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SHORT COMMUNICATION

NEOFLAVANOIDS OF *DALBERGIA CULTRATA*[*]

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Abstract—In addition to the known neoflavanoids (S)-4-methoxydalbergione, dalbergin, and stevenin, the heartwood of *Dalbergia cultrata* Grah. contains a new 3,3-diphenylprop-l-ene (Ia). The assigned structure is based on data acquired mainly by physical methods. The softwood of *D. ferruginea* Roxb.[†] yielded sitosterol and friedelin.

INTRODUCTION

Dalbergia cultrata Grah. (Leguminosae–Lotoideae), a moderate sized deciduous tree indigenous to the forests of Burma,[1] belongs to a family of plants known to contain neoflavanoids.[2]

We now report results of a phytochemical study on the presently available sample (17·3 g) of the heartwood.

Besides fatty acids, fractionation of the *n*-hexane extract gave (S)-4-methoxydalbergione[2,3] (II), dalbergin[4] (IIIa) and a compound isolated as its *O*-diacetate which is assigned structure (Ib). The ethanol extract yielded stevenin[5] (IIIb) (3′,6-dihydroxy-7-methoxy-4-phenylcoumarin) and a further sample of the phenol (Ia).

RESULTS AND DISCUSSION

The spectroscopic properties of (S)-4-methoxydalbergione, dalbergin and stevenin easily permitted their identification and this was confirmed by comparison with authentic specimens isolated from other *Dalbergia* species.

The *O*-diacetate (Ib) has UV [$\lambda_{\max}^{\mathrm{MeOH}}$ 285 nm (log ϵ 3·7), 233 nm (log ϵ 4·1)sh.] and mass spectra which showed features common to 3,3-diphenylprop-1-enes. Its structure as 3-(5-acetoxy-2,4-dimethoxyphenyl)-3-(3′-acetoxyphenyl)prop-1-ene is defined by its NMR spectrum. A comparison (see Table 1) with the spectra of model compounds indicates the

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[*] Part VIII of the series "Dalbergia Species". For Part VII see B. J. Donnelly, D. M. X. Donnelly A. M. O'Sullivan and J. P. Prendergast, *Tetrahedron* **25**, 4409 (1969).

[†] syn. *Dalbergia stipulacea* F. -Vill. Merr. En. Philip Fl. PL **2**, 294 (1923).

[1] J. S. Gamble, *A Manual of Indian Timbers*, p. 253, Sampson Low, Marston, London (1922).

[2] W. B. Eyton, W. D. Ollis, I. O. Sutherland, O. R. Gottlieb, M. Taveira Magalhães and L. M. Jackman, *Tetrahedron* **21**, 2683 (1965).

[3] B. J. Donnelly, D. M. X. Donnelly and C. B. Sharkey, *Phytochem.* **4**, 337 (1965).

[4] V. K. Ahluwalia, P. L. Sawhney and T. R. Seshadri, *J. Sci. Industr. Res.* **15B**, 66 (1956).

[5] This compound was isolated from *Dalbergia stevensonii* Standl. and was synthesized. Details of this work will be published shortly.

TABLE 1. ORD, UV AND NMR (τ, $CDCl_3$, J IN Hz) DATA FOR COMPOUND (Ib) AND MODEL COMPOUNDS

Compound	m.p.	ORD* $\{\phi\}$	ORD* λ (nm)	ORD* $a \times 10^{-2}$	UV λ (nm)	max* log ϵ
(R)-2'-*O*-Acetyl-5-*O*-methyllatifolin (IVc)	91–92°	−1420tr	287†	−30	293	3·72
		+1530sh	282		232i	3·93
		+6780pk	250	+401	214	4·27
		−33,300tr	224			
(R)-3,4-Dimethoxydalbergione quinol diacetate (IVb)	b.p. 100°/ 10^{-3} mm	−420tr	278†	−7	270	3·00§
		+340sh	263			
		+715pk	242	+55		
		+4800tr	226			
(S)-4,4'-Dimethoxydalbergione quinol diacetate (V)	113–114°	—			278	3·31§
(R)-2',5-*O*-Diacetyllatifolin (IVa)	124°	+1020tr	278†	−55	285	3·62
		+6400i	254			
		+12,700pk	242	+589	230i	3·98
		−46,200tr	218			
Diacetate (Ib)	93–95°	−4460	296‡		285	3·7
		−2240sh	279			
		−15,600tr	248	−646	233	4·1
		+49,000pk	225			

Location of protons‖ Ring A 2 OMe	2 OAc	3 OMe	3 H	4 OMe	5 OAc	5 OMe	6 H	Ring B
6·24	—	—	3·46	6·18	—	6·15	3·3	2·94 (4)m 7·8 (2'-OAc)
—	7·9	6·12	—	6·12	7·72	—	3·3	2·5–2·9 (5)m
—	7·9	—	3·3	6·25	7·7	—	3·2	2·85 (2), 3·08 (2) J 9·0 Hz; A_2B_2 system 6·25 (4'-OMe)
6·24	—	—	3·45	6·18	7·7	—	3·2	2·6–3·0 (4)m 7·8 (2'-OAc)
6·24	—	—	3·46	6·18	7·7	—	3·2	2·6–3·15 (4)m 7·7 (3'-OAc)

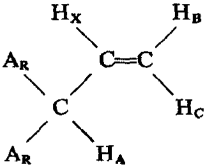
pk = peak; tr = trough; sh = shoulder; i = inflection.

* Solvent MeOH.

† Ref. 8.

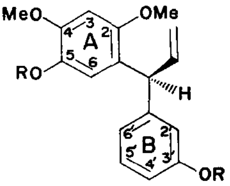
‡ Concentration 0·982 mg/3 ml; cell path-length 0·1 cm.

§ Solvent EtOH.

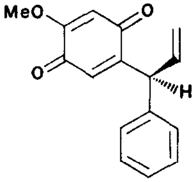
‖ The residue 

was identified by a quartet of triplets ($H_B + H_C$) and a broad doublet (H_A) {τ 4·5–5·5} and a multiplet (H_X) {τ 3·6–4·2}.

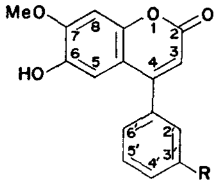
similarity of its A-ring with accompanying substitution pattern to that of the A-ring in 2′,5-*O*-diacetyllatifolin[6] (IVa).



(I) a R = H
b R = Ac

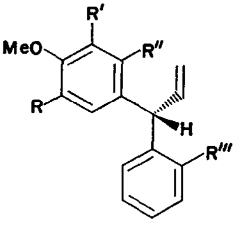


(II)

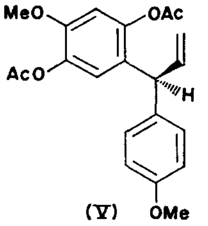


(III) a R = H
b R = OH

The para protons (A-ring) in compounds (Ib) and (IVa) resonate as singlets and their chemical shift values (τ 3·2 and 3·46) compare favourably as do the methoxyl proton shifts on solvation ($CDCl_3 \rightarrow C_6D_6$).[7] The location of the hydroxy-group at position-3′ in ring B is based on the following facts: (a) the non-existence of an A_2B_2 pattern for the four aromatic protons (compare with compound V); (b) the dissimilarity to 2′,5-*O*-diacetyllatifolin (IVa); and (c) the similarity of oxygenation pattern in the co-occurring 4-phenylcoumarin, stevenin (IIIb). The absolute (S)-configuration is assigned to compound (Ib) from analysis of the Cotton effects in its ORD curve. ORD curves for 2′,5-*O*-diacetyllatifolin (IVa) and several quinol diacetates related to 4-methoxydalbergione have been studied.[8] The co-occurring 4-methoxydalbergione in *D. cultrata* has an absolute (S)-configuration.



(IV)
(a) R = R‴ = OAc; R′ = H; R″ = OMe.
(b) R = R″ = OAc; R′ = OMe; R‴ = H.
(c) R = R″ = OMe; R′ = H; R‴ = OAc.



(V)

On receipt of a further sample of the heartwood a more detailed study shall be undertaken. We have also examined the softwood of *D. ferruginea* Roxb. sitosterol and friedelin[9] were isolated, and shown to be identical with authentic samples.

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[6] C. B. Dempsey, D. M. X. Donnelly and R. A. Laidlaw, *Chem. & Ind.* 491 (1963).
[7] A. Pelter and P. I. Amenechi, *J. Chem. Soc.* C, 887 (1969).
[8] D. M. X. Donnelly, B. J. Nangle, P. B. Hulbert, W. Klyne and R. J. Swan, *J. Chem. Soc.* C, 2450 (1967).
[9] O. R. Gottlieb, A. M. Bittencourt and M. Taveira Magalhães, *Anais da Assoc. Brazil de Quinca* **21**, 33.

EXPERIMENTAL

M.ps were measured on a Kofler hot-stage apparatus and are uncorrected. 60 MHz NMR spectra were measured in $CDCl_3$ (Me_4Si as internal reference). Merck Kiselgel G was used for TLC.

Examination of D. cultrata *heartwood.* (a) The powdered heartwood (17·3 g) was continuously extracted with hot *n*-hexane. The residue (1·1 g), when freed from solvent, was chromatographed on silica (70 g) with $CHCl_3$ as eluent. The first cut gave a fatty material, which on GLC analysis of the CH_2N_2 treated fraction showed the presence of a series of *n*-saturated acids (C_{19}–C_{27} inclusive). GLC peaks were identified by direct comparison with standards (arachidic, behenic and lignoceric methyl esters).

The second fraction was crystallized from *n*-hexane yielding (S)-4-methoxydalbergione (180 mg) as yellow needles (m.p., mixed m.p., $[\alpha]_D$, IR and NMR). A later fraction yielded dalbergin (15 mg) (m.p., mixed m.p., NMR); its acetate, (m.p., mixed m.p.).

(b) The residual heartwood was further extracted with cold ethanol. The ethanol extract was concentrated and re-extracted with $CHCl_3$. The solvent was evaporated and the residue (3·5 g) was chromatographed on silica giving the following fractions with the indicated eluents: I ($CHCl_3$), II ($CHCl_3$–acetone, 9:1), III ($CHCl_3$–acetone, 3:1). Fraction I gave a further quantity of (S)-4-methoxydalbergione and dalbergin. Fraction II (20 mg) was crystallized from a mixture of benzene–acetone in needles, m.p. 250–254° (decomp.) diethyl ether m.p. 123° (EtOH) (UV, TLC, (six solvents) identical with sample of stevenin diethyl ether).

Fraction III was plated (solvent $CHCl_3$) and the major component eluted (NMR spectrum τ 3·54, 4·95 s (2 × OH) exchangeable D_2O). Acetylation (Ac_2O–pyridine), TLC (solvent $CHCl_3$), and subsequent elution of the deep purple band gave a solid which crystallized from benzene–light petroleum (b.p. 60–80°) as prisms (25 mg) m.p. 93–95°, $[\alpha]_D^{21^\circ} + 8{\cdot}25^\circ$ ($CHCl_3$). (Found: C, 67·73; H, 5·7; M^+-370. $C_{21}H_{22}O_6$ requires C, 68·1; H, 5·9%).

Examination of D. ferruginea *softwood.* The powdered softwood (2·5 kg) was exhaustively extracted with *n*-hexane (72 hr) and subsequently with benzene. Evaporation of the solvents gave a dark yellow oil (38 g). An aliquot (14 g) was chromatographed over silica (800 g). The column was developed with $CHCl_3$: friedelin, $C_{30}H_{50}O$ as needles from di-*iso*propyl ether, m.p. 250° (mixed m.p.; $[\alpha]_D$, mass of triterpene); sitosterol, $C_{29}H_{50}O$ as needles from Et_2O m.p. 145° (mixed m.p.; $[\alpha]_D$, mass IR of sterol).

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Key Word Index—Dalbergia cultrata; Leguminosae; neoflavanoids; 3,3-diphenylprop-l-ene; *Dalbergia erruginea*; sitosterol; friedelin.