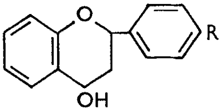
662. *Polymerisation of Flavans. Part III.* The Action of Lead Tetra-acetate on Flavans.*

By M. M. Bokadia, B. R. Brown, and W. Cummings.

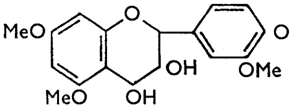
Lead tetra-acetate converts flavans into flavan-4α-yl acetates which on hydrolysis yield the 4α-alcohols. Flavan-3,4-diols are split by lead tetra-acetate into 2-aryl-2-formyl-2,3-dihydro-3-hydroxybenzofurans which are converted by acid into 2-arylbenzofurans. Increased methoxyl-substitution of the flavans results in decreased yields in both these reactions as a result of acetoxylation of the aromatic nuclei and the methoxyl groups. Despite this, tetra-*O*-methyl-(+)-catechin has been converted into 4α-hydroxy-tetra-*O*-methyl-(+)-catechin (a tetramethyl-leucocyanidin). The tetramethyl-leucocyanidin racemates from the reduction of dihydrotetramethylquercetin have afforded the corresponding benzofuran.

Polymers of flavans produced by the action of acids or by autoxidation are thought to contain new carbon–carbon links.[1] Determination of the positions of these links is structurally important, but progress has been hindered by the vigorous nature of the available degradative methods which result in very low yields of significant products. The most widely used methods have been oxidation of methylated polymers by permanganate and fusion of the polymers with potassium hydroxide.[2] We have investigated the possibility of first weakening a flavan structure by mild oxidation before applying more vigorous techniques.

Cavill and Solomon [3] found that the methyl group of substituted toluenes was attacked by lead tetra-acetate in acetic acid at 80°, a benzyl acetate being obtained, and that the yield increased when electron-repelling groups were present in the *para*-position. We have checked the efficiency of the method with 4-methoxydiphenylmethane and isolated, after hydrolysis, 80% of α-*p*-methoxyphenylbenzyl alcohol. Flavans are attacked first at the 4-position and yield 4α-acetoxy-derivatives from which, on hydrolysis, flavan-4α-ols (I) have been isolated and characterised. Flavan-4α-ol (I; R = H), from flavan itself, corresponded in properties with the compound, m. p. 119°, first obtained by Freudenberg and Orthner.[4] Subsequently, by reduction of flavanone with titanium chloride, Karrer *et al.*[5] isolated two compounds, m. p. 120° and 148°, which they designated respectively as the 4α-ol and the 4β-ol (these α and β designations are purely trivial, for reference, and have no stereochemical significance). Bognár and Rákosi [6] isolated the same 4β-alcohol on reduction of flavanone with lithium aluminium hydride. More recently [7] flavan-4α-ol has been obtained from 4-aminoflavan by reaction with nitrous acid. 4′-Methoxyflavan, on treatment with lead tetra-acetate and hydrolysis of the product, yielded the 4α-alcohol (I; R = OMe), m. p. 131—132°, which by Oppenauer oxidation gave 4′-methoxyflavanone. The 4β-alcohol, m. p. 152—153°, has been prepared by reduction of the flavanone with lithium aluminium hydride. The compound, m. p. 144—145°, obtained by Karrer *et al.*,[5]



(I)



(II)

---

* Part II, *J.*, 1958, 4302.

[1] Freudenberg and Maitland, *Annalen*, 1934, **510**, 193; Hathway and Seakins, *J.*, 1957, 1562.

[2] Stephen, *J.*, 1949, 3082.

[3] Cavill and Solomon, *J.*, 1954, 3945.

[4] Freudenberg and Orthner, *Ber.*, 1922, **55**, 1748.

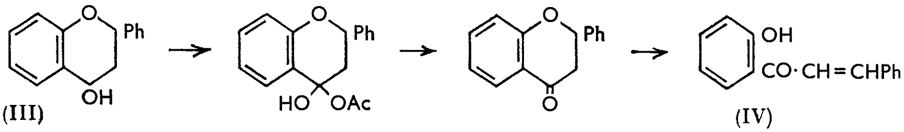
[5] Karrer, Yen, and Reichstein, *Helv. Chim. Acta*, 1930, **13**, 1308.

[6] Bognár and Rákosi, *Acta Chim. Acad. Sci. Hung.*, 1957, **13**, 217.

[7] Bognár, Rákosi, Fletcher, Philbin, and Wheeler, *Tetrahedron Letters*, 1959, **19**, 4.

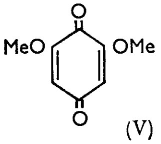
must be a mixture of these two isomers, especially as these authors isolated both alcohols on similar reduction of flavanone itself. When the method was applied to (+)-catechin tetramethyl ether in acetic acid, side reactions predominated and no 3,4-diol was isolated. However, in benzene solution at room temperature, a 10% yield of a tetra-*O*-methylleucocyanidin (II), m. p. 189—190°, $[\alpha]_D^{19}$ +34°, was obtained, together with unchanged starting material and alkali-soluble products. Thus a method is available for the conversion of a catechin into a leucoanthocyanidin, albeit in small yield.

The yields of 4α-alcohols drop as the flavan nucleus is more highly substituted with methoxyl groups. One of the side reactions responsible for this is attack by lead tetra-acetate on the 2-position, especially when a 4′-methoxyl group is present, with subsequent ring-fission on hydrolysis and production of alkali-soluble products. This has been well exemplified by Robertson and his co-workers [8] in their study of lead tetra-acetate oxidation of flavanones. Further, we have shown that flavan-4β-ol (III) is attacked by lead tetra-acetate in acetic acid at the 4-position and hydrolysis yields 40% of 2′-hydroxychalcone (IV) with 20% of unchanged starting material (see annexed scheme).

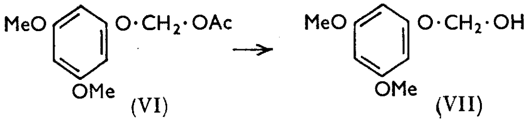


(III) (IV)

A second, and more serious, side reaction with highly substituted compounds of the type of 1,3,5-trimethoxybenzene is attack of the lead tetra-acetate both on the methoxyl groups and on the benzene ring. It is known [9] that *p*-dimethoxybenzene in this way yields a variety of products, and we have found that 1,3,5-trimethoxybenzene also reacts readily, and gives <1% of a nuclear-acetoxylated compound (infrared absorption band at 1780 cm.$^{-1}$, typical of an acetate of a phenol), 2,6-dimethoxybenzo-1,4-quinone (V) (17%), 5-acetoxymethoxy-1,3-dimethoxybenzene (VI) (32%), and unchanged starting material (24%). The identity of the quinone was proved by a mixed melting-point determination and ultraviolet and infrared comparisons. The compound (VI) is assigned this structure on the following evidence. It has an infrared band at 1754 cm.$^{-1}$ and hydrolysis with potassium carbonate in acetone yields a hydroxy-compound (VII) which gave no colour with ferric chloride. Hydrolysis of the acetate (VI) with hot dilute mineral acid or aqueous sodium hydroxide yielded intractable products, thought to be polymers of the phenol–formaldehyde type.



(V)



(VI) (VII)

As expected, flavan-3,4-diols (leucoanthocyanidins) are split by lead tetra-acetate. Flavan-3,4-diol (VIII) in acetic acid at room temperature thus yields small amounts of benzaldehyde and salicylaldehyde and a compound (76%) formulated as 2-formyl-2,3-dihydro-3-hydroxy-2-phenylbenzofuran (IX) because it yields a monoxime whose infrared spectrum does not contain a carbonyl peak. We believe that the first-formed dialdehyde undergoes an aldol condensation.[10] Oxidation of the dihydrobenzofuran (IX) with silver oxide in methanol or with potassium permanganate in acetone gave 20% each of benzoic acid and salicylic acid which were separated and identified. Treatment of the dihydrobenzofuran (IX) or its oxime with dilute sulphuric acid or sublimation of the aldehyde

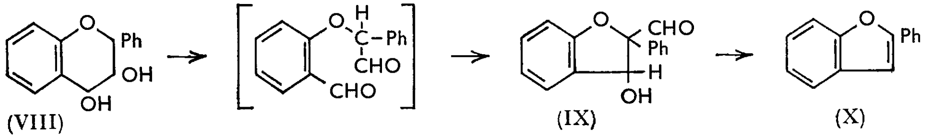
---

[8] Cavill, Dean, McGookin, Marshall, and Robertson, *J.*, 1954, 4573.

[9] Preuss and Menzel, *Arch. Pharm.*, 1958, **291**, 350, 377.

[10] Cf. Brown, Henbest, and Jones, *J.*, 1950, 3634.

gave 2-phenylbenzofuran (X) in good yield by the loss of the elements of formic acid.[11] In the same way, 4′-methoxyflavan-3,4-diol has been converted into 2-*p*-methoxyphenylbenzofuran (70%). Oxidation by lead tetra-acetate in acetic acid of the tetramethylleucocyanidin racemates obtained from the reduction of dihydrotetra-*O*-methylquercetin with sodium borohydride,[12] was not encouraging; but with benzene as solvent, the product yielded, on acid treatment, 5% of 2-(3,4-dimethoxyphenyl)-4,6-dimethoxybenzofuran. This method can therefore be applied to differentiate between flavan-3,4- and -2,3-diols since the latter cannot yield benzofurans in this way.[13]



(VIII) (IX) (X)

We had hoped in similar ways to convert catechins into leucoanthocyanidins and then to split these and to oxidise the products to acids which would enable the structures of monomers and eventually polymers to be determined. The low yields of desired products prevent this, but work is still in progress.

EXPERIMENTAL

Acetic acid was purified by distillation from lead tetra-acetate. Light petroleum refers to the fraction of b. p. 40—60°. Alumina was Spence's grade H deactivated with 10% acetic acid (10 ml. per 100 g.).

Oxidation of p-*Methoxydiphenylmethane by Lead Tetra-acetate.*—A mixture of lead tetra-acetate (13 g.), *p*-methoxydiphenylmethane (4·9 g.), and acetic acid (14 ml.) was heated at 80° for 5 hr. after which a starch–iodide test showed the absence of quadrivalent lead. Removal of the acetic acid *in vacuo* and ether-extraction of the residue gave an oil (5·9 g.) which was boiled with 5% ethanolic potassium hydroxide (100 ml.) for 30 min. and then diluted with water (1 l.). The precipitated α-*p*-methoxyphenylbenzyl alcohol (4·25 g.) separated from light petroleum (b. p. 60—80°) as needles, m. p. and mixed m. p. 66—67°.

Oxidation of Flavan by Lead Tetra-acetate.—Flavan (1·02 g.), lead tetra-acetate (3·23 g.), and acetic acid (25 ml.), treated as above, gave, after hydrolysis with potassium hydroxide, flavan-4α-ol (0·67 g.) which separated from light petroleum (b. p. 30—40°) as needles, m. p. 119·5—120·5° (Found: C, 79·5; H, 5·95. Calc. for $C_{15}H_{14}O_2$: C, 79·65; H, 6·2%). Karrer *et al.*[5] record m. p. 120—120·5°. The acetate separated from light petroleum (b. p. 30—40°) as colourless rods, m. p. 86—87° (lit.,[4] m. p. 85—86°).

Oxidation of Flavan-4β-ol by Lead Tetra-acetate.—Flavan-4β-ol (100 mg.), lead tetra-acetate (240 mg.), and dry benzene (25 ml.) were boiled under reflux for 6 hr. The mixture was filtered and the filtrate was washed with water and dried. Removal of the solvent yielded a solid which on hydrolysis with 5% methanolic potassium hydroxide gave unchanged starting material (20 mg.), m. p. and mixed m. p. 139—141°. Acidification of the alkali-soluble part yielded 2′-hydroxychalcone (40 mg.), m. p. and mixed m. p. 89°. The infrared spectrum was identical with that of an authentic specimen and a ferric chloride test was positive.

Oxidation of 4′-Methoxyflavan by Lead Tetra-acetate.—(a) *In acetic acid.* 4′-Methoxyflavan (0·98 g.), lead tetra-acetate (3·26 g.), and acetic acid (25 ml.) yielded, as above, a gum (1·1 g.) which was hydrolysed with 5% ethanolic potassium hydroxide. Dilution of the solution with water gave *4′-methoxyflavan-4α-ol* (0·35 g.) which separated from light petroleum (b. p. 30—40°) as needles, m. p. 131—132° (Found: C, 74·6, 75·35; H, 6·3, 6·2. $C_{16}H_{16}O_3$ requires C, 75·0; H, 6·25%). Acetylation with acetic anhydride and pyridine gave the acetyl derivative, m. p. and mixed m. p. 71° (see below).

4′-Methoxyflavan-4α-ol (200 mg.), *p*-benzoquinone (1·0 g.; freshly sublimed), toluene (25 ml.), and aluminium isopropoxide (300 mg.) were boiled under reflux for 40 min. Water

[11] Cf. Bottomley, *Chem. and Ind.*, 1956, 170.

[12] Ganguly and Seshadri, *Tetrahedron*, 1959, **6**, 21.

[13] Cf. Gramshaw, Johnson, and King, *J.*, 1958, 4040.

(100 ml.) was added and toluene and benzoquinone were removed by steam-distillation. Acidification of the residue with dilute sulphuric acid and ether-extraction gave an oil which was dissolved in benzene–light petroleum (1 : 4 v/v) and filtered through alumina (5 g.). The eluate (160 ml.) yielded 4′-methoxyflavan-4-one (120 mg.), needles, m. p. and mixed m. p. 90—91° (from light petroleum). The infrared spectrum was identical with that of an authentic specimen.

(b) *In benzene.* 4′-Methoxyflavan (0·60 g.), lead tetra-acetate (1·8 g.), and dry benzene (20 ml.) were boiled under reflux for 6 hr. after which no quadrivalent lead remained. The mixture was filtered, and the filtrate was washed with water and dried. Removal of the solvent under reduced pressure yielded a gum which was dissolved in light petroleum–benzene (3 : 2 v/v) and chromatographed on alumina (40 g.). Elution with the same solvent mixture yielded unchanged 4′-methoxyflavan (0·12 g.), m. p. and mixed m. p. 82—83°. Elution with benzene yielded 4α-*acetoxy*-4′-*methoxyflavan* (0·27 g.) which separated from light petroleum as colourless needles, m. p. 71° (Found: C, 72·5; H, 6·3; Ac, 14·9. $C_{18}H_{18}O_4$ requires C, 72·5; H, 6·05; 1Ac, 14·4%). Hydrolysis with 5% methanolic potassium hydroxide yielded 4′-methoxyflavan-4α-ol (90%), m. p. and mixed m. p. 131—132°. Elution with benzene–ether (1 : 1 v/v) gave a brown mass (0·10 g.) which could not be purified.

4′-*Methoxyflavan*-4β-*ol* (By G. A. SOMERFIELD).—4′-Methoxyflavan-4-one (2·0 g.), reduced in the usual way with lithium aluminium hydride (0·18 g.) in ether, gave 4′-*methoxyflavan*-4β-*ol* (1·8 g.) which separated from aqueous methanol as needles, m. p. 152—153° (Found: C, 74·75; H, 6·05. $C_{16}H_{16}O_3$ requires C, 75·0; H, 6·25%).

Oxidation of Tetramethyl-(+)-*catechin by Lead Tetra-acetate.*—Tetra-*O*-methylcatechin (2·70 g.), lead tetra-acetate (3·60 g.), and benzene (40 ml.) were shaken at room temperature for 11 days; a starch–iodide test was then negative. The mixture was worked up and hydrolysed in the usual way with methanolic potassium hydroxide. The product was dissolved in benzene (10 ml.) and put on alumina (50 g.). Elution with benzene yielded tetra-*O*-methylcatechin (0·50 g.) which, after crystallisation, had m. p. and mixed m. p. 145°. Elution with benzene–chloroform (3 : 1 v/v) yielded a *tetra*-O-*methyl-leucocyanidin* which on crystallisation from methanol and then from glycol monomethyl ether gave colourless rods (0·24 g.), m. p. 189—190°, $[\alpha]_D^{19}$ +34° (*c* 2·27 in $CHCl_3$) (Found: C, 62·85; H, 6·3. $C_{19}H_{22}O_7$ requires C, 63·0; H, 6·1%). Treatment of the compound with boiling methanolic hydrogen chloride gave tetra-*O*-methylcyanidin, R_F in 2N-hydrochloric acid–acetic acid (7 : 3 v/v) 0·62, and $\lambda_{max.}$ 535 mμ in EtOH–HCl.

The alkali-soluble part afforded, on acidification, a brown mass which could not be purified.

Oxidation of 1,3,5-*Trimethoxybenzene by Lead Tetra-acetate.*—The trimethoxybenzene (3·5 g.), lead tetra-acetate (10·5 g.), and benzene (50 ml.) were boiled under reflux for 6 hr. The product, isolated in the usual way, was put on alumina (200 g.) in benzene. Elution was as follows:

(i) Light petroleum gave unchanged trimethoxybenzene (0·83 g.), m. p. and mixed m. p. 51°.

(ii) Light petroleum–benzene (75 : 25 v/v) gave 1-*acetoxymethoxy*-3,5-*dimethoxybenzene*, prisms (1·5 g.), m. p. 101° (from methanol and ethyl acetate) (Found: C, 58·65; H, 6·35; Ac, 20·4. $C_{11}H_{14}O_5$ requires C, 58·4; H, 6·2; 1Ac, 19·0%), $\nu_{max.}$ (in Nujol) 1754s cm.$^{-1}$, hydrolysed by potassium carbonate in boiling acetone (24 hr.) to 1-*hydroxymethoxy*-3,5-*dimethoxybenzene* (purified on alumina), needles, m. p. 63° (Found: C, 58·4; H, 6·5. $C_9H_{12}O_4$ requires C, 58·7; H, 6·5%), $\nu_{max.}$ 3425 cm.$^{-1}$ (in Nujol), giving no colour with ferric chloride. Attempts to hydrolyse it with dilute mineral acid or with aqueous sodium hydroxide gave insoluble, amorphous products.

(iii) Light petroleum–benzene (25 : 75 v/v) afforded 2,6-dimethoxy-*p*-benzoquinone which, after crystallisation from benzene (orange prisms; 0·6 g.), was further purified by sublimation at 140—170°/0·5 mm. It had m. p. and mixed m. p. 249° (Found: C, 57·05; H, 4·3. Calc. for $C_8H_8O_4$: C, 57·15; H, 4·75%). The infrared spectrum in Nujol had a strong absorption at 1695 cm.$^{-1}$ and its ultraviolet spectrum in ethanol had $\lambda_{max.}$ 285 mμ (log ε 4·19). The spectra were identical with those of an authentic sample.

(iv) Benzene–ether (75 : 25 v/v) gave a colourless solid (5 mg.) which melted at 197° after crystalisation from ethyl acetate and had $\nu_{max.}$ (in CH_2Cl_2) 1780s cm.$^{-1}$.

Oxidation of Flavan-3,4-*diol by Lead Tetra-acetate.*—A mixture of flavan-3,4-diol (0·50 g.), lead tetra-acetate (1·0 g.), and acetic acid (95 ml.) was stirred at room temperature. After 8 hr. 0·98 mol. of lead tetra-acetate had been consumed. Acetic acid was removed in a vacuum and the residue was taken up in chloroform and washed with water and with sodium hydrogen carbonate solution. Removal of the solvent yielded a yellow oil with a smell of almonds and a violet ferric chloride colour. Steam-distillation yielded a turbid distillate which gave an orange-red precipitate (34 mg.) with dinitrophenylhydrazine. The dinitrophenylhydrazones were chromatographed in benzene (10 ml.) on bentonite (7 g.)–kieselguhr (1 g.; acid-washed). Elution with benzene afforded a dinitrophenylhydrazone which, after crystallisation from methanol, gave orange needles, m. p. and mixed m. p. with benzaldehyde dinitrophenylhydrazone 237°. Elution with benzene–ethanol (75 : 25 v/v) gave a dark orange dinitrophenylhydrazone which, after crystallisation from benzene, had m. p. and mixed m. p. 252° with salicylaldehyde dinitrophenylhydrazone.

The residue in the distillation flask gave an amorphous powder (0·38 g.), m. p. 60—63°, $\nu_{max.}$ (in Nujol) 3352 (OH) and 1739 cm.$^{-1}$ (C=O). The powder was boiled with hydroxylamine hydrochloride (0·5 g. in 2 ml. of water), 10% sodium hydroxide solution (2 ml.), and a few drops of ethanol for 30 min. The precipitated *oxime* separated from methanol as prisms (0·35 g.), m. p. 170° (Found: C, 70·5; H, 5·1; N, 5·3. $C_{15}H_{13}O_3N$ requires C, 70·6; H, 5·1; N, 5·5%), $\lambda_{max.}$ (in EtOH) 221, 280, and 287 mμ (log ε 4·12, 3·50, and 3·47). Its infrared spectrum had no bands in the carbonyl region. Hydrolysis of the oxime with dilute sulphuric acid gave 2-phenylbenzofuran as plates (from ethanol), m. p. and mixed m. p. 120° (Found: C, 86·3; H, 5·15. Calc. for $C_{14}H_{10}O$: C, 86·6; H, 5·15%), $\lambda_{max.}$ (in EtOH) 210, 302, and 316 mμ (log ε 4·29, 4·52, and 4·39). The infrared and ultraviolet spectra were identical with those of an authentic sample, prepared by the method of Kawai *et al.*[14] With concentrated sulphuric acid the benzofuran gave a yellow colour in the cold and a blue fluorescence on being warmed.

Sublimation of the amorphous powder (28 mg.) at 130—150°/10 mm. yielded 2-phenylbenzofuran (21 mg.), m. p. and mixed m. p. 120°.

The powder (20 mg.) was boiled for 2 hr. with 2N-sulphuric acid (10 ml.). 2-Phenylbenzofuran (14 mg.), m. p. and mixed m. p. 120°, was isolated.

Oxidation of the powder with potassium permanganate in acetone or with silver oxide in methanol at room temperature gave benzoic acid and salicylic acid in 20% yields. The acids were identified by their R_F values and were separated by esterification followed by alkali-treatment and hydrolysis, and further identified by m. p. and mixed m. p. determinations.

3-Hydroxy-4′-methoxyflavan-4-one.—To a cold solution of 2′-hydroxy-4-methoxychalcone (2·19 g.) in methanol (20 ml.) was added 2N-sodium hydroxide (1·8 ml.) and 30% hydrogen peroxide (2·8 ml.), and the mixture was kept at 0° overnight. Acidification gave a product which was only partially soluble in hot ethanol. The soluble portion, the *dihydroflavonol*, crystallised as colourless needles (1·4 g.), m. p. 168° (Found: C, 71·2; H, 5·45; OMe, 12·1. $C_{16}H_{14}O_4$ requires C, 71·2; H, 5·2; 1OMe, 11·5%), $\lambda_{max.}$ (in EtOH) 216, 252·5, and 320 mμ (log ε 4·45, 4·02, and 3·64), $\nu_{max.}$ (in Nujol) 3436 and 1692 cm.$^{-1}$. The insoluble portion (0·3 g.) was 4′-methoxyflavonol (see below).

4′-Methoxyflavonol.—(*a*) The insoluble portion from the preceding experiment crystallised from glacial acetic acid to yield *4′-methoxyflavonol* as pale yellow needles (0·2 g.), m. p. 236° (Found: C, 71·45; H, 4·55; OMe, 11·7. $C_{16}H_{12}O_4$ requires C, 71·65; H, 4·5; 1OMe, 11·55%), $\lambda_{max.}$ (in EtOH) 232, 253, 316, and 354 mμ (log ε 4·30, 4·20, 4·08, and 4·39), $\nu_{max.}$ (in Nujol) 3185 and 1631 cm.$^{-1}$.

(*b*) 3-Hydroxy-4′-methoxyflavan-4-one (1·3 g.) in methanol (25 ml.) was treated with 15% aqueous sodium hydroxide (45 ml.) and 100-vol. hydrogen peroxide (3 ml.) and kept at 0° for 24 hr. The mixture was acidified and the precipitate was recrystallised from acetic acid, to give 4′-methoxyflavonol (0·95 g.), m. p. and mixed m. p. 236°.

Acetylation with acetic anhydride and pyridine gave the *acetate* which separated from ethanol as colourless needles, m. p. 130—131° (Found: C, 69·2; H, 4·5; Ac, 14·7. $C_{18}H_{14}O_5$ requires C, 69·65; H, 4·5; 1Ac, 13·9%).

4′-Methoxyflavan-3,4-diol.—3-Hydroxy-4′-methoxyflavan-4-one (0·86 g.) was reduced with sodium borohydride to the *diol* (0·71 g.), colourless needles (from methanol), m. p. 172—174° (Found: C, 70·8; H, 6·15; OMe, 10·8. $C_{16}H_{16}O_4$ requires C, 70·6; H, 5·9; 1OMe, 11·4%).

Oxidation of 4′-Methoxyflavan-3,4-diol by Lead Tetra-acetate.—4′-Methoxyflavan-3,4-diol (0·50 g.), lead tetra-acetate (0·90 g.), and acetic acid (50 ml.) yielded, after removal of the solvent and isolation of the product in chloroform, an amorphous powder which with hot dilute sulphuric acid gave a solid. Filtration in light petroleum through alumina yielded *2-*p*-methoxyphenylbenzofuran*, which separated from ethanol as colourless plates (0·30 g.), m. p. 152° (Found:

---

[14] Kawai, Nakamura, and Sugiyama, *Proc. Imp. Acad.* (*Tokyo*), 1939, **15**, 45.

C, 80·05; H, 5·45; OMe, 14·05. $C_{15}H_{12}O_2$ requires C, 80·35; H, 5·35; 1OMe, 13·85%), $\lambda_{max.}$ (in EtOH) 211, 246, and 307·5 mμ (log ε 4·29, 3·59, and 4·44).

Oxidation of 3′,4′,5,7-*Tetramethoxyflavan*-3,4-*diol by Lead Tetra-acetate.*—(a) *In acetic acid.* The diol racemates [12] (0·50 g.), lead tetra-acetate (0·70 g.), and acetic acid (25 ml.) at room temperature developed a cherry-red colour. Paper chromatography and the ultraviolet spectrum showed the presence of tetramethylcyanidin. A brown mass was isolated which did not give a crystallisable product after treatment with hot dilute sulphuric acid.

(b) *In benzene.* The diol racemates (0·45 g.), lead tetra-acetate (0·70 g.), anhydrous potassium carbonate (3·0 g.), and dry benzene (40 ml.) were kept at room temperature for 1 hr. and worked up to yield a gum (0·31 g.) which was boiled for 2 hr. with 2N-sulphuric acid (3 ml.) and ethanol (10 ml.). This gave a brown powder which was chromatographed in benzene on alumina. Elution with light petroleum and light petroleum–benzene (50 : 50 v/v) gave 2-(3,4-*dimethoxyphenyl*)-4,6-*dimethoxybenzofuran* (20 mg.) as colourless needles (from methanol), m. p. 124° (Found: C, 68·9; H, 5·95; OMe, 38·9. $C_{18}H_{18}O_5$ requires C, 68·5; H, 5·75; 4OMe, 39·5%), $\lambda_{max.}$ (in EtOH) 213, 319, and 333·5 mμ (log ε 4·46, 4·49, and 4·35).

We thank the Government of India for the award of a Central Overseas Scholarship (to M. M. B.) and the D.S.I.R. for a maintenance grant (to W. C.).

DYSON PERRINS LABORATORY, UNIVERSITY OF OXFORD. [*Received, February* 1*st*, 1960.]