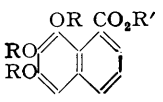
685. *Purpurogallin. Part II. Synthesis of Purpurogallone.*

By Robert D. Haworth, Barry P. Moore, and Peter L. Pauson.

Methods for the preparation of substituted 1-naphthoic acids suitable for the synthesis of purpurogallone (I; R = R′ = H) have been examined. Purpurogallone trimethyl ether (I; R = Me, R′ = H) and purpurogallone (I; R = R′ = H) have been synthesised from β-(3 : 4 : 5-trimethoxybenzoyl)propionic acid (VI). *iso*Purpurogallone "octamethyl ether" (III; R = R′ = Me) has also been synthesised.

Perkin and Steven (*J.*, 1903, **83**, 192) obtained a mixture of purpurogallone and *iso*purpurogallone by heating purpurogallin with concentrated potassium hydroxide solution. In a later paper (*J.*, 1912, **101**, 803) Perkin showed that purpurogallone ($C_{11}H_8O_5$) was a phenolic carboxylic acid yielding an ethyl ester with alcoholic hydrogen chloride, and methyl purpurogallone trimethyl ether with methyl sulphate and sodium hydroxide. The action of alcoholic potassium hydroxide at 160—170° on purpurogallin trimethyl ether yielded a purpurogallone dimethyl ether, which gave (*a*) a lactonic anhydro-derivative with acetic anhydride and (*b*) the methyl purpurogallone trimethyl ether with methyl sulphate and sodium hydroxide. Formulæ (I; R = R′ = H), (I; R = R′ = Me), and (II; R = Me) were suggested for purpurogallone, methyl purpurogallone trimethyl ether, and the lactonic anhydro-derivative respectively, and *iso*purpurogallone was regarded as the hexahydroxydinaphthyldicarboxylic



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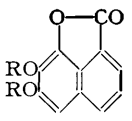

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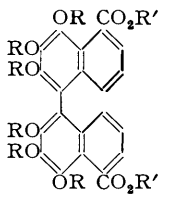
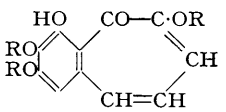


(III.)

acid (III; R = R′ = H). Willstätter and Heiss (*Annalen*, 1923, **433**, 17) suggested that purpurogallone arose by a benzilic acid rearrangement, and a similar explanation was advanced in Part I of this series (*J.*, 1948, 1045), although the phenyl*cyclo*pentadienolone structure for purpurogallin suggested by Willstätter and Heiss was rejected in favour of the benz*cyclo*heptatrienolone structure (IV; R = H).

Experiments aiming at the synthesis of purpurogallone were initiated at an early stage of our researches on purpurogallin, but unexpected difficulties were encountered, and the complete solution of this section of the problem has been considerably delayed. In the first place we found the preparation of purpurogallone (I; R = R′ = H) from purpurogallin to be unsatisfactory: the product consisted largely of *iso*purpurogallone (III; R = R′ = H), from which a small amount of purpurogallone could be separated as its diacetylanhydro-derivative (II; R = Ac), but Perkin's yields could not be approached either by the method described by



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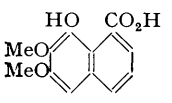

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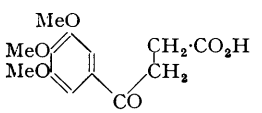


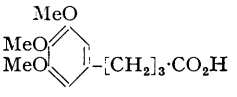
(VI.)

him or by slight modifications. Better results were, however, obtained by treating purpurogallin trimethyl ether with potassium hydroxide as described by Perkin (*loc. cit.*); although the

purification of the dimethyl ether (V)* of purpurogallone was difficult, methylation of the crude material afforded methyl purpurogallone trimethyl ether (I; R = R′ = Me) in fair yield, and the hydrolysis to *purpurogallone trimethyl ether* (I; R = Me; R′ = H) proceeded readily with sodium hydroxide solution.

Price *et al.* (*J. Amer. Chem. Soc.*, 1941, **63**, 1857; 1942, **64**, 2136; 1947, **69**, 2261) have prepared a number of α-naphthoic acids by condensation of furoic acid or its methyl ester with benzene, toluene, anisole, or chlorobenzene in the presence of aluminium chloride, and it was hoped that the use of 1 : 2 : 3-trimethoxybenzene might provide a synthesis of purpurogallone trimethyl ether, possibly together with the isomeric 5 : 6 : 7-trimethoxynaphthalene-1-carboxylic acid (XVI; R = Me). Although we have repeated the American work with anisole and also prepared 6-hydroxynaphthoic acid from phenol and furoic acid, the method failed completely with 1 : 2 : 3-trimethoxybenzene, pyrogallol, veratrole, and guaiacol.

For most synthetic routes β-(3 : 4 : 5-trimethoxybenzoyl)propionic acid (VI) was required, and this was obtained from ethyl 3 : 4 : 5-trimethoxybenzoylacetate and ethyl bromoacetate. The directions given by Haworth, Richardson, and Sheldrick (*J.*, 1935, 1580) gave erratic yields, but consistently good results are obtained by the slightly modified process described in the Experimental section. Reduction of the keto-acid (VI) to *γ-(3 : 4 : 5-trimethoxyphenyl)-butyric acid* (VII) was effected on a small scale either by Clemmensen reduction or by Minlon's modification of the Wolff–Kishner reduction, but on a larger scale both gave variable and frequently quite poor yields. Satisfactory reduction was realised by the employment of milder conditions for the Wolff–Kishner reduction; the keto-acid (VI) was converted into its hydrazone, which was isolated as a molecular compound of the normal hydrazone and the *anhydro*-derivative (VIII) and reduced smoothly to (VII) by boiling with 28% alcoholic sodium ethoxide.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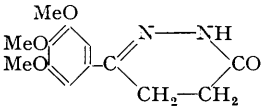
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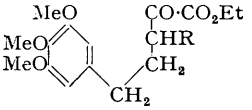
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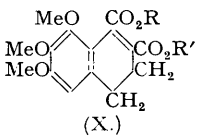
Reaction of γ-(3 : 4 : 5-trimethoxyphenyl)butyryl chloride with hydrogen cyanide and pyridine (Claisen, *Ber.*, 1898, **31**, 1024; Mauthner, *ibid.*, 1908, **41**, 921; 1909, **42**, 188) appeared to offer an approach to purpurogallone trimethyl ether, but tar formation and cyclisation of the acid chloride interfered. *Ethyl γ-(3 : 4 : 5-trimethoxyphenyl)butyrate* reacted readily with ethyl oxalate in the presence of potassium ethoxide to yield diethyl 1-keto-4-(3 : 4 : 5-trimethoxyphenyl)butane-1 : 2-dicarboxylate (IX; R = CO_2Et) as a crude oil, which we hoped to convert into ethyl 1-keto-4-(3 : 4 : 5-trimethoxyphenyl)butane-1-carboxylate (IX; R = H). Unfortunately, alkaline hydrolysis of (IX; R = CO_2Et) gave γ-(3 : 4 : 5-trimethoxyphenyl)-butyric acid, and the lowest concentration of sulphuric acid (18%) which had any effect caused ring closure to *diethyl 6 : 7 : 8-trimethoxy-3 : 4-dihydronaphthalene-1 : 2-dicarboxylate* (X; R = R′ = Et). Treatment of this diethyl ester (X; R = R′ = Et) with methanolic potassium hydroxide hydrolysed one ester group, but we failed to decarboxylate the half-ester, which is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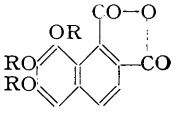
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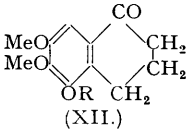
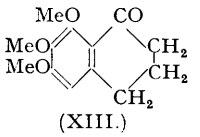

(XII.)

probably *1-carbethoxy-6 : 7 : 8-trimethoxy-3 : 4-dihydronaphthalene-2-carboxylic acid* (X; R = Et; R′ = H). Accordingly, an attempt was made to dehydrogenate and decarboxylate this half-ester in one operation, but heating it with sulphur or palladium-black resulted in the simultaneous elimination of ethyl alcohol with the formation of *6 : 7 : 8-trimethoxynaphthalene-1 : 2-dicarboxylic anhydride* (XI; R = Me). This stable yellow anhydride was demethylated with hydriodic acid, but the resultant red *6 : 7 : 8-trihydroxynaphthalene-1 : 2-dicarboxylic anhydride* (XI; R = H) resisted partial decarboxylation although its colour reactions with

* The formation of the lactonic anhydro-derivative establishes the structure (V) for purpurogallone dimethyl ether, m. p. 197—199°. Purpurogallin trimethyl ether, m. p. 176°, must consequently have structure (IV; R = Me) as its hydroxyl group has been shown to be in the benzene ring by the production of a phenolic tetrahydro-derivative (Part I, *loc. cit.*, p. 1047).

alkali and ferric chloride resembled very closely those exhibited by purpurogallone under similar conditions.

At this stage it was decided to carry out further exploratory experiments with γ-(2 : 3 : 4-trimethoxyphenyl)butyric acid, which was more accessible than the isomeric acid (VII) used above. 1 : 2 : 3-Trimethoxybenzene and succinic anhydride reacted in the presence of aluminium chloride to yield β-(2-hydroxy-3 : 4-dimethoxybenzoyl)propionic acid (Mitter and De, *J. Indian Chem. Soc.*, 1939, **16**, 35), which was reduced to γ-(2-hydroxy-3 : 4-dimethoxyphenyl)butyric acid as described by the Indian chemists and then cyclised by 92% sulphuric acid to 5-hydroxy-1-keto-6 : 7-dimethoxy-1 : 2 : 3 : 4-tetrahydronaphthalene (XII; R = H). The position of the free hydroxyl group in these compounds, assumed by Mitter and De (*loc. cit.*), was demonstrated by Manske and Holmes (*J. Amer. Chem. Soc.*, 1945, **67**, 97) by ethylation of the cyclic ketone (XII; R = H) and subsequent oxidation. The extensive demethylation occurring in the Friedel–Crafts reaction contrasts forcibly with the very slight demethylation occurring during the condensation of 1 : 2 : 3-trimethoxybenzene with glutaric anhydride * (Part I, *loc. cit.*). Both β-(2-hydroxy-3 : 4-dimethoxybenzoyl)propionic acid and its Clemmensen reduction product resist methylation, but the cyclic ketone (XII; R = H) was readily converted into 1-*keto*-5 : 6 : 7-*trimethoxy*-1 : 2 : 3 : 4-*tetrahydronaphthalene* (XII; R = Me). It has been shown that 6-methoxy-1 : 2 : 3 : 4-tetrahydronaphthalene is selectively oxidised by chromic acid to 1-keto-6-methoxy-1 : 2 : 3 : 4-tetrahydronaphthalene (see Thomas and Nathan, *J. Amer. Chem. Soc.*, 1948, **70**, 331, who give references to earlier work), and it was hoped that reduction of the ketone (XII; R = Me) to 5 : 6 : 7-*trimethoxy*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, followed by chromic acid oxidation, might provide a convenient route to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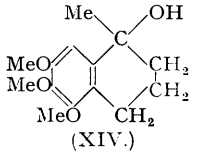
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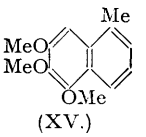
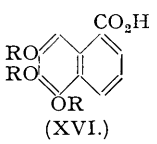

(XV.)

1-keto-6 : 7 : 8-trimethoxy-1 : 2 : 3 : 4-tetrahydronaphthalene (XIII). Reduction to the tetrahydronaphthalene was readily accomplished, but oxidation was not selective and both ketones were shown to be present in the oxidation product by chromatographic separation of the 2 : 4-*dinitrophenylhydrazones*. As 1-keto-5 : 6 : 7-trimethoxy-1 : 2 : 3 : 4-tetrahydronaphthalene (XII; R = Me) appeared to be formed in somewhat larger amount, presumably as a result of steric factors, this approach was abandoned.

The readily available 1-keto-5 : 6 : 7-trimethoxy-1 : 2 : 3 : 4-tetrahydronaphthalene (XII; R = Me) became the starting material for a number of experiments aiming at the introduction of a carboxyl group into position 1. A route *via* the carbinol and 1-halogeno-derivative was rapidly abandoned because the desired carbinol was too readily dehydrated, and 2 : 3 : 4-*trimethoxy*-5 : 6-*dihydronaphthalene* was obtained by Ponndorf reduction. The ketone (XII; R = Me) was therefore treated with methylmagnesium iodide to give 1-*hydroxy*-5 : 6 : 7-*trimethoxy*-1-*methyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene* (XIV). Dehydration of this compound with formic acid was accompanied by considerable polymerisation, and dehydrogenation of the resulting product with selenium at 310° or chloranil in boiling xylene (cf. Arnold and Collins, *J. Amer. Chem. Soc.*, 1939, **61**, 1407; 1940, **62**, 983) gave only poor yields of 1 : 2 : 3-*trimethoxy*-5-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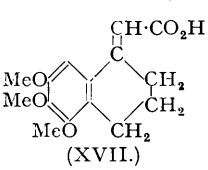
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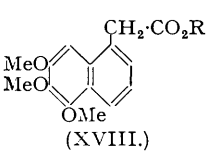
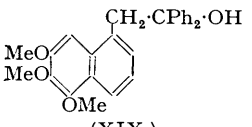

(XVIII.)

methylnaphthalene (XV). Good yields of (XV), however, were obtained by dehydrogenation of the carbinol (XIV), without prior dehydration, with palladium. The methoxylated ring of (XV) was oxidised more readily than the methyl group with selenium dioxide, and the product was identified as 3-methylphthalic acid, but the desired oxidation to 5 : 6 : 7-*trimethoxynaphthoic acid* (XVI; R = Me) was effected, though in yields of only 3—5%, by the use of potassium ferricyanide. Short boiling with hydriodic acid converted (XVI; R = Me) into 5 : 6 : 7-*tri*-

* In view of the work of Manske and Holmes (*loc. cit.*), there is little doubt that the demethylated acid obtained from this reaction is γ-(2-hydroxy-3 : 4-dimethoxybenzoyl)butyric acid.

hydroxynaphthoic acid (XVI; R = H), which gave a *triacetyl* derivative (XVI; R = Ac). Preliminary attempts to carry out a glycidic ester condensation with the tetralone (XII; R = Me) or to condense it with acetylene in the presence of potassium *tert.*-butoxide were unpromising, yielding much unchanged ketone and some tar in both cases, but by a Reformatsky reaction the tetralone (XII; R = Me) was readily converted into 5 : 6 : 7-*trimethoxy*-1 : 2 : 3 : 4-*tetrahydro*-1-*naphthylideneacetic acid* (XVII). Dehydrogenation of the ethyl ester of this acid (XVII) with palladium–charcoal yielded *ethyl* 5 : 6 : 7-*trimethoxy*-1-*naphthylacetate* (XVIII; R = Et), which gave the corresponding *acid* (XVIII; R = H) in dimorphous forms. Wieland degradation of this ester (XVIII; R = Et) proved unexpectedly difficult because the *carbinol* (XIX) obtained by the action of phenylmagnesium bromide resisted attempts at dehydration. This method of degradation was abandoned when it was found that ethyl 5 : 6 : 7-trimethoxy-1-naphthylacetate (XVIII; R = Et) was smoothly oxidised to the desired 5 : 6 : 7-trimethoxy-1-naphthoic acid (XVI; R = Me) by selenium dioxide at 140°, followed by treatment with alkaline hydrogen peroxide.

Equipped with the above two routes for the synthesis of 1-naphthoic acid derivatives, we turned our attention once again to the less accessible γ-(3 : 4 : 5-trimethoxyphenyl)butyric acid (VII). Cyclisation of the acid was effected in 45% yield by the action of phosphoric oxide in boiling benzene, or in 60% yield by conversion with phosphorus pentachloride into the acid chloride which was then treated with stannic chloride in benzene. 1-*Keto*-6 : 7 : 8-*trimethoxy*-1 : 2 : 3 : 4-*tetrahydronaphthalene* (XIII) did not give a cyanohydrin, but it reacted with methyl-



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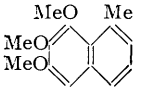

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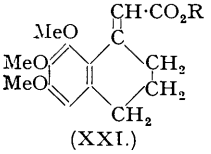
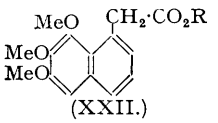


(XXI.)

magnesium iodide and the oily product yielded 1 : 2 : 3-*trimethoxy*-8-*methylnaphthalene* (XX) after dehydrogenation with palladium, but several unsuccessful attempts were made to oxidise this methylnaphthalene with potassium ferricyanide. The cyclic ketone (XIII) reacted smoothly with ethyl bromoacetate and zinc, yielding 6 : 7 : 8-*trimethoxy*-1 : 2 : 3 : 4-*tetrahydro*-1-*naphthylideneacetic acid* (XXI; R = H), the *methyl* ester of which was dehydrogenated with palladium to 6 : 7 : 8-*trimethoxy*-1-*naphthylacetic acid* (XXII; R = H) and a small quantity of 1 : 2 : 3-trimethoxy-8-methylnaphthalene (XX). The methyl ester (XXII; R = Me) was not oxidised smoothly by selenium dioxide and alkaline hydrogen peroxide, but it was converted into 6 : 7 : 8-trimethoxy-1-naphthoic acid (I; R = Me, R′ = H) by treatment with potassium ferricyanide. The same acid (I; R = Me, R′ = H) was also obtained during Wieland degradation of the methyl ester (XXII; R = Me); interaction with phenylmagnesium bromide yielded 1 : 1-*diphenyl*-2-(6 : 7 : 8-*trimethoxy*-1-*naphthyl*)*ethan*-1-*ol* (XXIII) and an oil, presumably containing phenyl 6 : 7 : 8-trimethoxy-1-naphthylmethyl ketone (XXIV), which



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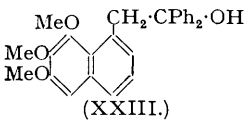

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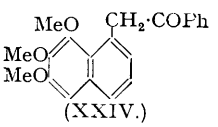

(XXIV.)

gave benzoic and the acid (I; R = Me, R′ = H) in small yield on oxidation with hydrogen peroxide. Comparison of the acid (I; R = Me, R′ = H) and the methyl ester (I; R = R′ = Me) showed complete identity with purpurogallone trimethyl ether and its methyl ester respectively, and demethylation of the acid (I; R = Me, R′ = H) with boiling hydriodic acid yielded purpurogallone.

Methyl 6 : 7 : 8-trimethoxy-1-naphthoate (I; R = R′ = Me) was iodinated to give *methyl* 5-*iodo*-6 : 7 : 8-*trimethoxy*-1-*naphthoate*, which on heating with copper powder yielded *dimethyl* 2 : 3 : 4 : 2′ : 3′ : 4′-*hexamethoxy*-1 : 1′-*dinaphthyl*-5 : 5′-*dicarboxylate* (III; R = R′ = Me), identical with *iso*purpurogallone octamethyl ether. Hydrolysis yielded 2 : 3 : 4 : 2′ : 3′ : 4′-*hexamethoxy*-1 : 1′-*dinaphthyl*-5 : 5′-*dicarboxylic acid* (III; R = Me, R′ = H).

The Experimental section also includes a description of the following new compounds prepared during this investigation: 3 : 4 : 5-*trimethoxyphenylglyoxal*, *methyl* 3 : 4 : 5-*trimethoxy*-2-*chloromethylbenzoate*, 4′-*hydroxy*-4 : 2′ : 3′-*triacetoxybenz*cyclo*heptatrien*-3-*one* (IV; R = Ac), and 1 : 4-*diphenoxy*cyclo*pent*-2-*ene*.

Experimental.

Purpurogallone Trimethyl Ether (I; R = Me; R′ = H).—Purpurogallin trimethyl ether (2 g.) was heated in a sealed tube with alcoholic potassium hydroxide at 160—170° as described by Perkin (*loc. cit.*). The resulting solution was acidified with hydrochloric acid and extracted with ether, and the crude product dissolved in aqueous sodium hydroxide and warmed with excess of methyl sulphate. The neutral material, isolated with ether, was distilled and the fraction, b. p. 180° (air-bath)/0·5 mm., crystallised from ether–light petroleum (b. p. 60—80°). Recrystallisation from *cyclo*hexane or aqueous ethanol gave colourless prisms of methyl purpurogallone trimethyl ether (I; R = R′ = Me), m. p. 80—81°. Hydrolysis, by heating for 12 hours with 4N-sodium hydroxide and sufficient ethanol to give a homogeneous solution when hot, gave purpurogallone trimethyl ether (I; R = Me, R′ = H) which crystallised from benzene–*cyclo*hexane in colourless plates, m. p. 145—146° (Found: C, 64·4; H, 5·4. Calc. for $C_{14}H_{14}O_5$: C, 64·1; H, 5·3%). Refluxing with constant-boiling hydriodic acid (50 parts) for 10 minutes yielded purpurogallone (I; R = R′ = H).

Condensation of Furoic Acid with Phenol.—Phenol (20 g.), furoic acid (2 g.), and aluminium chloride (7·5 g.) were heated at 60—70° for 10 hours. More aluminium chloride (2·5 g.) was then added and the heating continued for a further 24 hours. After decomposition of the complex with ice and hydrochloric acid and extraction with ether, the products were taken up in 5% sodium hydrogen carbonate solution, recovered, and extracted with ether. The crude oily product was crystallised first from acetone–benzene and then from water; 6-hydroxy-1-naphthoic acid (0·2 g.), m. p. 207—208° (Royle and Schedler, *J.*, 1923, **123**, 1641, give m. p. 208—209°), was obtained and was further characterised by methylation with methyl sulphate and sodium hydroxide to 6-methoxy-1-naphthoic acid, m. p. 181—182°, identical with a specimen synthesised from furoic acid and anisole.

β-3 : 4 : 5-Trimethoxybenzoylpropionic Acid (VI).—Ethyl 3 : 4 : 5-trimethoxybenzoylacetate (16·6 g.) was dissolved in sodium ethoxide solution (from 2 g. of sodium and 150 c.c. of anhydrous ethanol) and cooled below 10°, and ethyl bromoacetate (10 c.c.) added. After 48 hours at room temperature, the product was hydrolysed and the acid (VI) (9 g.), m. p. 122°, isolated as described by Haworth, Richardson, and Sheldrick (*loc. cit.*). The *methyl* ester, prepared with methanol and sulphuric acid, crystallised from methanol in needles, m. p. 94—95° (Found: C, 59·5; H, 6·3. $C_{14}H_{18}O_6$ requires C, 59·6; H, 6·4%).

γ-(3 : 4 : 5-Trimethoxyphenyl)butyric Acid (VII).—The keto-acid (VI) (1 g.) was dissolved in water (20 c.c.) containing sodium hydrogen carbonate (0·3 g.) and refluxed for 3 hours with 90% hydrazine hydrate (1 c.c.). The cooled solution was carefully acidified (litmus) and the product crystallised from benzene; the molecular compound was obtained as colourless prisms (0·85 g.) (Found: C, 57·3; H, 6·3; N, 10·5. $C_{13}H_{18}O_5N_2$ requires C, 55·3; H, 6·4; N, 9·9. $C_{13}H_{16}O_4N_2$ requires C, 59·1; H, 6·1; N, 10·6%) which melt to a turbid liquid at 110° and clear at 118°. The mother-liquors yielded the *anhydro*-derivative (VIII) which was purified by passing it in benzene through an alumina column and eluting it with benzene–acetone (10 : 1) and crystallised from benzene; stout needles, m. p. 139° (Found: C, 59·0; H, 6·3%), were obtained which were insoluble in cold alkali or dilute acid, but soluble in cold, concentrated hydrochloric acid. The mixed product (5 g.) from several operations was refluxed for 24 hours with a solution of sodium ethoxide from sodium (10 g.) and ethanol (125 c.c.). After diluting the mixture with water, shaking it with methyl sulphate (5 c.c.), and removing a trace of neutral matter with ether, acidification and crystallisation from benzene–light petroleum (b. p. 60—80°) gave *γ-(3 : 4 : 5-trimethoxyphenyl)butyric acid* (VII), colourless prisms (3·9 g.), m. p. 83—84° (Found: C, 61·1; H, 7·1. $C_{13}H_{18}O_5$ require C, 61·4; H, 7·1%). The *ethyl* ester, prepared with ethanolic hydrogen chloride, was an oil, b. p. 165—170°/0·3 mm.

Diethyl 6 : 7 : 8-Trimethoxy-3 : 4-dihydronaphthalene-1 : 2-dicarboxylate (X; R = R′ = Et).—A solution of ethyl oxalate (3·2 c.c.) in dry ether (10 c.c.) was added to a suspension of potassium ethoxide (from 0·7 g. of powdered potassium and 0·85 g. of ethanol) in ether (25 c.c.). A solution of the ethyl ester (2·7 g.) of the acid (VII) in ether (15 c.c.) was gradually introduced, and a red oil was precipitated. After 12 hours, water was added and the alkaline layers on acidification yielded diethyl 1-keto-4-(3 : 4 : 5-trimethoxyphenyl)butane-1 : 2-dicarboxylate (IX; R = CO_2Et) (2·8 g.) as a yellow oil which was not purified. This yellow oil (2·5 g.) was refluxed for 5 hours with 18% sulphuric acid (20 c.c.); the product (X; R = R′ = Et), isolated with ether and crystallised from light petroleum (b. p. 60—80°), was obtained as colourless prisms (1·3 g.), m. p. 89° (Found: C, 62·7; H, 6·6. $C_{19}H_{24}O_7$ requires C, 62·6; H, 6·8%). Hydrolysis of the above diethyl ester with excess of 20% methanolic potassium hydroxide for ½ hour gave the *half-ester* (X; R = Et, R′ = H), which separated from water in colourless plates, m. p. 178° (decomp.) (Found: equiv., 329. $C_{17}H_{20}O_7$ requires equiv., 336).

6 : 7 : 8-Trimethoxynaphthalene-1 : 2-dicarboxylic Anhydride (XI; R = Me).—The half-ester (X; R = Et, R′ = H) (0·7 g.) was heated with palladium-black (0·1 g.) for 1 hour at 250°. The *product*, isolated with chloroform, crystallised from acetic acid in yellow solvated needles, m. p. 167° (Found: C, 60·8, 60·5; H, 4·3, 4·2. $C_{15}H_{12}O_6,\frac{1}{2}CH_3{\cdot}CO_2H$ requires C, 60·4; H, 4·4%), which dissolved in warm alkali to a colourless solution; acidification then precipitated a colourless crystalline acid which reverted to the yellow anhydride on being heated. *6 : 7 : 8-Trihydroxynaphthalene-1 : 2-dicarboxylic anhydride* (XI; R = H), obtained by demethylation for ½ hour with boiling hydriodic acid (10 volumes; *d* 1·7), crystallised from ethyl acetate in deep-red prisms, m. p. >250° (Found: C, 58·4; H, 2·8. $C_{12}H_6O_8$ requires C, 58·5; H, 2·4%), which gave a reddish-brown ferric test and dissolved in alkali to a yellow solution becoming cherry-red on exposure to air.

1-Keto-5 : 6 : 7-trimethoxy-1 : 2 : 3 : 4-tetrahydronaphthalene (XII; R = Me).—The best yield of β-(2-hydroxy-3 : 4-dimethoxybenzoyl)propionic acid (8·75 g.) (Mitter and De, *loc. cit.*) was obtained from 1 : 2 : 3-trimethoxybenzene (8 g.), succinic anhydride (5 g.), and aluminium chloride (20 g.) in nitrobenzene (30 c.c.) after reaction for 40 hours at room temperature. Reduction and cyclisation to (XII; R = H) were effected by Mitter and De's method; 5-hydroxy-1-keto-6 : 7-dimethoxy-1 : 2 : 3 : 4-tetrahydronaphthalene (XII; R = H) gave a 2 : 4-*dinitrophenylhydrazone*, which crystallised from dioxan in red prisms, m. p. 284° (decomp.) (Found: N, 13·8. $C_{18}H_{18}O_7N_4$ requires N, 13·9%).

Methylation of the phenolic ketone (XII; R = H) with excess of methyl sulphate and 4N-sodium hydroxide gave 1-*keto*-5 : 6 : 7-*trimethoxy*-1 : 2 : 3 : 4-*tetrahydronaphthalene* (XII; R = Me), which separated from light petroleum (b. p. 60—80°) in colourless prisms, m. p. 74—74·5° (Found: C, 65·8; H, 6·7. $C_{13}H_{16}O_4$ requires C, 66·1; H, 6·8%), and yielded a 2 : 4-*dinitrophenylhydrazone* as long orange-red plates, m. p. 245°, from benzene (Found: N, 13·3. $C_{19}H_{20}O_7N_4$ requires N, 13·5%). The combined cyclisation and methylation processes gave the cyclic ketone (XII; R = Me) in 76% yield.

5 : 6 : 7-*Trimethoxy*-1 : 2 : 3 : 4-*tetrahydronaphthalene*.—The ketone (XII; R = Me) was reduced for 15 hours by Martin's modification of the Clemmensen reaction; the toluene layer was extracted with aqueous sodium hydroxide, and the alkaline extract methylated with methyl sulphate. The product was isolated with ether and purified first by distillation under reduced pressure and then by removing a small amount (2 : 4-dinitrophenylhydrazone test) of unchanged ketone (XII; R = Me) by passing a benzene–light petroleum (b. p. 60—80°) solution through a column of alumina. It crystallised from light petroleum (b. p. 40—60°) in rhombs, m. p. 43—44° (Found: C, 70·7; H, 8·1. $C_{13}H_{18}O_3$ requires C, 70·3; H, 8·1%). A solution of chromic acid (0·4 g.) in acetic acid (7 c.c.) and water (1 c.c.) was added during 20 minutes to a solution of 5 : 6 : 7-trimethoxy-1 : 2 : 3 : 4-tetrahydronaphthalene (0·55 g.) in a mixture of acetic (4 c.c.) and propionic (1 c.c.) acid at 5°. After 12 hours at 5°, the solution was evaporated under reduced pressure warmed with 5% sulphuric acid, and extracted with ether. The extract, after being washed with sodium hydroxide, was dried and evaporated, and the residue treated with methanolic 2 : 4-dinitrophenylhydrazine sulphate. The products were taken up in benzene, evaporated to remove methanol, redissolved in benzene, and passed through a 2-foot alumina column. Elution with benzene removed first the 2 : 4-dinitrophenylhydrazone (66·0 mg.) of 1-keto-5 : 6 : 7-trimethoxy-1 : 2 : 3 : 4-tetrahydronaphthalene (XII; R = Me) and then that (40 mg.) of 1-keto-6 : 7 : 8-trimethoxy-1 : 2 : 3 : 4-tetrahydronaphthalene (XIII) (see p. 3277).

2 : 3 : 4-*Trimethoxy*-5 : 6-*dihydronaphthalene*.—A mixture of 1-keto-5 : 6 : 7-trimethoxy-1 : 2 : 3 : 4-tetrahydronaphthalene (XII; R = Me) (1 g.) and aluminium *iso*propoxide (2·5 g.) in *iso*propyl alcohol (10 c.c.) was heated for 24 hours and decomposed with ice and dilute hydrochloric acid. Distillation yielded 2 : 3 : 4-*trimethoxy*-5 : 6-*dihydronaphthalene* (0·66 g.) as a colourless oil, b. p. 125°/0·5 mm. (Found: C, 70·8; H, 7·3. $C_{13}H_{16}O_3$ requires C, 70·9; H, 7·3%), and a viscous yellow oil (0·25 g.), probably a polymer, b. p. 240°/0·5 mm.

1-*Hydroxy*-5 : 6 : 7-*trimethoxy*-1-*methyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene* (XIV).—A solution of the cyclic ketone (XII; R = Me) (2·5 g.) in ether (25 c.c.) was added to methylmagnesium iodide (from 0·5 g. of magnesium) in ether (25 c.c.), and after 12 hours at room temperature the mixture was added to ice and ammonium chloride. The *carbinol* (XIV) crystallised from light petroleum (b. p. 60—80°) in long plates, m. p. 92—93° (Found: C, 66·6; H, 7·9. $C_{14}H_{20}O_4$ requires C, 66·7; H, 7·9%).

1 : 2 : 3-*Trimethoxy*-5-*methylnaphthalene* (XV).—Dehydration of the carbinol (XIV) (1 g.) by heating it for 15 minutes with 90% formic acid (5 c.c.) at 76—80° yielded an oil (0·35 g.), probably 5 : 6 : 7-trimethoxy-1-methyl-3 : 4-dihydronaphthalene, b. p. 140°/0·5 mm., and a polymer (0·55 g.), b. p. 200°/0·5 mm. The carbinol (XIV) (1 g.), heated with palladium-black (0·05 g.) at 260—300° for 4 hours, gave 1 : 2 : 3-*trimethoxy*-5-*methylnaphthalene* (XV) as a colourless oil, b. p. 135—140°/0·5 mm. (Found: C, 72·3; H, 6·7. $C_{14}H_{16}O_3$ requires C, 72·4; H, 6·9%), yielding a s-*trinitrobenzene* complex, which separated from aqueous methanol in orange needles, m. p. 88° (Found: C, 54·3; H, 4·4; N, 9·6. $C_{20}H_{19}O_9N_3$ requires C, 53·9; H, 4·3; N, 9·4%).

1 : 2 : 3-Trimethoxy-5-methylnaphthalene (XV) (1·2 g.) and selenium dioxide were heated in a sealed tube for 4 hours at 200—210°. The fraction of the product soluble in hydrogen carbonate yielded 3-methylphthalic acid which crystallised from ether–benzene in elongated plates, m. p. 154° (Jürgens, *Ber.*, 1907, **40**, 4409, gives m. p. 154°). Sublimation at 20 mm. gave the anhydride which separated from light petroleum (b. p. 60—80°) in needles, m. p. 116° (*idem*, *ibid.*, gives m. p. 114—115°) (Found: C, 66·6; H, 3·7. Calc. for $C_9H_6O_3$: C, 66·7; H, 3·7%).

5 : 6 : 7-*Trimethoxy*-1 : 2 : 3 : 4-*tetrahydro*-1-*naphthylideneacetic Acid* (XVII).—The tetralone (XII; R = Me) (1 g.) and ethyl bromoacetate (1·5 c.c.) in benzene (5 c.c.) were added dropwise to zinc needles (1 g.) and a small crystal of iodine under boiling benzene (10 c.c.); the reaction was completed by 1 hour's boiling after dissolution of the zinc. The cooled solution was decomposed with ice and hydrochloric acid and extracted with ether, the extract was washed with dilute sodium hydroxide solution and dried, and the solvent removed. The residual ethyl ester of (XVII) was distilled (b. p. 175°/0·5 mm.) and hydrolysed with aqueous-alcoholic potassium hydroxide; the *acid* (XVII) separated from *cyclo*hexane in colourless needles, m. p. 82—84° (Found: C, 64·4; H, 6·4. $C_{15}H_{18}O_5$ requires C, 64·7; H, 6·5%).

5 : 6 : 7-*Trimethoxy*-1-*naphthylacetic Acid* (XVIII; R = H).—The acid (XVII) was esterified with ethanol and sulphuric acid, and the distilled ethyl ester, b. p. 175°/0·5 mm. (2·5 g.), was heated with palladised charcoal (0·3 g. of 10%) for 3 hours at 280—320°. Distillation gave *ethyl* 5 : 6 : 7-*trimethoxy*-1-*naphthylacetate* (XVIII; R = Et), which separated from aqueous methanol in small plates, m. p. 66—67° (Found: C, 67·4; H, 6·7. $C_{17}H_{20}O_5$ requires C, 67·2; H, 6·6%). Hydrolysis afforded the *acid* (XVIII; R = H) which separated from *cyclo*hexane in either long needles, m. p. 97°, or rhombs, m. p. 113—115° (Found: C, 65·1; H, 5·6. $C_{15}H_{16}O_5$ requires C, 65·2; H, 5·8%), slow crystallisation favouring the latter variety.

1 : 1-*Diphenyl*-2-(5 : 6 : 7-*trimethoxy*-1-*naphthyl*)*ethan*-1-*ol* (XIX).—Ethyl 5 : 6 : 7-trimethoxy-1-naphthylacetate (1 g.) was added to a solution of phenylmagnesium bromide, prepared from bromobenzene (2 c.c.) and magnesium (0·4 g.) in ether (20 c.c.), and after ½ hour at room temperature and 1 hour's boiling the cooled mixture was decomposed with ice–hydrochloric acid. Evaporation of the dried ethereal extract and removal of a small amount of unchanged bromobenzene under reduced pressure yielded an oil from which the carbinol (0·4 g.) slowly solidified. Crystallisation from aqueous methanol and *cyclo*hexane yielded colourless prisms, m. p. 133—134° (Found: C, 78·1; H, 6·1. $C_{27}H_{26}O_4$ requires C, 78·3; H, 6·3%).

5 : 6 : 7-*Trimethoxynaphthalene*-1-*carboxylic Acid* (XVI; R = Me).—(*a*) 1 : 2 : 3-Trimethoxy-5-methylnaphthalene (XV) (2 g.), potassium ferricyanide (100 g.), and potassium hydroxide (18 g.) in

water (350 c.c.) were stirred for 24 hours at 60°. Further quantities of potassium ferricyanide (35 g.) and potassium hydroxide (6 g.) were added and the reaction continued for another 24 hours. After cooling, neutral material was removed in ether, and the aqueous solution was acidified and again extracted with ether. The product was dissolved in sodium hydrogen carbonate, recovered with hydrochloric acid, and collected.

(*b*) Ethyl 5 : 6 : 7-trimethoxy-1-naphthylacetate (XVIII; R = Et) (0·1 g.) was heated for 9 hours with selenium dioxide (0·15 g.) in dioxan (3 c.c.) in a sealed tube at 130—140°. The product was diluted with 2N-sodium hydroxide (5 c.c.), and warmed on a water-bath with hydrogen peroxide (5 c.c. of 100-vol.). The solution was extracted with ether, the aqueous alkaline layer was acidified, and the acid collected. 5 : 6 : 7-*Trimethoxynaphthalene*-1-*carboxylic acid* (XVI; R = Me) crystallised from benzene–light petroleum (b. p. 60—80°) in colourless needles, m. p. 159° (Found: C, 64·0; H, 4·9. $C_{14}H_{14}O_5$ requires C, 64·1; H, 5·3%).

5 : 6 : 7-*Trihydroxynaphthalene*-1-*carboxylic Acid* (XVI; R = H).—This acid was prepared by refluxing the trimethyl ether (XVI; R = Me) (50 mg.) with hydriodic acid (3 c.c.; *d* 1·7) for 10 minutes. After cooling, the solid was collected, washed with water, and crystallised from aqueous acetone; the acid (XVI; R = H) was obtained as grey elongated plates, decomposing above 270° without melting. The *triacetyl* derivative (XVI; R = Ac), prepared by heating the acid with acetic anhydride and sodium acetate on the water-bath for ½ hour, separated from aqueous methanol in colourless prisms (Found: C, 59·1; H, 4·3. $C_{17}H_{14}O_8$ requires C, 58·9; H, 4·0%) which sinter at 195° and on rapid heating melt to a clear liquid at 230°.

1-*Keto*-6 : 7 : 8-*trimethoxy*-1 : 2 : 3 : 4-*tetrahydronaphthalene* (XIII).—(*a*) γ-(3 : 4 : 5-Trimethoxyphenyl)butyric acid (VII) (1 g.) in benzene (40 c.c.) was refluxed for 3 hours with granulated phosphoric oxide (10 g.). The dark complex was decomposed with ice, made alkaline with sodium hydroxide, and extracted with ether, and the ketone (XIII) (0·4 g.) recovered.

(*b*) γ-(3 : 4 : 5-Trimethoxyphenyl)butyric acid (2·2 g.) in benzene (25 c.c.) was cooled in ice whilst phosphorus pentachloride (2·5 g.) was added. After 5 minutes at 0° and 25 minutes at room temperature, the mixture was warmed for 5 minutes on the water-bath. Stannic chloride (2·2 c.c.) in benzene (100 c.c.) was then added at 0°, and after 2 hours at 0° the mixture was decomposed with ice and hydrochloric acid, and the ketone (XIII) (1·25 g.) reovered by removal of the benzene. 1-*Keto*-6 : 7 : 8-*trimethoxy*-1 : 2 : 3 : 4-*tetrahydronaphthalene* (XIII) crystallised from aqueous methanol or ether–light petroleum (b. p. 60—80°) in colourless prisms, m. p. 125° (Found: C, 66·3; H, 6·5. $C_{13}H_{16}O_4$ requires C, 66·1; H, 6·8%). The 2 : 4-*dinitrophenylhydrazone* separated from ethyl acetate in long red plates, m. p. 205—206° (Found: N, 13·4. $C_{19}H_{20}O_7N_4$ requires N, 13·5%).

1 : 2 : 3-*Trimethoxy*-5-*methylnaphthalene* (XX).—Condensation of 1-keto-6 : 7 : 8-trimethoxy-1 : 2 : 3 : 4-tetrahydronaphthalene (XIII) with methylmagnesium iodide was carried out as described for the isomer (XII; R = Me) but appeared to be accompanied by dehydration. The product, which failed to crystallise and had b. p. 130°/0·5 mm., was dehydrogenated by heating it with palladium for 2 hours at 280—300° and yielded 1 : 2 : 3-*trimethoxy*-5-*methylnaphthalene* (XX), b. p. 130—135°/0·4 mm., which separated from aqueous methanol or light petroleum (b. p. 40—60°) in long prisms, m. p. 73—75° (Found: C, 72·6; H, 6·9. $C_{14}H_{16}O_3$ requires C, 72·4; H, 6·9%). The s-*trinitrobenzene* complex crystallised from methanol in orange needles, m. p. 91·5—93° (Found: N, 9·7. $C_{20}H_{19}O_9N_3$ requires N, 9·4%). This methylnaphthalene (XX) was recovered after being heated with alkaline potassium ferricyanide for 2 weeks.

6 : 7 : 8-*Trimethoxy*-1 : 2 : 3 : 4-*tetrahydro*-1-*naphthylideneacetic Acid* (XXI).—This *acid* (4 g.), obtained from 1-keto-6 : 7 : 8-trimethoxy-1 : 2 : 3 : 4-tetrahydronaphthalene (XIII) (5 g.) as described for the isomeric acid (XVII), crystallised from benzene–*cyclo*hexane in colourless prisms, m. p. 125—127° (Found: C, 64·9; H, 6·7. $C_{15}H_{18}O_5$ requires C, 64·7; H, 6·5%).

6 : 7 : 8-*Trimethoxy*-1-*naphthylacetic Acid* (XXII; R = H).—The *methyl* ester of the acid (XXI), prepared with excess of ethereal diazomethane, was dehydrogenated with palladium–charcoal as described in the preparation of the isomer (XVIII; R = H). The resultant oily *methyl* ester (XXII; R = Me) on hydrolysis yielded the *acid* (XXII; R = H) which crystallised from benzene in colourless plates, m. p. 158—159·5° (Found: C, 65·2; H, 5·7. $C_{15}H_{16}O_5$ requires C, 65·2; H, 5·8%). A small amount of 1 : 2 : 3-trimethoxy-5-methylnaphthalene (XX), m. p. 73—75°, was also obtained. The methyl ester (XXII; R = Me) resisted oxidation with selenium dioxide and hydrogen peroxide.

1 : 1-*Diphenyl*-2-(6 : 7 : 8-*trimethoxy*-1-*naphthyl*)*ethan*-1-*ol* (XXIII).—The methyl ester (XXII; R = Me) (0·5 g.), dissolved in ether (10 c.c.), was added to phenylmagnesium bromide [from magnesium (0·4 g.) and bromobenzene (2 g.) in ether (20 c.c.)]. After 2 hours' refluxing the product was set aside overnight and decomposed with ice and hydrochloric acid. The *product*, isolated with ether, separated from ether–light petroleum (b. p. 60—80°) in crystals (0·2 g.), which after recrystallisation from methanol or ethanol were obtained as colourless prisms, m. p. 152—153° (Found: C, 78·6; H, 6·5. $C_{27}H_{26}O_4$ requires C, 78·3; H, 6·3%). An oil (A), probably crude phenyl 6 : 7 : 8-trimethoxy-1-naphthylmethyl ketone (XXIV), was obtained from the mother-liquors.

6 : 7 : 8-*Trimethoxy*-1-*naphthoic acid* (I; R = Me, R′ = H).—(*a*) 6 : 7 : 8-Trimethoxy-1-naphthylacetic acid (XXII; R = H) (0·5 g.), potassium ferricyanide (35 g.), and potassium hydroxide (5 g.) were dissolved in water (100 c.c.) and heated at 75—80°. Two further portions of potassium ferricyanide (12 g.) and potassium hydroxide (2 g.) were added at 24-hours intervals. After 3 days' heating, the cooled and acidified solution was extracted with ether, and the acid (I; R = Me, R′ = H) (0·1 g.) was dissolved in sodium hydrogen carbonate solution, precipitated by acid, and collected.

(*b*) The crude oil (A) (0·3 g.) obtained from the mother-liquors from the preparation of the carbinol (XXIII) was refluxed for 3 hours with aqueous-alcoholic sodium hydroxide, and the neutral portion, obtained by removal of alcohol and extraction with ether was dissolved in ethanol and warmed on the water-bath with excess of hydrogen peroxide and 2N-sodium hydroxide. After removal of ethanol and cooling, ether extracted a further crop of carbinol (XXIII), and the acids liberated by acidification were fractionally sublimed under reduced pressure. The first fraction yielded benzoic acid, and at 120°/0·0005 mm. 6 : 7 : 8-trimethoxy-1-naphthoic acid (I; R = Me; R′ = H) sublimed.

6 : 7 : 8-*Trimethoxy*-1-*naphthoic acid* (I; R = Me, R′ = H) prepared by method (*a*) or (*b*) crystallised from benzene–light petroleum (b. p. 60—80°) in colourless prisms, m. p. 145—147°, undepressed by admixture with purpurogallone trimethyl ether. A portion was esterified with diazomethane and the resultant *ester*, m. p. 80—81°, was identified with methyl purpurogallone trimethyl ether.

Methyl 5-*Iodo*-6 : 7 : 8-*trimethoxynaphthalene*-1-*carboxylate*.—Iodine (0·1 g.) and mercuric acetate (0·08 g.) were added alternately in small portions during 15 minutes to a solution of methyl 6 : 7 : 8-trimethoxy-1-naphthoate (I; R = R′ = Me) (0·1 g.) in acetic acid (2 c.c.) at 50°. After being stirred for a further 5 minutes and then cooled, the mixture was diluted with water, extracted with chloroform, and filtered from mercuric iodide. The extract was washed with sodium hydrogen sulphite solution and water, and dried; removal of the solvent and crystallisation of the residue from aqueous methanol or light petroleum (b. p. 40—60°) yielded *methyl* 5-*iodo*-6 : 7 : 8-*trimethoxynaphthalene*-1-*carboxylate* as colourless prisms, m. p. 120—121° after softening at 119° (Found: C, 44·7; N, 3·7. $C_{15}H_{15}O_5I$ requires C, 44·8; H, 3·7%).

Dimethyl 2 : 3 : 4 : 2′ : 3′ : 4′-*Hexamethoxy*-1 : 1′-*dinaphthyl*-5 : 5′-*dicarboxylate* (III; R = R′ = Me).—The above iodo-compound (50 mg.) was mixed with copper bronze (0·1 g.), and the mixture heated for ½ hour at 260—275°. The product isolated with acetone solidified on trituration with cold methanol, and crystallised from ethanol in colourless prisms, m. p. 210—212°, alone or mixed with *iso*purpurogallone octamethyl ether. Hydrolysis with boiling aqueous-ethanolic sodium hydroxide for 12 hours gave the *dicarboxylic acid* (III; R = Me, R′ = H), which crystallised from glacial acetic acid in minute prisms, m. p. 300—305° (decomp.) (Found: C, 63·9; H, 5·1. $C_{28}H_{26}O_{10}$ requires C, 64·4; H, 5·0%).

3 : 4 : 5-*Trimethoxyphenylglyoxal*.—3 : 4 : 5-Trimethoxyacetophenone (1 g.) was dissolved in dioxan (4 c.c.) and boiled for 3 hours with a solution of selenium dioxide (0·8 g.) in water (2 c.c.). The cooled mixture was diluted. The product, isolated with ethyl acetate, was a yellow oil, b. p. 135—140°/0·4 mm., crystallising from water as a *hydrate*, colourless plates, m. p. 103—104° (decomp.) (Found: C, 54·6; H, 5·7. $C_{11}H_{14}O_6$ requires C, 54·6; H, 5·8%). Distillation of the pure hydrate at 0·4 mm. gave 3 : 4 : 5-trimethoxyphenylglyoxal as yellow prisms, m. p. 64°.

Methyl 3 : 4 : 5-*Trimethoxy*-2-*chloromethylbenzoate*.—Methyl 3 : 4 : 5-trimethoxybenzoate (2 g.), formaldehyde solution (15 c.c.), and concentrated hydrochloric acid (15 c.c.) were heated on a water-bath for 2 hours. *Methyl* 3 : 4 : 5-*trimethoxy*-2-*chloromethylbenzoate* which separated on cooling crystallised from light petroleum (b. p. 60—80°) or ether in colourless needles, m. p. 85° (Found: C, 52·8; H, 5·0. $C_{12}H_{15}O_5Cl$ requires C, 52·5; H, 5·5%).

4′-*Hydroxy*-4 : 2′ : 3′-*triacetoxybenz*cyclo*heptatrien*-3-*one* (*Purpurogallin Triacetate*) (IV; R = Ac).—Purpurogallin (4 g.) was warmed for 3 hours on the water-bath with acetic anhydride (20 c.c.) and anhydrous sodium acetate (5 g.). Water was added, and the tetra-acetate was collected and crystallised from benzene; colourless prisms, m. p. 184—186°, were obtained in quantitative yield. This tetra-acetate (1 g.) was suspended in methanol (40 c.c.) containing concentrated hydrochloric acid (1 c.c.) and shaken at room temperature for 14 hours. The filtrate from unchanged tetra-acetate was diluted, and the precipitate collected and crystallised from ethanol; the *triacetate* was obtained in golden needles, m. p. 138—140° (Found: C, 59·2; H, 4·2. $C_{17}H_{14}O_8$ requires C, 59·0; H, 4·0%).

1 : 4-*Diphenoxy*cyclo*pent*-2-*ene*.—*trans*-1 : 4-Dibromo*cyclo*pent-2-ene (Thiele, *Annalen*, 1901, **314**, 300) (4 g.) was dissolved in acetone (20 c.c.), and phenol (4 g.) and potassium carbonate (6 g.) were added. The mixture was refluxed for 3 hours, diluted, extracted with ether, and dried. Removal of the solvent gave 1 : 4-*diphenoxy*cyclo*pent*-2-*ene* which crystallised from ethanol in long prisms, m. p. 103° (Found: C, 80·8; H, 6·2. $C_{17}H_{16}O_2$ requires C, 81·0; H, 6·4%). The same product was obtained from *cis*-1 : 4-dibromo*cyclo*pent-2-ene.

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