Metabolites from the Purple Heartwood of Mimosoideae I, *Acacia peuce* F. Muell: The First Natural 2,3-*cis*-Peltogynoids

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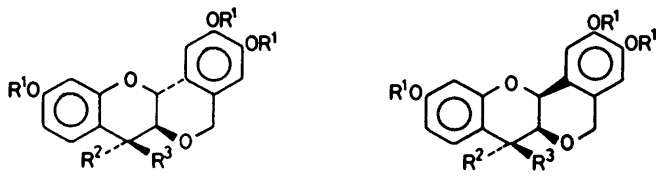
The presence of the first (+)-2,3-*cis*-3,4-*cis*- and (+)-2,3-*cis*-3,4-*trans*-peltogynols differentiates the purple heartwood of *A. peuce* from those of *A. crombei* and *A. carnei*. These compounds were obtained synthetically by epimerization of (+)-peltogynol. Other flavonoids included the known 2,3-*trans*-peltogynols, peltogynin, combenin, butin, fisetin, (+)-2,3-*trans*-fustin, and a novel optically active (+)-3-*O*-methyl-2,3-*trans*-fustin.

Acacia peuce F. Muell represents a rare species with distribution recorded in a few isolated localities, *i.e.* Andado Station, Northern Territory, as well as Birdsville and the Diamantina River in western Queensland. It is also differentiated, as its name implies from the vast majority of *ca.* 700 species of the same genus endemic to Australia, by its deep purple heartwood.[1]

Evidence of traces of the first natural 2,3-*cis*-peltogynoid, (−)-2,3-*cis*-3,4-*cis*-peltogynol (2d) in the heartwood of *A. peuce* was obtained by methylation of the appropriate fraction (R_F 0.55 in 2% AcOH) from preparative chromatography on paper. The trimethyl ether (2e), m.p. 216 °C, $J_{2,3}$ *ca.* 1 Hz, $J_{3,4}$ 4.4 Hz, was purified by t.l.c. and characterized as the acetate (2f), m.p. 230 °C, $[\alpha]_D^{28}$ −220°, which exhibits the same coupling constants as the methyl ether. The melting points of both natural derivatives differ from those of the corresponding synthetic racemates [2] [195—197 °C (decomp.) and 210—211 °C respectively], but their n.m.r. spectra are identical ($J_{2,3}$ *ca.* 1 Hz, $J_{3,4}$ 4.5 Hz) and the mass spectral fragmentations are consistent with the proposed structure.



(1) (2)

a; $R^1 = R^3 = H$; $R^2 = OH$
b; $R^1 = Me$; $R^2 = OH$; $R^3 = H$
c; $R^1 = Me$; $R^2 = OAc$; $R^3 = H$
d; $R^1 = R^2 = H$; $R^3 = OH$
e; $R^1 = Me$; $R^2 = H$; $R^3 = OH$
f; $R^1 = Me$; $R^2 = H$; $R^3 = OAc$

The free phenol (2d) is accompanied in even lower concentration by an isomer (R_F 0.59) presumed to be the (−)-2,3-*cis*-3,4-*trans*-diastereoisomer (2a) from the epimerizations described below.

The remarkably high relative mobilities in aqueous systems (R_F 0.55, 0.59 in 2% AcOH) of the free phenolic forms of (−)-2,3-*cis*-peltogynols (2d), (2a) contrast with those of the known (+)-2,3-*trans*-diastereoisomers (1a), (1d) (R_F 0.05, 0.09 respectively).[3] This behaviour is completely at variance with the R_F relationship between analogous flavan-3,4-diols, where the reverse generally pertains (2,3-*cis*: R_F 0.39—0.56; 2,3-*trans*: 0.53—0.58 for 3′,4′,7-trihydroxyflavan-3,4-diol [4,5]).

Epimerization of (+)-peltogynol ($2R:3S:4R$) [3] in aqueous solution under pressure [4,5] for 1.5 h affords an equilibrium mixture of four related (3*S*)-diastereoisomers consisting of starting material (1a), (+)-peltogynol B (1d), (−)-2,3-*cis*-3,4-*cis*-peltogynol (2d) identical to the natural product, and (−)-2,3-*cis*-3,4-*trans*-peltogynol (2a) {trimethyl ether (2b) $J_{2,3}$ 1.2 Hz, $J_{3,4}$ 2.8—2.9 Hz and its acetate (2c), m.p. 175 °C, $[\alpha]_D^{20}$ −154°} in the approximate ratio of 100 : 300 : 1 : 4. The latter compound (2a) has the same R_F values as the high R_F (0.59) compound on paper chromatograms, when utilizing the optically active substrate (cellulose).[6] The 2,3-*cis* pair from epimerization and thus also the corresponding natural products have $2S:3S:4S$ (2d) and $2S:3S:4R$ (2a) absolute configurations. Such unusual association of (3*S*)-diastereoisomers (1a), (1d), (2a), and (2d) was previously encountered only amongst ($2R:3S$)- and ($2S:3S$)-fisetinidols present in *Colophospermum mopane*.[3]

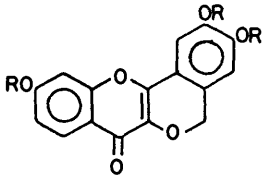
The stereochemical relationship of natural (−)-2,3-*cis*-3,4-*cis*-peltogynol and its 4-epimer (2d), (2a) with (+)-2,3-*trans*-peltogynol (1a) would suggest that *cis*-peltogynols represent artefacts of epimerization, but for the high-energy requirements of the conversion and for the fact that they are absent from closely related species of the same genus, *i.e. A. carnei*,[7] *A. crombei*,[8] where (+)-peltogynol is also present in excess. Another notable difference is that among the epimerization products, the thermodynamically more stable diastereoisomer of each pair with 4_{ax}-OH (1e), (2b) predominates by a factor of 3—4 (see above), whereas the natural mixture from *A. peuce* shows the exact reverse [*i.e.* those with 4_{eq}-OH (1b), (2e) predominate] as indicated below.

The strikingly low proportions of 2,3-*cis*- compared with 3,4-*trans* diastereoisomers formed by epimerization approximates to that found naturally in *A. peuce* (*ca.* 2 300 : 600 : 4 : 1), but contrasts with the high yields of 2,3-*cis*-flavan-3,4-diol analogues resulting from similar treatment of (+)-2,3-*trans*-3,4-*trans*-3′,4′,7-trihydroxyflavan-3,4-diol.[4] Clearly insertion of the D-ring as in 2,3-*cis*-peltogynoids introduces considerable strain into one or more of the heterocyclic ring systems, making these compounds thermodynamically less stable than 2,3-*trans*-isomers and conceivably contributing to the low concentrations of the former in nature. Difficulty anticipated with formation of 2,3-*cis*- compared with 2,3-*trans*-peltogynoids during cyclization of the appropriate chalcone analogue (peltogynochalcone) due to

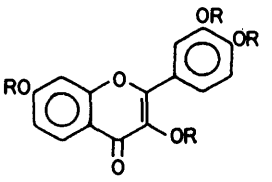
steric strain,[9] is evident from examination of Dreiding models. An excellent analogy for the above concordance between proportionate yields originating from synthetic and biogenetic processes, is to be found in the cyclization of 2'-hydroxy-α,3,4,4'-tetramethoxy-*trans*-chalcone which provides both 2,3-*cis*- and 2,3-*trans*-3-*O*-methylfustins in almost the exact ratio (1 : 2) in which they occur naturally.[8]

The coupling constants [$J_{2,3}$ 10.0 Hz, $J_{3,4}$ 8.8 Hz (1b); $J_{2,3}$ 10.0 Hz, $J_{3,4}$ 3.6 Hz (1e); $J_{2,3}$ *ca.* 1 Hz, $J_{3,4}$ 4.4 Hz (2e); $J_{2,3}$ 1.2 Hz, $J_{3,4}$ 2.8—2.9 Hz (2b)] taken in conjunction with Dreiding models, indicate differing sofa and twisted boat conformations respectively for the C-rings of 2,3-*trans*- (1b), (1e), and 2,3-*cis*-isomers (2e), (2b), but half-chair conformations for the D-rings of all diastereoisomers. The strained C-rings of 2,3-*cis*-diastereoisomers support the above observations as regards their relative thermodynamic stability. The coupling constants also require that aromatic B-rings be almost co-planar with A-rings for 2,3-*trans*-peltogynols (1a), (1d), but with planes *ca.* 45° relative to each other for 2,3-*cis*-isomers (2d), (2a). The proposed almost planar (2,3-*trans*) and twisted (2,3-*cis*) molecular conformations correlate with their relative mobilities (free phenolic forms) on cellulose in aqueous systems, since, amongst other factors,[7] planarity and non-planarity of flavonoids are closely associated with low and high mobilities under the conditions specified.

Other peltogynoids present in *A. peuce* are peltogynin (3a), previously found in *C. mopane*[10] and currently in *A. carnei*[11] and *A. crombei*,[12] in addition to optically active crombenin, the novel spirocoumaranone of *A.*



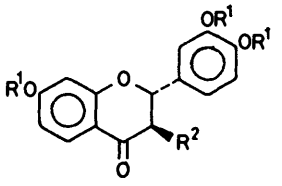
(3)



(4)

a; R = H
b; R = Me

crombei.[12,13] Both compounds were crystallized as their methyl ethers, the latter for the first time.



(5)

a; R^1 = H; R^2 = OH
b; R^1 = Me; R^2 = OH
c; R^1 = H; R^2 = OMe
d; R^1 = Me; R^2 = OMe
e; E^1 = R^2 = H
f; R^1 = Ac; R^2 = H

Notable amongst the conventional flavonoids, which include the flavanone analogue, butin (5e) and flavonol, fisetin (4a), are the optically pure dihydroflavonols, (+)-2,3-*trans*-fustin (5a) and (+)-3-*O*-methyl-2,3-*trans*-fustin (5c) identified as their methyl ethers (5b) and (5e). The 3-*O*-methylfustin was isolated as an optically active component for the first time, and is considered[14] as the offshoot of a biogenetic pathway leading *via* α-hydroxy- and α-methoxychalcones to peltogynols and mopanols on account of their regular association with these compounds in heartwoods (*Trachylobium verrucosum*,[8,15] *Peltogyne pubescens*, *P. venosa*, and *P. porphyrocardia*[16]).

EXPERIMENTAL

N.m.r. and mass spectra were recorded respectively on a Varian T60 (in $CDCl_3$ with $SiMe_4$ as internal reference unless otherwise stated) and an A.E.I. MS9 spectrometer. Jasco J20 (c.d./o.r.d.), Unicam SP 1000 (i.r.), Beckman DB-b (u.v.) and Hilger–Watts M412 ($[\alpha]_D$) instruments were employed as indicated.

Media used for preparative separation of components comprised Whatman No. 3 paper (p.p.c.) and Merck silica gel 60 PF_{254} (t.l.c.). Qualitative analyses were based mainly on two-dimensional chromatograms run by ascent on Whatman No. 1 paper (28 × 46 cm) in water-saturated Bu^sOH and in 20% (v/v) aq. AcOH (R_F values being indicated in this sequence). These were evaluated by u.v. illumination and/or spraying reagents ($AgNO_3$–NH_3, toluene-*p*-sulphonic acid, bis-diazotized benzidine or diazotized *p*-nitroaniline).

Authenticated samples of the cross-section of the stem of *A. peuce*, collected at ' North Bore ', Andado Station (December 1971) and at Birdsville, Queensland (August 1971), were kindly supplied by Dr. Mary D. Tindale, Royal Botanic Gardens and National Herbarium, Sydney, Australia.

Extraction and Fractionation of Compounds from A. peuce. —Drillings (451 g) from the heartwood of *A. peuce* were dewaxed with n-hexane (2 × 1.5 l × 12 h, *ca.* 25 °C) and extracted with MeOH (5 × 1.5 l) for 10 consecutive days at ambient temperatures (25—28 °C). Evaporation of the combined extracts yielded a dark brown amorphous powder (59.7 g).

A portion of the crude material (40 g) was fractionated by p.p.c., utilizing ascending development in 2% (v/v) aq. AcOH. Five bands yielded fractions A—E [R_F 0.47 (1.1 g), 0.24 (1.5 g), 0.17 (3.2 g), 0.13 (10.2 g), and 0.06 (12.8 g) respectively] on elution and evaporation. Subsequent two-dimensional paper chromatography showed fraction A to be a compound mixture which was accordingly rechromatographed by t.l.c. (benzene–acetone, 7 : 3) into four subfractions, A_1—A_4 (R_F 0.64, 0.60, 0.54, and 0.44 respectively), following methylation by diazomethane.

(+)-3,3',4',7-*Tetra*-O-*methyl*-2,3-trans-*fustin* (5d).—This compound crystallized from fraction A_1 in cyclohexane–acetone (8 : 2) as colourless needles (19.8 mg), m.p. 148 °C (lit.,[13] 153 °C: racemate); $[\alpha]_D^{24}$ +39° (*c* 0.31 in $CHCl_3$); n.m.r. identical to that in the literature.

(−)-4',5',7-*Tri*-O-*methyl*-2,3-cis-3,4-cis-*peltogynol* (2e) *and its Acetate* (2f).—Crystallization of fraction A_2 from acetone produced (−)-*cis,cis*-peltogynol trimethyl ether (2e) as yellow *needles* (13.5 mg), m.p. 216 °C (lit.,[2] 197 °C: synthetic racemate); M^+ 344; $J_{2,3}$ *ca.* 1 Hz, $J_{3,4}$ 4.4 Hz. This compound was acetylated to yield the monoacetate (2f) which readily crystallized from ethanol as colourless *needles* (11.2 mg), m.p. 230 °C (Found: M^+, 386.137. Calc. for

$C_{21}H_{22}O_7$: *M*, 386.137), *m/e* 386 (5.1%, M^+), 326 (11), 192 (100), 191 (12), 152 (4.4), and 151 (7.5), $[\alpha]_D^{28}$ −220° (*c* 0.40 in $CHCl_3$); τ($CDCl_3$) 2.81 (1 H, d, *J* 8.6 Hz, H-5), 3.00 (1 H, s, H-6'), 3.40 (1 H, s, H-3'), 3.47 (1 H, dd, *J* 8.6 Hz, *J* 2.0 Hz, H-6), 3.57 (1 H, d, *J* 2.0 Hz, H-8), 3.78 (1 H, d, *J* 4.4 Hz, H-4), 5.07 (3 H, s, H-2 and OCH_2), 5.66 (1 H, d, *J* 4.4 Hz, H-3), 6.05 (3 H, s, OMe), 6.11 (3 H, s, OMe), 6.25 (3 H, s, OMe), and 7.70 (3 H, s, 4-OAc).

(+)-3',4',7-*Tri*-O-*methyl*-2,3-trans-*fustin* (5b).—Purification of fraction A_3 by t.l.c. (1,2-dichloroethane–acetone, 19 : 1) produced the tri-*O*-methylfustin (R_F 0.21) which crystallized from EtOH as colourless needles (26.4 mg), m.p. 141 °C (lit.,[17] 138—140 °C); $[\alpha]_D^{28}$ −11° (*c* 0.51 in $CHCl_3$) {lit.,[1,11] $[\alpha]_D$ −44° (*c* 1.30 in C_2Cl_4)}; n.m.r. identical to that in the literature.[8]

(−)-4,6,6',7'-*Tetra*-O-*methylcrombenin*.—Fraction A_4 crystallized from acetone as colourless platelets (24.2 mg), m.p. 228 °C, $[\alpha]_D^{27}$ −9° (*c* 0.54 in pyridine) and n.m.r. identical to the same compound from *A. crombei*.[12,13]

2,3-cis-3,4-trans-*Peltogynol* (2a).—Due to extremely low concentrations, *cis,trans*-peltogynol was not isolated, but its presence in fraction A was ascertained with the aid of two-dimensional chromatography (R_F 0.70/0.69, purple with toluene-*p*-sulphonic acid). An identical synthetic compound (see below) served as authentic reference.

(±)-3',4',7-*Tri*-O-*acetylbutin* (5f).—Following acetylation of fraction B (1.1 g), the compound (5f) was isolated (R_F 0.46) and purified (R_F 0.52) by t.l.c. [1,2-dichloroethane–acetone (19 : 1) and benzene–acetone (8 : 2)], subsequently crystallizing from ethanol as colourless platelets (26.1 mg), m.p. 125 °C (lit.,[18] 124—126 °C: racemate); $[\alpha]_D^{24}$ +6° (*c* 0.35 in $CHCl_3$); n.m.r. [$J_{2,3(ax)}$ 10.0 Hz, $J_{2,3(eq)}$ 6.5 Hz and 2 H, m, τ 6.33—7.40, 3-CH_2 (*cf.* ref. 19)].

(+)-4',5',7-*Tri*-O-*methyl*-2,3-trans-3,4-cis-*peltogynol* (1e).—Methylation of a portion (1.0 g) of fraction C with dimethylsulphate gave tri-*O*-methylpeltogynol B after separation by t.l.c. (R_F 0.41; 1,2-dichloroethane–acetone, 9 : 1). Crystallization from ethanol produced colourless needles (52.1 mg), m.p. 141 °C (lit.,[20] 140 °C); $[\alpha]_D^{29}$ +242° (*c* 0.41 in $CHCl_3$) {lit.,[20] $[\alpha]_D$ +270° (in $CHCl_3$)}; n.m.r. identical to that in the literature.[3]

(+)-4-O-*Acetyl*-4',5',7-*tri*-O-*methyl*-2,3-trans-3,4-cis-*peltogynol* (1f).—Acetylated tri-*O*-methylpeltogynol B (50 mg) readily crystallized from EtOH as colourless needles (51.9 mg), m.p. 183 °C (lit.,[21] 182 °C); $[\alpha]_D^{26}$ +219° (*c* 0.49 in $CHCl_3$); n.m.r. identical to that in the literature.[3]

(+)-4',5',7-*Tri*-O-*methyl*-2,3-trans-3,4-trans-*peltogynol* (1b).—A portion (1.0 g) of fraction D, following methylation with dimethyl sulphate, was purified by t.l.c. (R_F 0.53; benzene–acetone, 7 : 3) and crystallized from EtOH as colourless needles (344.1 mg), m.p. 199 °C (lit.,[3] 200 °C); $[\alpha]_D^{24}$ +257° (*c* 0.48 in $CHCl_3$) {lit.,[20] $[\alpha]_D$ +250° (in $CHCl_3$)}; n.m.r. identical to that in the literature.[3]

(+)-4-O-*Acetyl*-4',5',7-*tri*-O-*methyl*-2,3-trans-3,4-trans-*peltogynol* (1c).—Acetylation of (1b) (50 mg) yielded the monoacetate which crystallized from EtOH as colourless needles (54.2 mg), m.p. 155 °C (lit.,[20] 156 °C); $[\alpha]_D^{29}$ +201° (*c* 0.47 in $CHCl_3$); n.m.r. identical to that in the literature.[3]

3,3',4',7-*Tetra*-O-*methylfisetin* (4b).—This compound was isolated from a methylated portion (1.0 g) of fraction E by t.l.c. (R_F 0.58, benzene–acetone, 7 : 3). Crystallization from ethyl acetate produced colourless needles (26.7 mg), m.p. 178 °C (lit.,[22] 180 °C); M^+ 342 and n.m.r. identical with those obtained from authentic samples.

4',5',7-*Tri*-O-*methylpeltogynin* (3b).—Tetra-*O*-methylfisetin is accompanied in the methylated fraction E by extreme low concentrations of tri-*O*-methylpeltogynin. This was established by t.l.c. [1,2-dichloroethane–acetone (9 : 1)] with a prepared sample[23] as reference (R_F 0.23, yellow with H_2SO_4–HCHO and intense turquoise fluorescence under u.v.).

Peltogynidin.—Individual treatment of phenolic material (2 mg) from respectively fraction A and D with isopropyl alcohol–3M-HCl, 4 : 1 (4 ml) for 30 min, under pressure at 96 °C, yielded the identical anthocyanidin, peltogynidin. This was confirmed by descending paper chromatography in formic acid–3M-HCl, 1 : 1 (R_F 0.58, $\lambda_{max.}$ 545 nm[3]).

Epimerization of (+)-*Peltogynol* (1a).—Natural authenticated (+)-*trans,trans*-peltogynol (9.8 g), dissolved in warm water (500 ml), was autoclaved under pressure (5 atm)[3,4] for 90 min with exclusion of air. An ethyl acetate extract (5 × 200 ml) of the rapidly cooled solution, after it had been dried with Na_2SO_4 and the solvent removed under reduced pressure at <60 °C, yielded a mixture of isomers (9.1 g). Application of p.p.c. (ascending development, 2% aqueous AcOH) separated this mixture into two distinct fractions, S_1 (R_F 0.46, 0.102 g) and S_2 (R_F 0.14, 7.997 g). Two-way chromatograms showed fraction S_2 to be composed of *trans,trans*- (R_F 0.56/0.29) and *trans,cis*-peltogynol (R_F 0.58/0.37) while fraction S_1 consisted of *cis,cis*- (R_F 0.62/0.63) and *cis,trans*-peltogynol (R_F 0.70/0.69) in the approximate ratio of 100 : 300 : 1 : 4. All appeared identical to the natural products and only fraction S_1 was further investigated.

Synthetic (−)-4',5',7-*Tri*-O-*methyl*-2,3-cis-3,4-cis-*peltogynol* (2e).—The *cis,cis*-isomer was isolated (R_F 0.38) from fraction S_1 (102 mg) by t.l.c. [1,2-dichloroethane–acetone (9 : 1)] following methylation with diazomethane. Subsequent crystallization from acetone produced colourless *needles* (18.2 mg), m.p. 216 °C (lit.,[2] 197 °C; synthetic racemate); mass spec. (M^+ 344) and n.m.r. identical to that of the natural derivative.

Synthetic (−)-4-O-*Acetyl*-4',5',7-*tri*-O-*methyl*-2,3-cis-3,4-cis-*peltogynol* (2f).—Acetylation of (2e) (23.6 mg) produced the monoacetate which crystallized from EtOH as colourless needles (18.9 mg), m.p. 230 °C (Found: M^+, 386.137. Calc. for $C_{21}H_{22}O_7$: *M*, 386.137), $[\alpha]_D^{25}$ −196° (*c* 0.36 in $CHCl_3$), mass spec. (M^+ 386) and n.m.r. identical to that of the natural derivative.

Synthetic (−)-4',5',7-*Tri*-O-*methyl*-2,3-cis-3,4-trans-*peltogynol* (2b) *and its Acetate* (2c).—Fraction S_1 following methylation and isolation (R_F 0.32) as for the *cis,cis*-isomer, yielded also (−)-*cis,trans*-peltogynol trimethyl ether as a white amorphous product (26.1 mg); M^+ 344; $J_{2,3}$ 1.2 Hz, $J_{3,4}$ 2.8 Hz. Subsequent acetylation produced the monoacetate (2c) which crystallized from EtOH as colourless *needles* (19.2 mg), m.p. 175 °C (Found: M^+, 386.136. Calc. for $C_{21}H_{22}O_7$: *M*, 386.136); M^+ 386, fragmentation virtually identical to that of *cis,cis*-tri-*O*-methylpeltogynol-acetate (2f); $[\alpha]_D^{20}$ −154° (*c* 0.51 in $CHCl_3$); τ($CDCl_3$) 2.67 (1 H, d, *J* 8.8 Hz, H-5), 2.95 (1 H, s, H-6'), 3.39 (1 H, d, *J* 2.0 Hz, H-8), 3.43 (1 H, dd, *J* 8.8 Hz, *J* 2.0 Hz, H-6), 3.52 (1 H, s, H-3'), 4.02 (1 H, d, *J* 2.8 Hz, H-4), 5.10 (4 H, s, H-2, H-3, OCH_2), 6.04 (3 H, s, OMe), 6.11 (3 H, s, OMe), 6.25 (3 H, s, OMe), 7.92 (3 H, s, OAc).

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