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ISOFLAVONOIDS OF *DALBERGIA ECASTOPHYLLUM**

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Key Word Index—*Dalbergia ecastophyllum;* Leguminosae; isoflavonoids; *R*-(8) demethylduartin.

Abstract—In addition to the known isoflavonoids formononetin and (±)-mucronulatol, the vine wood of *Dalbergia ecastophyllum* (L.) Taub. contains (*R*)-8-demethylduartin. The assigned structure (II) has been confirmed by synthesis. Its absolute stereochemistry is deduced from examination of the CD spectrum of its acetate.

INTRODUCTION

Dalbergia ecastophyllum (L.) Taub. (Leguminosae-Lotoideae) a vine indigenous to Africa and South America is the only recorded example of a species of *Dalbergia* which occurs on more than one continent. The result of a phytochemical analysis of a South American sample has been published[1] and this prompts us to record out independent examination of a sample of the wood from Nigeria. Our results are in agreement with the classification of *Dalbergia ecastophyllum* as belonging to the species-series *Dalbergia brasilianae*.[2]

The compounds identified in the extracts of a sample of South American wood were 4,2′,4′-trihydroxychalcone (isoliquiritigenin); 7,4′-dihydroxyisoflavone (daidzein); 7-hydroxy-4′-methoxyisoflavone (formononetin); (6*aS*, 11*aS*)-3-hydroxy-9-methoxypterocarpan (demethylhomopterocarpin); (±)-3-hydroxy-9-methoxypterocarpan; (3*S*)-2′-hydroxy-7,4′-dimethoxyisoflavan (7-*O*-methylvestitol); (3*S*)-7,2′-dihydroxy-4′-methoxyisoflavan (vestitol); (2*R*,3*R*)-3,7-dihydroxy-6-methoxyflavanone; sitosterol.

With the exception of (3*S*)-2′-hydroxy-7,4′-dimethylthoxyisoflavan and (2*R*,3*R*)-3,7-dihydroxy-6-methoxyflavanone, all the compounds were previously isolated from species of *Dalbergia* and *Macherium*.

RESULTS AND DISCUSSION

Dalbergia ecastophyllum vine wood, obtained from Nigeria was extracted with *n*-hexane and yielded only long chain saturated fatty acids (0·75% dry-wood basis). Their presence was identified by use of mass spectrometry and by a direct comparisn of the R_t of their methyl esters with those of standards (arachidic, behenic, lignoceric). Lignoceric acid was the principal component of the mixture and the relative proportions of the other acids increased in the order C_{19} to C_{23} and decreased from C_{25} to C_{28}. The co-occurrence of the fatty acids with even and odd carbon numbers in comparable concentrations is unusual.

The benzene extract of the shavings was chromatographed and afforded four main fractions, of which the least polar fraction, an oil, was a mixture of anethole and estragole. Their

* Part X in the series "*Dalbergia* Species".

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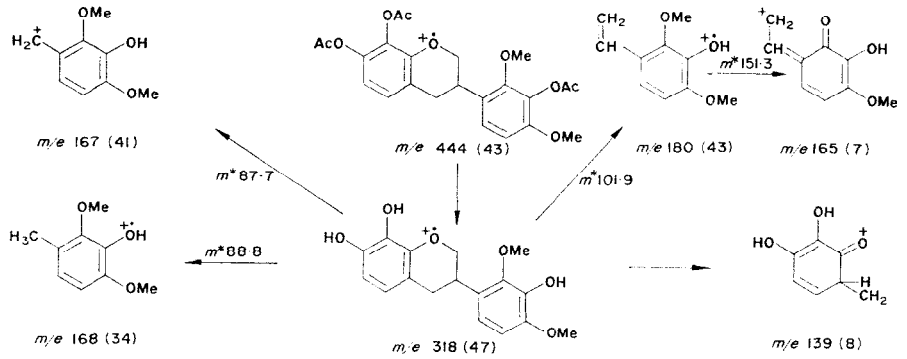
[1] DE ABREU MATOS, F. J., GOTTLIEB, O. R., OLLIS, W. D. and SOUZA ANDRADE, C. H. (1970) *An. Acad. Brasil. Ciênc* **42** (Supplemento), 61.

[2] BRAGA DE OLIVEIRA, A., GOTTLIEB, O. R., OLLIS, W. D. and RIZZINI, C. T. (1971) *Phytochemistry* **10**, 1863.

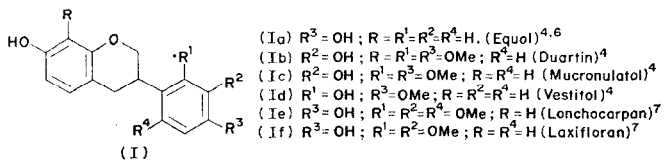
identification was based on GLC analysis and on comparison of spectra (NMR, UV, IR) with those of authentic samples. The closely related compound elemicin has been isolated from *Dalbergia spruceana*.[3]

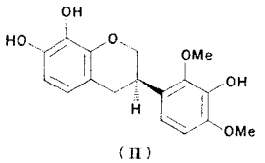
Sitosterol and formononetin were found to be present and are the only two extractives common to both American and African species. One isoflavan present proved to be (±)-mucronulatol (Ic). This compound has been isolated previously from *Dalbergia variabilis* and *Macherium mucronulatum*,[4] whilst the isomer (−)-mucronulatol is reported in five species of Macherium.[4]



SCHEME 1.

The second isoflavan was optically active and was isolated as its *O*-triacetate ($C_{23}H_{24}O_9$). Its UV and IR spectra demonstrated a close relationship to mucronulatol (Ic) and the NMR spectrum was consistent with a penta-substituted (trihydroxy-dimethoxy-)isoflavan.[4,5] The fragment ions in the MS of the *O*-triacetate indicated a similarity in B-ring substituents to mucronulatol-*O*-diacetate. The presence of two hydroxyl groups in ring-A (see Scheme 1) was apparent. From an analysis of the substitution patterns of known naturally occurring isoflavans (Ia–f), and from the observed co-occurrence [4]of duartin (Ib) and mucronulatol (Ic), the second hydroxyl group in ring-A was likely to be at position 8.





The relative positions of the hydroxyl groups in ring-A were assigned on the following evidence; (a) the triacetate was hydrolysed with HCl–NaOH and its UV spectrum obtained (λ_{max} 279, 282 nm). On addition of NaOH (0·25 N) a hypsochromic shift (14 nm) was observed. This behaviour implies oxidation to an *ortho-* or *para-* quinone, (b) the appearance

[3] OLLIS, W. D. (1966) *Experientia* **22,** 777.
[4] KUROSAWA, K., OLLIS, W. D., REDMAN, B. T., SUTHERLAND, I. O., BRAGA DE OLIVEIRA, A., GOTTLIEB O. R. and MAGALHÃES ALVES, H. (1968) *Chem. Commun.* 1263; and references therein.
[5] CLARK-LEWIS, J. W. (1968) *Australian J. Chem.* **21,** 2059.
[6] VERBIT, L. and CLARK-LEWIS, J. W. (1968) *Tetrahedron* **24,** 5519.
[7] PELTER, A. and AMENECHI, P. I. (1969) *J. Chem. Soc.* **C,** 888.

of two *AB* systems (*J* 9·0 Hz) in the aromatic region of the NMR spectrum of the triacetate indicates that the *A*- and *B*-rings each contain two *ortho*-hydrogens. The chemical shifts for these protons are consistent with those calculated[8] for the aromatic protons of 7,8,3′-triacetoxy-2′,4′-dimethoxyisoflavan (Table 1).

TABLE 1. NMR SPECTRA OF ISOFLAVANS

Compound	5-H	6-H	8-H	5′-H	6′-H
Unknown *O*-triacetate (obs)	3·0 (9·0)	3·28 (9·0)	—	3·28 (9·0)	3·00 (9·0)
Mucronulatol *O*-diacetate (obs)	2·92 (8·2)	3·38 (8·2, 2·2)	3·37	3·3 (8·5)	3·03 (8·5)
7,8,3′-Triacetoxy-2′,4′-dimethoxyisoflavan (calc)	3·0	3·3	—	3·45	3·1

Confirmation of the assignment of the oxygen functions was sought by synthesis of 7,8,3′-triacetoxy-2′,4′-dimethoxyisoflavan. The synthesis was effected by thallium (III) acetate oxidation[9] of 3,2′,3′,4′-tetrabenzyloxy-2,4-dimethoxychalcone in methanolic solution. The acetal obtained was debenzylated by hydrogenolysis and directly cyclised to give the isoflavone which was characterized as its triacetate. Catalytic reduction of the isoflavone afforded 7,8,3′-triacetoxy-2′,4′-dimethoxyisoflavan. This racemic isoflavan compared (IR, UV, NMR, MS) satisfactorily with the *O*-triacetate of the natural product. The unknown phenol is therefore 8-demethylduartin (I, R = R^2 = OH, R^1 = R^3 = OMe; R^4 = H).

TABLE 2.

Compound	(θ)	λnm	Compound	(θ)	λnm
(+)-8-Demethylduartin	+3400	279	(*S*)-(−)-5,7,3′,4′-tetramethoxyiso-		
	−3200	227	flavan	−1400	280
(*R*)-(−)-Dihydropterocarpin-*O*-				+4600	236
dimethyl ether	−2300	304	(*S*)-(−)-equol-*O*-dimethyl ether	−3500	285
	+2800	288		−3500	280
	−8000	236		+2500	236

The absolute configuration of (+)-8-demethylduartin-*O*-triacetate was deduced from an examination of its Cotton effects. A lack of material was a limiting factor, as confirmation of the absolute stereochemistry at C_3 by oxidative degradation was not feasible. A comparison (see Table 2) of the CD spectrum of the *O*-triacetate with the CD spectra[6,10] of (*R*)-(−)-dihydropterocarpin-*O*-dimethyl ether, (*S*)-(−)-5,7,3′,4′-tetramethoxyisoflavan and *S*-(−)-equol-*O*-dimethyl ether clearly indicated that 8-demethylduartin has an *R*-configuration and

[8] BALLANTINE, T. A. and PILLINGER, C. T. (1967) *Tetrahedron* **23**, 1691.
[9] OLLIS, W. D., ORMOND, K. L., REDMAN, B. T., ROBERTS, R. J. and SUTHERLAND, I. O. (1970) *J. Chem. Soc.* C, 125.
[10] KUROSAWA, K., OLLIS, W. D., REDMAN, B. T. SUTHERLAND, I. O., GOTTLIEB, O. R. and MAGALHÃES ALVES, H. (1968) *Chem. Commun.* 1265.

can be represented by structure (II). The absolute configuration of (3*S*)-5,7,3′,4′-tetramethoxyisoflavan is based on its stereospecific synthesis from (2*R*,3*S*)-catechintetramethyl ether and its chemical correlation[11] with *S*-(−)-methylsuccinic acid.

EXPERIMENTAL

M.ps were measured on a Kofler hot-stage apparatus and are uncorrected. Only significant bands from the IR spectra are quoted. Optical rotations were measured on a Perkin–Elmer Model 141 polarimeter. TMS was used as internal standard for NMR spectra. Merck Kieselgel $HF_{254+366}$ 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.

Extraction of Dalbergia ecastophyllum (*L*). *Taub.* Shavings of the vine *Dalbergia ecastophyllum* (1·14 kg) were exhaustively extracted with *n*-hexane and subsequently with C_6H_6. The fractions (7·5 g; 60 g) obtained on removal of the solvents were studied separately.

Examination of the n-*hexane extract.* Concentration of the *n*-hexane extract caused the precipitation of a yellow solid (4 g) which was collected. Further evaporation afforded a yellow oil (3·5 g). The solid m.p. 80–82° (ν_{max}^{KBr} 3425 cm^{-1} 1740 cm^{-1}) on MS analysis showed the presence of a C_{28} saturated acid and peaks at *m/e* 410 and *m/e* 396 due to the presence of C_{27} and C_{26} acids. Esterification with CH_2N_2 and subsequent GLC analysis showed lignoceric acid to be the principal component of the mixture. The methyl esters of arachidic, behenic and lignoceric acid were used as standards. The yellow oil (3·5 g) furnished a similar series of fatty acids.

Examination of the C_6H_6 *extract.* The C_6H_6 fraction was divided (a) a red solid (18 g) and (b) a red oil (42 g). Investigation of the solid (a) was unproductive. The red oil (b) was washed through silica gel (1500 g) with Et_2O to afford a pale red oil (23 g). An aliquot (15 g) was chromatographed (silica, 800 g) using C_6H_6–light petrol. (b.p. 40–60°) (1:1; 3:1); C_6H_6–$CHCl_3$ (1:1) and $CHCl_3$ as eluting solvents. Appropriate fractions were collected yielding four combinations (B i–iv). B(i) was fractionated using preparative tlc (Developer *n*-hexane–Et_2O (17:3)). Elution of the major band with Et_2O afforded an oil (aniseed odour). GLC analysis (Column 3% SE-30 on 80–100 mesh Chromosorb W; 75–150° in 9 min; 60 lb psi; 25 ml/min) showed two peaks (R_t: 3′ 38″ and 4′ 38″) identified as estragole and anethole respectively. NMR (estragole) τ: 6·69 (broad *d*, *J* 7·0 Hz), 4·03 (*m*), 5·01 (*t* × 4) (CH_2–CH=CH_2 system); 6·26 (*s*, OMe); 2·94 (2′-H, 6′-H), 3·23 (3′-H, 5′-H)/*J* 9·0 Hz, A_2B_2 system). NMR (anethole) τ: 8·15 (*d*, *J* 5·2 Hz), 3·86 (*m*), 3·72 (*q*) (ABX_3 system Me–CH=CH–); 6·26 (*s*, OMe); 2·79 (2′-H, 6′-H) 3·23 (3′-H, 5′-H) (*J* 9·0 Hz, A_2B_2 system). B(ii) was an intractable oil. B(iii) gave a white solid was purified by TLC (multiple development (5 ×)) with C_6H_6–$CHCl_3$ (1:1). Evaporation of the eluting solvent gave sitosterol $C_{29}H_{50}O$ as needles (25 mg) from MeOH m.p. 149–150·5° (m.m.p.; $[\alpha]_D$; MS IR of sterol). The monoacetate had a m.p. and m.m.p. 134–136°. B(iv) was subdivided. An aliquot was sublimed to give formononetin as white laths (25 mg) m.p. and m.m.p. 257–257·5°. NMR (DMSO-d_6): τ −0·60 (broad *s*, OH), 1·76 (*s*, 2H) 2·08 (*d*, *J* 9·0 Hz, 5-H); 2·54, 3·1 (*q*, *J* 8·8 Hz, A_2B_2 system, ring-B) 3·15 (*d*, *J* 9·0 Hz, 6-H), 3·18 (*s*, 8-H), 6·25 (*s*, OMe). The remainder of fraction B(iv) was crystallized from MeOH to yield 7,3′-dihydroxy-2′,4′-dimethoxyisoflavan (mucronulatol) (65 mg) as plates, m.p. and m.m.p. 224–225° $[\alpha]_D^{22}$ 0·0°. (Found C, 67·9; H, 5·9. Calc. for $C_{17}H_{18}O_5$: C, 67·5; H, 6·0%.) λ_{max}^{MeOH} 282 nm (log ϵ 3·62) 292 nm (log ϵ 3·79). NMR (DMSO-d_2): τ 0·86, 1·39 (*s*, 7-OH and 3′-OH, exchangeable D_2O), 3·1 (*d*, *J* 9·0 Hz, 5-H), 3·33 (*s*, 5′-H, 6′-H), 3·68 (*q*, *J* 2·3, 9·0 Hz, 6-H), 3·76 (8-H), 6·25 (*s*, OMe × 2) 5·8–6·95 (*m*, 2-H and 3-H), 7·28 (*d* (further splitting) *J* 8·0 Hz, 4-Hs); M^+ 386 (64%), *m/e* (%) 302 (64), 180 (100), 168 (79), 167 (29), 165 (11) and 123 (10). The mother liquor from the above crystallization was acetylated (Ac_2O (12 ml)–pyridine (10 ml)). Fractional crystallization of the crude acetate mixture with di-isopropyl ether gave plates of (±)-mucronulatol-*O*-diacetate (92 mg), m.p. 132–133°. The residue afforded (3R)-8-*demethylduartin*-O-*triacetate* which crystallized from MeOH in needles (15 mg) m.p. 223·5–225°. (Found C, 61·7; H, 5·6; MS M^+ 444. $C_{23}H_{24}O_9$ requires: C, 62·2; H, 5·4%; MS 444.) $[\alpha]_D^{22°}$ + 22·3° ($CHCl_3$); λ_{max}^{MeOH} 277 nm (log ϵ 3·8) IR (KBr) 1765 cm^{-1}. NMR ($CDCl_3$): 3·03 (*d*, *J* 9·0 Hz, 5-H, 6′-H) 3·28 (*d*, *J* 9·0 Hz, 6-H, 5′-H), 6·16 (*s*, OMe × 2), 5·65–6·55 (*m*, 2H, 3H) 7·2 (*d* (further splitting), *J* 7·6 Hz, 4-Hs), 7·63, 7·74 (*s*, OCOMe).

Synthesis of (±)-8-*demethylduartin*-O-*triacetate.* 2-*Benzyloxy*-1,3-*dimethoxybenzene.* Anhydrous K_2CO_3 (50 g) and NaI (2·0 g) were added to an equimolar solution of 2,6-dimethoxyphenol (51·4 g) and benzyl chloride (42·2 g) in anh. DMF (250 ml). The mixture was reflexed for 5 hr, cooled and poured onto ice. The brown oil obtained was extracted with Et_2O. The extract was washed successively with NaOH (5%), H_2O, NaCl (saturated) and dried. Evaporation of the solvent and distillation of the residual oil afforded 2-*benzyloxy*-1,3-*dimethoxybenzene* as an oil (56 g, 69%) b.p. 168°/2·2 mm Hg. (Found: C, 73·5; H, 6·4. $C_{15}H_{16}O_3$

[11] CLARK-LEWIS, J. W. (1962) *Rev. Pure Appl. Chem.* **12,** 96. CLARK-LEWIS, J. W., DAINIS, I. and RAMSAY, G. C. (1965) *Australian J. Chem.* **18,** 1035. WEINGES, K. (1964) *Proc. Chem. Soc.* 138; WEINGES, K. and PAULUS, E. (1965) *Annalen* **681,** 154.

requires: C, 73·8; H, 6·6%.) NMR (CCl_4): τ 2·58–3·68 (*m*, 8-Hs aromatic), 5·1 (*s*, $-O\cdot CH_2-\phi$), 6·27 (*s*, OMe × 2).

3-*Benzyloxy*-2,4-*dimethoxybenzaldehyde*. An equimolar mixture of $POCl_3$ (13·9 g) and *N*-methylformanilide (12·3 g) was stirred for 1 hr. 2-Benzyloxy-1,3-dimethoxybenzene (22·2 g; 1 m) was slowly added during 1·5 hr, and the temp. retained at 0·5°. The reaction mixture was stirred for a further 18 hr at 0·5°. The red oil was poured into ice which was kept neutral by controlled addition of NaOH (5%). The aq. solution was extracted with Et_2O, washed with NaOH (5%), H_2O, NaCl, (satd.) and dried. The oil, obtained on evaporation of the solvent, was distilled to give 3-*benzyloxy*-2,4-*dimethoxybenzaldehyde* (22 g, 90%) b.p. 142°/0·35 mm Hg. (Found: C, 70·8; H, 5·9. $C_{16}H_{16}O_4$ requires C, 70·6; H, 5·9%.) IR (liq. film)1675 cm^{-1}. NMR ($CDCl_3$): τ −0·35 (*s*, CHO); 2·27, 3·15 (*q*, *J* 9·0 Hz, *AB* system), 2·55 (*m*, aromatic), 4·9 (*s*, $-OCH_2-$) 5·93, 6·05 (*s*, OMe × 2). The 2,4-*D.N.P. derivative* had a m.p. 189–190°. (Found: C, 58·5; H, 4·4; N, 12·5. $C_{22}H_{20}O_7N_4$ requires: C, 58·4; H, 4·5; N, 12·4%.)

2′,3′,4′-*Tribenzyloxyacetophenone*. Anh. K_2CO_3 (100 g), NaI (10 g) were added to a soluton of 2′,3′,4′-trihydroxyacetophenone (33·6 g) and benzyl chloride (76 g) in anh. DMF (250 ml). The mixture was refluxed for 7·5 hr and the work up procedure was similar to the previous benzylation (see above). The 2′,3′,4′-tri-*benzyloxyacetophenone* was crystallized from MeOH as plates, m.p. 60–61°. (Found: C, 79·6; H, 5·8. $C_{29}H_{26}O_4$ requires: C, 79·4; H, 6·0%.) IR(KBr) 1663 cm^{-1}. NMR (CCl_4): τ 2·75 (*m*, 15 aromatic Hs), 3·33 (*d*, *J* 9·0 Hz, 6-H), 4·87, 4·89, 4·99 (*s*, 3 × $O-CH_2-\phi$), 7·55 (*s*, Me). The 2,4-*D.N.P. derivative* had m.p. 136–137°. (Found: C, 68·1; H, 4·9,; N, 9·0. $C_{35}H_{30}O_7N_4$ requires: C, 68·0; H, 4·9; N, 9·1%.)

3,2′,3′,4′,-*Tetrabenzyloxy*-2,4-*dimethoxychalcone*. Condensation of 3-benzyloxy-2,4-dimethoxybenzaldehyde (1·5 g) and 2′,3′,4′-tribenzyloxyacetophenone (2 g) in EtOH (40 ml) and KOH (10 ml, 50%) at R_t for 72 hr afforded a red oil. The Et_2O extract of the oil was washed with $NaHCO_3$ (5%), satd. $NaHSO_3$ and NaCl. The dried ethereal solution was evaporated to give a yellow oil. Purification by column chromatography (silica gel) yielded 3,2′,3′,4′-*tetrabenzyloxy*-2,4-*dimethyxychalcone* as an oil. (Found: C, 78·2; H, 5·9. $C_{45}H_{40}O_7$ requires: C, 78·0; H, 5·8%.) IR ($CHCl_3$) 1646 cm^{-1}.

1(2,3,4-*Tribenzyloxyphenyl*)-2(3-*benzyloxy*-2,4-*dimethoxyphenyl*)-3,3-*dimethoxypropan*-1-*one*. A mixture of 3,2′,3′,4′-*tetra*benzyloxy-2,4-dimethoxychalcone (1 g) and thallium (III) acetate (2 g) was dissolved in MeOH (10 ml) and the solution was refluzed for 24 hr. The reaction mixture was diluted (100 ml H_2O) and extracted with $CHCl_3$. Purification by TLC gave unreacted chalcone (540 mg) and 1(2,3,4-*tribenzyloxyphenyl*)-2(3-*benzyloxy*-2,4-*dimethoxyphenyl*)-3,3-*dimethoxypropan*-1-*one* (220 mg) as an oil. (Found: C, 74·7; H, 6·3. $C_{47}H_{46}O_9$ requires: C, 74·8; H, 6·1%.) IR (liq. film) 1678 cm^{-1}. NMR ($CDCl_3$): τ 2·42–2·8 (*m*, aromatic Hs), 3·2 (*d*) 3·34 (*d*) (*J* 8·5 Hz, 5-H, 5′-H), 4·47 (*d*) and 4·88 (*d*) (*J* 9·0 Hz, *AB* system, $CO.CH.CH(OMe)_2$) 4·96 (*s* × 4, $OC\underline{H}_2\phi$) 6·2 (*s*, OMe × 2); 6·47, 6·79 (*s*, aliphatic OMe).

7,8,3′-*Triacetoxy*-2′,4′-*dimethoxyisoflavone*. Palladised charcoal (50 mg, 10%) was added to 1(2,3,4-tribenzyloxyphenyl)-2(3-benzyloxy-2,4-dimethoxyphenyl)-3,3-dimethoxypropan-1-one (220 mg) in EtOAc (15 ml). The mixture ws stirred in an atmosphere of H_2 at R_t for 12 hr. The catalyst was removed and the filtrate was evaporated under reduced pressure. The debenzylated acetal (100 mg) had signals at τ −2·88 (OH) and τ 4·2 (3 × OH) (exchangeable D_2O). Concentrated HCl (6·2 ml) was added to the acetal (300 mg) in MeOH (20 ml) and the solution was warmed (2 hr) to 60°. Addition of H_2O to the reaction mixture and subsequent extraction with EtOAc afforded 7,8,3′-trihydroxy-2′,4′-dimethoxyisoflavone which was characterized by conversion (Ac_2O (2 ml)–pyidine (0·2 ml)) to its *triacetate*. Purification of the triacetate derivative by TLC (in $CHCl_3$–Me_2CO (19:1)) gave a solid which was crystallized from MeOH (85 mg) m.p. 192–193°. (Found: C, 60·5; H, 4·7. $C_{23}H_{20}O_{10}$ requires: C, 60·5; H, 4·4%.) IR(KBr) 1760 cm^{-1} 1652 cm^{-1}. λ_{max}^{MeOH} nm (log ϵ) 246 (4·22), 303 (3·86). NMR ($CDCl_3$): τ 1·67 (*d*, *J* 9·5 Hz, 5-H), 1·92 (*s*, 2-H), 2·66 (*d*, *J* 9·0 Hz, 6′-H), 2·67 (*d*, *J* 9·0 Hz, 5′-H), 3·13 (*d*, *J* 9·5 Hz, 6-H), 6·10, 6·26 (*s*, OMe) 7·56 (*s*) and 7·61 (2 × *s*) ($OCO\underline{CH}_3$).

7,8,3′-*Triacetoxy*-2′,4′-*dimethoxyisoflavan*. The 7,8,3′-triacetoxy-2′,4′-dimethoxyisoflavone (25 mg) was hydrogenated in HOAc (10 ml) containing Pd–C (9 mg; 10%) at 100° for 3 hr. The catalyst was removed and the filtrate was poured into H_2O. The $CHCl_3$ extract of the aq. solution was washed successively with $NaHCO_3$ (5%) and H_2O. Evaporation of the dried $CHCl_3$ solution yielded the isoflavan (18 mg) which was crystallized from MeOH in needles m.p. 236–237°. (MS M^+ 444). IR(KBr) 1764 cm^{-1}. λ_{max}^{MeOH} 277 nm (log ϵ 3·6). NMR ($CDCl_3$): τ 3·01 (*dd*, *J* 9·0 Hz, 5-H, 6′-H), 3·28 (*dd*, *J* 9·0 Hz, 6-H, 5′-H), 6·18 (*s*, OMe × 2), 5·55–6·55 (*m*, 2-H and 3-H), 7·14 (*d*, *J* 7·6 Hz 4-Hs), 7·67(*s*), 7·7(*s*) ($OCO\underline{CH}_3$).

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