# *Synthetic and Oxidative Studies in the Polyhydroxydiphenyl Series. Part I.*

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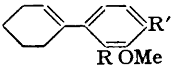
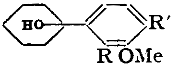
2 : 3-Dihydroxy- and 2 : 3 : 4-trihydroxy-diphenyl have been prepared from organometallic compounds and *cyclo*hexanone. Oxygenation of 2 : 3-dihydroxydiphenyl in a phosphate buffer at pH 8 gives only amorphous material, but treatment with silver oxide in ether yields the deeply coloured 2 : 3-diphenylbenzoquinone. Oxidation of 2 : 3 : 4-trihydroxydiphenyl in aqueous media yields a compound believed to be a diphenylpurpurogallin, probably 2′ : 3′ : 4′ : 4-tetrahydroxy-1′ : 5-diphenylbenzo*cyclo*heptatrien-3-one. The syntheses of several new derivatives of catechol and pyrogallol are described.

For a study of the mechanism of autoxidation of 5 : 6-dihydroxyindole (cf. Bruce, *Chem. and Ind.*, 1954, 310; *J. Appl. Chem.*, 1954, **4**, 469) we require certain indolyl derivatives of *vic.*-polyhydric phenols in which the heterocyclic ring is adjacent to a hydroxyl group. Before the preparation of these compounds, however, we found it necessary to investigate the synthesis, from organometallic compounds and *cyclo*hexanone, of some related polyphenols in which the indole nucleus is replaced by a phenyl group, and in the present paper the preparation and certain oxidative properties of 2 : 3-dihydroxy- and 2 : 3 : 4-trihydroxy-diphenyl are described.

1-(2 : 3-Dimethoxyphenyl)*cyclo*hexene (I) was prepared from 3-lithioveratrole and *cyclo*hexanone *via* the *tert.*-alcohol (IV) as described by Bergmann, Pappo and Ginsburg (*J.*, 1950, 1369) and Ginsburg and Pappo (*J.*, 1950, 516), and on dehydrogenation with chloranil in xylene it afforded 2 : 3-dimethoxydiphenyl from which 2 : 3-dihydroxydiphenyl was obtained in excellent yield by demethylation with aluminium chloride in chlorobenzene (cf. Dawson, Wasserman and Keil, *J. Amer. Chem. Soc.*, 1946, **68**, 534; Mason, *ibid.*, 1947, **69**, 2241).

(I) R = OMe; R′ = H
(II) R = H; R′ = OMe
(III) R = R′ = OMe





(IV) R = OMe; R′ = H
(V) R = H; R′ = OMe
(VI) R = R′ = OMe

Bergmann, Pappo, and Ginsburg (*loc. cit.*) based the orientation of compounds (I) and (IV) on the observation by Gilman, Swiss, and Cheney (*ibid.*, 1940, **62**, 1963) that metallation of veratrole with *n*-butyl-lithium in ether and subsequent carboxylation yielded 70% of 2 : 3-dimethoxybenzoic acid, indicating that the metal atom enters the veratrole nucleus in a position adjacent to a methoxyl group. In the present work this orientation has been confirmed by the synthesis, from 4-iodoveratrole, of the isomeric 1-(3 : 4-dimethoxyphenyl)*cyclo*hexanol (V) and the corresponding *cyclo*hexene (II), the physical properties of which differ considerably from those of (IV) and (I) respectively.

4-Iodoveratrole was readily prepared in over 70% yield from veratrole by treatment with iodine and mercuric oxide at 95°. By effecting the iodination in the presence of alcohol at room temperature Seer and Karl (*Monatsh.*, 1913, **34**, 647) and Ritchie (*J. Proc. Roy. Soc. N.S.W.*, 1945, **78**, 134) obtained yields of 31% and 56% respectively.

Attempts to prepare the 4-iodomagnesium derivative of veratrole were unsuccessful and consequently 4-lithioveratrole was prepared from 4-iodoveratrole by cross-metallation with phenyl-lithium. Reaction of 4-lithioveratrole with an excess of *cyclo*hexanone under the usual conditions afforded 1-(3 : 4-dimethoxyphenyl)*cyclo*hexanol (V), which was readily dehydrated to the *cyclo*hex-1-ene (II), and a quantity of 2-*cyclo*hexylidene*cyclo*hexanone.

Oxygenation of dilute solutions of 2 : 3-dihydroxydiphenyl in a phosphate buffer at pH 8 yielded only brown amorphous material; there was no indication of intramolecular reaction. Oxidation with silver oxide in anhydrous ether gave 2 : 3-diphenylbenzoquinone (VII), m. p. 92—94°, as deep brown crystals which had a green reflex. In aqueous-alcoholic solution the quinone decomposed to a dark polymer, the reaction being catalysed by acids and bases. Silver oxide oxidation of 3 : 4-dihydroxydiphenyl (Norris, Macintire, and Corse, *Amer. Chem. J.*, 1903, **29**, 120) yielded 3 : 4-diphenylbenzoquinone (VIII) as deep reddish-brown crystals, m. p. 105·5—107·5°.

Solutions of 2 : 3- and 3 : 4-diphenylbenzoquinones in dioxan showed light absorption maxima which slowly decreased in intensity and moved to slightly shorter wavelengths when the solutions were preserved in the dark at room temperature in the presence of air. Similar, though very much more pronounced, spectral shifts were observed by Mason (*J. Amer. Chem. Soc.*, 1948, **70**, 138) for solutions of 1 : 2-benzoquinone and its 3-*n*-pentadecyl derivative. In the solid state both diphenoquinones were spectroscopically almost unchanged after two months' storage in the dark at room temperature.

In the pyrogallol series, 1-(2 : 3 : 4-trimethoxyphenyl)*cyclo*hexanol (VI) was prepared from pyrogallol trimethyl ether by metallation with *n*-butyl-lithium and subsequent reaction of the 4-lithio-compound with *cyclo*hexanone as described by Ginsburg and Pappo (*ibid.*, 1953, **75**, 1094), but better yields were obtained when 4-lithiopyrogallol trimethyl ether was prepared by halogen–metal interchange between phenyl-lithium and 4-bromopyrogallol trimethyl ether.

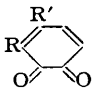
Pyrogallol trimethyl ether was brominated by treatment with bromine in carbon tetrachloride, this method giving good yields and being more convenient than the procedures of Kohn *et al.* (*Monatsh.*, 1925, **46**, 85; 1928, **49**, 178). Upon nitration as described by Kohn and Grün (*loc. cit.*, 1925) the bromo-compound yielded 4-bromo-5 : 6-dinitropyrogallol trimethyl ether whose orientation was established by reduction with zinc and acetic acid; the resulting diamine, which was not isolated, condensed readily with 9 : 10-phenanthraquinone to yield 10-bromo-11 : 12 : 13-trimethoxydibenzo[*a*, *c*]phenazine, and with benzil to give 5-bromo-6 : 7 : 8-trimethoxy-2 : 3-diphenylquinoxaline.

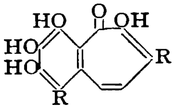
The *tert.*-alcohol (VI) prepared by either of the above procedures crystallised from light petroleum in rhombic platelets, m. p. 65°, in good agreement with the properties reported by Ginsburg and Pappo (*loc. cit.*). However, a preparation by halogen–metal interchange gave a dimorphic form which crystallised from light petroleum in short thick needles, m. p. 79·5°. This material was isolated from all subsequent preparations. On dehydration as described by Ginsburg and Pappo (*loc. cit.*), both forms yielded the *cyclo*hex-1-ene (III).

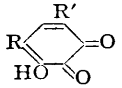
2 : 3 : 4-Trimethoxydiphenyl was prepared in 81% yield by dehydrogenation of the *cyclo*hexene (III) with chloranil; dehydrogenation with sulphur or palladium–charcoal gave lower yields. Demethylation, preferably with aluminium chloride in chlorobenzene, afforded 2 : 3 : 4-trihydroxydiphenyl, which crystallised from xylene under nitrogen in colourless blades. In air this compound slowly developed a violet colour which could only be removed by sublimation at reduced pressure; the change occurred more rapidly

when the polyphenol was dissolved in hydrocarbons. A similar effect was observed by Campbell (*J. Amer. Chem. Soc.*, 1951, **73**, 4190) in the case of 4 : 6-di-*tert.*-butylpyrogallol.

Owing to the low solubility of 2 : 3 : 4-trihydroxydiphenyl in water, oxidation was conducted in aqueous dioxan. Sodium iodate as oxidant afforded a 13% yield of golden-orange needles, m. p. 211°, which dissolved readily in 0·5% aqueous sodium hydroxide with an intense blue colour which in the air soon became green and then yellow. Very similar colour reactions are given by both purpurogallin (IX) and dimethylpurpurogallin (X), suggesting that the product is diphenylpurpurogallin (XI), and this view is supported by the similarity of the absorption spectra of the three compounds.


(VII) R = Ph; R′ = H
(VIII) R = H; R′ = Ph


(IX) R = H
(X) R = Me
(XI) R = Ph


(XII) R = Ph; R′ = H
(XIII) R = H; R′ = Ph

Yields of up to 70% of pure diphenylpurpurogallin were obtained when solutions of 2 : 3 : 4-trihydroxydiphenyl in aqueous dioxan containing a little sodium hydrogen carbonate or disodium hydrogen phosphate were oxidised with molecular oxygen. It is of interest that the product precipitated under these conditions consisted of small brick-red needles which when slowly heated had the same melting point as diphenylpurpurogallin prepared by iodate oxidation, but when placed on a block preheated to 117° melted completely and then rapidly re-solidified; on rise of temperature the normal melting point was observed. The primary melting appeared to occur without chemical change, suggesting that diphenylpurpurogallin is dimorphic. The change to the stable form took place extremely slowly in the solid state at room temperature, but quite rapidly in non-polar, and almost instantaneously in polar, solvents.

When 2 : 3 : 4-trihydroxytoluene was oxidised under similar conditions pure dimethylpurpurogallin (X), identical with material prepared by iodate oxidation as described by Critchlow, Haworth, and Pauson (*J.*, 1951, 1318), was precipitated in 50% yield as small orange needles which did not show a double melting point.

It is therefore apparent, if the mechanism postulated by Critchlow, Haworth, and Pauson (*loc. cit.*) for the formation of purpurogallin from pyrogallol is correct, that the first stage in the oxidation of 2 : 3 : 4-trihydroxydiphenyl under the above conditions must be the formation of 2-hydroxy-3 : 4-diphenoquinone (XII) and not of 4-hydroxy-2 : 3-diphenoquinone (XIII).

## EXPERIMENTAL

Reactions with organolithium compounds were carried out under oxygen-free nitrogen. The term (c) indicates that crystallisation was effected by cooling of the solution, prepared at room temperature, in solid carbon dioxide–acetone. Absorption spectra were measured in dioxan in a Unicam SP.500 spectrophotometer. M. p.s are corrected.

2 : 3-*Dimethoxydiphenyl.*—A mixture of 1-(2 : 3-dimethoxyphenyl)*cyclo*hexene (Bergmann, Pappo, and Ginsburg, *loc. cit.*) (21 g.), chloranil (47·5 g.), and dry xylene (220 c.c.) was refluxed for 8 hr., cooled, and filtered from tetrachloroquinol. The filtrate was washed with 10% aqueous sodium hydroxide and water, and dried ($Na_2SO_4$). Removal of the solvent left a deep red-brown oil which was distilled and the fraction with b. p. 100°/0·2 mm. was crystallised (c) from light petroleum (b. p. 40—60°), giving 2 : 3-*dimethoxydiphenyl* (11·2 g., 54%) as colourless needles, m. p. 46° (Found : C, 78·4; H, 6·3. $C_{14}H_{14}O_2$ requires C, 78·5; H, 6·5%).

2 : 3-*Dihydroxydiphenyl.*—2 : 3-Dimethoxydiphenyl (10·4 g.) was dissolved in dry chlorobenzene (120 c.c.), powdered anhydrous aluminium chloride (12·5 g.) added, and the mixture was refluxed for 3½ hr., then cooled, poured into ice-cold 15% hydrochloric acid (350 c.c.), and extracted with ether. The extract was washed with water and dried ($Na_2SO_4$). Removal of the solvent left a grey solid which was washed with cold light petroleum (b. p. 40—60°) and sublimed from the melt at 110°/0·05 mm., to give a colourless microcrystalline powder (8·4 g., 95%) which upon crystallisation from light petroleum (b. p. 80—100°) afforded 2 : 3-dihydroxydiphenyl as colourless needles, m. p. 114° (Loudon and Scott, *J.*, 1953, 265, report m. p. 111°)

(Found: C, 77·5; H, 5·3. Calc. for $C_{12}H_{10}O_2$: C, 77·4; H, 5·4%). The *diacetate* separated from benzene–light petroleum (b. p. 60—80°) in thick needles, m. p. 79—79·5° (Found: C, 70·9; H, 5·2; Ac, 31·1. $C_{16}H_{14}O_4$ requires C, 71·1; H, 5·2; Ac, 31·9%). Light absorption: 2 : 3-dihydroxydiphenyl, $\lambda_{max.}$ 253, 292 mμ (log ε 4·09, 3·44); 3 : 4-dihydroxydiphenyl (Norris *et al.*, *loc. cit.*), $\lambda_{max.}$ 267 mμ (log ε 4·12).

4-*Iodoveratrole*.—To stirred veratrole (13·8 g.) at 95° was added in small portions, during 20 min., an intimate mixture of iodine (30 g.) and mercuric oxide (14 g.), and the temperature was maintained at 95—100° for a further 30 min. The mixture was cooled and extracted with benzene, and the extract washed with sodium thiosulphate solution, then concentrated brine, and dried ($Na_2SO_4$). The solvent was removed and the residue distilled to give 4-iodoveratrole (18·8 g., 71%), b. p. 89—90°/0·2 mm., m. p. 34·5°. The brown residue from the distillation consisted mainly of 4 : 5-di-iodoveratrole.

1-(3 : 4-*Dimethoxyphenyl*)cyclo*hexanol* (V) *and* 2-cyclo*Hexylidene*cyclo*hexanone*.—To a vigorously stirred solution of phenyl-lithium, from lithium wire (0·8 g.), bromobenzene (9 g.), and ether (25 c.c.), at 0° was added, during 15 min., a solution of 4-iodoveratrole (13·2 g.) in ether (50 c.c.); a white precipitate was formed almost immediately. The suspension was stirred at 0° for a further 15 min. and at 20° for 1 hr., and was then cooled to 0° whilst a solution of *cyclo*hexanone (10 c.c.) in ether (30 c.c.) was added during 20 min.; the precipitate dissolved. After being stirred overnight at room temperature the mixture was cooled to 0° and decomposed by the dropwise addition of ice-cold water (75 c.c.), and the ethereal phase was washed with 5% aqueous sodium hydroxide, then with water, and dried ($Na_2SO_4$). Evaporation of the solvent left a light brown viscous oil which on distillation gave the fractions: (1) A fore-run of iodobenzene. (2) An oil (2·2 g.), b. p. 80—81°/0·3 mm., which solidified spontaneously and, crystallised (c), first, from light petroleum (b. p. 40—60°) and then from methanol, afforded 2-*cyclo*hexylidene*cyclo*hexanone (1·4 g.) as colourless needles, m. p. 55° (Reese, *Ber.*, 1942, **75**, 384, gives m. p. 57°) (Found: C, 80·8; H, 10·2. Calc. for $C_{12}H_{18}O$: C, 80·9; H, 10·1%) [semicarbazone, plates (from aqueous methanol), m. p. 180·5—181°, re-solidifying at 182·5°, and re-melting at 188·5—190° (Reese reports m. p.s 180° and 186—188°) (Found: N, 18·0. Calc. for $C_{13}H_{21}ON_3$: N, 17·9%)]. (3) An oil (5·6 g.), b. p. 136—142°/0·3 mm., which solidified spontaneously and on recrystallisation from light petroleum (b. p. 80—100°) afforded 1-(3 : 4-*dimethoxyphenyl*)cyclo*hexanol* (4·1 g., 35%), needles, m. p. 94·5° (Found: C, 71·5; H, 8·6. $C_{14}H_{20}O_3$ requires C, 71·2; H, 8·5%). 1-(2 : 3-Dimethoxyphenyl)-*cyclo*hexanol formed prisms, m. p. 50·5°.

1-(3 : 4-*Dimethoxyphenyl*)cyclo*hexene* (II).—A mixture of 1-(3 : 4-dimethoxyphenyl)*cyclo*hexanol (2·36 g.), anhydrous oxalic acid (0·4 g.), and dry toluene (15 c.c.) was refluxed, under an azeotropic water separator, until no further water was collected (30 min.). After cooling, the solution was filtered from oxalic acid, washed with water, dried ($Na_2SO_4$), and evaporated. Distillation of the residue gave a colourless oil (1·6 g., 74%), b. p. 120°/0·25 mm., which solidified spontaneously and on crystallisation (c) from light petroleum (b. p. 60—80°) afforded 1-(3 : 4-*dimethoxyphenyl*)cyclo*hexene* as needles, m. p. 58° (Found: C, 77·3; H, 8·2. $C_{14}H_{18}O_2$ requires C, 77·1; H, 8·3%). 1-(2 : 3-Dimethoxyphenyl)*cyclo*hexene had m. p. 15°.

2 : 3-*Dihydroxydiphenylmelanin*.—A rapid stream of oxygen was passed for 6½ hr. through a solution of 2 : 3-dihydroxydiphenyl (93 mg.) in a phosphate buffer (pH 8; 50 c.c.) at room temperature. The melanin was precipitated with hydrochloric acid, collected, and washed with water. After drying *in vacuo*, the brown amorphous product (39 mg.) had m. p. 110—140° (Found: C, 73·4; H, 4·1%).

2 : 3-*Diphenylbenzoquinone* (VII).—Silver oxide, prepared from silver nitrate (1 g.) as described by Willstätter and Müller (*Ber.*, 1908, **41**, 2581), and anhydrous sodium sulphate (2 g.) were suspended in dry ether (25 c.c.), and a solution of 2 : 3-dihydroxydiphenyl (186 mg.) in dry ether (25 c.c.) added all at once. After 15 minutes' shaking at room temperature the mixture was filtered and the deep red filtrate cooled to −75°; 2 : 3-*diphenylbenzoquinone* separated as a mixture of blades and prisms (114 mg., 62%), m. p. 92—94° (Found: C, 78·2; H, 4·6. $C_{18}H_{12}O_2$ requires C, 78·3; H, 4·4%). It was sparingly soluble in light petroleum, more soluble in ether, and readily soluble in benzene, dioxan, and alcohol. When hydrogenated at room temperature and atmospheric pressure in dioxan it absorbed 0·97 mol. of hydrogen. Light absorption: $\lambda_{max.}$ 241, 428 mμ (log ε 4·1, 3·5).

3 : 4-*Diphenylbenzoquinone* (VIII).—3 : 4-Dihydroxydiphenyl (Norris *et al.*, *loc. cit.*) (186 mg.) was oxidised under the conditions used for the preceding preparation. 3 : 4-*Diphenylbenzoquinone* separated from its deep green ethereal solution as a mixture of spikes and blades (111 mg., 60%), m. p. 105·5—107·5° (Found: C, 78·4; H, 4·6%). The quinone had similar solubility

properties to those of 2 : 3-diphenylbenzoquinone. Light absorption : $\lambda_{max.}$ 251, 308, 405 mμ (log ε 4·0, 3·8, 3·4).

4-*Bromopyrogallol Trimethyl Ether.*—Bromine (160 g.) in dry carbon tetrachloride (500 c.c.) was added during 7 hr. to a vigorously stirred solution of pyrogallol trimethyl ether (168 g.) in dry carbon tetrachloride (500 c.c.), the temperature being kept at 4—5°. After the mixture had been kept overnight at room temperature the solvent was removed and the residual yellow oil distilled through a short Dufton column; the fraction with b. p. 95—105°/0·45 mm. was redistilled to give almost pure 4-bromopyrogallol trimethyl ether (203 g., 82%), b. p. 95—100°/0·2 mm. (Found : C, 43·9; H, 4·6; Br, 31·8. Calc. for $C_9H_{11}O_3Br$ : C, 43·7; H, 4·5; Br, 32·4%). Upon nitration as described by Kohn and Grün (*loc. cit.*) this product afforded 4-bromo-5 : 6-dinitropyrogallol trimethyl ether, m. p. 137°, in 50% yield (Kohn and Grün, and Kohn and Gurewitsch, *locc. cit.*, report m. p. 134—135°) (Found : N, 8·0; Br, 23·5. Calc. for $C_9H_9O_7N_2Br$ : N, 8·3; Br, 23·7%).

10-*Bromo*-11 : 12 : 13-*trimethoxydibenzo*[a, c]*phenazine.*—4-Bromo-5 : 6-dinitropyrogallol trimethyl ether (1·7 g.) in glacial acetic acid (50 c.c.) at 90° was reduced by the portion-wise addition of zinc dust (5 g.). After addition of further acetic acid (50 c.c.) the mixture was boiled for ½ min., and then rapidly filtered into a solution of 9 : 10-phenanthraquinone (0·75 g.) in glacial acetic acid (50 c.c.) at 80°. The solution was boiled for 2 min., diluted with cold water (5 c.c.), and allowed to cool. The yellow solid which separated was collected and twice recrystallised from glacial acetic acid, to give 10-*bromo*-11 : 12 : 13-*trimethoxydibenzo*[a, c]-*phenazine* (0·9 g.) as bright yellow felted needles, m. p. 219·5° (Found : C, 61·6; H, 4·0; N, 6·4; Br, 18·3. $C_{23}H_{17}O_3N_2Br$ requires C, 61·5; H, 3·8; N, 6·2; Br, 17·8%).

5-*Bromo*-6 : 7 : 8-*trimethoxy*-2 : 3-*diphenylquinoxaline.*—4-Bromo-5 : 6-dinitropyrogallol trimethyl ether (1·7 g.) was reduced and the diamine condensed with benzil (0·75 g.) in acetic acid under the conditions of the previous preparation. The acetic acid solution was diluted with hot water (100 c.c.) and cooled, and the solid was collected, dissolved in benzene–light petroleum (b. p. 60—80°), and chromatographed on alumina. The column was eluted with benzene, the eluate evaporated, and the residue was recrystallised from ethanol to yield the *quinoxaline* (0·6 g.) as very pale yellow needles, m. p. 159° (Found : C, 61·3; H, 4·2; N, 5·8; Br, 17·9. $C_{23}H_{19}O_3N_2Br$ requires C, 61·2; H, 4·2; N, 6·2; Br, 17·7%).

1-(2 : 3 : 4-*Trimethoxyphenyl*)cyclo*hexanol* (VI).—To a stirred solution of phenyl-lithium, from lithium wire (6·4 g.) and bromobenzene (69 g.) in ether (200 c.c.), was added at 0° during 30 min. 4-bromopyrogallol trimethyl ether (99 g.) in ether (200 c.c.). Treatment with *cyclo*hexanone (53 c.c.) in ether (100 c.c.) and working up as for (V) gave a fraction, b. p. 123—128°/0·1 mm., which, crystallised from light petroleum (b. p. 40—60°), afforded 1-(2 : 3 : 4-trimethoxyphenyl)*cyclo*hexanol, rhombic platelets (36 g., 34%), m. p. 65° (Ginsburg and Pappo, *loc. cit.*, report m. p. 66—67°) (Found : C, 68·1; H, 8·5. Calc. for $C_{15}H_{22}O_4$ : C, 67·7; H, 8·3%). From a later preparation, thick needles, m. p. 79·5°, were obtained (Found : C, 67·6; H, 8·5 %).

1-(2 : 3 : 4-*Trimethoxyphenyl*)cyclo*hexene* (III).—1-(2 : 3 : 4-Trimethoxyphenyl)*cyclo*hexanol (22·5 g., m. p. 79·5°), anhydrous oxalic acid (4·5 g.) and dry toluene (200 c.c.), caused to react and worked up as for (II), gave an oil (19·8 g., 95%), b. p. 123—124°/0·2 mm., which solidified and crystallised (c) from light petroleum (b. p. 40—60°), affording the *cyclo*hexene (III) as hexagonal platelets, m. p. 40°, undepressed upon admixture with material similarly prepared from the low-melting form of the *tert.*-alcohol (Ginsburg and Pappo, *loc. cit.*, report this *cyclo*hex-1-ene as an oil) (Found : C, 72·6; H, 8·4. Calc. for $C_{15}H_{20}O_3$ : C, 72·6; H, 8·1%).

2 : 3 : 4-*Trimethoxydiphenyl.*—1-(2 : 3 : 4-Trimethoxyphenyl)*cyclo*hexene (14·8 g.) in xylene (130 c.c.) was dehydrogenated with chloranil (29·3 g.) as described for 2 : 3-dimethoxydiphenyl. Distillation of the crude product afforded a viscous red oil, b. p. 121—122°/0·1 mm., from which, by crystallisation (c) from light petroleum (b. p. 40—60°), 2 : 3 : 4-*trimethoxydiphenyl* (12·3 g., 85%) was obtained as colourless needles, m. p. 46·5° (Found : C, 73·6; H, 6·7. $C_{15}H_{16}O_3$ requires C, 73·8; H, 6·6%).

2 : 3 : 4-*Trihydroxydiphenyl.*—Demethylation of 2 : 3 : 4-trimethoxydiphenyl (10·6 g.) in chlorobenzene (110 c.c.) was effected with aluminium chloride (17·5 g.) as described for 2 : 3-dihydroxydiphenyl. The solid remaining after removal of the solvent was washed with cold benzene and sublimed at 165°/0·05 mm., the sublimate (7·8 g., 89%), on crystallisation from xylene under nitrogen, affording 2 : 3 : 4-*trihydroxydiphenyl* as colourless blades, m. p. 216° (Found : C, 71·2; H, 4·9. $C_{12}H_{10}O_3$ requires C, 71·3; H, 5·0%). The *triacetate* crystallised from benzene–light petroleum (b. p. 60—80°) in hexagonal plates, m. p. 111° (Found : C, 65·8; H, 4·8; Ac, 40·3. $C_{18}H_{16}O_6$ requires C, 65·9; H, 4·9; Ac, 39·3%).

*Diphenylpurpurogallin* (XI).—(*a*) 2 : 3 : 4-Trihydroxydiphenyl (0·5 g.) was dissolved in a mixture of dioxan (7·5 c.c.) and water (5 c.c.) at 0° and an ice-cold solution of sodium iodate (0·274 g. of $NaIO_3,H_2O$) in water (5 c.c.) added dropwise. The mixture was shaken for 10 min., water (10 c.c.) added, and shaking continued at room temperature for a further 20 min. The dark, granular solid was collected, washed with water, and dried *in vacuo*. Sublimation at 190°/6 × $10^{-6}$ mm. yielded a powder, which upon crystallisation from benzene–light petroleum (b. p. 60—80°) afforded *diphenylpurpurogallin* as golden-orange felted needles (59 mg., 13%), m. p. 211° (Found : C, 73·9; H, 4·4. $C_{23}H_{16}O_5$ requires C, 74·2; H, 4·3%). Light absorption : $\lambda_{max.}$ 223, 290, 325, 362, 445 mμ (log ε 4·26, 4·41, 4·66, 3·83, 3·64).

(*b*) 2 : 3 : 4-Trihydroxydiphenyl (100 mg.) in dioxan (5 c.c.) was added to a solution of sodium hydrogen carbonate (5 mg.; " AnalaR ") in water (10 c.c.) at room temperature, and a stream of small bubbles of oxygen passed through the mixture. After 12 hr. the diphenylpurpurogallin was collected. It consisted of brick-red needles (63 mg., 68%), m. p.s 117° and 209—210°. Similar results were obtained when disodium hydrogen phosphate was used instead of sodium hydrogen carbonate.

*Dimethylpurpurogallin* (X).—A solution of 2 : 3 : 4-trihydroxytoluene (140 mg.) and sodium hydrogen carbonate (10 mg.) in a mixture of water (16 c.c.) and dioxan (4 c.c.) was oxygenated at room temperature for 4 hr. Dimethylpurpurogallin separated as orange needles (62 mg., 50%), m. p. 201—202°, undepressed upon admixture with material prepared by iodate oxidation of 2 : 3 : 4-trihydroxytoluene. Recrystallised from toluene, dimethylpurpurogallin formed felted orange needles, m. p. 203° (Critchlow *et al.*, *loc. cit.*, give m. p. 185°) (Found : C, 62·9; H, 4·5. Calc. for $C_{13}H_{12}O_5$ : C, 62·9; H, 4·8%). Light absorption : $\lambda_{max.}$ 230, 245, 285, 309, 366, 388, 440 mμ (log ε 4·00, 4·09, 4·41, 4·52, 3·66, 3·72, 3·51).

*Purpurogallin* (IX).—This compound, prepared by the method of Dehn and Evans (*J. Amer. Chem. Soc.*, 1930, **52**, 3647) and Haworth, Moore, and Pauson (*J.*, 1948, 1045), was purified by sublimation at 230°/0·1 mm. followed by crystallisation from xylene, from which it separated as deep orange-red needles, m. p. 280° (decomp.). Light absorption : $\lambda_{max.}$ 230, 246, 281, 305, 359, 376, 420 mμ (log ε 4·10, 4·15, 4·38, 4·49, 3·73, 3·71, 3·50).

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