Phytochemistry, Vol. 26, No 2, pp. 531–535, 1987.
Printed in Great Britain.

0031–9422/87 $3.00 + 0.00

FLAVONOID ANALOGUES FROM *PTEROCARPUS* SPECIES

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(*Received* 16 *April* 1986)

Key Word Index –*Pterocarpus soyauxii*; *P. marsupium*; Leguminosae; isoflavonoids; 3′-*C*-glucosyl-α-hydroxydihydrochalcone; 5-deoxy-8-*C*-glucosylflavonols.

Abstract Two novel pterocarpans, 8-hydroxy-3,9-dimethoxy- and 3,8-dihydroxy-9-methoxypterocarpan and a new santal analogue were isolated from the heartwood of *P. soyauxii*. These are accompanied by several known pterocarpans, isoflavans, isoflavones and *trans*-pterostilbene. From the heartwood of *P. marsupium* were obtained 8-*C*-β-D-glucopyranosyl-3,7,4′-trihydroxy- and -3,7,3′,4′-tetrahydroxyflavone, representative of the first 5-deoxy *C*-*C*-coupled flavonol glucosides, and the rare 3′-*C*-β-D-glucopyranosyl-α-hydroxydihydrochalcone, their structures being determined by means of high resolution NMR techniques.

INTRODUCTION

We have recently indicated the co-existence of α-hydroxydihydrochalcones, α-methyldeoxybenzoins and isoflavonoids in the heartwood of *Pterocarpus angolensis* DC. and also demonstrated the *in vitro* transformation of α-hydroxydihydrochalcones into α-methyldeoxybenzoins [1]. This prompted reinvestigation of the heartwoods of *P. soyauxii* [2] and *P. marsupium* [3–7] in order to give credence to the presumed biogenetic relationship between these different classes of natural products.

RESULTS AND DISCUSSION

Successive extraction of the heartwood of *P. soyauxii* with *n*-hexane and methanol led to the isolation of (−)-homopterocarpin [8], (−)-vestitol* [9], (+)-mucronulatol* [10], formononetin [11], prunetin (**1**) [12], *trans*-pterostilbene [13], the rare (3*R*)-claussequinone* [9] and santal (**3**) [8]—the latter two being obtained from the title species for the first time. These compounds are accompanied by the novel (6a*R*,11a*R*)-8-hydroxy-3,9-dimethoxy- (**7**) and (6a*R*,11a*R*)-3,8-dihydroxy-9-methoxypterocarpan (**9**) and the new santal analogue (**5**).

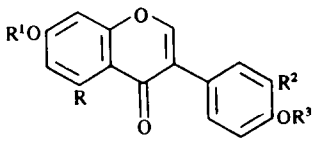
The pterocarpanoid character of both (**7**) and (**9**) is apparent from their ^{1}H NMR spectra which revealed the characteristic chemical shifts and coupling patterns [e.g. δ5.45 (*d*, *J* = 6.8 Hz, H-11a), 4.23 (*dd*, *J* = 4.9, 11.0 Hz, H-6_{eq}), 3.64 (*dd*, *J* = 10.5, 11.0 Hz, H-6_{ax}), and 3.50 (*ddd*, *J* = 4.9, 6.8, 10.5 Hz, H-6a) for (**7**)] associated with the ABMX system of ring B. The aromatic substitution pattern was defined in each case by an ABX system (A-ring) and two high field singlets (D-ring) in the benzenoid region. While chemical shift differences between aromatic protons of the phenolic compounds **7** and **9** and their acetates **8** and **10** allowed the allocation of methoxyl groups, definition of the 6a*R*,11a*R* absolute configurations [14–16] for both **7** and **9** follows from their CD curves which exhibit Cotton effects almost identical to that of (−)-homopterocarpin.

The ^{1}H NMR spectrum of the diacetate (**6**) of the novel santal analogue (**5**) revealed a low field singlet (δ7.86), characteristic of the H-2 vinylic proton of isoflavones. Two *meta*-coupled doublets (δ6.78 and 6.63; A-ring) and an ABX system for the B-ring partially define the aromatic oxygenation pattern. Comparison of the chemical shifts of the A-ring doublets with those of di-*O*-acetylprunetin (**2**) and tri-*O*-acetylsantal (**4**) indicated identical A-ring substitution in all three cases. The ABX pattern is compatible with four B-ring arrangements, i.e. two each for 3,4- and 2,4-disubstitution (e.g. 3-methoxy-4-acetoxy vs 3-acetoxy-4-methoxy). Long range decoupling of the methoxyl group at δ3.88 led to sharpening of the *m*-doublet (δ7.14) of the ABX system only. This taken in conjunction with the absence of prominent loss of methoxyl radical, a typical MS fragmentation of 2′-methoxyisoflavones [12], strongly indicates structure **5** for the isoflavone derivative.

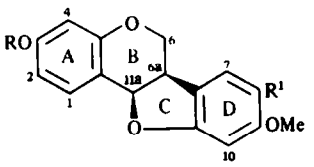
The methanol extract of the heartwood of *P. marsupium* gave in addition to *trans*-pterostilbene and the known 2′,4,4′-trihydroxychalcone/4,4′-dihydroxyflavanone pair (isoliquiritigenin/liquiritigenin) [3, 17] also the rare 3′-*C*-β-D-glucopyranosyl-α-hydroxydihydrochalcone, coatline A (**11**) [18] which was characterized as full acetate (**12**) by comparison of 300 MHz ^{1}H NMR data at 90° with that previously recorded [18]. Spin–spin decoupling of the two-proton doublet at δ7.16 (H-2,6; B-ring) led to selective sharpening of the non-equivalent methylene resonances (δ3.15 and 2.97) thus defining the aglycone moiety unambiguously as an α-hydroxydihydrochalcone analogue. The chemical shift value and coupling constant of the anomeric proton (δ4.74, *J* = 10.0 Hz; *cf.* [18], δ4.78, *J* = 10.0 Hz) taken in conjunction with *J*-values for the methine protons (*J* = 9.1–10.0 Hz) established the $C_{14}H_{19}O_9$ residue as a C_1-coupled β-D-tetra-*O*-acetylglucopyranosyl group.

*Absolute configurations were determined by comparison of CD data with that of (3*R*)-7-*O*-methylvestitol obtained by hydrogenolysis of (−)-homopterocarpin.

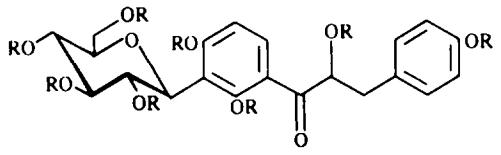
PHOTO 26/2-N



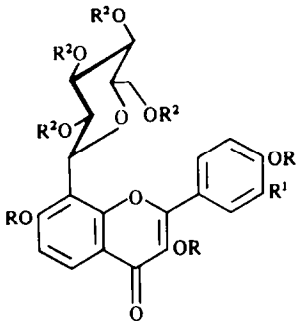
1 R = OH, R^1 = Me, R^2 = R^3 = H
2 R = OAc, R^1 = Me, R^2 = H, R^3 = Ac
3 R = R^2 = OH, R^1 = Me, R^3 = H
4 R = R^2 = OAc, R^1 = Me, R^3 = Ac
5 R = OH, R^1 = Me, R^2 = OMe, R^3 = H
6 R = OAc, R^1 = Me, R^2 = OMe, R^3 = Ac



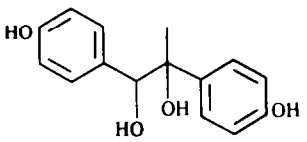
7 R = Me, R^1 = OH
8 R = Me, R^1 = OAc
9 R = H, R^1 = OH
10 R = Ac, R^1 = OAc



11 R = H
12 R = Ac



13 R = R^1 = R^2 = H
14 R = Me, R^1 = H, R^2 = Ac
15 R = R^2 = H, R^1 = OH
16 R = Me, R^1 = OMe, R^2 = Ac



17

Despite the availability of a well-defined CD curve, the absolute configuration of the chiral α-carbon could not be determined by direct comparison with CD data of (α*R*)-α,2′-dihydroxy-4,4′-dimethoxydihydrochalcone [1] due to complexity introduced by the chiral centres of the pyranosyl unit. Attempts aimed at its removal either failed (M HCl or β-glucosidase) or led to destruction (HI/phenol) of the dihydrochalcone moiety.

The compound pterosupin, from the rootwood of *P. marsupium*, with the molecular formula ($C_{21}H_{24}O_{10}$) and an aromatic substitution pattern identical to that of coatline A (**11**), had been designated the β-hydroxydihydrochalcone configuration by Adinarayana *et al.* [3] mainly by comparison of chemical shift values of the propanoid ABMX system with that of known α- and β-hydroxydihydrochalcones but in *different* solvent systems. The literature reveals a high degree of confusion regarding differentiation between these closely related classes of natural products. In the absence of synthetic evidence, detection of long-range coupling between H-2/6 (B-ring) and the adjacent methylene (α-hydroxydihydrochalcone) or methine (β-hydroxydihydrochalcone) protons, provides a powerful and reliable method for distinction between the α- and β-hydroxy analogues. This has been elegantly demonstrated by Beltrami *et al.* [18] in the case of coatline A (**11**) and its 3-hydroxy analogue coatline B.

The above-mentioned compounds in *P. marsupium* are accompanied by two novel 8-*C*-β-D-glucopyranosylflavonols **13** and **15**, representative of the first 5-deoxy *C*-*C*-coupled flavonol glucosides. Due to the complexity of the phenolic mixture these were identified as methyl ether acetates **14** and **16***.

*Acetylation of the phenolic fraction led to an inseparable mixture of the peracetates of **13** and **15**. The absence of methoxyl resonances in the 80 MHz ^{1}H NMR spectrum of this mixture excludes the possibility of **13** and **15** being present as partially *O*-methylated analogues.

^{1}H NMR spectra (300 MHz) of **14** and **16** in $CDCl_3$ displayed extensive broadening of signals in the aromatic and heterocyclic regions both at 27° and 90°. At higher temperatures (180°) in DMSO-d_6 the spectrum of the methyl ether acetate (**14**) reflected two low field benzenoid *o*-coupled doublets representative of an AB (δ 8.07) and AA'BB' (δ 8.10) system characteristic of the H-5 and H-2',6' resonances of flavonol-*O*-methyl ethers [19] thus typifying the compound as a C-8 substituted 3,7,4'-trimethoxyflavonol. Comparison of the heterocyclic regions revealed a strong resemblance of chemical shift values and coupling constants to that of coatline A which established the $C_{14}H_{19}O_9$ residue as a C_1-coupled β-D-tetra-*O*-acetylglucopyranosyl moiety and thus the structure of **14** as 8-(2″,3″,4″,6″-tetra-*O*-acetyl-*C*-β-D-glucopyranosyl)-3,7,4'-trimethoxyflavone. The *C*-*C*-coupling was exemplified by ^{1}H–^{13}C heteronuclear correlation of the anomeric proton (δ 5.43 at 27°) with a carbon doublet (δ 70.7) in the region characteristic of C_1-substituted glucosides [20].

The structure of the remaining methyl ether acetate (**16**) followed from that of **14**, since **16** exhibited spectroscopic properties very similar to those for **14**, except for changes due to the presence of an extra aromatic methoxyl group. Thus the ^{1}H NMR of **16** in DMSO-d_6 at 180° showed a typical ABX system for the B-ring protons which identified **16** as 8-(2″,3″,4″,6″-tetra-*O*-acetyl-*C*-β-D-glucopyranosyl)-3,7,3',4'-tetramethoxyflavone.

The high temperature required to induce free rotation of the pyranosyl- and B-ring originates from steric crowding of the *C*-2″-*O*-acetyl group with the heterocyclic oxygen and C-2, as well as between the C-3″ and C-5″ substituents and the B-ring. Since the latter interaction is increased by introduction of a C-3' functionality, this presumably also explains the remaining low degree of line-broadening of the B-ring protons of the tetramethoxyflavonol (**16**) even at 180°.

Although we were not able to detect α-hydroxydihydrochalcones or α-methyldeoxybenzoins in the heartwood of *P. soyauxii*, the present identification of coatline A in *P. marsupium*, taken in conjunction with the presence [5] of the α-methylhydrobenzoin, marsupol (**17**), in the same species is considered as additional evidence towards the tentative biogenetic relationship between the above-mentioned groups of natural products.

EXPERIMENTAL

Mps are uncorr. ^{1}H NMR spectra were recorded at 300 MHz in $CDCl_3$ (19°) with the $CHCl_3$ signal (δ 7.24) as reference, unless otherwise stated. Prep. TLC was carried out using 20 × 20 cm plates with 1.0 mm layers of silica gel. Zones were detected by UV and eluted with Me_2CO. Prep. PC comprised of 46 × 57 cm Whatman No. 3 sheets (100 mg/sheet), which were developed in 2% aq. HOAc. Bands were detected by UV and ammoniacal $AgNO_3$ solution and eluted with 80% EtOH. Column chromatography (CC) was done with Kieselgel 60 as stationary phase.

Extraction and isolation of the compounds from P. soyauxii. Drillings (1.5 kg) of the heartwood of *P. soyauxii* were extracted with hexane (3 × 3 l., 24 hr each) followed by MeOH (6 × 3 l., 48 hr each) producing on evaporation of the solvents a brown oil (37 g) and a dark brown resin (180 g) respectively. The hexane extract (37 g) was fractionated by CC [C_6H_6–Me_2CO (95:5)] to yield eleven fractions, while similar treatment [C_6H_6–Me_2CO–MeOH (14:5:1)] of the MeOH extract (25 g) led to eight fractions. Fractions 4 (RR_t 73 hr, 3.04 g) and 5 (RR_t 81 hr, 1.86 g) of the MeOH extract were further fractionated by CC [both C_6H_6–Me_2CO (9:1)] to yield subfractions 4.1–4.6 and 5.1–5.6 respectively, while subfraction 5.3 (RR_t 21 hr, 680 mg) was subjected to another fractionation by CC [hexane–$CHCl_3$–MeOH (10:9:1)] leading to five more subfractions (5.3.1–5.3.5).

(6a*R*,11a*R*)-3,9-*Dimethoxypterocarpan*[(−)-*homopterocarpin*]. Crystallization of fraction 4 (RR_t 74 hr, 11.85 g) of the hexane extract from EtOH yielded (−)-homopterocarpin as white needles (7.34 g), mp 86° (lit. [8] 85°); $[\alpha]_D^{25}$ −205° ($CHCl_3$, *c* 0.0210 g/ml), lit. [8] $[\alpha]_D^{30}$ −207° ($CHCl_3$); CD: $[\theta]_{205}$ 0, $[\theta]_{232}$ −51 100, $[\theta]_{253}$ 0, $[\theta]_{280}$ +21 010, $[\theta]_{300}$ 0, (MeOH, *c* 0.0650 mg/ml); ^{1}H NMR: δ 3.53 (1H, *ddd*, $J_{6a,6eq}$ = 4.8 Hz, $J_{6a,11a}$ = 6.8 Hz, $J_{6a,6ax}$ = 11.0 Hz, H-6a), 3.63 (1H, *dd*, $J_{6ax,6eq}$ = 10.3 Hz, $J_{6a,6ax}$ = 11.0 Hz, H-6*ax*), 3.77 (3H, *s*, OMe), 3.79 (3H, *s*, OMe), 4.25 (1H, *dd*, $J_{6eq,6a}$ = 4.8 Hz, $J_{6eq,6ax}$ = 10.3 Hz, H-6*eq*), 5.51 (1H, *d*, $J_{11a,6a}$ = 6.8 Hz, H-11a), 6.43 (1H, *d*, $J_{10,8}$ = 2.5 Hz, H-10), 6.46 (1H, *dd*, $J_{8,10}$ = 2.5 Hz, $J_{7,8}$ = 8.8 Hz, H-8), 6.46 (1H, *d*, $J_{4,2}$ = 2.5 Hz, H-4), 6.64 (1H, *dd*, $J_{2,4}$ = 2.5 Hz, $J_{2,1}$ = 8.5 Hz, H-2), 7.13 (1H, *d*, $J_{7,8}$ = 8.8 Hz, H-7), 7.42 (1H, *d*, $J_{1,2}$ = 8.5 Hz, H-1); MS *m/z* (rel. int.): 284 $[M]^+$ (100).

(6a*R*,11a*R*)-8-*Hydroxy*-3,9-*dimethoxypterocarpan* (**7**). Successive prep. TLC purification [cyclohexane–Me_2CO (7:3), × 2, R_f 0.38; hexane–1,2-dichloroethane–Me_2CO (50:48:2), R_f 0.39 and hexane–Me_2CO (7:3) × 2] of fraction 8 (RR_t 125 hr, 280 mg) of the hexane extract yielded the pterocarpan (**7**) (R_f 0.50) as brown needles (76 mg) from EtOH, mp 129° (found: C, 67.8; H, 5.2. $C_{17}H_{16}O_5$ requires: C, 67.9; H, 5.3%); CD: $[\theta]_{205}$ 0, $[\theta]_{230}$ −50 000, $[\theta]_{270}$ 0, $[\theta]_{290}$ 12 000, $[\theta]_{320}$ 0 (MeOH, *c* 0.0596 mg/ml); ^{1}H NMR: δ 3.50 (1H, *ddd*, $J_{6a,6eq}$ = 4.9 Hz, $J_{6a,11a}$ = 6.8 Hz, $J_{6a,6ax}$ = 10.5 Hz, H-6a), 3.64 (1H, *dd*, $J_{6ax,6eq}$ = 11.0 Hz, $J_{6a,6ax}$ = 10.5 Hz, H-6*ax*), 3.78 (3H, *s*, OMe), 3.83 (3H, *s*, OMe), 4.23 (1H, *dd*, $J_{6eq,6a}$ = 4.9 Hz, $J_{6eq,6ax}$ = 11.0 Hz, H-6*eq*), 5.24 (1H, *br s*, 8-OH), 5.45 (1H, *d*, $J_{6a,11a}$ = 6.8 Hz, H-11a), 6.45 (1H, *d*, $J_{2,4}$ = 2.3 Hz, H-4), 6.46 (1H, *s*, H-10), 6.62 (1H, *dd*, $J_{2,4}$ = 2.3 Hz, $J_{1,2}$ = 8.5 Hz, H-2), 6.82 (1H, *s*, H-7), 7.39 (1H, *d*, $J_{1,2}$ = 8.5 Hz, H-1); MS *m/z* (rel. int.): 300 $[M]^+$ (100).

(6a*R*,11a*R*)-8-*Acetoxy*-3,9-*dimethoxypterocarpan* (**8**). Acetylation of pterocarpan (**7**) yielded the monoacetate (**8**) as an amorphous brown solid; ^{1}H NMR: δ 2.33 (3H, *s*, OAc), 3.55 (1H, *ddd*, $J_{6a,6eq}$ = 4.9 Hz, $J_{6a,11a}$ = 6.8 Hz, $J_{6a,6ax}$ = 10.5 Hz, H-6a), 3.69 (1H, *dd*, $J_{6ax,6a}$ = 10.5 Hz, $J_{6ax,6eq}$ = 11.0 Hz, H-6*ax*), 3.79 (3H, *s*, OMe), 3.81 (3H, *s*, OMe), 4.26 (1H, *dd*, $J_{6eq,6a}$ = 4.9 Hz, $J_{6eq,6ax}$ = 11.0 Hz, H-6*eq*), 5.52 (1H, *d*, $J_{6a,11a}$ = 6.8 Hz, H-11a), 6.49 (1H, *d*, $J_{2,4}$ = 2.3 Hz, H-4), 6.56 (1H, *s*, H-10), 6.66 (1H, *dd*, $J_{2,4}$ = 2.3 Hz, $J_{1,2}$ = 8.5 Hz, H-2), 6.95 (1H, *s*, H-7), 7.42 (1H, *s*, $J_{1,2}$ = 8.5 Hz, H-1).

trans-*Pterostilbene*. The stilbene was obtained as needles (30 mg) by crystallization (petrol) of fraction 11 (RR_t 175 hr, 80 mg) of the hexane extract, mp 82° (lit. [13] 85–86°).

5,4'-*Diacetoxy*-7,3'-*dimethoxyisoflavone* (**6**). Acetylation and crystallization of subfraction 4.3 (RR_t 58 hr, 90 mg) from EtOH yielded the isoflavone as colourless needles (34 mg), mp 179° (found: C, 63.3; H, 4.5. $C_{21}H_{18}O_8$ requires: C, 63.3; H, 4.6%); ^{1}H NMR: δ 2.36 (3H, *s*, OAc), 2.45 (3H, *s*, OAc), 3.88 (3H, *s*, OMe), 3.93 (3H, *s*, OMe), 6.63 (1H, *d*, $J_{6,8}$ = 2.4 Hz, H-8), 6.78 (1H, *d*, $J_{6,8}$ = 2.4 Hz, H-6), 6.98 (1H, *dd*, $J_{2',6'}$ = 1.9 Hz, $J_{5',6'}$ = 8.3 Hz, H-6'), 7.07 (1H, *d*, $J_{5',6'}$ = 8.3 Hz, H-5'), 7.14 (1H, *d*, $J_{2',6'}$ = 1.9 Hz, H-2'), 7.86 (1H, *s*, H-2); MS *m/z* (rel. int.): 398 $[M]^+$ (100), 356 $[M - CH_2CO]^+$ (26), 340 (11), 324 (11), 312 (35), 303 (13), 301 (12), 299 (18), 298 $[M - CH_2CO–OAc + H]^+$ (100), 256 (22), 209 $[M - 190 + H]^+$ (1.7), 190 $[M - 208]^+$ (0.7), 151 $[B - 148 + H]^+$ (8.9), 148 $[B - 150]^+$ (4.5).

5,4'-*Diacetoxy*-7-*methoxyisoflavone* (5,4'-*di*-O-*acetylprunetin*) (**2**). Crystallization of subfraction 4.4 (RR_t 68 hr, 70 mg) from C_6H_6 followed by acetylation and recrystallization from MeOH

gave (2) as colourless platelets (15 mg), mp 223° (lit. [21] 222.5°); ^{1}H NMR (80 MHz, $CDCl_3$, TMS, 30°): δ2.28 (3H, *s*, OAc), 2.41 (3H, *s*, OAc), 3.88 (3H, *s*, OMe), 6.61 (1H, *d*, $J_{6,8}$ = 2.5 Hz, H-8), 6.77 (1H, *d*, $J_{6,8}$ = 2.5 Hz, H-6), 7.09 (2H, *d*, *J* = 8.8 Hz, H-3',5'), 7.48 (2H, *d*, *J* = 8.8 Hz, H-2',6'), 7.81 (1H, *s*, H-2); MS *m/z* (rel. int.): 368 $[M]^+$ (7.9), 326 $[M-CH_2CO]^+$ (33), 284 $[M-2\times CH_2CO]^+$ (100).

(3R)-7,2'-*Dihydroxy-4'-methoxyisoflavan*[(−)-*vestitol*]. Successive purification by CC [hexane–$CHCl_3$–MeOH (10:9:1), *RR*, 66 hr] and prep. TLC [1,2-dichloroethane–EtOAc (9:1) × 2] of subfraction 4.6 (*RR*, 99 hr, 290 mg) gave (−)-vestitol (R_f 0.52) as white plates (50 mg), mp 157° (lit. [9] 154–157°).

(3R)-2-*Methoxy*-5-(7-*hydroxychroman*-3-*yl*)-1,4-*benzoquinone* [(3R)-*claussequinone*]. Crystallization of subfraction 5.3.2 (*RR*, 20 hr, 66 mg) from MeOH yielded the isoflavanquinone as brown cubes (11 mg), mp 186° decomp. (lit. [9] 189–194°); CD: $[\theta]_{220}$ 0, $[\theta]_{250}$ −9900, $[\theta]_{272}$ 0, $[\theta]_{282}$ 3500, $[\theta]_{297}$ 1200, $[\theta]_{315}$ 1600, $[\theta]_{340}$ 600 (MeOH, *c* 0.0472 mg/ml); ^{1}H NMR (80 MHz, acetone-d_6, TMS, 30°): δ2.72–3.06 (2H, *m*, 4-CH_2), 3.19–3.56 (1H, *m*, H-3), 3.82 (3H, *s*, OMe), 4.00 (1H, *dd*, $J_{2ax,3}$ = 7.0 Hz, $J_{2ax,2eq}$ = 10.5 Hz, H-2*ax*), 4.27 (1H, *dd*, $J_{2eq,3}$ = 3.5 Hz, $J_{2ax,2eq}$ = 10.5 Hz, H-2*eq*), 6.06 (1H, *s*, H-3'), 6.25 (1H, *d*, $J_{6,8}$ = 2.5 Hz, H-8), 6.36 (1H, *dd*, $J_{6,8}$ = 2.5 Hz, $J_{5,6}$ = 8.1 Hz, H-6), 6.48 (1H, *d*, *J* = 1.0 Hz, H-6'), 6.89 (1H, *d*, $J_{5,6}$ = 8.1 Hz, H-5), 8.13 (1H, *br s*, 7-OH); MS *m/z* (rel. int.): 286 $[M]^+$ (100).

(3R)-7,3'-*Dihydroxy*-2',4'-*dimethoxyisoflavan*[(+)-*mucronulatol*]. The isoflavan was obtained as colourless cubes (60 mg) from EtOH after purification of subfraction 5.3.3 (*RR*, 27 hr, 172 mg) by CC [1,2-dichloroethane–EtOAc (94:6), *RR*, 37 hr], mp 147° (lit. [10] 147–149°).

(6*a*R,11*a*R)-3,8-*Dihydroxy*-9-*methoxypterocarpan* (**9**). Successive purification of subfraction 5.3.4 (*RR*, 33 hr, 160 mg) by CC [1,2-dichloroethane–EtOAc (94:6), *RR*, 27 hr] and prep. TLC [hexane–$CHCl_3$–MeOH (50:45:5) × 3] yielded the pterocarpan (**9**) (R_f 0.24) as a light brown amorphous solid (16 mg), CD: $[\theta]_{205}$ 0, $[\theta]_{230}$ −61 000, $[\theta]_{264}$ 0, $[\theta]_{291}$ 14 000, $[\theta]_{320}$ 0, (MeOH, *c* 0.0556 mg/ml); ^{1}H NMR: δ3.50 (1H, *ddd*, $J_{6a,6eq}$ = 4.9 Hz, $J_{6a,11a}$ = 6.5 Hz, $J_{6a,6ax}$ = 10.4 Hz, H-6a), 3.62 (1H, *dd*, $J_{6ax,6a}$ = 10.4 Hz, $J_{6ax,6eq}$ = 10.9 Hz, H-6*ax*), 3.84 (3H, *s*, OMe), 4.24 (1H, *dd*, $J_{6eq,6a}$ = 4.9 Hz, $J_{6eq,6ax}$ = 10.9 Hz, H-6*eq*), 5.07 (1H, *br s*, OH), 5.27 (1H, *br s*, OH), 5.45 (1H, *d*, $J_{6a,11a}$ = 6.5 Hz, H-11a), 6.41 (1H, *d*, $J_{2,4}$ = 2.5 Hz, H-4), 6.48 (1H, *s*, H-10), 6.55 (1H, *dd*, $J_{2,4}$ = 2.5 Hz, $J_{1,2}$ = 8.4 Hz, H-2), 6.84 (1H, *s*, H-7), 7.37 (1H, *d*, $J_{1,2}$ = 8.4 Hz, H-1); MS *m/z* (rel. int.): 286 $[M]^+$ (100); found: M^+, 286.083. $C_{16}H_{14}O_5$ requires: M, 286.084.

(6*a*R,11*a*R)-3,8-*Diacetoxy*-9-*methoxypterocarpan* (**10**). Acetylation of pterocarpan (**9**) yielded the diacetate (**10**) as an amorphous brown solid, ^{1}H NMR: δ2.30 (6H, *s*, 2 × OAc), 3.58 (1H, *ddd*, $J_{6a,6eq}$ = 4.3 Hz, $J_{6a,11a}$ = 6.5 Hz, $J_{6a,6ax}$ = 10.5 Hz, H-6a), 3.66 (1H, *dd*, $J_{6a,6ax}$ = 10.5 Hz, $J_{6ax,6eq}$ = 10.5 Hz, H-6*ax*), 3.79 (3H, *s*, OMe), 4.27 (1H, *dd*, $J_{6eq,6a}$ = 4.3 Hz, $J_{6eq,6ax}$ = 10.5 Hz, H-6*eq*), 5.53 (1H, *d*, $J_{6a,11a}$ = 6.5 Hz, H-11a), 6.54 (1H, *s*, H-10), 6.71 (1H, *d*, $J_{2,4}$ = 2.5 Hz, H-4), 6.80 (1H, *dd*, $J_{2,4}$ = 2.5 Hz, $J_{1,2}$ = 8.4 Hz, H-2), 6.93 (1H, *s*, H-7), 7.52 (1H, *d*, $J_{1,2}$ = 8.4 Hz, H-1).

7-*Acetoxy*-4'-*methoxyisoflavone* (7-O-*acetylformononetin*). Acetylation of subfraction 5.4 (*RR*, 28 hr, 240 mg) followed by crystallization from EtOH yielded acetylformononetin as colourless needles (108 mg), mp 169° (lit. [11] 172–173°).

5,3',4'-*Triacetoxy*-7-*methoxyisoflavone* (5,3',4'-*tri*-O-*acetylsantal*) (**4**). Crystallization (C_6H_6) of subfraction 5.5 (*RR*, 33 hr, 238 mg) followed by acetylation and recrystallization from MeOH gave (**4**) as colourless needles (35 mg), mp 147° (lit. [8] 144–146°); ^{1}H NMR (80 MHz, $CDCl_3$, TMS, 30°): δ2.31 (6H, *s*, 2 × OAc) 2.44 (3H, *s*, OAc), 3.91 (3H, *d*, OMe), 6.64 (1H, *d*, $J_{6,8}$ = 2.5 Hz, H-8), 6.80 (1H, *d*, $J_{6,8}$ = 2.5 Hz, H-6), 7.22 (1H, *d*, $J_{5',6'}$ = 8.8 Hz, H-5'), 7.39 (1H, *d*, $J_{2',6'}$ = 1.9 Hz, H-2'), 7.40 (1H, *dd*, $J_{2',6'}$ = 1.9 Hz, $J_{5',6'}$ = 8.8 Hz, H-6'), 7.88 (1H, *s*, H-2); MS *m/z* (rel. int.): 426 $[M]^+$ (6.0), 384 $[M-CH_2CO]^+$ (23), 342 $[M-2\times CH_2CO]^+$ (24), 300 $[M-3\times CH_2CO]^+$ (100).

Extraction and isolation of the components from P. marsupium. Heartwood drillings (880 g) of *P. marsupium* were successively extracted with hexane (4 × 3 l., 24 hr each) and MeOH (6 × 3 l., 24 hr each). Evaporation of the MeOH extract yielded a brown resin (97 g). Prep. PC of a portion (30 g) of the MeOH extract produced eight fractions.

α,2',4,4'-*Tetra-acetoxy*-3'-(2'',3'',4'',6''-*tetra*-O-*acetyl*-C-β-D-*glucopyranosyl*) *dihydrochalcone* (*coatline A*) (**12**). Acetylation and prep. TLC [hexane–C_6H_6–Me_2CO (4:4:2) × 2] of a portion (150 mg) of fraction 2 (R_f 0.87, 13.0 g) gave the dihydrochalcone (**12**) (R_f 0.34, 99 mg) as an amorphous solid, $[\alpha]_D^{26}$ −18° ($CHCl_3$, *c* 0.0077 g/ml); CD: $[\theta]_{210}$ 0, $[\theta]_{230}$ 12 900, $[\theta]_{240}$ 9000, $[\theta]_{243}$ 9700, $[\theta]_{265}$ 3000, $[\theta]_{273}$ 3600, $[\theta]_{300}$ 1200 (MeOH, *c* 0.3520 mg/ml); ^{1}H NMR (300 MHz, $CDCl_3$, $CDCl_3$, 90°): δ1.76 (3H, *s*, OAc), 1.97 (3H, *s*, OAc), 2.00 (6H, *s*, 2 × OAc), 2.02 (3H, *s*, OAc), 2.22 (3H, *s*, OAc), 2.29 (3H, *s*, OAc), 2.36 (3H, *s*, OAc), 2.97 (1H, *dd*, $J_{\alpha,\beta}$ = 8.5 Hz, $J_{\beta,\beta}$ = 15.0 Hz) and 3.15 (1H, *dd*, $J_{\alpha,\beta}$ = 4.3 Hz, $J_{\beta,\beta}$ = 15.0 Hz) (β-CH_2), 3.70–3.79 (1H, *m*, H-5''), 4.02 (1H, *dd*, $J_{5'',6''}$ = 2.4 Hz, $J_{6'',6''}$ = 12.5 Hz) and 4.33 (1H, *dd*, $J_{5'',6''}$ = 4.9 Hz, $J_{6'',6''}$ = 12.5 Hz) (6''-CH_2), 4.74 (1H, *d*, $J_{1'',2''}$ = 10.0 Hz, H-1''), 5.12 (1H, *dd*, $J_{4'',5''}$ = 9.5 Hz, $J_{3'',4''}$ = 9.1 Hz, H-4''), 5.24 (1H, *dd*, $J_{2'',3''}$ = 9.5 Hz, $J_{3'',4''}$ = 9.1 Hz, H-3''), 5.63 (1H, *dd*, $J_{2'',3''}$ = 9.5 Hz, $J_{1'',2''}$ = 10.0 Hz, H-2''), 5.82 (1H, *dd*, *J* = 4.3 Hz, *J* = 8.5 Hz, H-α), 6.99 (2H, *d*, *J* = 8.5, H-3,5), 7.10 (1H, *d*, $J_{5',6'}$ = 8.5 Hz, H-5'), 7.16 (2H, *d*, *J* = 8.5 Hz, H-2,6), 7.70 (1H, *d*, $J_{5',6'}$ = 8.5 Hz, H-6').

8-(2'',3'',4'',6''-*Tetra*-O-*acetyl*-C-β-D-*glucopyranosyl*)-7,3,4'-*trimethoxyflavone* (**14**). Methylation followed by prep. TLC [$CHCl_3$–MeOH (95:5), R_f 0.29], acetylation and a further prep. TLC separation [hexane–C_6H_6–Me_2CO (4:4:2) × 3] of a portion (400 mg) of fraction 6 (R_f 0.19) yielded two compounds with R_f 0.27 (75 mg) and 0.20 (17 mg) respectively. Crystallization of the former from EtOH–Me_2CO (min. Me_2CO) yielded (**14**) as needles (29 mg), mp 214° (found: C, 59.7; H, 5.4. $C_{32}H_{34}O_{14}$ requires: C, 59.8; H, 5.3%); ^{1}H NMR (300 MHz, DMSO-d_6, DMSO-d_6, 180°): δ1.66 (3H, *s*, OAc), 1.86 (3H, *s*, OAc), 1.92 (3H, *s*, OAc), 2.05 (3H, *s*, OAc), 3.87 (3H, *s*, OMe), 3.89 (3H, *s*, OMe), 3.99 (3H, *s*, OMe), 4.04 (1H, *dt*, $J_{5'',6''}$ = 4.0 Hz, $J_{4'',5''}$ = 9.5 Hz, H-5''), 4.16 (2H, *d*, $J_{5'',6''}$ = 4.0 Hz, 6''-CH_2), 5.17 (1H, *dd*, $J_{3'',4''}$ = 9.5 Hz, $J_{4'',5''}$ = 9.5 Hz, H-4''), 5.33 (1H, *dd*, $J_{3'',4''}$ = 9.5 Hz, $J_{2'',3''}$ = 9.5 Hz, H-3''), 5.34 (1H, *d*, $J_{1'',2''}$ = 9.8 Hz, H-1''), 5.75 (1H, *dd*, $J_{2'',3''}$ = 9.5 Hz, $J_{1'',2''}$ = 9.8 Hz, H-2''), 7.15 (2H, *d*, *J* = 9.0 Hz, H-3',5'), 7.17 (1H, *d*, $J_{5,6}$ = 8.9 Hz, H-6), 8.07 (1H, *d*, $J_{5,6}$ = 8.9 Hz, H-5), 8.10 (2H, *d*, *J* = 9.0 Hz, H-2',6'); ^{13}C NMR (75.4 MHz, DMSO-d_6, DMSO-d_6, 27°): δ19.9, 20.4, 20.5, 20.7 (each *q*, 4 × OCO<u>C</u>H_3), 55.4, 57.0, 59.6 (each *q*, 3 × OMe), 62.0 (*t*, C-6''), 68.0 (*d*, C-2''), 69.6 (*d*, C-4''), 70.7 (*d*, C-1''), 73.0 (*d*, C-3''), 75.1 (*d*, C-5''), 109.7 (*d*, C-6), 110.8 (*s*, C-8), 114.3 (*d*, C-3',5'), 117.7 (*s*, C-10), 122.8 (*s*, C-1'), 127.7 (*d*, C-5), 129.8 (*d*, C-2',6'), 139.4 (*s*, C-3), 154.0 (*s*, C-2),* 154.4 (*s*, C-9),* 161.2 (*s*, C-7),† 161.3 (*s*, C-4'),† 168.8, 169.5, 169.6, 170.0 (each *s*, 4 × OAc), 173.1 (*s*, C=O); MS *m/z* (rel. int.): 642 $[M]^+$ (100).

8-(2'',3'',4'',6''-*Tetra*-O-*acetyl*-C-β-D-*glucopyranosyl*)-3,7,3',4'-*tetramethoxyflavone* (**16**). The second fraction (R_f 0.20; *cf.* (**14**) gave the glucoside (**16**) as an amorphous solid (17 mg) (found: C, 58.4; H, 5.6. $C_{33}H_{36}O_{15}$ requires: C, 58.9; H, 5.4%); ^{1}H NMR (300 MHz, DMSO-d_6, DMSO-d_6, 180°): δ1.65, 1.88, 1.95, 2.05 (each 3H, each *s*, 4 × OAc), 3.88, 3.93, 3.94, 4.00 (each 3H, each *s*, 4

*Signals denoted by the same sign may be interchanged.

× OMe), 4.00–4.09 (1H, *m*, H-5″), 4.14–4.23 (2H, *m*, 6″-CH_2), 5.14 (1H, *dd*, $J_{3'',4''}$ = 9.5 Hz, $J_{4'',5''}$ = 9.5 Hz, H-4″), 5.36 (1H, *dd*, $J_{2'',3''}$ = 9.5 Hz, $J_{3'',4''}$ = 9.5 Hz, H-3″), 5.38 (1H, *d*, $J_{1'',2''}$ = 10.0 Hz, H-1″), 5.80 (1H, *dd*, $J_{2'',3''}$ = 9.5 Hz, $J_{1'',2''}$ = 10.0 Hz, H-2″), 7.21 (1H, *d*, $J_{5,6}$ = 8.9 Hz, H-6), 7.22 (1H, *d*, $J_{5',6'}$ = 8.9 Hz, H-5′), 7.74 (1H, *d*, $J_{2',6'}$ = 2.1 Hz, H-2′), 7.75 (1H, *dd*, $J_{2',6'}$ = 2.1 Hz, $J_{5',6'}$ = 8.9 Hz, H-6′), 8.11 (1H, *d*, $J_{5,6}$ = 8.9 Hz, H-5); MS *m/z* (rel. int.): 672 $[M]^+$ (100).

4,4′-*Dihydroxyflavanone* (*liquiritigenin*). Prep. TLC [cyclohexane–Me_2CO (6:4)] of a portion (100 mg) of fraction 5 (R_f 0.29) yielded liquiritigenin (R_f 0.33) as white needles (21 mg) from EtOH, mp 200° (lit. [22] 207°).

2′,4,4′-*Trihydroxychalcone* (*isoliquiritigenin*). The chalcone (R_f 0.65) was isolated by prep. TLC [C_6H_6–Me_2CO–MeOH (70:25:5)] from a portion (300 mg) of fraction 8 (R_f 0.00) and yielded yellow needles (11 mg) from aq. EtOH, mp 196° (lit. [17] 200°).

trans-*Pterostilbene* (130 mg), identical to that obtained from *P. soyauxii*, was isolated from a portion (300 mg) of fraction 8 (R_f 0.00) by prep. TLC [C_6H_6–Me_2CO–MeOH (70:25:5), R_f 0.83].

Acknowledgements—Support by the Sentrale Navorsingsfonds of this University and by the Foundation for Research Development, Council for Scientific and Industrial Research, Pretoria, South Africa is gratefully acknowledged. Wood samples of *P. soyauxii* and *P. marsupium* were supplied, respectively, by Prof. M. Mbona, University of Zaïre, B.P. 28, Yangambi, Zaïre and by the Conservator of Forests, P.O. Box 509, Colombo, Sri Lanka.

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