benzene (Found C, 61·7; H, 3·3. $C_{19}H_{12}O_8$ requires C, 61·96; H, 3·3%.)

6-Acetoxy-5,7-dimethoxy-11,12-methylenedioxycoumestone. M.p 241–243° from benzene (Found: C, 60·0; H, 3·4 $C_{20}H_{14}O_9$ requires C, 60 3; H, 3·6%) NMR τ 2·53 (s, 10-H), 2 86 (s, 13-H), 3 14 (s, 8-H), 3·92 (s, O.CH_2.O), 5 93 (s, OMe), 6·07 (s, OMe), 7·59 (s, OCOCH_3).

2,5-Dihydroxy-ω,4-dimethoxyacetophenone. A mixture of 1,4-dihydroxy-2-methoxybenzene (20 g), methoxyacetonitrile (12 g) in dry ether (250 ml) was saturated with dry HCl. The reaction mixture was kept for 24 hr then hydrolysed. The 2,5-dihydroxy-ω,4-dimethoxyacetophenone was collected and crystallized from EtOH as needles (4 g), m.p. 150°. (Found: C, 56·4; H, 5·7. $C_9H_{12}O_5$ requires C, 56 6; H, 5·7%.) *2,5-Dibenzyloxy-ω-4-dimethoxyacetophenone* crystallized in needles from MeOH m p 113–114°. (Found: C, 73·7, H, 6·2. $C_{24}H_{24}O_5$ requires C, 73 5; H, 6 2%); IR 1660 cm^{-1}.

[20] Information on the use of *m*-chloroperpenzoic acid for hydroxylation, was obtained from M Bennet personal communication.

2-(2,5-*Dibenzyloxy*-4-*methoxyphenyl*)-5,6-*methylenedioxybenzofuran*-3-*carboxylic acid methyl ester*. A solution of 2,5-dibenzyloxy-ω-4-dimethoxyacetophenone (3·2 g) and 2-hydroxy-4,5-methylenedioxybenzaldehyde (1·4 g) in Et_2O–EtOAc (7:3) (500 ml) was saturated with dry HCl. The reaction mixture was kept at room temp. for 24 hr and the red crystals of flavylium chloride (3 g) were collected m.p. 166–167°. The flavylium chloride was dissolved immediately in MeOH (100 ml) and the solution treated, slowly with stirring, with aq. H_2O_2 (80 ml; 15%). The reaction mixture was diluted with water and extracted with ether. The residue obtained on evaporation of the dried ethereal solution, was crystallized from MeOH yielding prisms of 2(2,5-*dibenzyloxy*-4-*methoxyphenyl*)-5,6-*methylenedioxybenzofuran*-3-*carboxylic acid methyl ester*, m.p. 130–132°. (Found: C, 71·7; H, 5·0. $C_{32}H_{26}O_8$ requires C, 71·4, H, 4·9%.)

6-*Acetoxy*-7-*methoxy*-11,12-*methylenedioxycoumestone* (*synthetic*). Conc. HCl (20 ml) was added slowly to a solution of 2(2,5-dibenzyloxy-4-methoxyphenyl)-5,6-methylenedioxybenzofuran-3-carboxylic acid methyl ester in HOAc (20 ml). The reaction mixture was kept at 100° for 30 min and then diluted with H_2O. The product was collected and acetylated to yield 6-acetoxy-7-methoxy-11,12-methylenedioxycoumestone m.p. 255–256°, mixed m.p. with natural 6-acetoxy-7-methoxy-11,12-methylenedioxycoumestone m.p. 255–256°.

6-*Acetoxy*-5,7-*dimethoxy*-11,12-*methylenedioxycoumestone* (*synthetic*). Dry HCl gas was passed into a solution of 2-hydroxy-4,5-methylenedioxybenzaldehyde (332 mg) and 2,5-dibenzyloxy-ω-3,6-trimethoxyacetophenone (844 mg) in Et_2O–EtOAc (4:1) (20 ml) at 0°. After 16 hr, an amorphous red solid (100 mg) was collected, washed and air dried. The crude product was dissolved in MeOH (10 ml) and treated with H_2O_2 (3 ml; 30%). The reaction mixture was then diluted with H_2O and extracted with ether. The solvent was evaporated, the residue was dissolved in HOAc (2 ml), HCl (2 ml) and heated on a steam-bath for 30 min. The reaction was diluted, and the product collected and acetylated (Ac_2O–pyridine). The acetate was purified by preparative TLC using benzene as eluent. The 6-acetoxy-5,7-dimethoxy-11,12-methylenedioxycoumestone crystallized from benzene in fine needles, melting point 241–243°, mixed m.p. with the natural product showed no depression.

Acknowledgements—The authors thank Professor E. M. Philbin for her constant interest, the Minister for Education, Republic of Ireland, for award of a maintenance grant (to M.A.F.). They are indebted to Dr. J. D. Brazier, Forest Products Research Laboratory, Princes Risborough, for a gift of *Swartzia leiocalycina*; Professor Klyne and Dr. P. M. Scopes for ORD; Professor A. J. Brink for a sample of 6aR,11aR-2-hydroxy-3-methoxy-8,9-methylenedioxypterocarpan.