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(+)-2,3-*TRANS*-PUBESCHIN, THE FIRST CATECHIN ANALOGUE OF PELTOGYNOIDS FROM *PELTOGYNE PUBESCENS* AND *P. VENOSA*

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Key Word Index—*Peltogyne pubescens*, *P venosa*, Leguminosae, catechin analogue of peltogynol, 3-*O*-methyldihydroflavonols, 5,6-dihydroxyphthalide, α-hydroxychalcones, synthesis of (+)-2,3-*trans*-pubeschin

Abstract—The heartwoods of *Peltogyne pubescens* and *P venosa* contain the predominant pair (+)-peltogynol and (+)-mopanol, their 4-epimers, (+)-peltogynol B and (+)-mopanol B, together with the first catechin analogue of peltogynol, (+)-2,3-*trans*-pubeschin These are accompanied by (±)-2,3-*cis*- and (±)-2,3-*trans*-3-*O*-methylfustins, and by α,2',3,4,4'-pentahydroxychalcone Other minor metabolites are 4',7-dihydroxy- and 3',4',7-trihydroxyflavanones and 5,6-dihydroxyphthalide (+)-2,3-*Trans*-pubeschin trimethyl ether was synthesized by reduction of the corresponding (+)-2,3-*trans*-peltogynone analogue with $NaBH_4/BF_3$ in diglyme, and its absolute configuration shown to be 2R 3S

INTRODUCTION

FOLLOWING early indications by Robinson and Robinson[1] of the presence of (+)-peltogynol in a number of *Peltogyne* spp. ("purple heart", from the West Indies, Northern Brazil and French Guiana); subsequent revision of its structure by Chan *et al.*;[2] determination of its absolute configuration (**1.** R_1=OH, R_2=H) by Drewes and Roux[3] and isolation of its structural isomer (+)-mopanol (**1.** R_1=H, R_2=OH) from *Colophospermum mopane* by Drewes and Roux,[3] both (+)-peltogynol and (+)-mopanol together with their 4-epimers[2,3] (**2.** R_1=OH, R_2=H and **2.** R_1=H, R_2=OH) were shown present by chromatography in *P. porphyrocardia*, *P. venosa* and *P. pubescens*.[4] In the first-mentioned pair the peltogynols predominate, but in the latter peltogynols and mopanols exist in equivalent concentration, as in the case of *C. mopane*.[3] (+)-Peltogynol and (+)-mopanol were accordingly isolated from *P. pubescens*.[4]

In the present extension of this work the woods of *P. pubescens* and *P. venosa* are examined in greater detail for minor concentrations of novel flavonoids and peltogynoids.

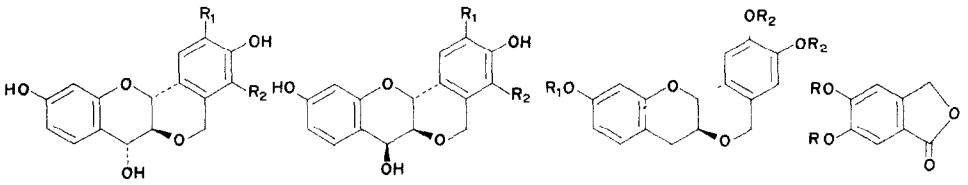
RESULTS AND DISCUSSION

Complete analysis of the purple heartwoods has confirmed the presence of (+)-2,3,-*trans*-3,4-*trans*-peltogynol (**1.** R_1=OH, R_2=H) and -mopanol (**1.** R_1=H, R_2=OH) and their 4-epimers, (+)-2,3-*trans*-3,4-*cis*-peltogynol (**2.** R_1=OH, R_2=H) and -mopanol (**2.** R_1=H,

[1] ROBINSON, G M and ROBINSON, R (1935) *J Chem Soc.* 744
[2] CHAN, W R., FORSYTH, W G C and HASSALL, C H (1958) *J Chem. Soc* 3174
[3] DREWES, S E and ROUX, D G (1966) *J Chem Soc (C)* 1644
[4] DREWES, S E. and ROUX, D G (1967) *J. Chem Soc (C)* 1407

R_2=OH) as predominant metabolites The latter pair are probably mainly responsible for the purple colour of the woods due to the relative ease of 3,4-*trans*-elimination (3-*ax*.-H, 4-*ax*.-OH) of the elements of water and subsequent anthocyanidin formation [5]

The above peltogynoids were accompanied by very low concentrations of a number of interesting components, requiring stabilization by methylation to facilitate their isolation on TLC, after initial fractionation of the free phenolic forms on silica gel The most notable of these represents the first catechin analogue amongst peltogynoids This compound (**3.** R_1=R_2=H), named pubeschin, was isolated as the trimethyl ether (**3.** R_1=R_2=Me), previously synthesized by Hassall and Weatherston,[6] and also as the 4',5'-dimethyl ether (**3.** R_1=H, R_2=Me), following methylation with diazomethane of the appropriate fractions from column chromatography of extracts from both *P. pubescens* and *P. venosa* The dimethyl ether was converted to the acetate (**3.** R_1=Ac, R_2=Me), and the 7-position of the acetyl group deduced from the chemical shifts of the A-ring protons of the acetate compared with those of the di- and trimethyl ethers.



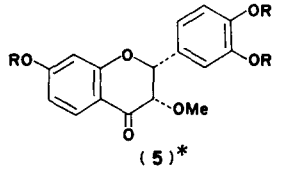
Synthesis of the trimethyl ether of (+)-pubeschin by another route was effected by reduction of (+)-tri-*O*-methyl-2,3-*trans*-peltogynone[6] [MnO_2-oxidation product of (2R:3S:4R)-tri-*O*-methylpeltogynol[3]] with $NaBH_4/BF_3$ in diglyme. The absolute configuration of (+)-tri-*O*-methyl-2,3-*trans*-pubeschin may accordingly be assigned as 2R·3S. Coupling constants of the heterocyclic C-ring protons of the trimethyl ether ($J_{2,3}$ 10·0, $J_{3,4eq} \leq 1$; $J_{3,4ax}$ − 4·8; $|J_{4ax,4eq}$ 9·4|) correlate with $\frac{1}{2}$-chair conformations for the C- and D-rings, and almost coplanar arrangement of the benzene A- and B-rings. The general planarity of the molecule is reflected in its lack of mobility (R_f 0·0) in 2% acetic acid on paper chromatograms

Related to the above peltogynoids is 5,6-dihydroxyphthalide (**4.** R=H), identified as meconine (**4.** R=Me) after methylation of fractions of both *Peltogyne* spp. with diazomethane, and comparison with a synthetic specimen [7] Meconine was previously isolated by our research group from *Acacia carnei*[8] after similar methylation, and the original phthalide (**5.** R=H) may in both instances represent the biochemical oxidation product of the associated (+)-peltogynol, its 4-epimer (**1, 2.** R_1=OH, R_2=H), or of (+)-pubeschin (**3.** R_1=R_2=H)

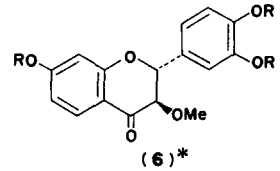
Some of the associated flavonoids, namely (±)-3-*O*-methyl-2,3-*cis*-fustin (**5.** R=H), (±)-3-*O*-methyl-2,3-*cis*-fustin (**6.** R=H) and α,2',3,4,4'-pentahydroxychalcone (**7.** R=H), identified as methyl ethers (**5, 6, 7.** R=Me) were previously found in association with mopanols and peltogynols in the heartwood of another genus of the Caesalpinioideae. *Trachylobium*

[5] FOURIE, T G., FERREIRA, D and ROUX, D G unpublished work on *Acacia xanthophloea*.
[6] HASSALL, C H and WEATHERSTON, I (1965) *J. Chem. Soc.* 2844.
[7] EDWARDS, G A., PERKIN, W H and SUDBOROUGH, F W (1925) *J. Chem. Soc.* **127**, 195.
[8] BRANDT, E V., FERREIRA, D and ROUX, D G unpublished work on *Acacia carnei*.

verucosum.[9] The natural presence of the 3-*O*-methyl function in the 2,3-*cis*- and 2,3-*trans*-fustins (**5, 6.** R=H) is beyond doubt,[9] since dihydroflavonols do not methylate at the 3-OH-position with diazomethane.



(5)*



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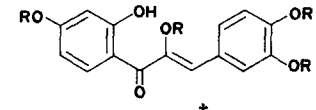
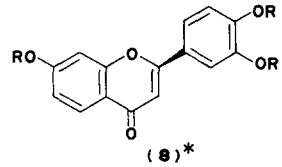


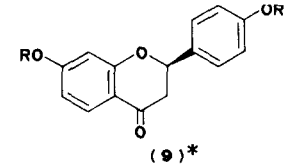
(7)†

* Racemates: only 2R-enantiomers shown.
† Only *trans*-enolic form shown

Two partly-racemized flavanones, (±)-3′,4′,7-trihydroxy (**8.** R=H) and (±)-4′,7-dihydroxy (**9.** R=H) (butin and liquiritigenin respectively) represent minor components which were isolated as partially racemized[10] (+)-methyl ethers (**8, 9.** R=Me). Both flavanones thus exhibit an excess of (2R)-enantiomers,[10] whereas (2S)-forms usually predominate in Nature.[11]



(8)*



(9)*

* Partial racemates (2R)-enantiomers, as illustrated predominate

The series of components **1–9** are common to *P. pubescens* and *P. venosa* with little difference in their relative concentrations. Compounds **5–8** are of interest as metabolites which may possibly represent precursors (α-hydroxychalcone) or offshoots (3-*O*-methyldihydroflavonols) of a biogenetic path[12] which leads to peltogynols (**1, 2.** R_1=OH, R_2=H), mopanols (**1, 2.** R_1=H, R_2=OH) and pubeschin (**3.** R_1=R_2=H), and eventually by oxidation of peltogynols to 5,6-dihydroxyphthalide (**4.** R=H). *Peltogyne* spp. represents the fourth source of the recently-discovered class of α-hydroxychalcones (*cf.* lit.[9]), amongst which *cis-trans* isomerism[13] resulting from keto-enol tautomerism[9,11,12] has been shown to exist.

TABLE 1 PHENOLIC FRACTIONS OF *P. pubescens* EXTRACT FROM CHROMATOGRAPHY ON SILICA GEL

R_f as indicated by TLC in C_6H_6–EtOAc–Me_2CO (7 2 2)	Colour on TLC with $HCHO/H_2SO_4$ (1·40) spray	Yield (g)
0 16	Red–black	2 21
0 20	Red–black	0 28
0 27	Orange–brown	0 67
0·33	Pink–brown	0 22
0 38	Green	
0 42	Yellow	0 31
0 46	Green	
0 52	Black	0·14

[9] VAN DER MERWE, J P., FERREIRA, D, BRANDT, E V and ROUX, D G (1972) *J Chem Soc Chem Commun* 521
[10] DU PREEZ, I. C, FERREIRA, D and ROUX, D G (1971) *J Chem Soc* (*C*) 336, ROUX, D G and PAULUS, E (1961) *Biochem. J* **80,** 62
[11] DEAN, F. M (1963) *Naturally Occurring Oxygen Ring Compounds*, p. 357, Butterworths, London
[12] ROUX, D G and FERREIRA, D (1974) *Phytochemistry* to be published.
[13] VOLSTEEDT, F DU R., RALL, G J H and ROUX, D G (1973) *Tetrahedron Lett* 1001

EXPERIMENTAL

Authenticated samples were kindly supplied by Professor D Normand, Centre Technique Forestier Tropical, Nogent-sur-Marne. *Peltogyne pubescens* Bentham (CTF W 18146, herbarium No 214, collected by I Petrov in the Kaw mountains, South Cayenne, French Guiana), and *P venosa* Bentham (CTF W 18155, herbarium No 223, collected by I Petrov in the Saint Laurent area of Maroni and Iracoubo)

NMR spectra were recorded in $CDCl_3$, unless otherwise specified, with TMS as internal standard, optical rotations on a Hilger and Watts M-412 polarimeter using $CHCl_3$, and CD-curves on a JASCO J-20 spectropolarimeter 2-D chromatograms were run by ascent on Whatman No 1 (28 × 46 cm) sheets in water-satd *sec*-BuOH and in 2% HOAc TLC was on Kieselgel PF_{254} (0 25 mm) and on preparative scale on the same substrate (1 mm) Plates were air-dried and unactivated, and sprayed with H_2SO_4 40% formaldehyde (40 1) Column chromatography was on Kieselgel 60 (120–230 mesh) introduced with the solvent as a slurry and compacted with a PIFCO orthopaedic vibrator Columns were used in conjunction with an ISCO model 273 fraction collector

Extraction and preliminary separation Drillings (1 94 kg) from each of the heartwoods of *P pubescens* and *P venosa* were dewaxed with petrol (b p 40–60°) in two successive extractions (24 hr each) at ambient temp., and thereafter extracted similarly with EtOAc–Et_2O (3 2) Evaporation under reduced pressure gave light brown solids (8 2 g) Thereafter extraction was continued with Me_2CO (3 1 successive extractions for 24 and 48 hr) yielding a red–brown solid (53 6 g) under reduced pressure The powdered extract was shaken with water-satd EtOAc to free it of oxidized material, the solubles giving a reddish solid (30 2 g)

The products of EtOAc–Et_2O and Me_2CO–wet EtOAc extractions were chromatographed on a column (extract substrate ratio 1 50) to give fractions represented in Table 1 The higher R_f fractions (0 33–0 52) predominated amongst the EtOAc–Et_2O extractives, while those of lower R_f (0 16–0 38) were emphasized in the acetone extract The band at R_f 0 52 represented a steroid fraction

(+)-2 3-Trans-3,4-trans-*peltogynol* (**1.** R_1=*OH*, R_2=*H*) *and -mopanol* (**1.** R_1=*H*, R_2=*OH*) *and their* 4-*epimers* (+)-*Tri*-O-*methyl*-2,3-trans-3 4-trans-*peltogynol* The red–black fractions (R_f 0 16, 0 20) were examined by two-way PC and the presence of (+)-peltogynol, (+)-peltogynol B, (+)-mopanol and (+)-mopanol B established by comparison with reference compounds

Methylation of these fractions with CH_2N_2 and subsequent separation of the methyl ethers by TLC in MeCOEt-toluene (3 7)[4] confirmed the presence of the trimethyl ethers of both (+)-peltogynol (R_f 0 40) and in low concentration of (+)-peltogynol B (0·71) [4] The former was separated, and the solids from the fraction crystallized as prisms (400 mg) from Me_2CO–EtOH, m p 194–198° with sintering from 157°, M^+ 344 (18%), $[\alpha]_D^{22}$ + 252° (*c* 0 46) {lit [2] m p 196–200°, $[\alpha]_D$ + 250°} The NMR spectrum was identical to that in the literature [3]

(+)-*Tri*-O-*methyl*-2,3-trans-3,4-trans-*mopanol* The above methylated fractions also showed the presence of the tri-*O*-methyl ethers of (+)-mopanol (0 54) and low concentrations of (+)-mopanol B (0 88) under the same conditions Separation of the former on preparative TLC gave needles (35 mg) from Me_2CO–EtOH, m p 193–195°, M^+ 344, $[\alpha]_D^{22}$ + 231° (*c* 0 88) {lit [3] m p 193–195°, $[\alpha]_D^{20}$ + 235°} The NMR spectrum was identical with that in the literature [3]

(+)-2,3-trans-*Pubeschin* (**3.** R_1=R_2=*H*) [(+)-2,3-trans-4-*desoxypeltogynol*] The pink-brown fraction (R_f 0 33) from the primary fractionation was methylated with diazomethane to give three products (R_f 0 26, 0 48 and 0 51) on TLC separation in C_6H_6–EtOAc–Me_2CO (20 2 1)

(+)-4′,5′-*Di*-O-*methyl*-2,3-trans-*pubeschin* (**3.** R_1=*H*, R_2=*Me*) The compound with R_f 0 26 proved to be partially methylated pubeschin, affording the same red colour with H_2SO_4/HCHO spray as the trimethyl ether The band gave an *amorphous solid* (40 mg), m p 69–71°, M^+ 314 (2%), [τ 2 77 (*s*, 6′-H), 3 00 (*d* 5-H) 3 44 (*s*, 3′-H), 3 44 (*d*, 8-H), 3,53 (*q*, 6-H), 5 12 {*s*, CH_2(D-ring)}, 5 26 (*d*, 2-H), 6 03, 6 13 (*s* 2 × OMe), 6 20 (*m*, 3-H), 7 04 (*m*, 4-CH_2), $J_{2,3}$ 10 Hz]

(+)-7-O-*Acetyl*-4′,5′-*di*-O-*methyl*-2,3-trans-*pubeschin* (**3.** R_1=*Ac*, R_2=*Me*) The 4′ 5′-dimethyl ether of pubeschin (35 mg) was acetylated with Ac_2O/pyridine and purified by TLC in C_6H_6–Me_2CO (8 1) (R_f 0 45) The *amorphous solid* (31 mg), m p 58–60°, M^+ 356, $\upsilon_{max}^{CHCl_3}$ 1755 cm^{-1} (acetyl), [τ 2 77 (*s*, 6′-H), 2 85 (*d*, 5-H), 3 20 (*d*, 8-H), 3 30 (*q*, 6-H), 3 43 (*s*, 3′-H), 5 06 (*d*, 2-H), 5 30 {*s*, CH_2(D-ring)}, 6 03 6 12 (*s*, 2 × OMe), 6 17 (*m*, 3-H), 6 97 (*m*, 4-CH_2), 7 69 (*s*, OAc), $J_{2,3}$ 10 0 Hz], Found C 67 3, H 5 7 Calculated for $C_{20}H_{20}O_6$ C 67 4, H 5 65%

(+)-4′,5′,7-*Tri*-O-*methyl*-2,3-trans-*pubeschin* (**3.** R_1=R_2=*Me*) Solids from the band R_f 0 48 crystallized from Me_2CO–C_6H_6–EtOH as needles (53 mg) with a slight yellow tinge, m p 157° (sintering from 146) (lit [6] 165°), M^+ 328 (2 5%), $[\alpha]_D^{21}$ + 188° (*c* 0 49), [τ 2 73 (*s*, 6′-H), 2 92 (*d*, 5-H), 3 37 (*s*, 3′-H), 3 43 (*q*, 6-H) 3 43 (*d* 8-H), 5 10 {*s*, CH_2(D-ring)}, 5 23 (*d*, 2-H), 6 14 (*m*, 3-H), 6 02, 6 11, 6 20 (*s*, 3 × OMe), 7 03 (*m* 4-CH_2), $J_{2,3}$ 10 0, $J_{3\,4eq} \leq 1$, $J_{3\,4ax} = 4\,8$, $|J_{4ax\,4eq}|$ 9 4] The complex AB part of the ABXY spin system is in agreement with an analysis of the corresponding portion of an ABX system by Bovey[14]] Found C 69 8, H 5 5 Calculated for $C_{19}H_{20}O_5$ C 69 9, H 5 5% Repeated recrystallization did not increase the m p or the rotation to that of the synthetic product (*loc cit*) However, the NMR spectrum of the natural derivative showed no impurities and its CD-curve was similar to that of the synthetic product

(±)-3′,4′,7-*Trihydroxy-and* (±)-4′,7-*dihydroxyflavanones* (**8, 9.** *R*=*H*) (+)-4′,7-*Di*-O-*methylflavanone* The fraction R_f 0 51 from the methylated band, which also yields the di- and trimethyl ethers of pubeschin gave a *wax*

[14] BOVEY F A (1969) *Nuclear Magnetic Resonance Spectroscopy*, p. 111, Academic Press, London

(22 mg), M^+ 284 (28%), $[\alpha]_D^{26°}$ + 29° (*c* 0 4), $\nu_{max}^{CHCl_3}$ 1679 cm^{-1} (C=O stretching), [τ 2 07 (*d*, 5-H), 2 53 (*d*, 2'-H + 6'-H), 3 03 (*d*, 3'-H + 5'-H), 3 36 (*q*, 6-H), 3 43 (*d*, 8-H), 4 55 (*q*, 2-H), 6 13 (*s*, 2 × OMe), 6 90–7 17 (*m*, CH_2)]

(+)-3',4',7-*Tri*-O-*methylflavanone* Methylation of the orange–brown fraction (0 27) from the primary fractionation with CH_2N_2, followed by separation of TLC with C_6H_6–EtOAc–Me_2CO (7 2 2) gives a solid (37 mg) which separates from C_6H_6–MeOH in yellow crystals, m p 108° (lit [10] 73°, 114–115°, 120–121° according to degree of racemization), M^+ 314, $[\alpha]_D^{26°}$ + 11° (*c* 0 4), $\nu_{max}^{CHCl_3}$ 1677 cm^{-1} (*C*=O stretching), [τ 2 06 (*d*, 5-H), 2 95 (*q*, 6'-H), 2 97 (*d*, 2'-H), 3 07 (*d*, 5'-H), 3 33 (*q*, 6-H), 3 40 (*d*, 8-H), 4 53 (*q*, 2-H), 6 91–7 15 (*m*, CH_2), 6·03, 6 13 (*s*, 3 × OMe)]

5,6-*Dihydroxyphthalide*, (±)-3',4',7-*trihydroxy*-3-O-*methyl*-2,3-cis-*dihydroflavonol*, (±)-3',4',7-*trihydroxy*-3-O-*methyl*-2,3-trans-*dihydroflavonol and* α,2',3,4,4'-*pentahydroxychalcone* Due to the low individual concentrations of fractions R_f 0 38–0 46 from the primary fractionation and some degree of mutual contamination, they were combined and methylated with CH_2N_2 The methylated product was separated by column chromatography (loading 1 100) when four "components" were obtained which showed R_f 0 23, 0·34, 0 42 and 0 46 by TLC in C_6H_6–EtOAc–Me_2CO (20 2 1)

5,6-*Dimethoxyphthalide* (m-*meconine*) (**4.** *R*=*Me*) The methylated component of R_f 0 23 from TLC gave rosettes (18 mg) from C_6H_6–Me_2CO–MeOH, m p 154–155° (lit [7] 155–157°), $\nu_{max}^{CHCl_3}$ 1775 cm^{-1} (C=O stretching lactone), M^+ 194 (70%), *m/e* 165 (100), [τ (acetone-d_6) 2 69 (*s*, 7-H), 2 76 (*s*, 4-H), 4·72 (*s*, CH_2), 6 03, 6 07 (*s*, 2 × OMe)]

(±)-3,3',4',7-*Tetra*-O-*methyl*-2,3-cis-*fustin* (**5.** *R*=*Me*), The band, R_f 0 42 (TLC) from the column gave a non-crystalline waxy compound (21 mg), M^+ 344, $[\alpha]_D$ 0° (*c* 0 4), $\nu_{max}^{CHCl_3}$ 1685 (C=O stretching), [τ 2·05 (*d*, 5-H), 2 83 (*q*, 6'-H), 3 00 (*d*, 2'-H), 3 07 (*d*, 5'-H), 3 32 (*q*, 6-H), 3 44 (*d*, 8-H), 4 65 (*d*, 2-H), 6 27 (*d*, 3-H), 6 05, 6 15, 6 62 (*s*, 4 × OMe), $J_{2,3}$ 2 0 Hz (*cf* lit[9,15])]

(±)-3,3',4',7-*Tetra*-O-*methyl*-2,3-trans-*fustin* (**6.** *R*=*H*) The band, R_f 0 34 (TLC) yielded crystals (57 mg) from ethanol, m p 140° (lit [9,14] 143°), M^+ 334, $[\alpha]_D$ 0° (*c* 0 4), $\nu_{max}^{CHCl_3}$ 1685 cm^{-1} (C=O stretching), [τ 2 10 (*d*, 5-H), 2 87 (*q*, 6'-H), 2 93 (*d*, 2'-H), 3 10 (*d*, 5'-H), 3 35 (*q*, 6-H), 3 52 (*d*, 8-H), 4 73 (*d*, 2-H), 5 92 (*d*, 3-H), 6 07 (*s*, 2 × OMe), 6 12, 6 57 (*s*, 2 × OMe), $J_{2,3}$ 10 2 Hz]

2'-*Hydroxy*-α,3,4,4'-*tetramethoxy*-trans-*chalcone* (**7.** *R*=*Me*) A yellow waxy amorphous compound (25 mg) was obtained from the band with R_f 0 46, $\nu_{max}^{CHCl_3}$ 1633 cm^{-1} (C=O stretching), M^+ 344 (100%), [τ −2 64 (*s*, 2'-OH), 1 95 (*d*, 6'-H), 2 48 (*d*, 2-H), 2 66 (*q*, 6-H), 3 10 (*d*, 5-H), 3 46 (*d*, 3'-H), 3 53 (*q*, 5'-H), 3 59 (*s*, β-H), 6 05, 6 12 (*s*, 3 × OMe), 6 25 (*s*, α-OMe)] (cf lit [9]) Refluxing of the chalcone with NaOAc in ethanol gave a 1.2 ratio of (±)-3,3',4',7-tetra-*O*-methyl-2,3-*cis*- and -2,3-*trans*-fustins (**5, 6.** R=Me) respectively (cf lit [9])

Synthesis of m-*meconine* (**4.** *R*=*Me*) [7] Veratric acid (2 g), formaldehyde (3 ml, 35% v/v) and conc HCl (8 ml) were heated on a waterbath for 12 hr After cooling an equal volume of water was added with shaking The solution was extracted with ether, and the residue obtained purified by TLC in C_6H_6–EtOAc–Me_2CO (20 2 1) The band R_f 0 23 gave *m*-meconine (210 mg) from aqueous ethanol as crystals, m p 155–157°, with physical properties identical to the natural product

Synthesis of (±)-*tri*-O-*methyl*-2,3-trans-*pubeschin* (**3.** R_1=R_2=*Me*) The trimethylether (200 mg) of (+)-2,3-*trans*-peltogynol in $CHCl_3$ (25 ml) was stirred with activated MnO_2 (1 6 g) for 24 hr at ambient temperatures. The product was filtered through celite and the residue washed with $CHCl_3$ (3 × 10 ml) The combined solvent was removed under vacuum to give a residue (180 mg) (+)-Tri-*O*-methyl-2,3-*trans*-peltogynone crystallized readily from ethanol in off-white crystals, m p 215° (lit [2] 211–213°), $\nu_{max}^{CHCl_3}$ 1688 cm^{-1}, M^+ 342, [τ 2 30 (*d*, 5-H), 2·82 (*s*, 2'-H), 3 36 (*q*, 6-H), 3 39 (*s*, 5'-H), 3 39 (*d*, 8-H), 4 73 (*d*, 2-H), 5 07 (*s*, CH_2), 5 70 (*d*, 3-H), 6 03 (*s*, OMe), 6 11 (*s*, 2 × OMe), $J_{2,3}$ 12 Hz]. The peltogynone (170 mg) in diglyme (2 ml) and dry ether (5 ml) was added slowly together with BF_3 (850 mg) in diglyme (1 ml) and dry ether (5 ml) to $NaBH_4$ (200 mg) in diglyme (1 ml) and dry ether (5 ml) cooled in an ice/salt mixture over 20 min (cf lit [16]) After a further 30 min at ambient temperature the mixture was refluxed for 1 hr Additional $NaBH_4$ (100 mg) was added and refluxing continued for another hour The mixture was acidified with dilute 0 3 N HCl, the ether layer separated and washed successively with N HCl, aqueous $NaHCO_3$ and water The ether solution was dried (Na_2SO_4), evaporated to dryness and the product separated by preparative TLC (R_f 0 49) with C_6H_6–EtOAc–Me_2CO (20 2 1), crystallized as needles from ethanol (115 mg), m p. 160–161° (lit [6] 165°), $[\alpha]_D$ + 261° (*c* 0 4) (lit [6] + 258° in tetrachloroethane) The NMR spectrum was identical to that of the corresponding natural derivative

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