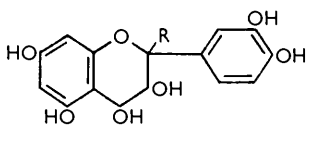
644. *The Constitution of the* leuco*Anthocyanidin, Peltogynol.*

By W. R. Chan, W. G. C. Forsyth, and C. H. Hassall.

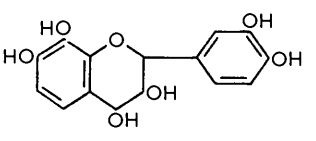
New evidence leads to the proposal that the structure of the *leuco*anthocyanidin peltogynol should be modified to (IV), which relates it to the flavan-3 : 4-diols. The stereochemistry of peltogynol and an isomer, peltogynol B, which accompanies it in the extract of *Peltogyne porphyrocardia*, is discussed.

There is extensive evidence of the occurrence in plant tissue of colourless substances that afford anthocyanidin-like pigments on treatment with acids.[1] There is relatively little direct evidence, however, concerning the molecular structures of these *leuco*anthocyanins and *leuco*anthocyanidins. Robinson and Robinson [1] suggested that *leuco*cyanidin might be formulated as (I). Elucidation [2] of the structure of melacacidin as (II) and the observation that cyanidin chloride is readily formed from the corresponding flavan-3 : 4-diol (III) on treatment with acid [3] in the presence of oxygen, have led to the proposal [2,3] that natural *leuco*anthocyanidins are derivatives of flavan-3 : 4-diols. However, the constitution assigned earlier [4] to peltogynol, a constituent of the heartwood of *Peltogyne porphyrocardia* and the first *leuco*anthocyanidin to be isolated, is at variance with this hypothesis. We have studied some further reactions of peltogynol and suggest the structure (IV) which may be regarded as being derived from a flavan-3 : 4-diol.

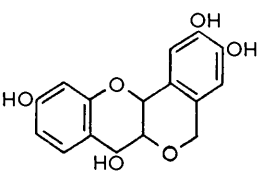


(I) : R = OH

(III) : R = H



(II)



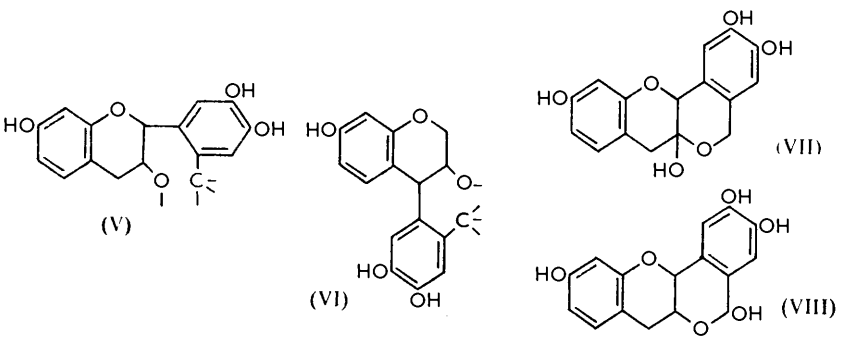
(IV)

Robinson and Robinson's structure [4] (VII) for peltogynol, $C_{16}H_{14}O_6$, was based largely on the following evidence. The substance is optically active. It forms a pyrylium salt. It gives tetra-acyl derivatives but a trimethyl ether which is insoluble in alkali and gives no colour with ferric chloride solution, which suggests that one of the four hydroxyl groups is non-phenolic. As peltogynol gives a 2 : 4-dinitrophenylhydrazone it appears that this hydroxyl group is associated with a semi-acetal structure. Nitric acid oxidises peltogynol to 2 : 4 : 6-trinitroresorcinol, and tri-*O*-methylpeltogynol to 4 : 5-dinitroveratrole, while treatment of tri-*O*-methylpeltogynol with potassium permanganate yields *m*-hemipinic acid, showing that peltogynol contains a resorcinol as well as a catechol nucleus which has

[1] Robinson and Robinson, *Biochem. J.*, 1933, **27**, 206.
[2] King and Bottomley, *J.*, 1954, 1399.
[3] Bauer, Birch, and Hillis, *Chem. and Ind.*, 1954, 433.
[4] Robinson and Robinson, *J.*, 1935, 744.

carbon atoms attached to positions 4 and 5. The similarity of peltogynidin chloride to known anthocyanidins suggested that the skeletons (V) and (VI) should be considered. *X*-Ray data favoured (V) as it was difficult to arrange models based on (VI). The free hydroxyl group of the resorcinol nucleus was placed at position 7 and not 5 in view of the fluorescent properties of the methylated peltogynidin salts. Alternative structures (VII) and (VIII) were suggested but the former was favoured on the grounds that a compound with the structure (VIII) resembles catechin and should, therefore, be relatively resistant to the formation of a flavylium salt.

Although these reactions make it evident that peltogynol contains both a catechol and a resorcinol nucleus in a C_6–C_3–C_6 flavonoid structure they do not define the substitution on the C_3 portion with certainty. It appeared possible that the formation of the 2 : 4-dinitrophenylhydrazone from peltogynol could be attributed to oxidation of an alcohol group in an activated position. We have obtained support for this view from experiments on the oxidation of trimethylpeltogynol with manganese dioxide in chloroform. The product, tri-*O*-methylpeltogynone, $C_{19}H_{18}O_6$, is optically active and gives a cherry-red colour with magnesium–hydrochloric acid. Treatment with sodium borohydride regenerates the original tri-*O*-methylpeltogynol. The infrared absorption spectrum of trimethylpeltogynone shows no maximum in the hydroxyl stretching region but a band

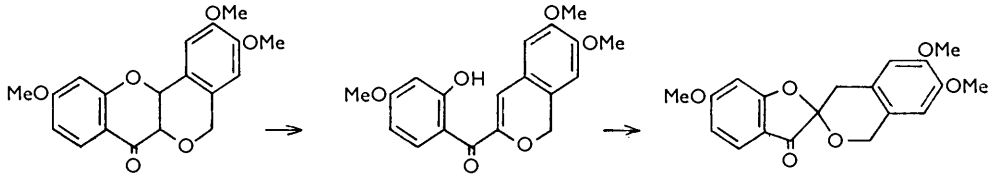


at 1687 cm.$^{-1}$ is in the position expected of a carbonyl group conjugated to an aromatic nucleus and lying in a six-membered ring.[5] The ultraviolet absorption spectrum is typical of compounds in which a carbonyl group is in conjugation with a resorcinol or a phloroglucinol nucleus.[6] This evidence led us to favour the structure (IX) for tri-*O*-methylpeltogynone. In support of this tri-*O*-methylpeltogynol was converted by alkali almost quantitatively into a yellow, alkali-soluble compound $C_{19}H_{18}O_6$ with the properties of the chalcone (X). It gives an alkali-insoluble methylation product $C_{20}H_{20}O_6$ and a colourless dihydro-derivative with ketonic properties. The carbonyl bands in the infrared spectrum of the chalcone and the methylation product are at 1615 and 1650 cm.$^{-1}$ respectively. The shift in wavelength is that expected when comparing a hydrogen-bonded 2′-hydroxychalcone with the corresponding 2′-methoxychalcone.[7] The chalcone was converted by dilute sulphuric acid into an isomer which is assigned structure (XI) on the basis of a negative magnesium–hydrochloric acid test, resistance to acetylation, and an infrared absorption spectrum with no hydroxyl bands but with a carbonyl band [8] at 1720 cm.$^{-1}$.

Oxidation of the chalcone (X) with potassium permanganate yielded 2-hydroxy-4-methoxybenzoic acid. This confirms Robinson and Robinson's placing of the hydroxyl group at position 7.

[5] Shaw and Simpson, *J.*, 1955, 655.
[6] Morton and Sawires, *ibid.*, 1940, 1052; Valyashko and Rozum, *J. Gen. Chem.* (*U.S.S.R.*), 1947, **17**, 783.
[7] Hergert and Kurth, *J. Amer. Chem. Soc.*, 1953, **75**, 1622.
[8] Gutsche, *ibid.*, 1951, **73**, 786.

The new information leads unambiguously to structure (IV) for peltogynol. It could arise biogenetically by condensation of formaldehyde (or its equivalent) with the corresponding flavan-3 : 4-diol.[9] There are various biogenetic schemes in which similar condensations with formaldehyde are postulated.[10] Among flavonoids, peltogynol shares

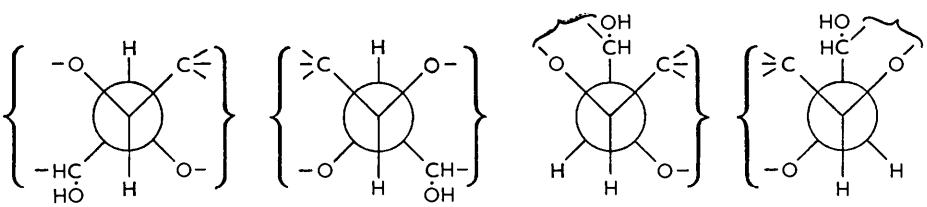


with distemonanthin [11] the unusual attachment of a carbon substituent to the 2′-position of the aromatic ring attached to the benzopyran nucleus.

Attention has already been drawn to the necessity of including an oxidation in the conversion of peltogynol into peltogynidin. There is experimental evidence for this. Hydrolysis of peltogynol with dilute acid, in an inert atmosphere, gives less than 1% of peltogynidin but, in the presence of oxygen, a yield of more than 80% has been obtained.

Aqueous extracts of the heartwood of *Peltogyne porphyrocardia* contain a second *leuco*anthocyanidin, peltogynol B, which yields peltogynidin on treatment with acid. Its relation to peltogynol is clear from oxidation of its trimethyl derivative to tri-*O*-methylpeltogynone: peltogynol and peltogynol B differ only in the mode of attachment of the 4-hydroxyl group. As tri-*O*-methylpeltogynol is formed exclusively when tri-*O*-methylpeltogynone, with a relatively unhindered carbonyl group, is reduced with sodium borohydride, peltogynol must be assigned a constitution with an equatorial 4-hydroxyl group [12] while peltogynol B has an axial 4-hydroxyl group.

The evidence does not permit complete definition of the stereochemistry of the peltogynols. However, it favours limitation to two pairs of isomers (XIIa, b) and (XIIc, d). Peltogynol B, unlike peltogynol, yields peltogynidin when heated in air at the relatively low temperature of 130°. This reaction involves elimination of the axial 4-hydroxyl group. It will occur most readily when the 3-hydrogen atom, the 4-hydroxyl



group, and the 3- and 4-carbon atoms are coplanar.[12] This is achieved when both the 3-hydrogen atom and 4-hydroxyl group have axial conformations. The relation between peltogynol and peltogynol B indicates that peltogynol has also an axial 3-hydrogen atom.

Peltogynol has one of the structures (XIIa—d) in which the 4-hydroxyl group is equatorial; peltogynol B has the corresponding structure with an axial hydroxyl group.

Experimental

M. p.s were determined by means of a Kofler block and are uncorrected. Rotation measurements employed chloroform solutions at 28—30° except where other solvents are specified.

[9] Keppler, *J.*, 1957, 2721; Roux, *Chem. and Ind.*, 1958, 161; White and King, *ibid.*, p. 291.
[10] Robinson, " The Structural Relations of Natural Products," Oxford Univ. Press, 1955; Woodward, *Angew. Chem.*, 1956, **68**, 13.
[11] King, King, and Stokes, *J.*, 1954, 4594.
[12] Barton, *J.*, 1953, 1027.

Ultraviolet spectra were determined for EtOH solutions on a Beckman spectrophotometer, model D.U. Infrared spectra were measured with potassium bromide discs unless otherwise stated. We are grateful to Dr. S. M. Nagy, Massachusetts Institute of Technology, and Dr. H. E. Hallam, University College, Swansea, for the determinations of infrared absorption spectra.

Isolation of Peltogynol and Peltogynol B by Partition Chromatography.—Fresh sawdust (500 g.) of *Peltogyne porphyrocardia* heartwood was stirred with successive amounts of water (8 l., 5 l., 5 l.) on a steam-bath for 20 min. each. The extraction, filtration, and all subsequent operations were carried out in apparatus shielded from light. Paper chromatography on Whatman No. 1 paper with (*A*) butan-1-ol–acetic acid–water (4 : 1 : 5) [13] or with water [14] showed the presence of the two major phenolic components: peltogynol [R_F (H_2O) 0·04; (*A*) 0·45] and peltogynol B [R_F (H_2O) 0·10; (*A*) 0·52]. The phenols were detected with a ferric chloride–potassium ferricyanide spray.[15] Peltogynol and peltogynol B were present in the crude aqueous extract in the ratio 4 : 3 when determined by quantitative paper chromatography with permanganate titration.[16]

The combined extract was added to a column (25 × 10 cm.) of dry cellulose powder (Solka floc.; 200 mesh) which was developed with water. The first 9 l. of eluate contained no peltogynol B and was discarded. The following 5760 c.c. contained only peltogynol B. The following 9240 c.c. contained both peltogynol and peltogynol B, and the final 5020 c.c. contained only peltogynol. Each of the two fractions containing peltogynol B was saturated with sodium chloride and extracted twice with one-quarter of its volume of ethyl acetate. The extracts were dried (Na_2SO_4–$NaHCO_3$, 1 : 1), concentrated under reduced pressure to approximately 150 c.c., and poured into light petroleum (1 l.; b. p. 40—60°). Peltogynol B (2·85 g.), the precipitate from the first fraction, recrystallized from chloroform, containing 2·5% (v/v) of ethanol, as colourless prisms which held chloroform tenaciously even at 100°.

The mixed fraction was worked up for peltogynol by Robinson and Robinson's method.[4] The last aqueous fraction, containing only peltogynol, was directly concentrated *in vacuo* without decomposition. It crystallized from the aqueous concentrate (yield 4·63 g.) and had $[\alpha]_D^{21}$ +273° (*c* 0·6 in ethyl acetate) (Found: C, 63·6; H, 4·7. Calc. for $C_{16}H_{14}O_6$: C, 63·6; H, 4·6%).

Peltogynidin.—Treatment of peltogynol with acid gave two coloured products, peltogynidin and so-called phlobaphen. The yield of peltogynidin was determined in the following way. The solution obtained when peltogynol (10 mg.) was heated with dilute hydrochloric acid was added to a cellulose powder column (10 × 2 cm.) and washed with N-hydrochloric acid (5 × 2 c.c.). The colour was all adsorbed on the top 2 cm. of the column. Butanol (12 c.c.) equilibrated with an equal volume of N-hydrochloric acid was then added. The peltogynidin band separated from the faster-moving phlobaphen band. The column was extruded. The peltogynidin band was cut out and extracted with methanolic 0·1N-hydrochloric acid. The colour intensity of the solution was compared with a standard prepared from crystalline peltogynidin chloride.

The maximum yield (11·5 ± 0·5%) by this procedure was obtained by using 2N-hydrochloric acid for 15 min. at 100°. The production of phlobaphen, but not peltogynidin, was greatly increased by increasing the concentration of acid or the time of heating, or substituting alcoholic for aqueous acid.

However, when oxygen was bubbled through the heated mixture, yields of peltogynidin of over 80% were obtained. When nitrogen was used the yield was less than 1%. Peltogynol and peltogynol B gave very similar yields of peltogynidin.

Peltogynidin gives R_F values on paper which differ from the common anthocyanidins which occur in flower pigments: Butan-1-ol–acetic acid–water (4 : 1 : 5), 0·65; butanol–2N-HCl, 0·38; "Forestal" solvent, 0·72. Unlike the common anthocyanidins it was stable during chromatography in butanol–acetic acid–water. When 100 mg. of peltogynol were boiled with acid as above and chromatographed on a column, crystalline peltogynidin hydrochloride (64 mg.) was recovered (Found: C, 54·3; H, 4·5; Cl, 9·7. Calc. for $C_{16}H_{11}O_5Cl,2H_2O$: C, 54·0; H, 4·2; Cl, 10·0%).

[13] Partridge, *Biochem. J.*, 1948, **42**, 238.
[14] Roberts and Wood, *ibid.*, 1953, **53**, 332.
[15] Barton, Evans, and Gardner, *Nature*, 1952, **170**, 249.
[16] Forsyth, *Biochem. J.*, 1955, **60**, 108.

Tri-O-methylpeltogynol.—This was prepared most conveniently from a crude extract of *Peltogyne porphyrocardia*. It was identical with material prepared from pure peltogynol by Robinson and Robinson's procedure.[4]

The ethyl acetate-soluble fraction was methylated with diazomethane, and purified by chromatography in benzene–chloroform (9 : 1) on ethyl acetate-washed alumina.[7] *Tri-O-methylpeltogynol* has m. p. 203—205°, $[\alpha]_D$ +250° (*c* 1·4), $\lambda_{max.}$ 280 and 286 mμ (log ε 3·84 and 3·87 respectively), $\nu_{max.}$ 3484 cm.$^{-1}$ [Found: C, 66·35; H, 5·9; O, 27·7; OMe, 27·6%; *M*, 332. $C_{16}H_{11}O_3(OMe)_3$ requires C, 66·3; H, 5·85; O, 27·9; OMe, 27·0%; *M*, 344]. The compound gave no colour with ferric chloride but a violet colour with the Fearon–Mitchell reagent. An alcoholic solution quickly gave a red solution with a green fluorescence on addition of a few drops of hydrochloric acid.

The *acetate* was prepared in the usual way with fused sodium acetate and acetic anhydride. It crystallized from light petroleum (b. p. 60—80°)–benzene or from aqueous acetic acid, as white needles, m. p. 154—156° [Found: C, 65·7; H, 5·8; OMe, 24·15. $C_{18}H_{13}O_4(OMe)_3$ requires C, 65·3; H, 5·7; OMe, 24·1%].

Tri-O-methylpeltogynone.—Manganese dioxide[18] (14 g.) was added to a solution of tri-*O*-methylpeltogynol (1·0 g.) in chloroform (125 c.c.). The suspension was stirred at room temperature for 18 hr., then filtered. The manganese dioxide was washed with chloroform (100 c.c.), and the combined filtrates were evaporated to dryness. The white residue, after one recrystallization from ethanol, afforded needles (685 mg.), m. p. 211—213°, $[\alpha]_D$ +279° (*c* 1·2) [Found: C, 66·5; H, 5·4; O, 28·0; OMe, 27·0. $C_{16}H_9O_3(OMe)_3$ requires C, 66·6; H, 5·3; O, 27·9; OMe, 27·2%], $\lambda_{max.}$ 276 mμ (log ε 4·23), infl. 230 and 306 mμ (log ε 4·30 and 3·87 respectively), $\nu_{max.}$ 1687 cm.$^{-1}$ (CO) (in $CHCl_3$). The compound was recovered unchanged after attempted acetylation by acetic anhydride–sodium acetate. It gave no colour with ferric chloride or with the Fearon–Mitchell reagent. Attempted oximation in a solution buffered with sodium acetate gave unchanged material. The ketone dissolves in hot hydrochloric acid to a yellow solution. Reduction of an ethanolic solution with magnesium and hydrochloric acid gave an immediate cherry-red colour.

Reduction of Tri-O-methylpeltogynone with Sodium Borohydride.—A solution of sodium borohydride (25 mg.) in water (2 c.c.) was added to a suspension of the ketone (20 mg.) in methanol. The suspension started clearing immediately. The solution was shaken for 2 hr., then diluted with water (10 c.c.). After filtration and washing with water, the residue was dried and recrystallized from benzene as white needles, m. p. 202—203° alone or mixed with natural tri-*O*-methylpeltogynol.

Degradation of Tri-O-methylpeltogynone with Alkali.—A stirred suspension of the ketone (300 mg.) in 10% aqueous potassium hydroxide (72 c.c.) was heated on a boiling-water bath for 75 min. The orange solution was filtered and acidified, to give a yellow precipitate which was collected after 12 hr. This (298 mg.) had m. p. 121—124° and recrystallized from ethanol to give the chalcone, 3-(2-*hydroxy*-4-*methoxybenzoyl*)-6 : 7-*dimethoxy*iso*chromen* (X) as golden-yellow plates, m. p. 124—125°, $\lambda_{max.}$ 251, 295, and 395 mμ (log ε 4·07, 4·05, and 4·31 respectively), $\nu_{max.}$ 1615 cm.$^{-1}$ (CO) [Found: C, 66·6; H, 5·3; O, 27·7; OMe, 27·55. $C_{16}H_9O_3(OMe)_3$ requires C, 66·7; H, 5·3; O, 28·0; OMe, 27·2%]. It gave a brown colour with ferric chloride. There was no change in colour in the magnesium–hydrochloric acid test.

Oxidation of 3-(2-*Hydroxy*-4-*methoxybenzoyl*)-6 : 7-*dimethoxy*iso*chromen with Potassium Permanganate.*—5% Aqueous potassium permanganate (30 c.c.) was added, with vigorous stirring, at room temperature to a solution of the chalcone (X) (425 mg.) in acetone (50 c.c.). Stirring was continued for a further 6 hr., then the mixture was left undisturbed for 12 hr. The supernatant solution was then completely colourless. After dissolution of the suspended solid by sulphur dioxide, the solution was treated with dilute sulphuric acids, warmed on a water-bath for 10 min., and cooled. The acetone was removed *in vacuo*. The product, which separated on cooling, recrystallized from benzene as white needles, m. p. 163—164° alone or mixed with 2-hydroxy-4-methoxybenzoic acid (Found: C, 57·2; H, 4·8; O, 38·1. Calc. for $C_8H_8O_4$: C, 57·1; H, 4·8; O, 38·1%). The infrared spectra of the " natural " and authentic 2-hydroxy-4-methoxybenzoic acid were identical over the region 2—15 μ.

3-(2 : 4-*Dimethoxybenzoyl*)-6 : 7-*dimethoxy*iso*chromen.*—The chalcone (X) (100 mg.) was methylated with dimethyl sulphate and 10% aqueous potassium hydroxide. The product

[17] Mancera, Barton, Rozenkranz, and Djerassi, *J.*, 1952, 1021.
[18] Attenburrow, Cameron, Chapman, Evans, Hems, Jansen, and Walker, *ibid.*, p. 1097.

crystallized from benzene–light petroleum (b. p. 60—80°) as pale yellow hexagonal plates (55 mg.), m. p. 137—138°, $\lambda_{max.}$ 252 and 375 mμ (log ε 4·19 and 4·24 respectively), infl. 315 mμ (log ε 3·85), $\nu_{max.}$ 1650 cm.$^{-1}$ (CO) [Found: C, 67·6; H, 5·8; O, 27·1; OMe, 35·3. $C_{16}H_8O_2(OMe)_4$ requires C, 67·4; H, 5·7; O, 26·9; OMe, 34·8%]. In ethanol it gave no colour with ferric chloride.

3-(2-*Hydroxy*-4-*methoxybenzoyl*)-6 : 7-*dimethoxy*iso*chroman*.—The ketone (X) (81 mg.) was hydrogenated in ethyl acetate with 10% palladium–charcoal (104 mg.). One mol. of hydrogen was taken up smoothly. The residue, after removal of catalyst and solvent, crystallized from ethanol as colourless needles, m. p. 139—140°, $\lambda_{max.}$ 230 mμ (log ε 4·24) (Found: C, 66·45; H, 5·85; O, 27·6. $C_{19}H_{20}O_6$ requires C, 66·3; H, 5·85; O, 27·9%). It gave a brown colour with ferric chloride.

Action of Sulphuric Acid on 3-(2-*Hydroxy*-4-*methoxybenzoyl*)-6 : 7-*dimethoxy*iso*chromen*.—A solution of the compound (X) (200 mg.), ethanol (20 c.c.), and 8N-sulphuric acid (10 c.c.) was heated on a boiling-water bath for 24 hr. Removal of ethanol *in vacuo* gave 2 : 3-*dihydro*-6 : 6′ : 7′-*trimethoxy*-3-*oxobenzofuran*-2-spiro-3′-iso*chroman* (XI) which recrystallized as white needles, m. p. 183—185° (from ethanol), $\lambda_{max.}$ 232, 278, and 322 mμ (log ε 4·26, 4·23, and 3·98, respectively) [Found: C, 66·6; H, 5·6; O, 28·3; OMe, 27·7. $C_{19}H_9O_3(OMe)_3$ requires C, 66·7; H, 5·3; O, 28·0; OMe, 27·2%]. The compound gave no ferric chloride colour and was insoluble in aqueous sodium hydrogen carbonate or warm 10% potassium hydroxide solution. Attempted acetylation (pyridine–acetic anhydride) gave unchanged material. It gave no colour in the magnesium–hydrochloric acid test.

Periodic Acid Oxidation of Tri-O-*methylpeltogynol and Tri*-O-*methylpeltogynone*.—0·773M-Periodic acid (1 c.c.) was added to a solution of the derivative (25 mg.) in ethanol (20 c.c.) and was estimated in the usual way. There was no uptake of periodic acid.

Peltogynol B (*with* J. B. Roberts).—Our product had $[\alpha]_D$ +270°, m. p. 130—140° (decomp. with formation of about 15% of peltogynidin). Satisfactory analyses have not been obtained on the crystalline material from chloroform owing to retention of solvent. The *tetra-acetate*, prepared with pyridine and acetic anhydride, crystallized from ethanol as white needles, m. p. 240°, $[\alpha]_D$ +262° (Found: C, 61·2; H, 4·6; Ac, 35·0. $C_{16}H_{10}O_6Ac_4$ requires C, 61·3; H, 4·7; Ac, 36·6%).

Tri-O-*methylpeltogynol B* was obtained by methylation of peltogynol B with diazomethane as needles, m. p. 140° [Found: C, 66·6; H, 5·9; OMe, 26·6. $C_{16}H_{11}O_3(OMe)_3$ requires C, 66·3; H, 5·8; OMe, 27·0%], $\lambda_{max.}$ 283 mμ (log ε 3·82). Its *monoacetate*, prepared with pyridine and acetic anhydride, and crystallized from ethanol, had m. p. 182° [Found: Ac, 13·0. $C_{16}H_{10}O_3Ac(OMe)_3$ requires Ac, 12·9%].

Peltogynol B (0·77 g.) was heated at 70° for 1 hr. in 1% aqueous oxalic acid. The solution so obtained was fractionated on a cellulose column for isolation of peltogynol and peltogynol B as described above. Peltogynol (0·25 g.) and unchanged peltogynol B (0·24 g.) were isolated. When peltogynol (2 g.) was heated at 70° for 1 hr. in 1% aqueous oxalic acid, peltogynol B (0·25 g.) and unchanged peltogynol (1·2 g.) were isolated. The products were identified by conversion into the tetra-acetates and by mixed m. p. determination.

Tri-*O*-methylpeltogynol B (0·33 g.) was oxidised with manganese dioxide in chloroform according to the procedure for trimethylpeltogynol. The product, after crystallization from ethanol, yielded needles (0·1 g.), m. p. and mixed m. p. 211°, $[\alpha]_D$ +280°. Reduction with sodium borohydride then gave tri-*O*-methylpeltogynol, m. p. and mixed m. p. 203°. The chalcone, prepared by treatment with alkali, was identical with that from tri-*O*-methylpeltogynone.

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