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ISOFLAVANOIDS OF *DALBERGIA OLIVERI**

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Key Word Index—*Dalbergia oliveri*; Leguminosae; isoflavanoids; 3-phenylcoumarins; (±) pterocarpans, coumestones.

Abstract—The heartwood of *Dalbergia oliveri* has yielded 11 natural products of which two are new 3-phenylcoumarins. The structures of the extractives have been examined by physical methods and in addition the assigned structures have been confirmed by synthesis. The oxygenation pattern relating the structures of chalcone, isoflavone, pterocarpans, 3-arylcoumarins, coumestones and the isoflavan and isoflavanone suggests a common biosynthetic origin.

INTRODUCTION

Dalbergia oliveri Gamble (Leguminosae–Lotoideae) is a large tree indigenous to the forest of Upper Burma, and is the source of Burma tulipwood. The results of the phytochemical examination, showed the lack of neoflavanoids, and thus favours the placement of *D. oliveri* in the species series Dalbergiae brazilianae.[1]

Extracts of the heartwood afforded 11 natural products of which two are new 3-arylcoumarins (**3**a,b). We report here on the isolates, discuss the methods of identification and the synthesis of the new compounds.

RESULTS AND DISCUSSION

The heartwood of *D. oliveri* was extracted, in turn, with *n*-hexane, acetone and 2-butanone. Attempted fractionation of the yellow oil from the *n*-hexane extract left insufficient material in the purified isolates for the assignment of structures. From the behaviour on TLC, GLC and the spectral data, the compounds resembled triterpenoids.

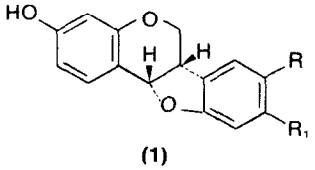
The extractives from acetone afforded a series of isoflavanoids, which included the two unknown coumarins $C_{16}H_{12}O_5$ and $C_{16}H_{10}O_6$. Isoflavanoids are widely distributed in the subfamily Lotoideae and *D. oliveri* contains an isoflavone, an isoflavanone (**5**), an isoflavan (**4**) pterocarpans (**1**a,b), coumestones (**2**a,b) and 3-arylcoumarins (**3**a,b). The optically active pterocarpans (**1**a,b) were found to be the major components of *D. oliveri*. Their separation was achieved after acetylation to give (6*aS*, 11*aS*)-3-acetoxy-9-methoxypterocarpan and (6*aS*, 11*aS*)-3-acetoxy-8,9-methylenedioxypterocarpan. The dextrorotatory form (**1**a)

* Part XI in the series "*Dalbergia* species".

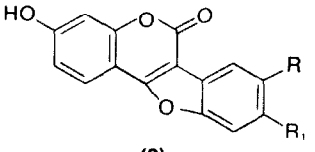
[1] BRAGA DE OLIVEIRA, A., GOTTLIEB, O. R., OLLIS, W. D. and RIZZINI, C. T. (1971) *Phytochemistry* **10**, 1863.

[2] OLLIS, W. D. (1966) *Experientia* **22**, 777; DONNELLY, D. M. X., THOMPSON, J. C., WHALLEY, W. B. and AHMED, S. (1973) *J. Chem. Soc. Perkin I* 1737; ALENCAR, R., FILHO, R. B., GOTTLIEB, O. R., OLLIS, W. D. and SOUZA ANDRADE, C. H. (1970) *An Acad. Brasil Ciênc.* **42**, 61.

occurs in other *Dalbergia* species.[1,2] The (+)-pterocarpan (**1**b) is new to the genus but was found previously in *Aldina heterophylla*[3] and as its glucoside in *Sophora japonica*.[4]



(1)



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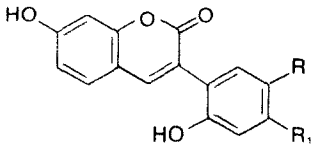
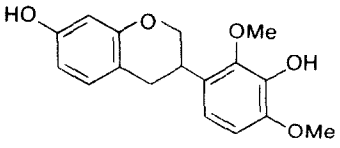


(3)

(a) R = H; R_1 = OMe (b) R,R_1 = $O.CH_2.O$



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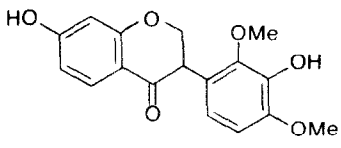


(5)

The presence of the coumestones, 12-*O*-methylcoumestrol (**2**a) and medicagol (**2**b), were recognized from their TLC behaviour and confirmed by UV and MS analyses. The oxygenation pattern of the pterocarpans and coumestones was repeated in the two new 3-arylcoumarins. This isoflavanoid series presumably arises biosynthetically from a chalcone precursor by an enzyme mediated aryl migration. However only isoliquiritigenin could be found (GLC/MS) in the extracts, but no butein.

The arylcoumarins (**3**a,b) were isolated as an acetate mixture and separated by TLC. The tentative assignment of a coumarin structure was based on a comparison with standard 7-acetoxy-4′-methoxy-3-phenylcoumarin. The molecular formulae for the diacetates were $C_{20}H_{16}O_7$ (M^+ 368) and $C_{20}H_{14}O_8$ (M^+ 382) and the 14 mass unit difference supported the existence of a methylenedioxy group in the higher molecular weight compound. The presence of the acetoxyl groups was evident in the individual mass spectra by the consecutive losses of *m/e* 42 fragments, and the subsequent loss of an *m/e* 28 fragment ion confirmed the coumarin skeleton.

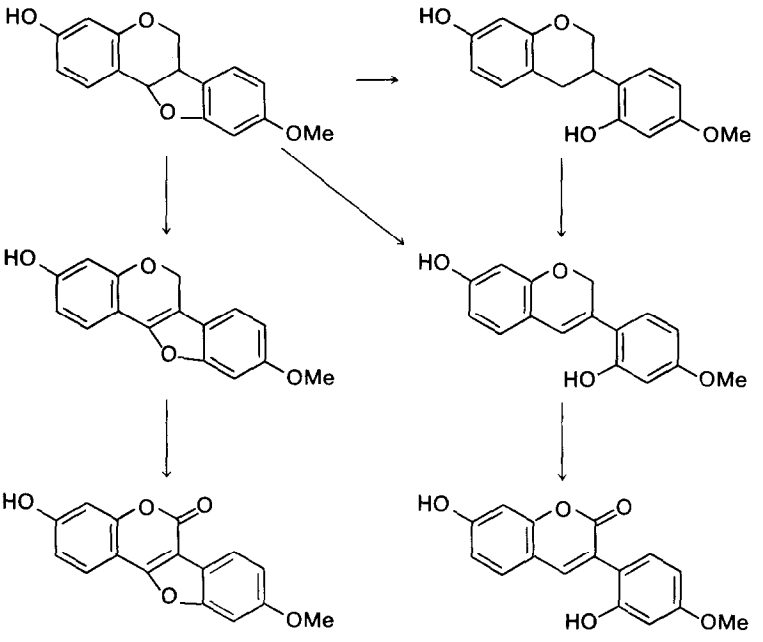
Signals at τ 2·2 in the NMR spectra were assigned to the C-4 protons and each compound had a distinctive ABX pattern in the aromatic region which would agree with a 7-oxygenated system as in the co-occurring pterocarpans and coumestones. Similarly the likely positions for the oxygen functions in the B-rings would be 2′,4′ and 2′,4′,5′. A doublet, *ortho* coupled (τ 2·52) in the NMR spectrum of the methoxycoumarin supported the 2′,4′ pattern and methylation gave the known 7,2′,4′-trimethoxy-3-phenylcoumarin. The structures (**3**a) and (**3**b) for the natural products were confirmed by comparison with authentic samples. The diacetate of the coumarin (**3**a) was synthesized by the Perkin–Oglialoro reaction of 2′-hydroxy-4′-methoxyphenylacetic acid[5] with 2,4-dihydroxybenzaldehyde in Ac_2O. Deacylation of the synthetic 3-phenylcoumarin by NH_3 in EtOH gave 2′,7-dihydroxy-4′-methoxy-3-phenylcoumarin identical with the natural product. The diacetate of

[3] BRAZ FILHO, R., GOTTLIEB, O. R., PINHO, S. L. V., MONTE, F. J. Q. and ROCHA, A. I. DA (1973) *Phytochemistry* **12**, 1184.

[4] SHIBATA, S. and NISHIKAWA, Y. (1963) *Chem. Pharm. Bull. (Tokyo)* **11**, 167.

[5] DANN, O., LANG, J. and VOHL, H. (1960) *Annalen* **631**, 116.

coumarin (**3b**) was synthesized by condensation of the 2-benzyloxy-4,5-methylenedioxyphenylacetic acid and 2,4-dihydroxybenzaldehyde.



These two coumarins are the third and fourth members of this class to be found in nature and are the first isolated from the *Dalbergia* genus. Those previously isolated were pachyrrhizin and neofolin from *Pachyrrhizus erosus*[6] and *Neoratanenia ficifolia*[7] respectively. The 3-arylcoumarins are isoflavanoids in a high oxidation state and their biosynthesis may involve allylic oxidation of an "isoflav-3-ene" by analogy to the proposals in the pterocarpan, pterocarpene coumestone series.

The isoflavan (**4**) obtained, was optically inactive and its m.p. and spectroscopic properties were in agreement with those of (±)-mucronulatol. The laevorotatory form accompanied by the racemate have been isolated from the closely related *Macherium* genus[8] and a racemate alone is present in *D. ecastophyllum*.[9] There are, at present, 12 known natural isoflavans,[2d,8–10] none of which carries a methylenedioxy group, even though their proposed precursors isoflavones and pterocarpans do. The same oxygenation pattern to that of mucronulatol was present in an isoflavanone and it was shown to be (±)-violanone (**5**)[2a]. The 2′-substituent, preventing free rotation of the aryl group, results in the distinctive

[6] SIMONITSCH, E., FREI, H. and SCHMID, H. (1957) *Monatsch. Chem.* **88**, 54.

[7] BRINK, C.V.D.M., NEL, W., RALL, G. J. H., WEITZ, J. C. and PACHLER, K. G. R. (1966) *J. S. A. Chem. Inst.* **19**, 24.

[8] 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.

[9] DONNELLY, D. M. X., KEENAN, P. J. and PRENDERGAST, J. P. (1973) *Phytochemistry* **12**, 1157.

[10] SHIBATA, S. and SAITOH, T. (1968) *Chem. Pharm. Bull.* (Tokyo) **16**, 1932; BURDEN, R. S., BAILEY, J. A. and DAWSON, G. W. (1972) *Tetrahedron Letters*, 4175; PELTER, A. and AMENECHI, P. I. (1969) *J. Chem. Soc.* (*C*), 887; BRAGA DE OLIVEIRA, A., GOTTLIEB, O. R., GONÇALVES, T. M. M. and OLLIS, W. D. (1971) *An Acad. Brasil Ciênc.* **42**, 1291; INGHAM, J. W. and MILLAR, R. L. (1973) *Nature* **242**, 125.

but more complex NMR spectrum.[2b] Provided the 2′-position is protected, isoflavanones may be prepared *in vitro* from the corresponding isoflavans by addition of DDQ.[11] Only two of the 14 known isoflavanones are optically active, (−)-sophorol from *Sophora japonica*[12] and (−)-4′,7′-dihydroxyisoflavanone from *Pericopsis mooniana*.[13] Formononetin and (+)-liquiritigenin were also present in the extracts of *D. oliveri*.

EXPERIMENTAL

Unless otherwise stated, m.ps. were determined on a Kofler hot-stage apparatus. IR spectra were measured for KBr discs UV spectra were determined for solutions in MeOH and 60 MHz. NMR spectra for solutions in $CDCl_3$ (tetramethylsilane as internal reference). Only significant bands in IR and NMR spectra are quoted. MS were obtained with an AEI MS 902 (direct inlet) instrument. Optical rotations were measured on a Perkin–Elmer Model 141 Polarimeter. Separations by column chromatography were carried out using Merck silica gel. Merck Kieselgel HF_{254} and $HF_{254+366}$ were used for TLC. During isolation processes, the appropriate combination of fractions were determined by TLC. TLC plates were examined with UV illumination and by spraying with chlorosulphonic acid in HOAc.

Isolation of the constituents of Dalbergia oliveri. The heartwood shavings (1 kg) were extracted with hot *n*-hexane (3 days) and subsequently with hot acetone (2 days). The latter extract (26 g) was re-extracted with Et_2O. The soluble material (14 g) constituted the sample analysed and was fractionated by column chromatography (silica-gel; 750 g). Elution with $CHCl_3$ gave fractions 1–3, the first of which was discarded. Elution then with $CHCl_3$–Me_2CO (19:1) gave fractions 4 and 5 and finally with $CHCl_3$–Me_2CO (9:1) gave fraction 6. Fraction (2), a brown oil (1·75 g), was rechromatographed (silica gel column (70 g); eluent Et_2O). The major fraction afforded an impure solid (1·4 g) m.p. 130–132°. An NMR spectrum indicated a mixture (1:1) of 3-hydroxy-9-methoxypterocarpan and 3-hydroxy-8,9-methylenedioxypterocarpan. Acetylation (Ac_2O-pyridine) and subsequent separation of the pterocarpan acetates (TLC: eluent–EtOAc: petrol, b.p. 60–80° (7:3) gave 3-acetoxy-9-methoxypterocarpan as needles from EtOAc and petrol, (bp. 60–80°), m.p. 120–121° (Lit.[14] m.p. 127–128°) $[\alpha]_D^{31}$ + 170° ($CHCl_3$); NMR τ 7·69 (*s*, OAc), 6·2 (*s*, OMe), 6·3–6·45 (*m*, 6a-H, 6-Hax), 5·64–5·95 (*m*, 6-Heq), 4·4–4·5 (*m*, 11a-H), τ_X 3·2 (*d*, 4-H) τ_B 3·12 (*q*, 2-H) τ_X 2·38 (*d*, 1-H) (ABX system $J_{1,2}$ 8 Hz, $J_{2,4}$ 2 Hz), τ_X 3·55 (*q* 8-H) τ_B 3·54 (*d*, 10-H) τ_X 2·8 (*d*, 7-H) ABX system ($J_{7,8}$ 8·5 Hz $J_{8,10}$ 2·5 Hz). The more polar fraction gave 3-acetoxy-8,9-methylenedioxypterocarpan as needles (EtOAc) m.p. 174–175° (lit.[3] m.p. 176–177°), $[\alpha]_D^{31}$ + 173° ($CHCl_3$) NMR τ 4·02 (*s*, $O.CH_2.O$). Fraction 3 was a brown oil, which solidified on adding MeOH. Acetylation and separation of the acetates by TLC with $CHCl_3$ yielded 7-acetoxy-11,12-methylenedioxy-coumestone and 7-acetoxy-12-methoxycoumestone (12 mg)[2b] m.p. 310–315° and (±)-mucronulatol diacetate.[9] Fraction 4 was a brown solid (90 mg) which when crystallized (MeOH) afforded 7-hydroxy-4′-methoxyisoflavone as needles (m.m.p.; NMR, IR, MS of formononetin). The monoacetate had a m.p. and m.m.p. 170–171°. Fraction 5 was a brown oil (980 mg) which on TLC in Et_2O gave a yellow solid m.p. 183° (440 mg). Acetylation, followed by TLC in Et_2O–petrol (2:1) gave a faster moving component, which yielded (±)-violanone, m.p. 200–202°[11] after deacetylation. The slower moving material was treated with EtOH to give the solid 2′,7-diacetoxy-4′-methoxy-3-phenylcoumarin (80 mg) as plates. The filtrate, following TLC (in $CHCl_3$ × 3) gave 2′,7-diacetoxy-4′,5-methylenedioxy-3-phenylcoumarin (12 mg).

(±)-3′,7-*Diacetoxy-2′,4′-dimethoxyisoflavanone*, an oil, $[\alpha]_D$ 0°; MS (rel int.) M^+ 400 (10), 358 (40) 316 (12) 222 (10) 180 (100) 137 (80). Calc. for $C_{21}H_{20}O_8$ M^+ 400. NMR τ 7·69, 7·66 (*s*, 2 × OAc), 6·2, 6·18 (*s*, 2 × OMe), 5·82–5·25 (*m*, 2-H, 3-H) 3·26 (*d*, *J* 9 Hz, 5′-H) 2·97 (*d*, *J* 9 Hz, 6′-H) 1·95 (*d*, *J* 9 Hz, 5-H). Deacetylation (dilute acid EtOH) gave (±)-3′,7-dihydroxy-2′,4′-dimethoxyisoflavanone m.p. 200–201° (from C_6H_6).

2′,7-*Diacetoxy-4′-methoxy-3-phenylcoumarin* was crystallized (EtOH) m.p. 159–161°. (Found: C, 65·0; H, 4·3. $C_{20}H_{16}O_7$ requires C, 65·2; H, 4·3%). λ_{max} (nm) (log ϵ) 235 sh (4·24), 280 (4·06) 327 (4·36); ν_{max} 1760 cm^{-1} 1720 cm^{-1} 1620 cm^{-1}. NMR τ 7·8, 7·62 (*s*, 2 × OAc), 6·11 (*s*, OMe), 2·24 (*s*, 4-H).

2′,7-*Diacetoxy-4′,5′-methylenedioxy-3-phenylcoumarin* crystallized in needles (aq. EtOH) m.p. 195–196°. (Found: C, 62·4; H, 3·8. $C_{20}H_{14}O_8$ requires C, 62·8; H, 3·7%); λ_{max} (nm) (log ϵ) 238 (4·08) 282 (4·14), 328 (4·13); ν_{max} 1750 cm^{-1}, 1720 cm^{-1} and 1605 cm^{-1}.

2′,7-*Dihydroxy-4′-methoxy-3-phenylcoumarin*. Deacetylation of 2′,7 diacetoxy-4′-methoxy-3-phenylcoumarin in ethanolic ammonium hydroxide afforded the *dihydroxy* compound which crystallized from aq. EtOH as light yellow rhombs, m.p. 258–260°. (Found: C, 67·5; H, 4·1. $C_{16}H_{12}O_5$ requires C, 67·5; H, 4·2%); ν_{max} 3300 cm^{-1}, 1680 cm^{-1} and 1610 cm^{-1}; λ_{max} (nm) (log ϵ) 243 (4·24), 285 sh (4·03), 343 (4·5); $\lambda_{max}^{MeOH+NaOMe}$ 260 (sh), 295 (4·08), 385 (4·52). NMR (DMSO-d_6) τ 6·25 (*s*, OMe), 2·77 (*d*, *J* 9 Hz 6′-H), 2·41 (*d*, *J* 9 Hz, 5-H), 2·19 (*s*, 4-H).

2′,4′,7-*Trimethoxy-3-phenylcoumarin*. Methylation (CH_2N_2) of the yellow solid (m.p. 183°) (12 mg) (see above) and subsequent purification by preparative TLC (eluent: $CHCl_3$) afforded 2′,4′,7-trimethoxy-3-phenylcoumarin (5 mg)

[11] KAVANAGH, P. J. (1974) Ph.D. Thesis (NUI). Unpublished results.
[12] SUGINOME, H. (1959) *J. Org. Chem.* **24**, 1655.
[13] FITZGERALD, M. (1972) Ph.D. Thesis (NUI). Unpublished results.

(m.m.p; UV of authentic sample). Fraction 6. Addition of $CHCl_3$ to the brown oil gave a solid (285 mg). Purification by TLC [$CHCl_3$: $(Me)_2CO$/9:1; double development] afforded 2',4',4-trihydroxychalcone (180 mg) as an amorphous powder (aq. EtOH) (m.m.p; UV, NMR, IR, MS of the chalcone).[14] Acetylation of the second component afforded (+)-4',7-diacetoxyflavanone as needles from $CHCl_3$/MeOH m.p. 179–181°. (lit. 178°[15]; $[\alpha]_D^{24}$ + 11; NMR τ 7·65 (*s*, OAc), 6·98 (*d*, $J_{2,3}$ 10 Hz, 3-H_{ax}), 7·02 (*d*, $J_{2,3}$ 4 Hz, 3-H_{eq}) 4·42 (*q*, *J* 10, 4 Hz, 2-H), 3·1 (*q*, *J* 9·3, 2 Hz, 6-H), 3·05 (*d*, *J* 2 Hz, 8-H), 2·56 (*q* A_2B_2 system J_{AB} 9·3 Hz, ring B), 1·93 (*d*, *J* 9·3 Hz, 5-H).

Synthesis of 2',7'-Dihydroxy-4'-methoxy-3-phenylcoumarin. 2-Hydroxy-4-methoxyphenylthiomorpholide, as pale yellow plates (EtOH) m.p. 132–133° (lit. m.p.[5] 133°) resulted from the admixture of 2-hydroxy-4-methoxyacetophenone (20 g), morpholine (40 g) and sulphur (14 g) at 140° for 3 hr and 160° for a further 1 hr. The crude morpholide was hydrolysed with NaOH (200 ml; 10%). The hydrolysate was acidified (pH 2) and purified through celite and charcoal (2 g) to afford 2'-hydroxy-4'-methoxyphenylacetic acid m.p. 131–133°. (lit.[5] m.p. 133°); NMR (DMSO-d_6) τ 6·59 (*s*, $-CH_2-$), 6·31 (*s*, OMe). The phenylacetic acid, under acetylation, afforded *3-acetoxy-2-(2-hydroxy-4-methoxyphenyl)crotonic acid* as needles (HOAc) m.p. 142–144° (lit.[16] m.p. 143°). Condensation of 2,4-dihydroxybenzaldehyde and the above phenylacetic acid with anhydrous KOAc and Ac_2O for 8 hr. gave *2',7-diacetoxy-4'-methoxy-3-phenylcoumarin* as plates from EtOH, m.p. 159–161°. (Found: C, 65·1; H, 4·3. $C_{20}H_{16}O_7$ requires C, 65·2; H, 4·3%) The NMR, IR and UV spectra were identical with those of the natural product. Deacylation of the *diacetate* (300 mg) in EtOH (10 ml) and NH_3 (15 ml, 10%) afforded *2',7-dihydroxy-4'-methoxy-3-phenylcoumarin* as yellow rhombs (aq. EtOH) m.p. and m.m.p. (with natural product) 258–260°.

Synthesis of 2',7-diacetoxy-4',5'-methylenedioxy-3-phenylcoumarin. 1-Benzyloxy-3,4-methylenedioxybenzene (22·8 g) was added with stirring (over 80 min) to an equimolar mixture of $POCl_3$ (15·3 g) and *N*-methylformanilide (13·5 g). During the addition the internal temperature was maintained at 23°. Dilution and subsequent extraction with Et_2O gave 2-benzyloxy-4,5-methylenedioxybenzaldehyde (18·7 g) as yellow needles from EtOH, m.p. 95° (lit.[17] m.p. 95–96°). NMR τ 4·82 (*s*, O–CH_2–ϕ), 3·95 (*s*, O–CH_2O), 3·32 (*s*, 3-H), 2·64 (*s*, 5-H), −0·40 (*s*, –CHO). $NaBH_4$ (3 g) was added to a solution of the aldehyde (18 g) in aqueous dioxan (250 ml; 80%). Addition of HOAc (3 ml) gave a crystalline product (18 g). The *2-benzyloxy-4,5-methylenedioxybenzyl alcohol* was crystallized from C_6H_6 in needles, m.p. 108–109° (lit.[17] m.p. 109–110°). NMR [$(CD_3)_2CO$]τ 6·85 (broad *s*, –OH), 5·3 (*s*, $-CH_2$.OH), 4·84 (*s*, O.CH_2–ϕ), 4·0 (*s*, O.CH_2.O), 3·19 (*s*, 3-H), 2·93 (*s*, 6-H). The alcohol was converted via the chloride to 2-benzyloxy-4,5-methylenedioxybenzyl cyanide m.p. 115–117° (lit.[17] m.p. 117–118°); NMR τ 6·35 (*s*, $-\underline{CH_2}CN$).

Evaporation of the solvent from the reaction of the benzyl cyanide (5·5 g) with ethanolic KOH (65 g; 20%) afforded a residue which was diluted and acidified. The precipitate was crystallized from EtOH and gave needles of 2-benzyloxy-4,5-methylenedioxyphenylacetic acid (2·5 g) m.p. 127–128° (lit. m.p. 130°). A mixture of this acid (2·5 g) was refluxed with 2,4-dihydroxybenzaldehyde (1·2 g), anhydrous KOAc (1·5 g) and Ac_2O (6 ml) for 9 h. Dilution of the reaction mixture afforded *7-acetoxy-2'-benzyloxy-4',5'-methylenedioxy-3-phenylcoumarin* as yellow prisms ($CHCl_3$/EtOH) m.p. 209–210° (Found: C, 69·6, H, 4·1. $C_{25}H_{18}O_7$ requires: C, 69·7; H, 4·2%). λ_{max} nm (log ϵ) 232 (4·07) 285 (4·23) 3·1 (4·12) 3·45 (4·0); ν_{max} 1720 cm^{-1} and 1610 cm^{-1}. NMR (DMSO-d_6) τ 7·7 (*s*, OAc) 4·92 (*s*, O–CH_2–Ph) 3·92 (*s*, O–CH_2.O), 2·97 (*s*, 3'-H, 6'-H) 2·86 (*q*, *J* 2·5, 9 Hz 6-H) 2·62 (*s*, 8-H), 2·2 (*d*, *J* 9 Hz 5-H), 1·94 (*s*, 4-H). Debenzylation (HOAc; 80 ml)/HCl, 30 ml) and subsequent acetylation (Ac_2O/pyridine) afforded *2',7-dimethoxy-4',5'-methylenedioxy-3-phenylcoumarin* as yellow needles (aq. EtOH) m.p. and m.m.p. (with the diacetate of the natural product) 196–198°; NMR τ 7·83, 7·62 (*s*, 2 × OAc), 3·9 (*s*, O.CH_2.O), 3·19 (*s*, 3'-H), 3·04 (*s*, 6'-H), 2·82 (*m*, 6-H, 8-H), 2·39 (*d*, *J* 9·3 Hz, 5-H), 2·25 (*s*, 4-H).

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