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PTEROCARPANS FROM *DALBERGIA SPRUCEANA**

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Key Word Index—*Dalbergia spruceana*; Leguminosae–Lotoideae; neoflavonoids; isoflavones; pterocarpans.

Abstract—The wood of *Dalbergia spruceana* contains, besides *O*-acetyloleanolic acid, elemicin and 3,4,5-trimethoxycinnamaldehyde; the neoflavonoids (*S*)-4-methoxydalbergione and dalbergin; the isoflavones biochanin-A, formononetin, pseudobaptigenin and caviunin; and the pterocarpans (±)-medicarpin, (±)-maackiain, as well as the 3,4-dihydroxy-, 3-hydroxy-4-methoxy- and 4-hydroxy-3-methoxy-derivatives of (6*aR*,11*aR*)-8,9-methylenedioxypterocarpan. The constitutions of the three last named compounds were deduced by spectra and confirmed by synthesis of (±)-4-hydroxy-3-methoxy-8,9-methylenedioxypterocarpan.

INTRODUCTION

Dalbergia spruceana Benth., resembling the true jacarandá timber tree *D. nigra* (Vell.) Fr. Allem., occurs in the 'terra firme' upland forests of the Amazonas and Pará States, Brasil. Benzene extraction of its softwood yielded sitosterol, *O*-acetyloleanolic acid [2], benzoic acid, elemicin and 3,4,5-trimethoxycinnamaldehyde, besides the neoflavonoids (*S*)-4-methoxydalbergione [3] and dalbergin [4], the isoflavones biochanin-A [5], caviunin [6] and formononetin [1], and five pterocarpans, (±)-medicarpin [7], (±)-maackiain [8], as well as the 3,4-dihydroxy- (**1a**), 3-hydroxy-4-methoxy- (**1b**) [9] and 4-hydroxy-3-methoxy- (**1c**) derivatives of (−)-8,9-methylenedioxypterocarpan. Benzene extraction of the heartwood yielded again benzoic acid and (*S*)-4-methoxydalbergione, this time accompanied by the isoflavone pseudobaptigenin [10] and the pterocarpans (±)-maackiain, (−)-**1a** and (−)-**1c**.

* Part 5 in the series 'Isoflavonoid Constituents of *Dalbergia* and *Machaerium* Species'. For Part 4 see ref. [1].

RESULTS AND DISCUSSION

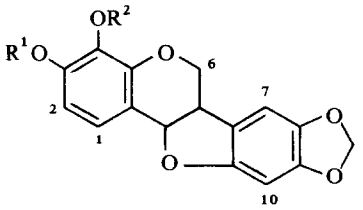
PMR and MS data indicated that both novel compounds, $C_{15}H_8O_2(OH)_2O_2CH_2$ (**1a**) and $C_{15}H_8O_2.OH.OMe.O_2CH_2$ (**1c**) are pterocarpans. Their methyl ethers are identical with the methyl ether of (−)-3-hydroxy-4-methoxy-8,9-methylenedioxypterocarpan, i.e. **1d** [9], and this established their constitutions as (−)-3,4-dihydroxy-8,9-methylenedioxypterocarpan (**1a**) and (−)-4-hydroxy-3-methoxy-8,9-methylenedioxypterocarpan (**1c**).

The synthesis of racemic **1c**, undertaken in order to confirm these structural assignments, used a method which has previously been applied to the synthesis of other pterocarpan derivatives [11, 12]. The chalcone **2a**, synthesised by the condensation of 6-benzyloxypiperonal with 2,3-dibenzyloxy-4-methoxyacetophenone,

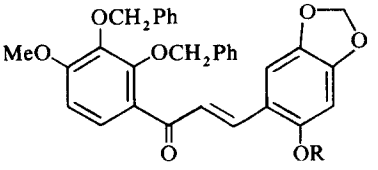
Table 1. Pterocarpans of *Dalbergia* and *Machaerium* species

Compound	Substituent at position 2	3	4	6	8	9	10	Plant Source*
(+)-Mucronucarpan	OH	OMe	—	—	—	OMe	OH	Mmu
(+)-Homopterocarpin	—	OMe	—	—	—	OMe	—	Mve, Mvi
(+)-Medicarpin	—	OH	—	—	—	OMe	—	Dde, Dri, Dva, Mku, Mni, Mve
(+)-Vesticarpan	—	OH	—	—	—	OMe	OH	Mve
(+)-Variabilin	—	OMe	—	OH	—	OMe	—	Dva
(±)-Medicarpin	—	OH	—	—	—	OMe	—	Dce, Dde, Dec, Dsp, Dst, Dva
(±)-Maackiain	—	OH	—	—	OCH_2	O	—	Dsp, Dst
(−)-Medicarpin	—	OH	—	—	—	OMe	—	Dst
(−)-Maackiain	—	OH	—	—	OCH_2	O	—	Dst
(−)-**1a**	—	OH	OH	—	OCH_2	O	—	Dsp
(−)-**1b**	—	OH	OMe	—	OCH_2	O	—	Dsp
(−)-**1c**	—	OMe	OH	—	OCH_2	O	—	Dsp

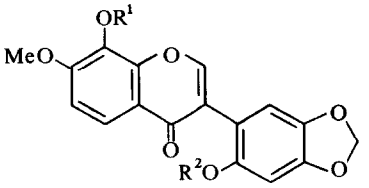
* Dce *D. cearensis* Ducke [16]; Dde *D. decipularis* Rizz. et Matt. [17]; Dec *D. ecastophyllum* (L.) Taub. [7]; Dri *D. riparia* (Mart.) Benth. [18]; Dsp *D. sprucceana* Benth.; Dst *D. stevensonii* Standl [8]; Dva *D. variabilis* Vog. [1]; Mac *M. acutifolium* Vog. [19]; Mku *M. kuhlmannii* Hoehne [20]; Mmu *M. mucronulatum* (Mart.) Benth. [21]; Mni *M. nictitans* (Vell.) Benth. [20]: Mve *M. vestitum* Vog. [22]; Mvi *M. villosum* Vog. [21].



1a $R^1 = R^2 = H$
1b $R^1 = H$, $R^2 = Me$
1c $R^1 = Me$, $R^2 = H$
1d $R^1 = R^2 = OMe$



2a $R = CH_2Ph$
2b $R = Me$



3a $R^1 = R^2 = CH_2Ph$
3b $R^1 = H$, $R^2 = Me$
3c $R^1 = CH_2Ph$, $R^2 = Me$

was converted into its epoxide, which was rearranged with simultaneous monodebenzylation to the isoflavone **3a**. This was debenzylated and reduced to a 2′-hydroxyisoflavanol which cyclised to a racemic pterocarpan, identical (IR, MS, TLC) with natural (−)-**1c**. An alternative synthesis of **1c** was attempted which required selective demethylation of **3b**. Although this reaction had been accomplished for other 2′-methoxyisoflavones [13], it failed in the present case.

The ORD curves of the three (−)-pterocarpans **1a**, **1b**, **1c** from *D. spruceana* are characterised by similar multiple Cotton effects in the 250–350 nm region, and are approximately the mirror images of the curves shown by the (+)-pterocarpans isolated from other *Dalbergia* and *Machaerium* species (Table 1). For (+)-homopterocarpin we established the 6*aS*, 11*aS*-configuration in connection with an ORD study of isoflavans [14], and since all pterocarpans listed in Table 1 have approximately the same value for $J_{H\text{-}6a,H\text{-}11a}$ and should adopt analogous conformations of their *cis*-fused rings B and C [15], all (+)-pterocarpans must possess the same 6*aS*, 11*aS*-configuration. The 6*aR*,11*aR*-configuration can thus be assigned to the (−)-pterocarpans of *D. spruceana*.

EXPERIMENTAL

Unless otherwise stated spectra were measured in EtOH (UV), $CHCl_3$ (IR), $CDCl_3$ (60 MHz PMR) and MeOH (ORD). All evapns of volatile material were performed under diminished pressure.

Isolation of the constituents of D. spruceana. A specimen was collected near Manaus, AM, Brasil and identified by the botanist Apparício Pereira Duarte. Ground sapwood (10·4 kg) was extracted with hot C_6H_6. The extract (50 g) was chromatographed on Si gel to the following products (eluant, method of purification and quantity indicated): fatty material (C_6H_6, 3.6 g), sitosterol (C_6H_6, cryst. from petrol, 170 mg), elemicin (C_6H_6, rechromatography, 500 mg), (*S*)-4-methoxydalbergione (C_6H_6, C_6H_6–$CHCl_3$ (9·1) cryst. from C_6H_6, 200 mg), benzoic acid (C_6H_6–$CHCl_3$ (4:1) cryst. from MeOH, 2 mg), a mixture [C_6H_6–$CHCl_3$ (1:1) rechromatography to benzoic acid (4 mg) and (−)-**1b** (20 mg)], a mixture [C_6H_6–$CHCl_3$ (1:1) fract. cryst. from MeOH to *O*-acetyloleanolic acid (174 g), (±)-maackiain (274 mg) and (−)-**1c** (30 mg)], a mixture [C_6H_6–$CHCl_3$ (1:1) fract. cryst. from MeOH to biochanin A (110 mg) and (±)-medicarpin (70 mg), rechromatography of the residual material to 3,4,5-trimethoxycinnamaldehyde (14 mg), dalbergin (2 mg) and (±)-medicarpin (45 mg)], (−)-**1a** (C_6H_6–$CHCl_3$ (1:1 and 2:3) rechromatography, 40 mg), a mixture [C_6H_6–$CHCl_3$ (2:3) fract. cryst. from MeOH to caviunin (105 mg) and (−)-**1c** (55 mg)], caviunin (C_6H_6–$CHCl_3$ (2:3) $CHCl_3$, cryst. from MeOH, 500 mg), formononetin ($CHCl_3$, cryst. from MeOH, 30 mg). Ground heartwood (1.9 kg) was extracted with hot C_6H_6. The conc C_6H_6 soln was first washed with aq. $NaHCO_3$. The aq. soln was acidified and extracted with $CHCl_3$. Evapn of the $CHCl_3$ gave benzoic acid. The conc C_6H_6 soln was next treated with Et_2O. The ppt. was chromatographed on acid-washed Al_2O_3 to (*S*)-4-methoxydalbergione, (−)-**1c**, (±)-maackiain, pseudobaptigenin and (−)-**1a**. Ground bark (2.1 kg) was extracted with hot C_6H_6. The extract (29 g) gave a large amount of fatty material and a small quantity of caviunin.

Identifications Sitosterol, *O*-acetyloleanolic acid [2], (*S*-4-methoxydalbergione [3], dalbergin [4], (±)-medicarpin [7], (±)-maackiain [8], biochanin-A [5], caviunin [6], formononetin [1], pseudobaptigenin [10], were identified by direct comparison with authentic samples of natural products. Benzoic acid, elemicin and 3,4,5-trimethoxycinnamaldehyde were identified by direct comparison with synthetic samples. 3,4,5-Trimethoxycinnamaldehyde, yellow needles, mp 109–111° ($CHCl_3$), was prepared in 2 steps: (1) $LiAlH_4$ reduction of the corresponding acid; (2) active MnO_2 oxidation of the intermediate alcohol.

(−)-3,4-*Dihydroxy*-8,9-*methylenedioxypterocarpan* (**1a**, α-6aH, α-11aH). Mp 85–87° and 186–187° (aq. MeOH), $[\alpha]_D^{20}$ − 233° (MeOH). [Found: C, 61.27; H, 4.87. $C_{16}H_{12}O_6$. MeOH requires. C, 61.45; H, 4.82%] ν_{max} (cm^{-1}): 3500, 1635, 1610, 1500. λ_{max} (nm): 235, 312 (ε 8400, 6250). MS (*m/e*): 300 (100%) M, 163 (7), 175 (4), 162 (36), 150 (10), 87·7 (metastable ion for 300 → 162). ORD (*c* 0.0036): $[\phi]_{330}$ + 6900, $[\phi]_{279}$ − 10200, $[\phi]_{255}$ − 22500, $[\phi]_{250}$ − 12930. Positive $FeCl_3$-reaction on TLC. *Diacetate*, needles, mp 142–145° (MeOH). PMR (CCl_4, τ): 2.65 (*d*, *J* = 9 Hz, H-1), 3.20 (*d*, *J* = 9 Hz, H-2), 3.37 (*s*, H-7), 3·67 (*s*, H-10), 4.13 (*s*, O_2CH_2), 7.77 (*s*, 2 OAc), 5.6–6.6 (*m*, 2 H-6, H-6a), 4.5 (*d*, *J* = 7 Hz, H-11a).

Dimethyl ether (**1f**, α-6aH, α-11aH), rhombs, mp 218–220° (C_6H_6–petrol) (lit. [7] mp 245–247°). $[\alpha]_D^{20}$ − 134° ($CHCl_3$). MS (*m/e*): 328 (100%) M, 191 (2), 175 (6), 162 (14), 178 (6). ORD (*c* 0.0052): $[\phi]_{351}$ − 1490, $[\phi]_{323}$ 0, $[\phi]_{290}$ − 5300, $[\phi]_{278}$ − 4960, $[\phi]_{256}$ − 7630, $[\phi]_{250}$ − 6620.

(−)-3-*Hydroxy*-4-*methoxy*-8,9-*methylenedioxypterocarpan* (**1b**, α-6aH, α-11aH). Needles, mp 156–159° (MeOH) (lit. [7] mp 159–161°). ν_{max} (cm^{-1}): 3500, 1630 *sh*, 1615, 1500. λ_{max} (nm): 229, 283, 312 (ε 10050, 2800, 7400). PMR (τ): 2.85 (*d*, *J* = 9 Hz, H-1), 3.33 (*d*, J = 9 Hz, H-2), 3.25 (*s*, H-7), 3.55 (*s*, H-10), 4.15 (*s*, OH-3), 4.10 (*s*, O_2CH_2), 5.93 (*s*, OMe-4), 4.50 (*d*, *J* = 7 Hz, H-11a), 5.6–6.6 (*m*, 2 H-6, H-6a). MS (*m/e*): 314 (100%) M, 177 (3), 175 (8), 162 (32), 164 (10), 83.6 (metastable ion for 314 → 162). ORD (*c* 0.0036): $[\phi]_{328}$ + 2210, $[\phi]_{256}$ − 10150, $[\phi]_{274}$ − 8390, $[\phi]_{256}$ − 17610, $[\phi]_{250}$ − 14180, $[\phi]_{244}$ − 8350.

(−)-4-*Hydroxy*-3-*methoxy*-8,9-*methylenedioxypterocarpan* (**1c**, α-6aH, α-11aH). Needles (MeOH), rhombs, mp 172–174° (petrol), $[\alpha]_D^{20}$ −300° (MeOH). [Found: C, 63.01; H, 4.46; OMe, 13.77. $C_{17}H_{14}O_6$. 1/2MeOH requires: C, 63.60; H, 4.25; OMe, 14.10%]. ν_{max} (cm^{-1}): 3500, 1640, 1600 *sh*, 1500. λ_{max} (nm): 236, 312 (ε 7500, 4950). PMR (τ): 2.93 (*d*, *J* = 9 Hz, H-1), 3.33 (*d*, *J* = 9.Hz, H-2), 3.25 (*s*, H-7), 3.55 (*s*, H-10), 4.09 (*s*, O_2CH_2), 4.51 (*s*, OH-4), 6.09 (*s*, OMe-3), 4.50 (d, *J* = 7 Hz, H-11a), 5.6–6.6 (*m*, 2 H-6, H-6a). MS (*m/e*): 314 (100%) M, 177 (3), 175 (6), 162 (35), 164 (5). ORD (*c* 0.0055): $[\phi]_{345}$ − 1950, $[\phi]_{328}$ − 654, $[\phi]_{284}$ − 16340, $[\phi]_{256}$ − 34000, $[\phi]_{254}$ − 22280. Positive $FeCl_3$-reaction on TLC.

Synthesis of (±)-4-*hydroxy*-3-*methoxy*-8,9-*methylenedioxypterocarpan* (**1c**). (a) *Preparation of* 6-*benzyloxypiperonal*. 6-Hydroxypiperonal [23] (4.5 g), K_2CO_3 (25 g), $PhCH_2Cl$ (8 ml) and Me_2CO (80 ml) were heated under reflux (24 hr). The usual work up led to the benzyl derivative (3.5 g), needles, mp 97–98° (EtOH). [Found: C, 70.15; H, 4.62. $C_{15}H_{12}O_4$ requires: C, 70.04; H, 4.69%]. (b) *Preparation of* 2,3-*dibenzyloxy*-4-*methoxyacetophenone*. 2,3-Dihydroxy-4-methoxyacetophenone (1 g) was benzylated analogously to the dibenzyl derivatives (1.1 g), rhombs, mp 40–41° (MeOH). [Found: C, 76.07; H, 6.08. $C_{23}H_{22}O_4$ requires: C, 76.20; H, 6.07%]. (c) *Preparation of* 2,2',3'-*tribenzyloxy*-4'-*methoxy*-4,5-*methylenedioxychalcone* (**2**). To the aldehyde (1 g) and acetophenone (1.5 g) (see preparations a and b) in warm EtOH (10 ml) 60% aq. NaOH soln (25 ml) was added with stirring. Stirring was continued (1 hr). The ppt. was collected, washed with H_2O, dil. HCl, H_2O and cryst. to **2** (1.9 g), yellow rhombs, mp 141–142° (EtOH). [Found: C, 76.40; H, 5.58. $C_{38}H_{32}O_7$ requires: C, 76.10; H, 5.33%]. (d) *Preparation of* 8,2'-*dibenzyloxy*-7-*methoxy*-4',5'-*methylenedioxyisoflavone* (**3a**). The chalcone **2a** (4 g) in Me_2CO (240 ml) and MeOH (80 ml) was treated with 30% H_2O_2 (3 ml) and 8% aq. NaOH (3 ml). The mixture was shaken, brought to boiling twice during 1 hr, kept at room temp. (2 hr), further treated with 30% H_2O_2 (1.5 ml) and 8% aq. NaOH (1.5 ml) and kept *ca* 18 hr. H_2O (200 ml) was then added, the Me_2CO and MeOH evapd and the mixture extracted with $CHCl_3$. Evapn. of the $CHCl_3$ gave the chalcone epoxide (4 g) as a pale yellow oil. This was dissolved in dry C_6H_6 (30 ml) and treated with BF_3–Et_2O (4 ml) dropwise and with stirring. After 20 min Et_2O (100 ml) was added and the soln washed with H_2O and extracted with 5% aq. NaOH. The basic soln was acidified and extracted with AcOEt. Evapn. of the AcOEt gave the monobenzyl isoflavone (400 mg). ν_{max} (cm^{-1}): 3500, 1640, 1610, 1570, 1500. PMR (τ): 2.06 (*s*, H-2). Evapn of the C_6H_6–Et_2O soln and purification of the residue by chromatography gave the dibenzyl isoflavone (**3a**, 500 mg). ν_{max} (cm^{-1}): 1640, 1630, 1600, 1500, 1480. (e) *Preparation of* (±)-4-*hydroxy*-3-*methoxy*-8,9-*methylenedioxypterocarpan* (**1c**). Hydrogenation of **3a** (500 mg) in AcOEt (10 ml) over 10% Pd/C (50 mg) gave a product which was dissolved in MeOH, treated with $NaBH_4$ (50 ml) in H_2O (5 ml), kept *ca* 18 hr, then treated with a few drops of HCl and extracted with Et_2O. Evapn of the Et_2O and TLC (Si gel, $CHCl_3$) of the residue gave two compounds: **1c** (15 mg), needles, mp 213–215° (EtOH); rhombs, mp 191–193° (C_6H_6–petrol), identical (IR, MS, TLC) with the natural product. *Acetate*, mp 195–196° (EtOH–H_2O). The second compd, strong $FeCl_3$-reaction, was presumed to be the intermediate 2'-hydroxyisoflavonol, since on brief treatment with warm dil. HCl further **1c** was formed.

Synthesis of 8-*hydroxy*-7,2'-*dimethoxy*-4',5'-*methylenedioxyisoflavone*. (a) *Preparation of* 2',3'-*dibenzyloxy*-2,4'-*dimethoxy*-4,5-*methylenedioxychalcone* (**2b**). 6-Methoxypiperonal (1 g) [23] and 2, 3-dibenzyloxyacetophenone (2 g) as in (c) above, gave **2b** (2.8 g), yellow clusters, mp 91–92° (EtOH). [Found: C, 73.20; H, 5.45. $C_{32}H_{28}O_7$ requires: C, 73.40; H, 5.34%]. ν_{max} (cm^{-1}): 1640. λ_{max} (nm): 245, 314, 398 (ε 10300, 9050, 15600). (b) *Preparation of* 2',3'-*dibenzyloxy*-2,4'-*dimethoxy*-4,5-*methylenedioxychalcone epoxide*. The chalcone **2b** (3 g), treated with H_2O_2 as in (d) above, gave the epoxide (1.6 g), needles, mp 111–113° ($CHCl_3$–EtOH). [Found: C, 71.01; H, 5.34. $C_{32}H_{28}O_8$ requires: C, 71.10; H, 5.17%]. ν_{max} (cm^{-1}): 1660. λ_{max} (nm): 233, 295, 293 (ε 18300, 10700, 6300). PMR (τ): 5.65 (*s*, COCHCHAr). (c) *Preparation of* 8-*hydroxy*-7,2'-*dimethoxy*-4',5'-*methylenedioxyisoflavone* (**3b**). The epoxide (1 g) was treated with BF_3–Et_2O as in (d) above. The C_6H_6–Et_2O soln gave **3c** (*ca* 10 mg). PMR (τ): 2.09 (*s*, H-2). Evapn of the AcOEt soln and sublimation of the residue gave **3b**, needles, mp 233–234°. ν_{max} (cm^{-1}): 3560, 1640, 1620, 1600, 1570, 1015, 940. λ_{max} (nm): 221, 262, 304 (ε 18800, 24000, 10900). *Acetate*, needles, mp 226–228° (EtOH). [Found: C, 62.83; H, 4.29. $C_{20}H_{16}O_8$ requires: C, 62.50; H, 4.17%]. PMR (τ): 2.12 (*s*, H-2).

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