Phytochemical Examination of *Pericopsis* Species

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From the heartwood extractives of *P. mooniana* Thw., *P. elata* Harms., *P. laxiflora* Benth., *P. schliebenii* Harms., and *P. angolensis* Baker, seventeen natural products were isolated, of which one, (*R*)-2-*O*-methylangolensin, is a new member of the monotypic α-methyldeoxybenzoin class. Natural 4',7-dihydroxyisoflavanone was obtained for the first time and shown to have the *R*-configuration. The structures of the extractives have been examined by physical methods and the new compounds have been synthesised. The bark of *P. schliebenii* was found to contain *N*-methylcytisine. The relevance of the compilation to the proposed reduction of *Afrormosia* to *Pericopsis* is discussed.

FROM a morphological study Knaap-van Meeuwen [1] has shown that the species of *Afrormosia* would be more accurately classified if listed with *Pericopsis mooniana*. He concluded that *Afrormosia* must be reduced to *Pericopsis*, being the older generic name for the combined genera. *Pericopsis mooniana*, a tree first considered to be indigenous to Ceylon, was later found in Sumatra, Borneo, Celebes, the Talaud Islands, Micronesia, and New Guinea. This distribution resembles the ' tropical South Tethyan ' pattern. The genus *Pericopsis*, previously considered monotypic, now comprises five species: *P. mooniana* and the former *Afrormosia* members, *A. laxiflora*, *A. schliebenii*, *A. angolensis*, and *A. elata*. To establish if chemical evidence supports the conclusions of the morphological study, the heartwood extractives of these five species have now been investigated. A summary of the isolates identified is given in Table 1.

TABLE 1

Heartwood extractives of *Pericopsis* species

	Fatty acids	Sitosterol	4-Hydroxy-*N*-methylproline	1-*O*-Methyl-(+)-inositol	Vanillin	Syringaldehyde	Stilbene-3,3',4,5'-tetraol	(−)-(*S*)-4',7-Dihydroxyflavanone	(*RS*)-Angolensin [a]	(−)-(*R*)-Angolensin	(+)-(*R*)-2-*O*-Methylangolensin	(*R*)-4',7-Dihydroxyisoflavanone	Biochanin-A	Genistein	Irisolidone	Formononetin	Afromosin	8-*O*-Methylretusin	(6a*R*,11a*R*)-3,9-Dimethoxypterocarpan	(6a*R*,11a*R*)-3-Hydroxy-2-methoxypterocarpan	(6a*R*,11a*R*)-3-Hydroxy-8,9-methylenedioxypterocarpan	Ref.
P. mooniana Thw.	*	*						*	†	*		*	†*		*	†*	†*					*b*
P. elata Harms.			†	†			*	*		†*	*		*			†*						20, *c*
P. laxiflora Benth.					*	*								*		*						
P. schliebenii Harms.							*												*	*	*	
P. angolensis Baker							†												†*			

* Present paper. † Previous work.

[a] Racemic angolensin is reported [2] in the sample of heartwood obtained in Japan; however in the present study the sample of *P. mooniana* was obtained from Ceylon. [b] H. Imamura, Y. Tanno, and T. Takahashi, *J. Japan Wood Res. Soc.*, 1968, **14** (5), 295. [c] T. B. H. McMurry and V. Y. Theng, *J. Chem. Soc.*, 1960, 1491. [d] S. H. Harper, A. D. Kemp, W. G. E. Underwood, and R. V. M. Campbell, *J. Chem. Soc.* (*C*), 1969, 1109. [e] Von H. H. Dietrichs and M. H. Simatupang, *Holzforschung*, 1974, **28**, 186.

Members of the isoflavanoid class were present in all species. Isoflavones predominated in the extracts of three of the heartwoods, whereas pterocarpans were the major components of the extracts of the other two. The members of the isoflavone and pterocarpan classes co-occur only in *P. schliebenii*, in which the former is a minor component. A feature of the pterocarpan-producing species (*P. angolensis* and *P. schliebenii*) is the high yield of (6a*R*,11a*R*)-3,9-dimethoxypterocarpan and stilbene-3,3',4,5'-tetraol, to the almost complete exclusion of other products. As both these species are of similar provenance,[1] environmental factors may play a role in stimulating formation of the pterocarpan and stilbene.

P. mooniana and *P. elata* yielded a range of secondary metabolites. Particularly interesting is their ability to synthesise the α-methyldeoxybenzoin system as depicted in the major isolate, (−)-angolensin (I; R = H).[2] Co-occurring with (−)-angolensin in *P. elata* is (+)-2-*O*-methylangolensin (I; R = Me). The assigned structure was confirmed by comparison with an authentic sample prepared from (−)-angolensin by benzylation to afford 4-*O*-benzylangolensin, and subsequent methylation and debenzylation. (+)-2-*O*-Methylangolensin has therefore the same stereochemistry as (−)-angolensin, which was

[1] M. S. Knapp-van Meeuwen, *Bull. Jard. bot. Bruxelles*), 1962, **32**, 213.

[2] F. E. King, T. J. King, and A. J. Warwick, *J. Chem. Soc.*, 1952, 1920.

defined as *R* by its degradation to (−)-2-(4-methoxyphenyl)propionic acid.[3] A summary of some physical data for angolensin and its methyl ethers is given in Table 2.

TABLE 2

Physical data for angolensin and its methyl ethers

	M.p. (°C)	$[\alpha]_D^{24}(CHCl_3)$(°)	ν_{CO}/cm^{-1}	Ref.
(*R*)-Angolensin	120.5	−114	1631	3
Angolensin	86—88		1631	2, [a]
(*R*)-2-*O*-methylangolensin	Oil	+5.3	1664	
(*R*)-4-*O*-methylangolensin	62	−142	1631	20, [b]
(*R*)-2,4-di-*O*-methylangolensin	49	+26	1664	3,20, [b]
2,4-Di-*O*-methylangolensin	70		1664	2

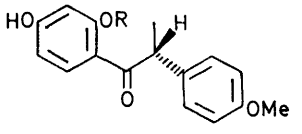
[a] V. N. Gupta and T. R. Seshadri, *J. Sci. Ind. Res., India*, 1956, **B15**, 146. [b] Footnote *c*, Table 1.

Both species (*P. mooniana* and *P. elata*) produce (−)-(*S*)-4′,7-dihydroxyflavanone (II), identified by comparison with the authentic synthetic racemate. The similarly substituted isoflavanone occurs only in *P. mooniana*, and was isolated as its diacetate. A sample of racemic 4′,7-diacetoxyisoflavanone was synthesised for comparison. The stereochemistry of (−)-4′,7-diacetoxyisoflavanone is defined as 3*R* by comparison of its o.r.d. curve (negative Cotton effect at 327 nm) with the c.d. curve of (*S*)-2′,4′,7-trimethoxyisoflavanone [positive maximum (*a* 249.7) at 325 nm]. A sample of this latter isoflavanone was obtained from (−)-(6a*R*,11a*R*)-3,9-dimethoxypterocarpan by hydrogenolysis, methylation, and subsequent oxidation.[4]

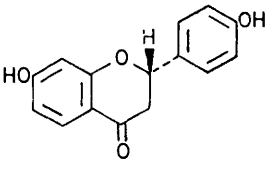
(−)-Angolensin and (−)-4′,7-diacetoxyisoflavanone from *P. mooniana* have a similar stereochemistry, which may arise from a common biogenetic origin, for example, from (−)-(*S*)-4′,7-dihydroxyflavanone. With the exception of (+)-sophorol, all the known isoflavanones were isolated in their optically inactive form. Keto–enol tautomerism may account for this optical inactivity.[5] The *R* configuration assigned to 4′,7-dihydroxyisoflavanone is opposite to that found for (+)-sophorol by Suginome,[6] who based the assignment on a plain dispersion curve.

As mentioned earlier, *P. angolensis* and *P. schliebenii* are of similar provenance. The heartwood of the former has been analysed by several workers and, irrespective of the source of the wood, a high yield of (−)-(6a*R*,11a*R*)-3,9-dimethoxypterocarpan (IV) was obtained. The same pterocarpan occurs in *P. schliebenii*, accompanied by minor quantities of (6a*R*,11a*R*)-3-hydroxy-8,9-methylenedioxypterocarpan and (6a*R*,11a*R*)-3-hydroxy-9-methoxypterocarpan, which were isolated as a 1 : 3 mixture. A similar mixture was found to occur in *Dalbergia oliveri*.[7] Besides the pterocarpanoids, *P. schliebenii* contains 8-*O*-methylretusin in small amounts. The identity of this isoflavone was confirmed by direct comparison with 8-*O*-methylretusin isolated from *Dalbergia retusa*.[8]

The major component in the heartwood extract of *P. schliebenii* is stilbene-3,3′,4,5′-tetraol. This is present in lesser amounts in *P. angolensis* and *P. elata*, and its decomposition is considered as being responsible for the darkening of these timbers on exposure to light.[9]



(I) R = H or Me



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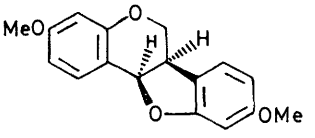
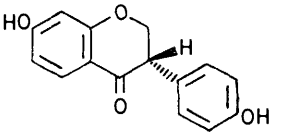


(IV)



(III)

P. laxiflora, like *P. schliebenii*, is an African hardwood, and is of commercial value as a satinwood.[10] The five compounds isolated from *P. laxiflora* were vanillin, syringaldehyde, formononetin, biochanin-A, and genistein. The vanillin and syringaldehyde are more likely to be breakdown products of lignin than intermediates in the biosynthesis of more complex molecules. Genistein (major isolate) and biochanin-A possess a 5-hydroxy-group, which would antagonise pterocarpan formation if the latter arises through direct oxidative cyclisation of the carbonyl oxygen to the 2′-hydroxy-group. The quantity of the heartwood available was small. A sample of the chloroform extract was acetylated and the product mixture analysed * by field desorption mass spectrometry. It showed major peaks at *m/e* 368, 398, and 426. The peak at *m/e* 368 possibly arises from prunetin diacetate (V) or 5-*O*-methylgenistein diacetate (VI). This suggestion is made on biosynthetic grounds since genistein and biochanin-A are present in the plant. The mass spectrum shows a peak at *m/e* 326 corresponding to loss of acetyl (VII).

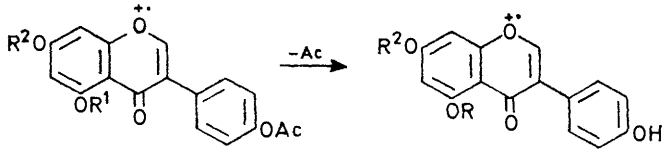
The hexane extract of *P. schliebenii* has a bright yellow colour. The pigment could not be isolated owing to its labile nature, but its spectrum [$\lambda_{max.}$ (MeOH) 420, 445, and 475 nm] resembles those of xanthophyll and ε-carotene. It did not run concurrently with ε-carotene

* We thank Dr. D. E. Games, University College, Cardiff, for the analysis and assignments.

[3] W. D. Ollis, M. V. J. Ramsay, and I. O. Sutherland, *Austral. J. Chem.*, 1965, **18**, 1787.
[4] T. B. H. McMurry, E. Martin, D. M. X. Donnelly, and J. C. Thompson, *Phytochemistry*, 1972, **11**, 3283.
[5] J. W. Clark-Lewis, *Rev. Pure Appl. Chem.*, 1962, **12**, 96.
[6] H. Suginome, *Bull. Chem. Soc. Japan*, 1966, **39**, 1544.
[7] D. M. X. Donnelly and P. J. Kavanagh, *Phytochemistry*, 1974, **13**, 2587.
[8] L. Jurd, K. Stevens, and G. Manners, *Phytochemistry*, 1972, **11**, 2535.
[9] J. W. W. Morgan and R. J. Orsler, *Holzforschung*, 1968, **22**, (1), 11.
[10] A. H. Unwin, 'West African Forests,' Unwin, London, 1920, p. 66.

in chromatography and its R_F value is higher than that reported for xanthophyll. It is possibly an ester of xanthophyll since these compounds have a wide natural distribution.[11]

The bark extracts of the five species have not been investigated. However, the use of leaves, root, and bark



m/e 368 (V) R^1 = Ac R^2 = Me (VI) R^1 = Me R^2 = Ac

m/e 326 (VII)

of *P. laxiflora* and *P. elata* in traditional medicinal preparations led to an analysis of basic constituents of their barks. Both species were reported [12] to contain the lupin-type alkaloid, *N*-methylcytisine. This alkaloid was also found by us in the bark of *P. schliebenii*. Chromatography of the acetone extract showed the presence of two other basic components, probably lupin-type alkaloids, in the bark of *P. schliebenii*, but lack of material prevented their being fully investigated. Lupin-type alkaloids are widespread in the Lotoideae.[13]

Samples of the bark from *P. angolensis* and *P. mooniana* were not available.

The reduction of the genus *Afrormosia* to *Pericopsis* could not have been proposed on purely chemical grounds but, taken in conjunction with the morphological study, our results enable definite intrageneric relationships to be discerned.

EXPERIMENTAL

Unless otherwise stated, m.p.s were determined with a Kofler hot-stage apparatus. Spectroscopic data, where indicated with an asterisk, are available as Supplementary Publication No. SUP 21593 (13 pp., 1 microfiche).† Optical rotations were measured with a Perkin-Elmer 141 polarimeter. During isolation processes, the appropriate combination of fractions was determined by t.l.c. T.l.c. plates were examined by u.v. illumination and by spraying with chlorosulphuric acid in acetic acid. Light petroleum refers to the fractional b.p. 40—60°.

Pericopsis mooniana *Thw.*—The heartwood shavings (2.64 kg) of *P. mooniana* were exhaustively extracted with n-hexane, benzene, and acetone. The acetone extract was subsequently extracted with ether.

The n-hexane extract (5 g), on addition of acetone gave a white solid (2 g), m.p. 65—72°. Methylation with diazomethane and g.l.c. analysis (2.8% SE30) of the product mixture showed the presence of a series of unbranched saturated acid esters (C_{16}—C_{28} inclusive). The methyl esters of palmitic, stearic, arachidic, behenic, and lignoceric acids were used as standards.

The filtrate remaining after collection of the above solid was fractionated by column chromatography [silica gel (120 g)]. Elution with chloroform afforded (i) sitosterol, mixed m.p. 138° (from benzene–methanol) and (ii) a fraction (200 mg) further purified by t.l.c. (benzene–light petroleum) to give (—)-angolensin (40 mg), m.p. 119°; $[\alpha]_D^{24}$ —114° (lit.,[3] m.p. 119°).

The residue from the benzene extract, a brown oil (14 g) was placed on a silica column (1 kg). Elution with chloroform–ethyl acetate (9 : 1 and 7 : 3) gave a series of fractions which yielded (i) 5,7-dihydroxy-4′,6-dimethoxyisoflavone (eluant chloroform) (140 mg), crystallised as needles (from benzene–light petroleum), m.p. 188° (lit.,[14] 191°) [dimethyl ether, m.p. 184 (lit.,[15] 181°)]; biochanin-A [eluant chloroform–ethyl acetate (9 : 1)] (400 mg) (identified by m.p. and mixed m.p., i.r., u.v., and n.m.r. of acetate); (—)-angolensin [eluant chloroform–ethyl acetate (9 : 1)] (600 mg), crystallised from benzene–light petroleum; and formononetin [eluant chloroform–ethyl acetate (7 : 3)] (200 mg), m.p. 255° (from ethanol) (identified by mixed m.p., u.v., and i.r. data) [monoacetate, m.p. 170° (identified by mixed m.p., i.r., and n.m.r.)].

The acetone extract (64 g) was re-extracted with one portion of ether (500 ml). Evaporation afforded a brown oil (50 g). A sample (20 g) was placed on a silica gel column (1 kg). Elution with chloroform–ethyl acetate (9.5 : 0.5, 9 : 1, and 4 : 1) gave a series of fractions. The products were purified by acetylation and by p.l.c.

Fraction (i) (100 mg) [eluant chloroform–ethyl acetate (9.5 : 0.5)] was acetylated and the product purified by p.l.c. [developer chloroform–acetone (4.9 : 1)] to give *4′,7-diacetoxyisoflavanone* (20 mg), m.p. 153° (from ethanol), $[\alpha]_D^{24}$ —20.7° (2.8 mg in 1.12 ml of $CHCl_3$) (Found: C, 66.5; H, 4.9. $C_{19}H_{16}O_6$ requires C, 67.0; H, 4.8%) (u.v., i.r., mass, and n.m.r.*), o.r.d. (1.002 mg in 3 ml of MeOH) $[\phi]_{327}$ —2 030°, $[\phi]_{295}$ 0°, $[\phi]_{261}$ —6 080°, $[\phi]_{238}$ 0°. Fractions (ii)—(iv) [eluant chloroform–ethyl acetate (9 : 1)] gave more biochanin A (100 mg), (—)-angolensin (9 g), and formononetin (40 mg). Fraction (v) [eluant chloroform–ethyl acetate (9 : 1)] (2.7 g) was acetylated and afforded (*S*)-4′,7-diacetoxyflavanone, m.p. 178°, $[\alpha]_D^{24}$ +11.1 ($CHCl_3$) (u.v., i.r., and n.m.r.*). Hydrolysis of the diacetate (10 mg) in ethanol (3 ml) and hydrochloric acid (0.2 ml; 10%) at 100 °C for 1 h gave 4′,7-dihydroxyflavanone, m.p. 201°. Fraction (vi) was an intractable oil. Fraction (vii) [eluant chloroform–methanol (4 : 1)] (2.6 g) was acetylated and the product fractionated by p.l.c. (developer chloroform). An unidentified compound crystallised from ethanol in needles (100 mg), m.p. 169° (Found: C, 65.6; H, 4.8. Calc. for $C_{21}H_{18}O_7$: C, 65.96; H, 4.75%), $\lambda_{max.}$ 210 (log ε 4.69), 2.67 (4.24), 274 (4.23), 310 (4.28), and 334 nm (4.24), $\nu_{max.}$ 1 740 and 1 630 cm^{-1}.

Synthesis of 4′,7-Diacetoxyisoflavanone.—2′4′-Bisbenzyloxyacetophenone (10 g) and *p*-benzyloxybenzaldehyde (10 g) were dissolved in sodium ethoxide [sodium (2 g) in ethanol (100 ml)]. The mixture was kept at 25 °C for 12 h. The product crystallised from chloroform–ethanol to give *2,4,4′-trisbenzyloxychalcone* (8 g), m.p. 114—116° (Found: C, 81.8; H, 5.8. $C_{36}H_{30}O_4$ requires C, 82.1; H, 5.7%), $\lambda_{max.}$ 338 nm (log ε 4.36), ν_{CO} 1 661 cm^{-1}, δ 5.1 (6 H, s, OCH_2Ph).

† For details of Supplementary Publications see Notice to Authors No. 7, *J.C.S. Perkin I*, 1974, Index issue.

[11] P. Karrer and E. Jucker, ' Carotenoids,' Elsevier, Amsterdam, 1950. p. 198.
[12] C. W. L. Bevan and A. W. Ogan, *J. West African Sci. Ass.*, 1964, **9** (1), 1.
[13] N. J. Leonard in ' The Alkaloids,' eds. R. H. F. Manske and H. L. Holmes vol. III, Academic Press, London, 1953, p. 120.
[14] L. Farkas, J. Varady, and A. Gottsegan, *Magyar Kém. Folyóirat*, 1962, **68**, 238.
[15] K. W. Gopinath, A. R. Kidwai, and L. Prakash, *Tetrahedron*, 1961, **16**, 201.

A mixture of the chalcone (10 g) and thallium(III) acetate (12 g) was dissolved in methanol and the solution was refluxed for 100 h. When kept at 25 °C the solution deposited starting material (4 g). The filtrate was diluted with water and extracted with chloroform. P.l.c. (developer chloroform–light petroleum) gave 2-(4-*benzyloxyphenyl*)-1-(2,4-*bisbenzyloxyphenyl*)-3,3-*dimethoxypropan*-1-*one* (1.5 g) as an oil (Found: C, 77.4; H, 6.1. $C_{38}H_{36}O_6$ requires C, 77.5; H, 6.2%), ν_{CO} 1 650 cm^{-1} (n.m.r.*).

Palladised charcoal (50 mg; 10%) was added to the foregoing ketone (1 g) in ethyl acetate (50 ml). The mixture was stirred in hydrogen at room temperature for 12 h. The catalyst was removed and the filtrate evaporated under reduced pressure. The debenzylated acetal crystallised from ethanol in needles (200 mg), ν_{OH} 3 200, ν_{CO} 1 630 cm^{-1}. Concentrated hydrochloric acid (0.1 ml) was added to the acetal (70 mg) in methanol (10 ml) and the solution was warmed (0.5 h) to 100 °C. 4',7-Dihydroxyisoflavone separated, and crystallised from aqueous ethanol in plates (40 mg), m.p. 320° (lit.,[16] 325°).

A solution of 4',7-dihydroxyisoflavone (30 mg) in acetic acid (20 ml) was hydrogenated [palladium–charcoal (10%; 25 mg)] until 1 mol. equiv. of hydrogen had been absorbed. Filtration and evaporation were followed by dissolution of the residue in acetic anhydride–pyridine (1 : 1); the solution was kept at 25 °C for 12 h, and the resulting 4',7-diacetoxyisoflavanone crystallised from ethanol as needles (6 mg), m.p. 174° (identified by u.v., i.r., and n.m.r. comparison with the natural product acetate) (lit.,[17] m.p. 173—175°).

Synthesis of (S)-2',4',7-*Trimethoxyisoflavanone*.—A solution of (6a*R*,11a*R*)-3,9-dimethoxypterocarpan (300 mg) in ethanol (50 ml) was hydrogenated over palladium–charcoal (100 mg; 10%). The catalyst was removed and the filtrate was evaporated to afford the corresponding isoflavan, which crystallised from aqueous ethanol as prisms (215 mg), m.p. 152° (lit.,[17] 154°). Methylation [dimethyl sulphate (170 mg) and potassium carbonate (500 mg) in acetone] afforded 2',4',7-trimethoxyisoflavan, which crystallised from aqueous ethanol in prisms (130 mg), m.p. 60° (lit.,[17] 60°). A solution of 2',4',7-trimethoxyisoflavan (200 mg) and potassium permanganate (1 g) in acetone (50 ml) was stirred at 25 °C (72 h). Water (100 ml) was added and sulphur dioxide was bubbled through the mixture until the latter was colourless. The solution was extracted with chloroform. Evaporation and p.l.c. [developer chloroform–light petroleum (1 : 1)] afforded a band (R_F *ca.* 0.3) which was eluted with chloroform. The resulting (S)-2',4',7-trimethoxyisoflavanone crystallised from ethanol; yield 70 mg, m.p. 124° (lit.,[18] 127°), ν_{CO} 1 685 cm^{-1} (n.m.r.*), c.d. (1.926 mg in 5 ml of MeOH) $[\theta]_{326}$ + 20 460, $[\theta]_{298}$ −8 613, $[\theta]_{278}$ −10 758, $[\theta]_{237}$ −34 386.

Pericopsis elata *Harms*.—The heartwood shavings (300 g) were exhaustively extracted with n-hexane (reflux) and aqueous butan-2-one (9 : 1) (room temperature). The latter extract was evaporated and the residual oil (17 g) was re-extracted with chloroform (500 ml), ethyl acetate (500 ml), and ethanol (500 ml). T.l.c. analysis showed that the chloroform and ethyl acetate extracts were similar. The combined fractions were chromatographed on silica gel (600 g). Elution with chloroform–ethyl acetate (9.5 : 0.5 and 9 : 1) and chloroform–ethyl acetate–acetone (8.5 : 1 : 0.5) gave fractions (i)—(iv) which yielded (i) a mixture (3.44 g) [eluant chloroform–ethyl acetate (9.5 : 0.5)] which was further purified by chromatography; (ii) afrormosin (750 mg), m.p. 228° (from ethanol) (identified by m.p., u.v., i.r., and n.m.r.); (iii) a solid (680 mg) (eluant chloroform–ethyl acetate–acetone) which was acetylated to give 4',7-diacetoxyflavanone (39 mg), m.p. and mixed m.p. 186°; (iv) stilbene-3,3',4,5'-tetraol (50 mg), m.p. 229—230° (from ethyl acetate–benzene) (lit.,[19] 225°). Rechromatography of fraction (i) on a silica column (160 g) [eluant ether–light petroleum (2 : 1 and 1 : 1)] afforded (−)-angolensin (90 mg), m.p. and mixed m.p. 119—120°; and biochanin-A, which crystallised from benzene as needles (40 mg), m.p. and mixed m.p. 212°. The 1 : 1 eluant yielded 2-O-*methylangolensin* as an oil (30 mg), $[\alpha]_D^{24}$ +5.3° ($CHCl_3$) (Found: C, 70.9; H, 6.4. $C_{17}H_{18}O_4$ requires C, 71.3; H, 6.3%); $\lambda_{max.}$ 270 (log ε 4.1) and 315 nm (3.98), $\nu_{max.}$ 3 370 and 1 660 cm^{-1}; δ 7.63 (1 H, d, *J* 9.0 Hz, H-5), 6.38 (1 H, d, *J* 2.0 and 9.0 Hz, H-6), 6.42 (1 H, d, *J* 2.0 Hz, H-8), 7.25 and 6.84 (4 H, q, *J* 9.0 Hz, H-2', -6', -3', and -5'), 4.78 (1 H, q, *J* 8.0 Hz, H-2), 1.44 (3 H, d, *J* 8.0 Hz, H-1), 3.76 and 3.74 (6 H, 2 × s, OMe), and 8—7.6br (1 H, s, OH).

4-O-*Benzyl*-2-O-*methylangolensin* was obtained from 2-*O*-methylangolensin (20 mg), benzyl chloride (30 mg), and potassium carbonate (100 mg) when the mixture was refluxed for 4 h in acetone (10 ml) as an oil (Found: C, 76.6; H, 6.5. $C_{24}H_{24}O_4$ requires C, 76.6; H, 6.4%), ν_{CO} 1 660 cm^{-1} (n.m.r.*), identical with the product from benzylation and methylation of (−)-angolensin.

Methylation of (−)-angolensin (500 mg) [dimethyl sulphate (360 mg) and potassium carbonate (1 g) in acetone (30 ml)] afforded the 4-methyl ether, which crystallised from methanol in prisms, m.p. 60° (lit.,[20] 62.5°), ν_{CO} 1 631 cm^{-1} (n.m.r.*).

Benzylation [benzyl chloride (500 mg) and potassium carbonate (1 g) in acetone (30 ml)] of (−)-angolensin (500 mg) for 8 h under reflux, removal of inorganic salts, evaporation of the filtrate, and p.l.c. (developer ether–light petroleum (3 : 2)] afforded a residue which crystallised from chloroform–light petroleum in needles of 4-O-*benzylangolensin* (337 mg), m.p. 92—93° (Found: C, 76.2; H, 6.2. $C_{23}H_{22}O_4$ requires C, 76.2; H, 6.1%), ν_{CO} 1 630 cm^{-1} (n.m.r.*).

(−)-Di-*O*-methylangolensin, obtained from (−)-angolensin (100 mg) and dimethyl sulphate (150 mg), potassium carbonate (1 g), and acetone (30 ml), crystallised from ethanol as needles (60 mg), m.p. 49° (lit.,[20] 50—51°), ν_{CO} 1 664 cm^{-1}.

Pericopsis laxiflora *Benth*.—The pulverised heartwood (25 mg) was extracted for 48 h with n-hexane. Evaporation gave a residue which was purified by p.l.c. (eluant chloroform) to afford an oil. No satisfactory separation technique was found. The heartwood was subsequently extracted with chloroform for 56 h. Evaporation gave a dark red oil (2.5 g). A preliminary separation of this oil was achieved by p.l.c. [ethanol–chloroform (4 : 96); double development]. Four major fractions (i)—(vi) were eluted with methanol.

Fraction (i) (130 mg) was a red oil. Acetylation followed by p.l.c. gave vanillin acetate (40 mg), which crystallised

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from ether as needles, m.p. 75° (identified by mixed m.p., n.m.r., i.r., and u.v.); and syringaldehyde acetate (25 mg), which crystallised from methanol as needles, m.p. 112—114° (identified by mixed m.p., n.m.r., i.r., and u.v.).

Fraction (ii) (110 mg) was a brown oil. Acetylation gave a mixture of acetates, separated into bands A—D by p.l.c. [developer ethanol–chloroform (1 : 99)]. Band A afforded material which crystallised from ethanol as needles (5 mg), m.p. 174—175°. Hydrolysis of a sample (3 mg) with methanolic ammonium hydroxide gave a compound showing spectroscopic data was consistent with a 5-hydroxyisoflavonoid. Lack of material prevented further characterisation. Band B (85 mg) afforded a mixture of formononetin acetate and biochanin-A acetate and was separated by p.l.c. into its components [developer benzene–ethyl acetate (9 : 1)]. Hydrolysis of the individual acetates gave formononetin, m.p. 250° (identified by m.p. and u.v.), and biochanin-A, m.p. 209° (identified by m.p. and u.v.). Acetylation of material from band C and subsequent p.l.c. [developer chloroform–ethanol (49 : 1)] gave genistein triacetate, which crystallised from ethanol as needles (50 mg), m.p. 196° (identified by m.p., u.v., i.r., and n.m.r.). Hydrolysis with methanolic ammonium hydroxide gave genistein. Material from band D, on acetylation and p.l.c. (developer chloroform), afforded an oil (30 mg), *m/e* (field desorption) 368.3 (100%), 398.2 (63), 426.4 (51), and 326.2 (8).

Pericopsis schliebenii *Harms*.—The pulverised heartwood and sapwood (1.7 kg) were extracted for 42 h with n-hexane. Evaporation gave a semisolid (22 g). Subsequently the sawdust was extracted with ether for 40 h. The extract was evaporated to 1 l and washed with water to remove peroxides, dried, and evaporated to give a dark green solid (7.6 g).

The semisolid (12.3 g) was chromatographed [silica (720 g); light petroleum and light petroleum–ether (19 : 1, 1 : 1, and 3 : 2)]. Fractions (i)—(iv) were collected. Fractions (i), (ii), and (iv) were unproductive. Fraction (i) was bright yellow in colour but the pigment responsible decomposed on removal of the solvent. Its spectrum [$\lambda_{max.}$ (MeOH) 420, 445, and 475; $\lambda_{max.}$ (C_6H_6) 435, 459, and 487; $\lambda_{max.}$ (light petroleum) 419, 445, and 472 nm] resembles those of xanthophyll and ε-carotene.[21] It did not run concurrently with ε-carotene and its R_F value [0.8 in ether–light petroleum (1 : 99)] is higher than reported values for xanthophyll.

Fraction (iii) afforded (—)-3,9-dimethoxypterocarpan (2.0 g), which crystallised as needles (from ethanol), m.p. 84—85° (identified by m.p., $[\alpha]_D$, n.m.r., i.r., and u.v.[18]).

A sample of the n-hexane extract was triturated with light petroleum to give a solid (7 g) which was fractionated by column chromatography [eluants ether–light petroleum (1 : 1 and 5 : 1) and ether]. Fraction (i) [eluant ether–light petroleum (1 : 1)] afforded more (6a*R*,11a*R*)-3,9-dimethoxypterocarpan (3.6 g). Fraction (ii) [eluant ether–light petroleum (5 : 1)], a red oil, was purified by p.l.c. [developer ether–light petroleum (1 : 2); double development] to yield a gum (150 mg) identified as a mixture of (—)-3-hydroxy-9-methoxypterocarpan and (—)-3-hydroxy-8,9-methylenedioxypterocarpan, δ 5.93 (s, O·CH_2·O), 5.5 (m, 11a-H), 4.2 (m, 6*eq*-H), 3.78 (s, OMe), and 3.63 (m, 6a-H and 6*ax*-H). Relative intensities of MeO and CH_2O_2 peaks indicate a ratio of 3.2 : 1. Acetylation of the mixture afforded a solid which crystallised from methanol; yield 80 mg, m.p. 115—135°, $[\alpha]_D^{24}$ —179° ($CHCl_3$), *m/e* 326 (3%), 312 (4.0), 284 (10.5), 283 (4.3), 270 (100), 269 (37.5), 255 (21), 175 (1.5), 161 (12), 148 (24), 147 (12), and 134 (9). The mixture of acetates ran concurrently in chromatography with a mixture isolated from *Dalbergia oliveri* [7] [ethyl acetate–light petroleum (1 : 3)].

Fraction (iii) was purified by p.l.c. [developer chloroform–ethanol (28 : 1)]. The major band was eluted (chloroform) and gave 8-*O*-methylretusin, which crystallised from benzene–methanol as cubes (4 mg), m.p. 228—230° (identified by m.p., u.v., and mass spectra [8]).

A sample (1 g) of the solid obtained from the ether extract was dissolved in ethyl acetate and fractionated by p.l.c. [developer benzene–ethyl acetate–acetic acid (9 : 6 : 1)] to give (A) (R_F 0.90) (—)-3,9-dimethoxypterocarpan (30 mg); (B) (R_F 0.75) (—)-3-hydroxy-9-methoxy- and (—)-3-hydroxy-8,9-methylenedioxy-pterocarpan (30 mg); and (C) (R_F 0.50) stilbene-3,3′,4,5′-tetraol (450 mg), m.p. 225—228° (decomp.) (from water) (lit.,[22] 229°), $\lambda_{max.}$ (MeOH) 221, 305, and 326, $\lambda_{max.}$ (MeOH–NaOAc–H_3BO_4) 305 and 338, $\lambda_{max.}$ (MeOH–NaOMe) 310 and 347 nm, $\nu_{max.}$ 3 300 and 1 600 cm^{-1} (n.m.r.*). Acetylation of the stilbene (100 mg) [pyridine (1 ml) and acetic anhydride (2 ml)] afforded the tetra-acetate, which crystallised from ethanol as needles (100 mg), m.p. 123—124° (lit.,[21] 114° and 125°) (Found: C, 63.7; H, 4.8. Calc. for $C_{22}H_{20}O_8$: C, 64.1; H, 4.9%) (u.v., i.r., and n.m.r.*).

Extractives of the Bark of P. schliebenii.—The pulverised bark (450 mg) was extracted successively with n-hexane (1.3 l; 48 h), chloroform (1.3 l; 24 h), and ethanol (1.5 l; 48 h). Concentration of the n-hexane extract caused precipitation of a white solid (1.5 g), which was collected. Further evaporation afforded a yellow semisolid (3.5 g). G.l.c. analysis of the latter, after treatment with diazomethane, showed palmitic acid to be a component of the extract. The methyl esters of arachidic, behenic, and lignoceric acid were used as standards. The other components were not identified. A sample of the ethanol extract (5.2 g) was warmed (100 °C) with hydrochloric acid (3 × 50 ml; 10%). The solution was brought to a pH 10 [potassium carbonate and ammonium hydroxide (25%)]. Extraction with chloroform afforded, on evaporation, a brown gum (70 mg). T.l.c. analysis [(i) chloroform–methanol (9 : 1); (ii) benzene–methanol (7 : 3)] showed the presence of *N*-methylcytisine and two unidentified alkaloids (positive Dragendorff reaction) [R_F values: *N*-methylcytisine (i) 0.53 (ii) 0.42; mixture in solvent (i) 0.20, 0.52, and 0.86; mixture in solvent (ii) 0.16, 0.49, and 0.81]. G.l.c. analysis (2.8% SE30) confirmed these results.

Pericopsis angolensis *Baker*.—The heartwood shavings of *P. angolensis* (650 g) were exhaustively extracted under reflux with n-hexane. Evaporation afforded a yellow oil (15 g). A sample (1.2 g) was fractionated by p.l.c. [developer light petroleum–chloroform (3 : 2)]. The major band, on elution with chloroform, gave a residue which crystallised from ethanol as needles of (6a*R*,11a*R*)-3,9-dimethoxypterocarpan (680 mg), m.p. 85°, $[\alpha]_D^{24}$ —223°. A second band of high R_F value yielded an oil (220 mg), which was not further investigated. In an attempt to find the stilbenetetraol, the heartwood shavings were extracted with butan-2-one–water (9 : 1). The residue from this extract yielded more (—)-(6a*R*,11a*R*)-3,9-dimethoxypterocarpan.

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