Metabolites from the Purple Heartwoods of the Mimosoideae. Part 4.† *Acacia fasciculifera* F. Muell ex. Benth: Fasciculiferin, Fasciculiferol, and the Synthesis of 7-Aryl- and 7-Flavanyl-peltogynoids

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Structural examination of the heartwood metabolites of *Acacia fasciculifera* revealed the presence of fasciculiferin, a novel peltogynoid, and fasciculiferol, a dibenzo-α-pyrone, in addition to known flavonoids, peltogynoids, and biflavanoids.

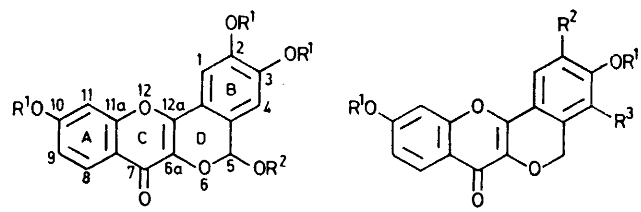
Synthesis of 7-aryl- and 7-flavanyl-peltogynoids as model tannins from peltogynol requires increasingly drastic conditions with decrease of nucleophilicity of the substrate. These condensations come progressively under thermodynamic control and proceed with greater difficulty than those involving the flavan-3,4-diol analogue.

THE 'arrested' metabolic pool represented in the heartwood of *Acacia fasciculifera* contains known flavonoids ‡ based on the 3′,4′,7-trihydroxy-substitution pattern or its equivalent: 3′,4′,7-trihydroxyflavone, fisetin (flavonol), (+)-2,3-*trans*-fustin (dihydroflavonol), (±)-butin (flavanone), 2-benzyl-2,3′,4′,6-tetrahydroxyfuran-3-one, (+)-2,3-*trans*-3,4-*trans*- and (+)-2,3-*trans*-3,4-*cis*-flavan-3,3′,4,4′,7-pentaols (flavan-3,4-diols); also peltogynoids based on the same phenolic pattern, (+)-6a,12a-*trans*-6a,7 *trans*- and (+)-6a,12a-*trans*-6a,7-*cis*-peltogynols, (+) 6a,12a-*trans*-peltogynone (dihydroflavonol analogue), and peltogynin and mopanin (flavonol analogues); and the known biflavanoid-3,4-diols, (+)-2,3-*trans*-3,4-*cis*:2,3-*trans*-3,4-*trans*- (10a) and (+)-2,3-*trans*-3,4-*cis*:2,3-*trans*-3,4-*cis*-[4,6]-(−)-fisetinidol-(+)-leucofisetinidins (11a).

Apart from the biflavanoids, the metabolite composition is broadly similar to that encountered in *A. peuce*,[1] *A. carnei*,[2] and *A. crombei*,[3] notable differences being the relatively low concentrations of peltogynols in *A. fasciculifera*; § this is the first indication in the Mimosoideae of the isomeric mopanoid group which characterizes some of the Anacardiaceae,[4] as evinced by the presence of mopanin;[5a] and only the second isolation of [4,6]-biflavanoids with a 'terminal' flavan-3,4-diol function.[6]

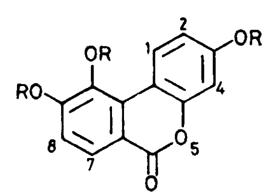
These known compounds are accompanied by the peltogynoid fasciculiferin [7] (1), isolated after methylation as its *O*-ethyl-2,3,10-tri-*O*-methyl derivative (2), and fasciculiferol (6), a dibenzo-α-pyrone. Proof of structure of the derivative (2) is provided by the oxidation of the trimethyl ether of peltogynin with DDQ in ethanol [8] in a one-step synthesis (4) ⟶ (2). The *O*-ethyl ether isolated from *A. fasciculifera* is considered to represent an artefact originating from the hydroxypeltogynin (1) due to handling in ethanol during preparative paper chromatography, thus providing indirect evidence of the presence of the parent compound. Fasciculiferin (1) represents the first peltogynoid with an intermediate stage of oxidation of the methylene function of the D-ring.[7]

The second novel compound, fasciculiferol (6), isolated

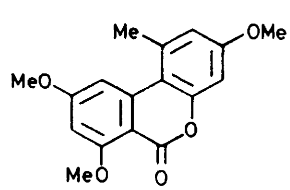


(1) R¹ = R² = H
(2) R¹ = Me, R² = Et
(3) R¹ = R³ = H, R² = OH
(4) R¹ = Me, R² = OMe, R³ = H
(5) R¹ = R² = H, R³ = OH

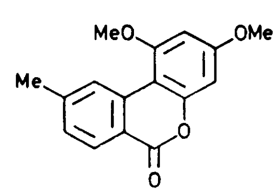
as the tri-*O*-methyl derivative (7), represents a 3,9,10-trihydroxydibenzo-α-pyrone. A carbonyl absorption at 1 720 cm^{-1} in the i.r. spectrum of the methyl ether (7) confirmed the presence of a lactone ring,[9] while the u.v. absorption spectrum was similar to that of the related 3,7,9-tri-*O*-methylalternariol (8).[10] In the n.m.r. spec-



(6) R = H
(7) R = Me



(8)



(9)

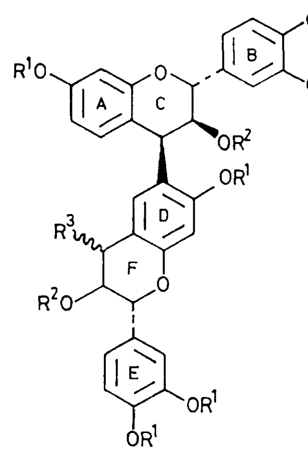
† Part 3 is ref. 3.

‡ Structural formulae of known flavonoids are illustrated in previous papers.[1–5]

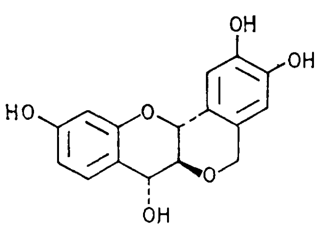
§ The heartwood accordingly exhibits a pale purple-brown rather than the striking purple characteristic of *A. peuce*, *A. carnei*, and *A. crombei*. *A. fasciculifera* is, nevertheless, included in this series since its peltogynoid content differentiates it chemically from related *Acacia* spp. (*cf.* M. D. Tindale and D. G. Roux, *Phytochemistry*, 1974, **13**, 829).

trum H-1 was strongly deshielded by the 10-methoxy-function, the chemical shift (δ 8.66) being in close agreement with that of H-10 of 1,3-dimethoxy-9-methyl-dibenzo-α-pyrone [11] (9) (δ 8.57). Hitherto the natural occurrence of dibenzo-α-pyrones, reputed to possess general cytotoxic properties,[12] was thought to be restricted to moulds of the genus *Alternaria* [10,12] and the plant *Eutomis autumnalis* Graeb. (Liliaceae).[13] Fasciculiferol is accordingly the second example of the occurrence of dibenzo-α-pyrones in higher plants.

However, our main interest centred around the isolation of two biflavanoids which proved to be known [6]



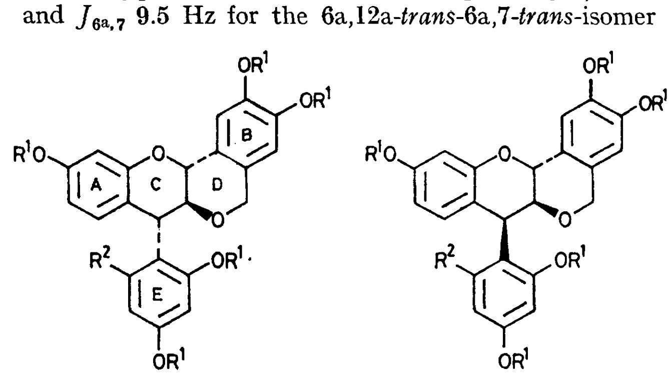
(10a)	$R^1 = R^2 = H$,	R^3 = ---OH	(3,4-*trans*)
(10b)	R^1 = Me, R^2 = Ac,	R^3 = ---OAc	(3,4-*trans*)
(11a)	$R^1 = R^2 = H$,	R^3 = ▬OH	(3,4-*cis*)
(11b)	R^1 = Me, R^2 = Ac,	R^3 = ▬OAc	(3,4-*cis*)



(12)

compounds, (+)-2,3-*trans*-3,4-*cis*:2,3-*trans*-3,4-*trans*- and (+)-2,3-*trans*-3,4-*cis*:2,3-*trans*-3,4-*cis*-[4,6]-(−)-fisetinidol-(+)-leucofisetinidin (10a) and (11a), and an assessment of the possible formation of related biflavanoids based on (+)-peltogynol. The latter aspect follows from the proposal [14,15] that flavan-3,4-diols (*via* 4-carbocations) and nucleophilic flavan-3-ols (or flavan-3,4-diols) represent the direct precursors of biflavanoids. This is apparently illustrated also in the present case by their association with (+)-2,3-*trans*-3,4-*trans*- and (+)-2,3-*trans*-3,4-*cis*-3′,4′,7-trihydroxyflavan-3,4-diol 'precursors'. Peltogynol (12) when considered as a flavan-4-ol has a similar potential for forming biflavanoids in which the peltogynoid moiety constitutes the 'upper' unit. This is now assessed by adopting the same synthetic approach as developed in these laboratories for the formation of 4-aryl- [16] and 4-flavanyl-flavan-3-ols.[17]

In order to establish the optimum reaction conditions required for the formation of 7-flavanylpeltogynans, (+)-peltogynol (12) was initially condensed with phloroglucinol and resorcinol, respectively. No reaction was observed under conditions (0.1M HCl, 20 °C, 1 h) used by Botha *et al.*[16,17] for similar condensations with the (+)-flavan-3,4-diol analogue. Reaction with phloroglucinol under more vigorous conditions (2M HCl, 40 °C, 2 h) gives two products, (6a*S*,7*S*,12a*R*)- and (6a*S*,7*R*,12a*R*)-2,3,10-trihydroxy-7-(2,4,6-trihydroxyphenyl)-peltogynans [(13) and (17)], characterized as the methyl ethers [(14) and (18)], each in 10% yield. Their stereochemistry is evident from the coupling constants of the C-ring protons derived from n.m.r. spectra [$J_{6a,12a}$ 9.0 and $J_{6a,7}$ 9.5 Hz for the 6a,12a-*trans*-6a,7-*trans*-isomer

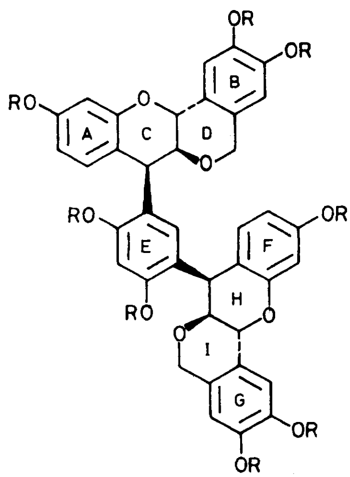


(13)	R^1 = H, R^2 = OH	(17)
(14)	R^1 = Me, R^2 = OMe	(18)
(15)	$R^1 = R^2$ = H	(19)
(16)	R^1 = Me, R^2 = H	(20)

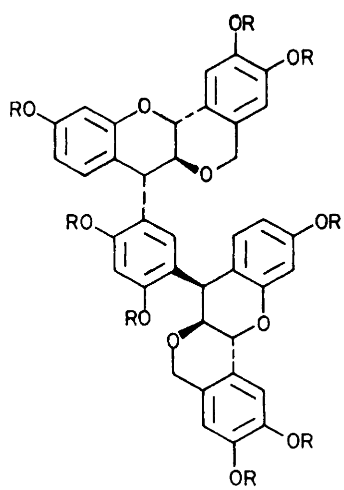
(14); $J_{6a,12a}$ 9.5 and $J_{6a,7}$ 7.0 Hz for the 6a,12a-*trans*-6a,7-*cis*-isomer (18)], and from the negative and positive high-amplitude Cotton effects respectively at *ca.* 240 nm.[16,17] Formation of these isomers in equal proportions contrasts with the stereoselectivity of the same reaction with flavan-3,4-diols, in which the 2,3-*trans*-3,4-*trans*-diastereoisomer predominates.[16,17] The loss of stereoselectivity may be due to the more drastic conditions which puts the reaction partly under thermodynamic control.

The same reaction performed with resorcinol, necessitating more drastic conditions (2M HCl, 60 °C, 4 h), generates two expected products [(15) and (19)], as well as two compounds [(21 and (23)] which originate from the condensation of two peltogynan moieties with a single resorcinol unit. The compounds were isolated as the corresponding methyl ethers in yields of 4% (16), 9% (20), 3% (22), and 3% (24). The predominance of the more stable 6a,7-*cis*- configuration in both pairs of structural types indicates that the reaction is mainly under thermodynamic control. The compounds were readily identified by n.m.r. and mass spectrometry of the methyl ethers, the mass spectra of the bis-peltogynan derivatives (22) and (24) being characterized (*a*) by retro-

Diels–Alder fragmentation, and (*b*) by subsequent loss of a methoxy-group [18] (*cf.* ions at *m/e* 599 and 567, respectively). The structural symmetry of compound (22) is evident from its ^{1}H n.m.r. spectrum, indicating that both peltogynan units attached to resorcinol must have the same stereochemistry. The assigned stereochemistry (6a*S*,7*S*,12a*R*) follows from coupling constants ($J_{6a,12a}$ 10.0



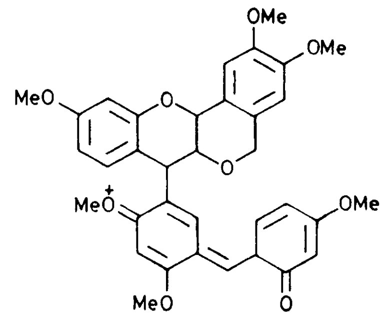
(21) R = H
(22) R = Me



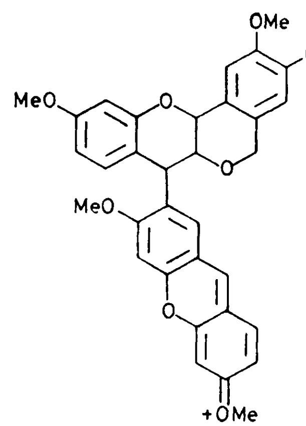
(23) R = H
(24) R = Me

$J_{6a,7}$ 5.0 Hz) and the circular dichroism spectrum where the sign of the high-intensity and low-wavelength (*ca.* 240 nm) Cotton effect is the same, but its amplitude is double that of (6a*S*,7*S*,12a*R*)-2,3,10-trimethoxy-7-(2,4-dimethoxyphenyl)peltogynan (20). The formation of bis-peltogynan derivatives of resorcinol [(21) and (23)] could be attributed to inadequate excess of the nucleophile (resorcinol) (although similar molar proportions were used as in the condensation with phloroglucinol), or to the relatively drastic reaction conditions required for reaction.

Condensations of (+)-peltogynol (12) with (+)-catechin (25) and with (−)-fisetinidol (26) were found to proceed best under conditions approximating to those

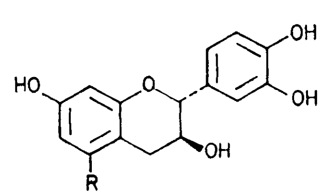


m/e 599
(a)



m/e 567
(b)

established for phloroglucinol and resorcinol, respectively, but with reduced yields in both instances. The two products [(27) and (29)] of the reaction of (+)-peltogynol with (+)-catechin were characterized as their methyl ether acetates [(28) and (30)], obtained in 8 and 9% yields, respectively. The one-proton singlets (δ 6.14) represented in the n.m.r. spectra of (28) and (30) are

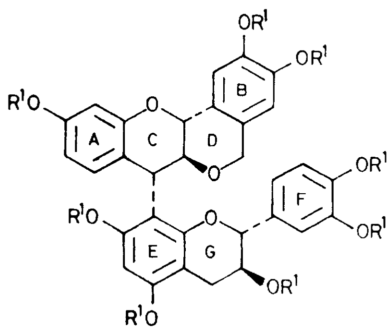


(25) R = OH
(26) R = H

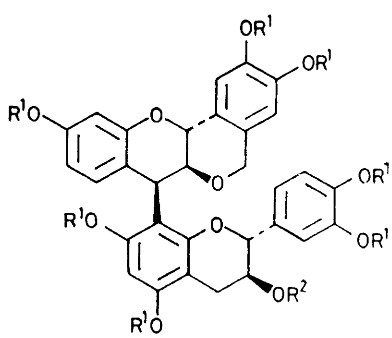
attributable [19] to H-6 (E-rings), and the peltogynan-type biflavanoids are accordingly [7,8]-linked. Their relative and absolute stereochemistry [6a,12a-*trans*-6a,7-*trans*:2′,3′-*trans*, (6a*S*,7*S*,12a*R*:2′*R*,3′*S*) (28); and 6a,12a-

trans-6a,7-*cis*:2′,-3′-*trans*, (6a*S*,7*R*,12a*R*:2′*R*,3′*S*) (30)] follows from coupling constants [$J_{6a,12}$ 10.0, $J_{6a,7}$ 8.0 Hz for (28); and $J_{6a,12a}$ 8.0, $J_{6a,7}$ 2.5 Hz for (30)]. The regiospecificity of this reaction contrasts somewhat with the course of analogous reactions involving flavan-3,4-diols where both [4,8] and [4,6] coupling occurs, albeit in low yields in the latter instance. The lack of stereoselectivity is in line with that observed for phloroglucinol as the nucleophile under identical conditions.

Condensation of (+)-peltogynol (12) with (−)-fisetinidol (26) necessitated more drastic conditions (1M HCl, 60 °C, 8 h) than those applicable with resorcinol, with consequent halving of the yields of the biflavanoids (31) and (33), reflected in the yields of the methyl ether acetates (32) and (34) (2% each).



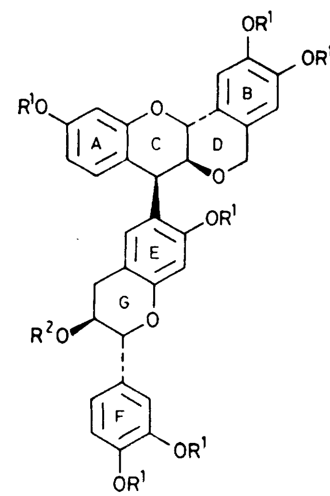
(27) $R^1 = R^2 = H$
(28) $R^1 = Me$, $R^2 = Ac$



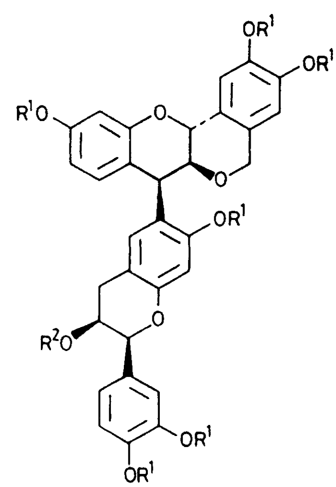
(29) $R^1 = R^2 = H$
(30) $R^1 = Me$, $R^2 = Ac$

The relative and absolute stereochemistry of the derivatives [6a,12a-*trans*-6a,7-*cis*:2′,3′-*trans*, (6a*S*,7*S*,12a*R*:2′*R*,-3′*S*) (32); and 6a,12a-*trans*-6a,7-*cis*:2′,3′-*cis*; (6a*S*,7*S*,-12a*R*:2′*S*,-3′*S*) (34)] is clearly defined by the coupling constants in the ^1H n.m.r. spectra [$J_{6a,12a}$ 9.7, $J_{6a,7}$ 6.3 Hz (C-rings in both cases); and $J_{2',3'}$ 7.5 Hz in (32) and $J_{2',3'}$ < 1 Hz (34) (G-rings)]. Notable are the resultant stable 6a,7-*cis* configurations at the point of coupling in both compounds, indicative of a reaction under thermodynamic control, and also the epimerization of the 'lower' (−)-fisetinidol to a (+)-epifisetinidol unit [4] under the conditions required for reaction. The aromatic regions of the 500-MHz spectra of the methyl ether acetates (32) and (34) exhibit, in addition to singlet resonances at low (δ 7.23, 7.26) and high (δ 6.44, 6.44) field attributed to H-1 and H-4 (B-rings) of the peltogynan units, second pairs of singlets assigned to H-8 (δ 6.53, 6.57) and H-5 (δ 6.49, 6.53) (E-rings) of the fisetinidol units, thus defining the anticipated [6,7] inter-flavanoids bonds in both instances.

Noteworthy is the exceptional magnetic non-equivalence of 2- and 6-methoxyl and 3- and 5-proton



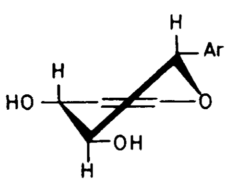
(31) $R^1 = R^2 = H$
(32) $R^1 = Me$, $R^2 = Ac$



(33) $R^1 = R^2 = H$
(34) $R^1 = Me$, $R^2 = Ac$

resonances of the 7-aryl E-rings of the 7-phloroglucinol-peltogynan methyl ethers (14) and (18), resonances which coalesce at higher temperatures. In the absence of line-broadening such non-equivalence at ambient temperatures is indicative of higher energy barriers to rotation in these 7-arylpeltogynans than in their 4-arylflavan-3-ol counterparts,[16] and possibly reflects the conformational rigidity of the heterocyclic C-ring of the former compared with corresponding conformational mobility of the latter class of compounds.

All condensations involving (+)-peltogynol (12) require conditions which are considerably more severe than those which lead to facile reaction of flavan-3,4-diols with the same nucleophile units.[16,17] This implies that generation of 7-carbocations occurs with greater difficulty in the case of peltogynols compared with the 4-carbocations of flavan-3,4-diols, and that reasons could be sought in differences in functionality and conformational stability of their C-rings. Thus, although the preferred conformation of the C-ring in flavan-3,4-diols is a half-chair [20] (35), contributions by the boat (36) and inverted half-chair (37) forms are feasible. In both the last-mentioned conformations the 3-hydroxy-group, located axially and therefore coplanar with the *p*-orbital of the forming carbocation (itself stabilized by alignment with the *p*-orbitals of the A-ring), may be involved in neighbouring-group participation, hence decreasing the activation energy required for condensation. By contrast the C-ring of (+)-peltogynol is not only restricted by the D-ring to a half-chair conformation (38)



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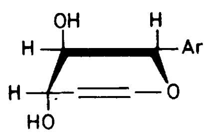

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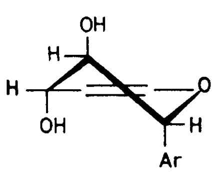

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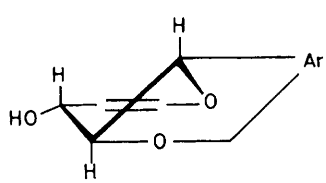

(38)

with the vacant *p*-orbital of the resultant 7-carbocation intermediate in the equatorial position, but in the absence of a 3-hydroxy-function (due to its replacement by an ether bridge) no neighbouring-group participation is possible during condensation. Coupled with this the higher temperature requirements for condensations with peltogynol lead to reactions which fall mainly under thermodynamic control compared with predominantly kinetic control [16] for similar couplings with flavan-3,4-diols.

Chromatographic comparison of the free phenolic forms of synthetic 7-flavanylpentogynans with the methanolic extracts of *A. fasciculifera*, *A. peuce*, *A. crombei*, and *A. carnei* indicates the absence of these compounds in the heartwoods. Their absence may be attributed to the high energy requirements for generating the peltogynoid carbocation, based on the foregoing *in vitro* studies.

EXPERIMENTAL

N.m.r. spectra were recorded for solutions in deuteriated chloroform ($SiMe_4$ as internal reference), u.v. spectra for solutions in methanol, and i.r. spectra for solutions in chloroform. Mass spectra were obtained with a Varian CH-5 instrument; c.d. determinations with a JASCO J-20 spectropolarimeter; specific rotations with a Bendix-NPL Automatic Polarimeter Type 132; and ^1H n.m.r. spectra with Bruker WP-80 and WM-500 Fourier-transform n.m.r. spectrometers.

Systems used for separation of components comprise Whatman No. 3 paper [preparative paper chromatography (p.p.c.)], Merck silica gel 60 (column chromatography), and Merck silica gel 60 PF_{254} [preparative thin layer chromatography (p.l.c.)]. T.l.c. bands were located by u.v. illumination and $HCHO–H_2SO_4$ spray reagent. Melting points are uncorrected.

The mass-spectral fragmentation data for compounds (14), (18), (16), (20), (22), (24), (28), (30), (32), and (34) are deposited as Supplementary Publication No. SUP 23060 (9 pp.).*

Isolation of Constituents from A. fasciculifera.—Drillings (1.9 kg) from the heartwood of *A. fasciculifera*, collected north of Rockhampton, Queensland, Australia, and kindly supplied by Dr. M. D. Tindale, Royal Botanic Gardens and National Herbarium, Sydney, were extracted with MeOH (6 × 1 l) at room temperature for 6 consecutive days, producing a brown solid (80 g) on evaporation of the combined extracts. The mixture was divided into 5 subfractions (fractions 1—5) with a 'Quickfit (Model 20) Steady State Distribution' apparatus [solvent, H_2O–butan-2-ol–n-hexane (5 : 3 : 2 v/v)]. After 150 transfers five fractions resulted; fractions 1 (tubes 28—67), 2 (68—81), 3 (82—99), 4 (100—132), and 5 (133—147).

Fraction 1 (4.65 g) was fractionated by p.p.c., using ascending development in 2% (v/v) aqueous AcOH. Three bands yielded fractions A_1—A_3 [R_F 0.71 (0.40 g), 0.48 (0.41 g), and 0.10 (2.10 g), respectively] on elution and evaporation. Fraction A_3 was a complex mixture of components.

(+)-trans-*Fustin*.—Fraction A_1 crystallized from water as colourless needles (350 mg), m.p. 227 °C (lit.,[21] 228 °C), c.d. (*c* 0.0618) $[\theta]_{350}$ 0, $[\theta]_{330}$ 7 700, $[\theta]_{318}$ 0, $[\theta]_{300}$ −21 000, $[\theta]_{275}$ 0, $[\theta]_{265}$ 5 800, and $[\theta]_{246}$ 0.

(±)-3′,4′,7-*Tri*-O-*methylbutin*.—Methylation of fraction A_2 (diazomethane) yielded colourless needles (MeOH), m.p. 118—120 °C (lit.,[22] 115 °C), $[\alpha]_D$ 0.

2-*Benzyl*-2,3′,4′-6-*tetramethoxyfuran*-3-*one*.—P.p.c. of fraction 2 (8.0 g) yielded subfractions B_1—B_3 [R_F 0.74 (1.5 g), 0.55 (3.0 g), 0.16 (2.4 g), respectively]. Fraction B_2 consisted of fustin (3.0 g). Methylation of fraction B_1 (diazomethane) yielded a light yellow oil,[5b] c.d. (*c* 0.0912) $[\theta]_{350}$ 0, $[\theta]_{325}$ 300, $[\theta]_{310}$ 0, $[\theta]_{280}$ 2 500, $[\theta]_{260}$ 700, and $[\theta]_{240}$ 0.

Fraction B_3 was identical to fraction A_3. After combination these fractions were methylated (diazomethane) and separated by column chromatography [benzene–acetone (4 : 1)] into 6 sub-fractions (C_1—C_6) with retention times 36, 42, 50, 63, 70, and 80 h, respectively, at a flow rate of *ca.* 20 ml h^{-1}.

3,9,10-*Trimethoxydibenzo*[b,d]*pyran*-6-*one* (7).—Crystallization of fraction C_1 from methanol yielded *white needles* (50 mg), m.p. 196 °C (Found: C, 67.0; H, 4.9. $C_{16}H_{14}O_5$ requires C, 67.1; H, 4.9%); *m/e* 286 (98%, M^+), 271 (100),

* For details see Notice to Authors No. 7, *J. Chem. Soc.*, *Perkin Trans. 1*, 1980, Index issue.

256 (13), 228 (22), 200 (11), 185 (16), 184 (19), and 127 (17); $\lambda_{max.}$ (log ε) 330 (6.04), 300 (6.23), 287 (6.26), and 260 (6.45); $\nu_{max.}$ 1 730 cm^{-1}; δ 8.66 (d, *J* 8.7 Hz, H-1), 8.14 (d, *J* 8.7 Hz, H-7), 6.96 (d, *J* 8.7 Hz, H-8), 6.78 (dd, *J* 8.7 and 2.5 Hz, H-2), 6.73 (d, *J* 2.5 Hz, H-4), and 3.94, 3.84, 3.81 (s, 3 × OMe).

(+)-2,3,10-*Tri*-O-*methylpeltogynone*.—Fraction C_2 (200 mg) was re-chromatographed [p.l.c., dichloroethane–acetone (9 : 1)]. The compound of higher R_F value (R_F 0.50) crystallized from methanol to yield (+)-2,3,10-tri-*O*-methylpeltogynone as colourless needles (30 mg), m.p. 212 °C (lit.,[23] 211—213 °C), c.d. (*c* 0.0716) $[\theta]_{350}$ 0, $[\theta]_{322}$ 23 200, $[\theta]_{305}$ 0, $[\theta]_{288}$ −12 900, $[\theta]_{274}$ 0, $[\theta]_{262}$ 9 300, $[\theta]_{245}$ 5 900, $[\theta]_{225}$ 40 600, and $[\theta]_{207}$ 0.

3,3′,4′,7-*Tetra*-O-*methylfisetin*.—The second compound (R_F 0.37) crystallized from acetone as colourless needles (50 mg), m.p. 154 °C (lit.,[5a] 152 °C). Fraction C_3 (400 mg) also consisted of 3,3′,4′,7-tetra-*O*-methylfisetin.

3,4,10-*Tri*-O-*methylmopanin*.—P.l.c. separation [$CHCl_3$–acetone (19 : 1)] of fraction C_4 (150 mg) yielded 3,3′,4′,7-tetra-*O*-methylfisetin (80 mg, R_F 0.75) and 3,4,10-tri-*O*-methylmopanin (30 mg, R_F 0.70), m.p. 191 °C (lit.,[5a] 190 °C).

3′,4′,7-*Trimethoxyflavone*.—Fraction C_5 (300 mg) was re-chromatographed [t.l.c., benzene–ethyl acetate (7 : 3)] to yield two compounds. The compound of higher R_F value (R_F 0.30) crystallized from methanol as colourless needles (200 mg), m.p. 176—178 °C (lit.,[24] 176 °C).

5-*Ethoxy*-2,3,10-*trimethoxy*-[1]*benzopyrano*[3,2-c][2]-*benzopyran*-7(5H)-*one* (2) *and its Synthesis*.—The second compound (R_F 0.25) was isolated as a *colourless amorphous solid* (30 mg), m.p. 160 °C (Found: M^+, 384.120. $C_{21}H_{20}O_7$ requires *M*, 384.121); *m/e* 384 (19%, M^+), 339 (100), 312 (15), 192 (10), 151 (14), and 109 (26); $[\alpha]_D$ 0; δ 8.10 (d, *J* 8.7 Hz, H-8), 7.28 (s, H-1), 6.88 (d, *J* 2.0 Hz, H-11), 6.85 (dd, *J* 8.7 and 2.0 Hz, H-9), 6.76 (s, H-4), 6.03 (s, H-5), 3.97, 3.92, 3.87 (s, 3 × OMe), 3.75 (q, *J* 7.5 Hz, OCH_2Me), and 1.18 (t, *J* 7.5 Hz, OCH_2Me).

Synthesis of the compound was achieved (*cf.* ref. 8) by slow addition of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (70 mg) to a solution of 2,3,10-tri-*O*-methylpeltogynin (100 mg) in benzene–ethanol (50.5 ml, 50 : 1 v/v). After refluxing for 1 h and p.l.c. [benzene–acetone (8 : 2 v/v) the resultant product (R_F 0.42, 30 mg) proved to be identical to that derived from *A. fasciculifera*.

2,3,10-*Tri*-O-*methylpeltogynin*.—Fraction C_6 was crystallized from ethanol to yield 2,3,10-tri-*O*-methylpeltogynin as yellow needles (300 mg), m.p. 158 °C (lit.,[5a] 160 °C).

(+)-2,3,10-*Tri*-O-*methylpeltogynol B*.—Fraction 3 (3.0 g) was chromatographed (ascending p.p.c., 2% AcOH) to yield two compounds (R_F 0.29, 0.30 g; R_F 0.22, 0.65 g respectively) which were characterized as their methyl ethers. Methylation (diazomethane) of the more polar compound yielded 2,3,10-tri-*O*-methylpeltogynol B as colourless needles (MeOH), m.p. 141 °C (lit.,[23] 140 °C); $[\alpha]_D$ +240° (lit.,[23] $[\alpha]_D$ +270°).

(+)-2,3,10-*Tri*-O-*methylpeltogynol*.—The second compound was methylated (diazomethane) to yield 2,3,10-tri-*O*-methylpeltogynol as colourless needles (MeOH), m.p. 200 °C (lit.,[4] 200 °C); $[\alpha]_D$ +253° (lit.,[23] $[\alpha]_D$ +250°).

(+)-2,3-trans-3,4-cis-3′,4′,7-*Trimethoxyflavan*-3,4-*diol*.—A portion (300 mg) of fraction 4 (2 g) was methylated (diazomethane) and chromatographed [p.l.c., dichloroethane–acetone (19 : 1)] to yield two compounds. The less polar compound (R_F 0.30), 2,3-*trans*-3,4-*cis*-3′,4′,7-trimethoxyflavan-3,4-diol, crystallized from methanol as colourless needles (50 mg), m.p. 186 °C (lit.,[25] 178.5 °C); $[\alpha]_D$ +38° lit.,[25] $[\alpha]_D$ +40°). N.m.r. and mass spectra were identical to those of an authentic specimen.[25]

(+)-2,3-trans-3,4-trans-3′,4′,7-*Trimethoxyflavan*-3,4-*diol*.—The second compound (R_F 0.28) was obtained as colourless needles (53 mg), m.p. 128 °C (lit.,[26] 129 °C); $[\alpha]_D$ −6.0° (lit.,[26] $[\alpha]_D$ −9.35°).

(+)-2,3-trans-3,4-cis-3-*Acetoxy*-4-(2,3-trans-3,4-trans-3,4-*diacetoxy*-3′,4′,7-*trimethoxyflavan*-6-*yl*)-3′,4′,7-*trimethoxyflavan* (10b).—Following methylation (diazomethane) and acetylation (Ac_2O–pyridine), fraction 5 (500 mg) was separated [p.l.c., benzene–ethyl acetate (9 : 1), 4×] into two compounds. The less polar substance (R_F 0.46) was isolated as an amorphous solid (20 mg), m.p. 112 °C (lit.,[6] 115 °C), c.d. (*c* 0.0520) $[\theta]_{300}$ 0, $[\theta]_{285}$ −6 700, $[\theta]_{270}$ 0, $[\theta]_{235}$ 35 600, $[\theta]_{215}$ 0.

(+)-2,3-trans-3,4-cis-3-*Acetoxy*-4-(2,3-trans-3,4-cis-3,4-*diacetoxy*-3′,4′,7-*trimethoxyflavan*-6-*yl*)-3′,4′,7-*trimethoxyflavan* (11b).—The second compound (R_F 0.37) was obtained as a colourless amorphous solid, m.p. 110 °C (lit.,[6] 125—127 °C), c.d. (*c* 0.0560) $[\theta]_{300}$ 0, $[\theta]_{285}$ −8 300, $[\theta]_{272}$ 0, $[\theta]_{235}$ 89 600, and $[\theta]_{215}$ 0.

N.m.r. and mass spectra of both biflavanoid derivatives (10b) and (11b) were identical to those of their known counterparts.[6]

Synthesis of 7-Aryl- and 7-Flavanyl-peltogynans

Acid-catalysed Condensation of (+)-6a,12a-trans-6a,7-trans-5,6a,7,12-*Tetrahydro*-[1]*benzopyrano*[3,2-c][2]*benzopyran*-2,3,7,10-*tetraol with Phloroglucinol*.—Compound (12) (300 mg) and phloroglucinol (260 mg), dissolved in methanol (5 ml), were treated with 2M hydrochloric acid (5 ml) at 40 °C for 2 h. After addition of water (50 ml), the solution was extracted with ethyl acetate (3 × 50 ml), the combined extracts dried (Na_2SO_4), and the solvent removed. The single fraction obtained [p.l.c., benzene–acetone–methanol (7 : 2 : 1), R_F 0.80) on methylation yielded two components [p.l.c., chloroform–acetone (98 : 2)].

(6a*S*,7*S*,12a*R*)-6a,12a-trans-6a,7-trans-2,3,10-*Trimethoxy*-7-(2,4,6-*trimethoxyphenyl*)-5,6a,7,12a-*tetrahydro*-[1]*benzopyrano*[3,2-c][2]*benzopyran* (14).—The compound with R_F 0.90 was obtained as a *colourless amorphous solid* (40 mg, 10%), m.p. 89 °C (Found: M^+, 494.196. $C_{28}H_{30}O_8$ requires *M*, 494.194); c.d. (*c* 0.0764) $[\theta]_{300}$ 0, $[\theta]_{280}$ −6 500, $[\theta]_{277}$ 0, $[\theta]_{265}$ 5 800, $[\theta]_{248}$ 0, $[\theta]_{237}$ −12 900, $[\theta]_{230}$ 0, $[\theta]_{220}$ 8 100, and $[\theta]_{210}$ 0; δ 7.11 (s, H-1), 6.56—6.25 (m, H-4, H-8, H-9, and H-11), 6.15 [d, *J* 2.5 Hz, H-3 or H-5 (E)], 6.00 [d, *J* 2.5 Hz, H-3 or H-5 (E)], 4.87 (d, *J* 9.0 Hz, H-12a), 4.72 (d, *J* 9.5 Hz, H-7), 4.60 [s, 5-CH_2], 4.31 (dd, *J* 9.0 and 8.0 Hz, H-6a), and 3.90, 3.81, 3.78, 3.75, 3.72, 3.31 (s, 6 × OMe).

(6a*S*,7*R*,12a*R*)-6a,12a-trans-6a,7-cis-2,3,10-*Trimethoxy*-7-(2,4,6-*trimethoxyphenyl*)-5,6a,7,12a-*tetrahydro*-[1]*benzopyrano*[3,2-c][2]*benzopyran* (18).—The second compound (R_F 0.85) was isolated as a *colourless amorphous solid* (40 mg, 10%), m.p. 94 °C (Found: M^+, 494.195. $C_{28}H_{30}O_8$ requires *M*, 494.194); c.d. (*c* 0.0740) $[\theta]_{300}$ 0, $[\theta]_{280}$ 6 700, $[\theta]_{260}$ 0, $[\theta]_{237}$ 70 700, and $[\theta]_{205}$ 0; δ 7.09 (s, H-1), 6.65 (d, *J* 8.7 Hz, H-8), 6.28 (d, *J* 2.5 Hz, H-11), 6.31 (s, H-4), 6.24 (dd, *J* 8.7 and 2.5 Hz, H-9), 6.10 [d, *J* 2.5 Hz, H-3 or H-5 (E)], 5.92 [d, *J* 2.5 Hz, H-3 or H-5 (E)], 5.23 (d, *J* 9.5 Hz, H-12a), 4.92 (d, *J* 7.0 Hz, H-7), 4.78 [d, *J* 13.7 Hz, H_{eq}-5], 4.56 [d, *J* 13.7 Hz, H_{ax}-5], 3.95 (dd, *J* 10.0 and 7.5 Hz, H-6a), and 3.87, 3.81, 3.75, 3.68, 3.72, 3.25 (s, 6 × OMe).

Acid-catalysed Condensation of Compound (12) [(+)-*Peltogynol*] *with Resorcinol*.—Compound (12) (600 mg) and resorcinol (440 mg) were dissolved in methanol (5 ml) and 2M hydrochloric acid (5 ml). The mixture was refluxed at 60 °C for 4 h. After addition of water (50 ml), the mixture was extracted with ethyl acetate (3 × 50 ml), the combined extracts dried (Na_2SO_4), and the solvent evaporated. Chromatography of the residue [p.l.c., benzene–acetone–methanol (7 : 2 : 1)] yielded two fractions (R_1 and R_2, R_F 0.85 and 0.60, respectively). Both fractions were methylated and re-purified by chromatography [p.l.c.; R_1, dichloroethane–acetone (9 : 1); R_2, benzene–ethyl acetate (9 : 1), 2×].

(6a*S*,7*R*,12a*R*)-6a,12a-trans-6a,7-trans-2,3,10-*Trimethoxy-7-(2,4-dimethoxyphenyl)*-5,6a,7,12a-*tetrahydro*-[1]*benzopyrano*-[3,2-c][2]*benzopyran* (16).—Compound (16) (R_F 0.58) was isolated from fraction R_1 as a *colourless amorphous solid* (35 mg, 4%), m.p. 94 °C (Found: M^+, 464.185. $C_{27}H_{28}O_7$ requires *M*, 464.183); c.d. (*c* 0.0480) $[\theta]_{300}$ 0, $[\theta]_{265}$ 3 900, $[\theta]_{248}$ 0, $[\theta]_{235}$ −16 400, $[\theta]_{229}$ 0, $[\theta]_{220}$ 8 200, and $[\theta]_{205}$ 0; δ 7.12 (s, H-1), 6.62—6.22 (m, aromatic H), 5.03—4.56 [m, 5-CH_2, H-12a, and H-7], 3.95 (m, H-6a), and 3.90, 3.78, 3.75, 3.72 (s, 5 × OMe).

(6a*S*,7*S*,12a*R*)-2,3-trans-3,4-cis-2,3,10-*Trimethoxy*-4-(2,4-*dimethoxyphenyl*)-5,6a,7,12a-*tetrahydro*-[1]*benzopyrano*-[3,2-c][2]*benzopyran* (20).—The second compound from fraction R_1 (R_F 0.55) was isolated as a *colourless amorphous solid* (80 mg, 9%), m.p. 86 °C (Found: M^+, 464.187. $C_{27}H_{28}O_7$ requires *M*, 464.183); c.d. (*c* 0.06) $[\theta]_{300}$ 0, $[\theta]_{270}$ −4 600, $[\theta]_{245}$ 0, $[\theta]_{235}$ 73 700, $[\theta]_{229}$ 0, $[\theta]_{219}$ 58 400, and $[\theta]_{205}$ 0; δ 7.06 [s, H-1], 7.34 [d, *J* 8.0 Hz, H-8], 6.64 [d, *J* 8.0 Hz, H-6 (E)], 6.46 [d, *J* 2.0 Hz, H-11], 6.37 [d, *J* 2.5 Hz, H-3 (E)], 6.34 [dd, *H* 8.0 and 2.0 Hz, H-9], 6.28 [s, H-4], 6.22 [dd, *J* 8.0 and 2.5 Hz, H-5 (E)], 4.95 [d, *J* 9.4 Hz, H-12a], 4.86 [d, *J* 6.3 Hz, H-7], 4.78 [d, *J* 15.0 Hz, H_{eq}-5], 4.50 [d, *J* 15.0 Hz, H_{ax}-5], 3.95 [dd, *J* 9.4 and 6.3 Hz, H-6a], and 3.84, 3,78, 3,68, 3.72, 3.64 (s, 5 × OMe).

2,4-*Dimethoxy*-1,5-*bis*-[(6a*S*,7*S*,12a*R*)-6a,12a-trans-6a,7-cis-2,3,10-*trimethoxy*-5,6a,7,12-*tetrahydro*-[1]*benzopyrano*-[3,2-c][2]*benzopyran-7-yl*]*benzene* (22).—The less polar compound of fraction R_2 (R_F 0.33) was isolated as a *colourless amorphous solid* (30 mg, 3%), m.p. 147 °C (Found: M^+, 790.303. $C_{46}H_{46}O_{12}$ requires *M*, 790.299); c.d. (*c* 0.0600) $[\theta]_{300}$ 0, $[\theta]_{285}$ −10 500, $[\theta]_{256}$ 0, $[\theta]_{253}$ 156 700, $[\theta]_{217}$ 0, and $[\theta]_{205}$ 26 000; δ 6.86 [s, H-1 (B)], 6.55 [d, *J* 8.7 Hz, H-8 (A)], 6.36 [d, *J* 2.5 Hz, H-11 (A)], 6.36 [s, H-6 (E)], 6.25 [s, H-4 (B)], 6.18 [dd, *J* 8.7 and 2.5 Hz, H-9 (A)], 5.98 [s, H-3 (E)], 4.69 [s, 5-CH_2], 4.58 [d, *J* 6.0 Hz, H-7 (C)], 4.31 [d, *J* 10.0 Hz, H-12a (C)], 3.89 [dd, *J* 10.0 and 5.0 Hz, H-6a (C)], and 3.92, 3.80, 3.77, 3.73 (s, 8 × OMe).

2,4-*Dimethoxy*-1-[(6a*S*,7*R*,12a*R*)-6a,12a-trans-6a,7-cis-2,3,10-*trimethoxy*-5,6a,7,12a-*tetrahydro*-[1]*benzopyrano*[3,2-c][2]*benzopyran-7-yl*]-5-[(6a*S*,7*S*,12a*R*)-6a,12a-trans-6a,7-trans-2,3,10-*trimethoxy*-5,6a,7,12-*tetrahydro*-[1]*benzopyrano*[3,2-c][2]*benzopyran-7-yl*]*benzene* (24).—The second compound of fraction R_2 (R_F 0.25) was obtained as a *colourless amorphous solid* (30 mg, 3%), m.p. 150 °C (Found: M^+, 790.301. $C_{46}H_{46}O_{12}$ requires *M*, 790.299); c.d. (*c* 0.0595) $[\theta]_{260}$ 0, $[\theta]_{225}$ 79 500, and $[\theta]_{210}$ 0; δ(C_6D_6) 4.12 [q, ΣJ_s 14.1 Hz, H-6a (H) and q, ΣJ_s 17.5 Hz, H-6a (C)], 4.41 [br s, 5-CH_2], 4.48 [d, *J* 8.5 Hz, H-7 (C)], 4.53 [dd, *J* 16.5 Hz, CH_2 (I)], 4.94 [d, *J* 9.0 Hz, H-12a (C)], 5.25 [d, *J* 5.6 Hz, H-7 (H)], 5.56 [d, *J* 8.5 Hz, H-12a (H)].

Acid-catalysed Condensation of Compound (12) [(+)-*Peltogynol*] *with* (2*R*,3*S*)-3,3′,4′,5,7-*Pentahydroxyflavan* [(+)-*Catechin*].—The reaction between compound (12) (1 g) and (+)-catechin (25) (1.9 g) was carried out as described for the reaction with phloroglucinol. The single fraction obtained [p.l.c., benzene–acetone–methanol (6 : 3 : 1)] yielded on methylation and acetylation two compounds [p.l.c., dichloroethane–acetone (9 : 1)].

(6a*S*,7*S*,12a*R*)-6a,12a-trans-6a,7-trans-7-[(2*R*,3*S*)-2,3-trans-3-*Acetoxy*-3′,4′,5,7-*tetramethoxyflavan-8-yl*]-2,3,10-*trimethoxy*-5,6a,7,12-*tetrahydro*-[1]*benzopyrano*[3,2-c][2]*benzopyran* (28).—The less polar compound (R_F 0.52 was obtained as *colourless needles* (MeOH, 150 mg, 8%), m.p. 244 °C (Found: C, 67.1; H, 5.9. $C_{40}H_{42}O_{12}$ requires C, 67.2; H, 5.9%); *m/e* 714 (43%, M^+); c.d. (*c* 0.0522) $[\theta]_{280}$ 0, $[\theta]_{270}$ 4 100, $[\theta]_{253}$ 0, $[\theta]_{235}$ −37 600, and $[\theta]_{215}$ 0; δ 7.00 [s, H-1 (B)], 6.58 [d, *J* 8.0 Hz, H-8 (A)], 6.44—6.22 (m, 5 × aromatic H), 6.14 [s, H-6 (E)], 5.87 [dd, *J* 7.5 and 2.0 Hz, H-6 (F)], 5.03—4.56 [m, H-12a and H-7 (C), 5-CH_2 (D), H-2 and H-3 (G)], 5.52 [dd, *J* 10.0 and 8.0 Hz, H-6a (C)], 3.84, 3.83, 3.76, 3.68, 3.66, 3.59 (s, 7 × OMe), 2.87 [dd, *J* 16.3 and 5.0 Hz, H-4_{eq} (G)], 2.56 [dd, *J* 16.3 and 5.0 Hz, H-4_{ax} (G)], and 1.84 (s, 3-OAc).

(6a*S*,7*R*,12a*R*)-6a,12a-trans-6a,7-cis-7-[(2*R*,3*S*)-2,3-trans-3-*Acetoxy*-3′,4′,5,7-*tetramethoxyflavan-8-yl*]-2,3,10-*trimethoxy*-5,6a,7,12a-*tetrahydro*-[1]*benzopyrano*[3,2-c][2]*benzopyran* (30).—The second compound (R_F 0.45) was isolated as a *colourless amorphous solid* (160 mg, 9%), m.p. 112 °C (Found: M^+, 714.271. $C_{40}H_{42}O_{12}$ requires *M*, 714.268); c.d. (*c* 0.1316) $[\theta]_{300}$ 0, $[\theta]_{285}$ 2 700, $[\theta]_{270}$ 0, $[\theta]_{265}$ −1 600, $[\theta]_{255}$ 0, $[\theta]_{240}$ 37 900, $[\theta]_{220}$ 0, $[\theta]_{210}$ −5 400; δ 6.84 [s, H-1 (B)], 6.75—6.18 (m, 6 × aromatic H), 6.13 [s, H-6 (E)], 5.78 [d, *J* 2.5 Hz, H-2 (F)], 5.31—4.50 [m, 5-CH_2 (D), H-12a and H-7 (C), H-2 and H-3 (G)], 3.97 [dd, *J* 8.0 and 2.5 Hz, H-6a (C)], 3.87, 3.84, 3.81, 3.79, 3,75, 3.67, 3.53 (s, 7 × OMe), 2.75 [dd, *J* 15.0 and 6.0 Hz, H-4_{eq} (G)], and 2.37 [dd, *J* 15.0 and 6.0 Hz, H-4_{ax} (G)].

Acid-catalysed Condensation of Compound (12) [(+)-*Peltogynol*] *with* (2*R*,3*S*)-3,3′,4′,7-*Tetrahydroflavan* (26) [(−)-*Fisetinidol*].—The reaction was carried out as described for resorcinol (60 °C), but with a more prolonged reaction time (8 h). P.l.c. (benzene–acetone–methanol (6 : 3 : 1)] yields a single fraction (R_F 0.40). After methylation (diazomethane) and acetylation two compounds were obtained [p.l.c., benzene–hexane–acetone (5 : 4 : 1)].

(6a*S*,7*R*,12a*R*)-6a,12a-trans-6a,7-cis-7-[(2*R*,3*S*)-2,3-trans-3-*Acetoxy*-3′,4′,7-*trimethoxyflavan-6-yl*]-2,3,10-*trimethoxy*-5,6a,7,12a-*tetrahydro*-[1]*benzopyrano*[3,2-c][2]*benzopyran* (32). The less polar compound (R_F 0.40) was obtained as a *colourless amorphous solid* (13 mg, 2%) (Found: M^+, 684.260. $C_{39}H_{40}O_{11}$ requires *M*, 684.257); c.d. (*c* 0.0596) $[\theta]_{300}$ 0, $[\theta]_{290}$ −2 300, $[\theta]_{279}$ 0, $[\theta]_{260}$ 4 600, $[\theta]_{237}$ 94 100, and $[\theta]_{210}$ 0; δ 7.23 [s, H-1 (B)], 6.89 [dd, *J* 8.0 and 2.0 Hz, H-6 (F)], 6.87 [d, *J* 2.0 Hz, H-2 (F)], 6.83 [d, *J* 8.5 Hz, H-8 (A)], 6.82 [d, *J* 8.0 Hz, H-5 (F)], 6.58 [d, *J* 2.2 Hz, H-11 (A)], 6.53 [s, H-8 (E)], 6.49 [dd, *J* 8.5 and 2.2 Hz, H-9 (A)], 6.49 [s, H-6 (E)], 6.44 [s, H-4 (B)], 5.24 [m, H-3 (G)], 5.07 [d, *J* 9.8 Hz, H-12a (C)], 4.96 [d, *J* 6.3 Hz, H-7 (C)], 4.90 [d, *J* 7.5 Hz, H-2 (G)], 4.88 [d, *J* 14.5 Hz, H_{ax}-5 (D)], 4.68 [d, *J* 14.5 Hz, H_{eq}-5 (D)], 4.05 [dd, *J* 9.8 and 6.3 Hz, H-6a (C)], 3.96, 3.86, 3.85, 3.84, 3.83, 3.80 (s, 6 × OMe), 2.90 [dd, *J* 15.5 and 5.4 Hz, H-4_{eq} (G)], 2.72 [dd, *J* 15.5 and 8.3 Hz, H-4_{ax} (G)], and 1.87 (s, 3-OAc).

(6a*S*,7*S*,12a*R*)-6a,12a-trans-6a,7-cis-7-[(2*S*,3*S*)-2,3-cis-3-*Acetoxy*-3′,4′,7-*trimethoxyflavan-6-yl*]-2,3,10-*trimethoxy*-5,6a,7,12a-*tetrahydro*-[1]*benzopyrano*[3,2-c][2]*benzopyran* (34). The second compound (R_F 0.34) was isolated as a *colourless amorphous solid* (13 mg, 2%) (Found: M^+, 684.258. $C_{39}H_{40}O_{11}$ requires *M*, 684.257); c.d. (*c* 0.0616)

$[\theta]_{300}$ 0, $[\theta]_{299}$ −3 300, $[\theta]_{275}$ 0, $[\theta]_{260}$ 2 200, $[\theta]_{235}$ 72 000, and $[\theta]_{210}$ 0; δ 7.26 [s, H-1 (B)], 6.98 [d, *J* 2 Hz, H-2 (F)], 6.92 [dd, *J* 8.2 and 2 Hz, H-6 (F)], 6.85 [d, *J* 8.5 Hz, H-8 (A)], 6.83 [d, *J* 8.2 Hz, H-5 (F)], 6.59 [d, *J* 2.5 Hz, H-11 (A)], 6.57 [s, H-8 (E)], 6.53 [s, H-6 (E)], 6.50 [dd, *J* 8.5 and 2.5 Hz, H-9 (A)], 6.44 [s, H-4 (B)], 5.3 [m, H-3 (G)], 5.07 [d, *J* 9.7 Hz, H-12a (C)], 4.99 [br s, *J* < 1 Hz, H-2, (G)], 4.96 [d, *J* 6.3 Hz, H-7 (C)], 4.88 [d, *J* 14.7 Hz, H_{ax}-5 (D)], 4.68 [d, *J* 14.7 Hz, H_{eq}-5 (D)], 4.06 [dd, *J* 9.7 and 6.3 Hz, H-6a (C)], 3.97, 3.87 (6H), 3.85, 3.83, 3.81 (s, 6 × OMe), 3.09 [dd, *J* 17.5 and 4.0 Hz, H-4_{eq} (G)], 2.77 [dd, *J* 17.5 and 2.5 Hz, H-4_{ax} (G)], and 1.86 (s, 3-OAc).

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