Studies in Mycological Chemistry. Part II. Proof of the Constitution of Flaviolin (2 : 5 : 7-Trihydroxy-1 : 4-naphthaquinone) by a Synthesis of Tri-O-methylflaviolin.*

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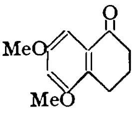
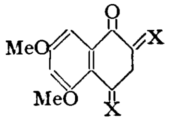
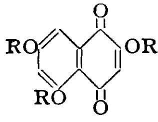
Syntheses of the isomeric 2 : 5 : 7- and 3 : 5 : 7-methoxy-1 : 4-naphthaquinones are described. It is shown that the 2 : 5 : 7-trimethyl ether is identical with tri-*O*-methylflaviolin, whence the constitution of flaviolin is established as the 2 : 5 : 7-trihydroxy-1 : 4-naphthaquinone.

ANALYTICAL and degradative methods have shown that flaviolin, a metabolic product of *Aspergillus citricus* (Wehmer) Mosseray, is 2(or 3) : 5 : 7-trihydroxy-1 : 4-naphthaquinone (Part I *). Further attempts to provide an unequivocal solution of the remaining structural problem have been directed towards the synthesis of the corresponding trimethyl ethers, and as already indicated (*Chem. and Ind.*, 1954, 1110) the results afford conclusive evidence that the structure of flaviolin is 2 : 5 : 7-trihydroxy-1 : 4-naphthaquinone.†

The usual methods for the hydroxylation of quinones, *viz.*, the hydrolysis and oxidation of products obtained therefrom by Thiele acetylation or the action of amines, are inapplicable in the present case since unsymmetrically *ar*-substituted 1 : 4-naphthaquinones give products of ambiguous constitution. An alternative route was therefore explored, based on the work of Pfeiffer and Hesse (*J. prakt. Chem.*, 1941, **158**, 315) and of Buu-Hoï and Cagniant (*Compt. rend.*, 1942, **214**, 87). This consists in the conversion of the appropriately substituted α-tetralone (*e.g.*, I) into a dianil (II), thus affording after hydrolysis a hydroxynaphthaquinone (III; R = Me, R′ = H) of unmistakable orientation.


(I)


(II) X = p-N·C_6H_4·NMe_2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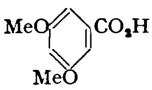
(IV)

2 : 5 : 7-Trimethoxy-1 : 4-naphthaquinone was synthesised in seven stages starting from resorcinol, which was converted by well-known methods into γ-(2 : 4-dimethoxyphenyl)butyric acid. Cyclisation of this acid proved to be extremely difficult and of the three different processes investigated the most efficient resulted in only 4—6% of 5 : 7-dimethoxytetral-1-one (I). Application of the Pfeiffer and Hesse reaction, followed by methylation, gave 2 : 5 : 7-trimethoxy-1 : 4-naphthaquinone (III; R = R′ = Me), m. p. 186—188°, unaltered on admixture with tri-*O*-methylflaviolin, m. p. 186—187°. The ultraviolet absorption spectrum of the synthetic compound also corresponded with that of tri-*O*-methylflaviolin.

3 : 5 : 7-Trimethoxy-1 : 4-naphthaquinone was synthesised in a twelve-stage process from benzoic acid, from which 3 : 5-dimethoxybenzoic acid was first prepared by standard procedures. The product (IV) was then homologated to the butyric acid (IX) by one of the annexed routes. Method A involved first the conversion of (IV) by the Arndt–Eistert reaction into the ester (V) and reduction of the latter by lithium aluminium hydride to the alcohol (VI). From the derived bromide (VII) the substituted malonic ester (VIII) was prepared and thence the butyric acid (IX). In method B the chloride of the acid (IV) was caused to react with ethyl sodioacetosuccinate [G. M. Robinson, *J.*, 1930, 745; cf. Thompson (*J.*, 1932, 2310) and Fieser and Dunn (*J. Amer. Chem. Soc.*, 1936, **58**, 572)], and the product (X) hydrolysed and decarboxylated to the keto-acid (XI). Reduction of the latter by the modified Wolff–Kishner method then gave (IX). Route C

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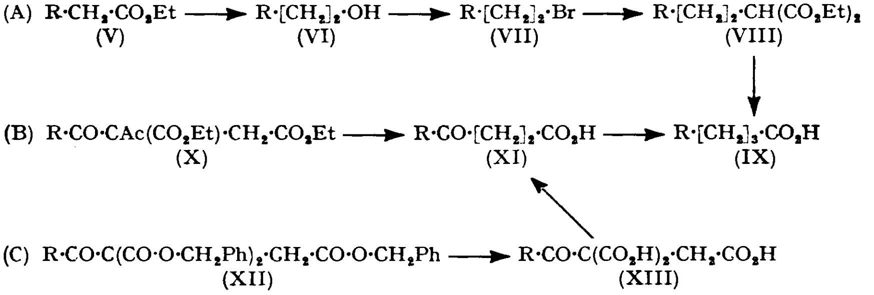
* Part I, *J.*, 1953, 3302. † A preliminary account of an alternative synthesis of 2 : 5 : 7-trimethoxy-1 : 4-naphthaquinone has been published by Birch and Donovan (*Chem. and Ind.*, 1954, 1047).

follows the elegant homologation method of Bowman (*J.*, 1950, 325). Reaction between the chloride of the acid (IV) and benzyl ethane-1 : 1 : 2-tricarboxylate led to the product (XII) which was catalytically debenzylated to the acid (XIII). Decarboxylation of this acid gave the keto-acid (XI) which was reduced as before.



(R = 3 : 5-dimethoxyphenyl)

The last-mentioned process (C) proved the most expeditious and was used for the completion of the synthesis. Cyclisation of the substituted butyric acid (IX) led to 6 : 8-dimethoxytetral-1-one which was converted *via* the dianil and its hydrolysis product into 3 : 5 : 7-trimethoxy-1 : 4-naphthaquinone, m. p. 197—199°. The ultraviolet absorption spectrum of this compound differed from that of its isomer especially in the regions 240—300 and 325—400 mμ.

EXPERIMENTAL

Di-O-methylresorcinol.—This was prepared either from resorcinol, methyl sulphate, and aqueous sodium hydroxide (Ullmann, *Annalen*, 1903, **327**, 104) or, with more consistent results, by heating resorcinol (22 g.), anhydrous potassium carbonate (92·4 g.), methyl sulphate (61 g.), and dry acetone (350 c.c.) under reflux for 24 hr. and isolating the product, b. p. 216—218°, in the usual way (17·8 g., 66%).

β-(2 : 4-*Dimethoxybenzoyl)propionic Acid.*—Powdered aluminium chloride (75 g,) was added to a solution of the above ether (40·7 g.) and succinic anhydride (29·75 g.) in nitrobenzene (193 c.c.). After having been kept at room temperature for 2 days with occasional shaking, the mixture was poured into 12% hydrochloric acid (133 c.c.). By a procedure similar to that used for isolating β-(2 : 4-dimethoxybenzoyl)-α-methylpropionic acid (Schmid and Burger, *Helv. Chim. Acta*, 1952, **35**, 928) there was obtained β-(2 : 4-dimethoxybenzoyl)propionic acid (32·8 g., 67%), m. p. (after crystallisation from ethanol) 146—147°. Perkin and Robinson (*J.*, 1908, 506) give m. p. 146—148°. Yields varied from 45 to 85%.

γ-(2 : 4-*Dimethoxyphenyl)butyric Acid.*—This acid was prepared (i) by the modified Clemmensen reduction of the recrystallised keto-acid (yield 57%) using the method described for the corresponding α-methylbutyric acid (Schmid and Burger, *loc. cit.*) or (ii) by the modified Wolff–Kishner procedure (Huang-Minlon, *J. Amer. Chem. Soc.*, 1946, **68**, 2487). β-(2 : 4-dimethoxybenzoyl)propionic acid (29·5 g. of unrecrystallised material), potassium hydroxide (32·5 g.), hydrazine hydrate (90% ; 23·5 c.c.), and ethylene glycol (250 c.c.) were heated under reflux for 1½ hr. at 130° (bath) and then, after distillation of water, for 4 hr. at 200° (bath). The mixture was cooled, diluted with water, and acidified to Congo-red. The product was collected in ether, and the acid (10 g., 37%), b. p. 152—154°/0·1 mm., m. p. 45—47°, was isolated in the usual way. Mitter and De (*J. Indian Chem. Soc.*, 1939, **16**, 35) give m. p. 49°.

5 : 7-*Dimethoxytetral*-1-*one* (I).—The best results were obtained by working in batches. The foregoing acid (3 g.) was added, with stirring, to " polyphosphoric acid " [phosphoric oxide (12 g.) and " syrupy " phosphoric acid (10 c.c.)] at 165°. After 3 min. at this temperature the mixture was cooled to *ca.* 90° and triturated with water. The product (from nine such batches) was collected in ether, and the ethereal solution, after having been washed successively with sodium hydrogen carbonate solution, sodium carbonate solution, and water, was dried (Na_2SO_4) and the solvent was evaporated. Distillation of the residue gave 5 : 7-dimethoxytetral-1-one, b. p. 120—124°/0·1 mm. (1·75 g., 4·5%) which, even after crystallisation from light petroleum (b. p. 40—60°) (to give pale yellow prisms, m. p. 66—68°) was still slightly impure [Found :

C, 69·0; H, 6·6; OMe, 30·0. Calc. for $C_{10}H_8O(OMe)_2$: C, 69·9; H, 6·8; OMe, 30·0%]. Its 2 : 4-*dinitrophenylhydrazone* crystallised from chloroform–methanol in needles, m. p. 246° (decomp.) (Found : C, 55·5; H, 4·9; N, 14·6. $C_{18}H_{18}O_6N_4$ requires C, 56·0; H, 4·7; N, 14·5%).

Attempts to improve the efficiency of the cyclisation by using (i) anhydrous hydrofluoric acid (with the butyric acid) or (ii) stannic chloride (with the acyl chloride) were unsuccessful.

2 : 4-*Bis*-p-*dimethylaminophenylimino*-1 : 2 : 3 : 4-*tetrahydro*-5 : 7-*dimethoxy*-1-*oxonaphthalene* (II).—A 10% solution (2·8 c.c.) of sodium hydroxide was added to a solution of 5 : 7-dimethoxytetral-1-one (2·5 g.) and *p*-nitrosodimethylaniline (5 g.) in ethanol (*ca.* 50 c.c.) (Pfeiffer and Hesse, and Buu-Hoï and Cagniant, *locc. cit.*). The solution was kept at room temperature for 2 days. The dark violet solid was filtered off, washed with ethanol, and crystallised from benzene–light petroleum (b. p. 40—60°), to give the *dianil* (II) (2·65 g., 47%) as clusters of permanganate-coloured needles, m. p. 179—182° (decomp.) (Found : N, 11·6. $C_{28}H_{30}O_3N_4$ requires N, 11·9%).

2 : 5 : 7-*Trimethoxy*-1 : 4-*naphthaquinone* (III; R = R′ = Me).—The dianil (2·5 g.) was heated under reflux for 1 hr. with 30% sulphuric acid (60 c.c.). The mixture was cooled, diluted with water, and extracted with (i) chloroform and (ii) ether. The combined extracts were shaken with successive portions of aqueous sodium hydrogen carbonate solution until the latter was no longer coloured. The combined aqueous solutions were acidified and the product was collected with chloroform and ether. The solution was dried (Na_2SO_4) and the solvents were evaporated to give crude 2-hydroxy-5 : 7-dimethoxy-1 : 4-naphthaquinone (III; R = Me, R′ = H). This material (*ca.* 0·3 g.) was heated under reflux for ½ hr. with methanolic hydrogen chloride (3%; 4 c.c.) (cf. Fieser, *J. Amer. Chem. Soc.*, 1926, **48**, 2932). The solution was cooled, diluted with water, and extracted several times with benzene. The combined, dried (Na_2SO_4) benzene solutions were poured on to a column (10 × 1·3 cm.) of acid-washed alumina. Development of the chromatogram with (i) benzene, (ii) benzene containing 10% v/v of ether, and (iii) benzene containing 2% v/v of ethanol produced a broad, bright-yellow band which was eluted. Removal of the solvents *in vacuo* from the eluate and crystallisation of the residue from benzene–light letroleum (b. p. 40—60°) gave 2 : 5 : 7-trimethoxy-1 : 4-naphthaquinone (85 mg.) as golden-yellow prisms [Found : C, 62·8; H, 4·7; OMe, 34·7. Calc. for $C_{10}H_3O_2(OMe)_3$: C, 62·9; H, 4·9; OMe, 37·5%], m. p. 186—188°, unaltered by admixture with tri-*O*-methylflaviolin, m. p. 186—187°. Ultraviolet light absorption : Synthetic : $\lambda_{max.}$, 215, 260, 295, 412 mμ (log ε 4·49, 4·18, 4·03, 3·49 respectively). Natural : $\lambda_{max.}$, 214, 260, 296, 414 mμ (log ε 4·51, 4·20, 4·05, 3·42 respectively).

3 : 5-*Dimethoxybenzoic Acid.*—3 : 5-Dihydroxybenzoic acid (*Org. Synth.*, 1941, **21**, 27) was methylated by Mauthner's procedure (*J. prakt. Chem.*, 1913, **87**, 403).

3 : 5-*Dimethoxybenzoyl Chloride.*—The method used was essentially that of Mauthner (*loc. cit.*) but more consistent yields (64%) were obtained by using the modified proportions of phosphorus pentachloride (11·5 g.) to acid (10 g.). Very variable yields (0—90%) were obtained when attempts were made to prepare the acyl chloride by heating under reflux the acid (1 mol.) and thionyl chloride (1—2 mols.) for 1—1½ hr.

Ethyl 3 : 5-*Dimethoxyphenylacetate* (V).—A solution of 3 : 5-dimethoxybenzoyl chloride (30 g.) in ether (75 c.c.) was added dropwise, with stirring, to an ethereal solution (750 c.c.) of diazomethane (made from 52·5 g. of *N*-nitrosomethylurea). The solution was kept at room temperature for several hours and the solvent was then evaporated, to give an oil which later solidified (36 g.). A solution of this diazo-ketone in ethanol (540 c.c.) at 60° was treated with a slurry of silver oxide (from 3·75 g. of silver nitrate) in ethanol (162 c.c.). The mixture was then heated under reflux for 2 hr., boiled for a few minutes with charcoal, and filtered. The solvent was removed and the residue distilled, to give the ester (25 g., 75%), b. p. 128—132°/0·1 mm. Mühlemann (*Pharm. Acta Helv.*, 1951, **26**, 198) gives b. p. 144—146°/5 mm.

2-(3 : 5-*Dimethoxyphenyl*)*ethanol* (VI).—An ethereal solution of the foregoing ester (24 g.) was added, at such a rate to produce a steady reflux, to a rapidly stirred solution of lithium aluminium hydride (4 g.) in ether (275 c.c.). After the solution had been heated under reflux for 1 hr. and cooled, the excess of hydride was decomposed by the cautious addition of water (Nystrom and Brown, *J. Amer. Chem. Soc.*, 1947, **69**, 1197). The mixture was stirred into dilute sulphuric acid and the ethereal layer was separated, washed, and dried (Na_2SO_4). Evaporation of the solvent and distillation of the residue gave 2-(3 : 5-*dimethoxyphenyl*)*ethanol*, b. p. 126—130°/0·1 mm., 112—116°/0·01 mm., in yields of 40—70% (Found : C, 66·1; H, 7·7. $C_{10}H_{14}O_3$ requires C, 65·9; H, 7·7%).

2-(3 : 5-*Dimethoxyphenyl*)*ethyl Bromide* (VII).—Phosphorus tribromide (17·4 g.) was added dropwise (but without cooling) to the foregoing alcohol (17·6 g.), and the mixture was heated on the steam-bath for 1½ hr. and then poured on ice. The product was collected in ether, and the ethereal solution was washed successively with aqueous sodium hydroxide solution (5%), water, 2N-hydrochloric acid, and water, and was then dried (Na_2SO_4). The solvent was evaporated and the residue distilled, without delay and at low pressure, to give slightly impure 2-(3 : 5-dimethoxyphenyl)ethyl bromide (9·52 g., 51%), b. p. 90—110°/0·05 mm. (Found: C, 49·9; H, 5·4; Br, 32·2. Calc. for $C_{10}H_{13}O_2Br$: C, 49·0; H, 5·3; Br, 32·5%). Barnes (*J. Amer. Chem. Soc.*, 1953, **75**, 3007) has experienced similar difficulties in attempting to obtain pure 2-(2 : 5-dimethoxyphenyl)ethyl bromide. These substances appear to lose hydrogen bromide with great ease.

β-(3 : 5-*Dimethoxybenzoyl)propionic Acid* (XI).—(i) *Route B*. A solution of 3 : 5-dimethoxybenzoyl chloride (37·1 g.) in ether (19 c.c.) was added slowly, with shaking, to an ethereal solution of ethyl sodioacetosuccinate [prepared from " powdered " sodium (4·5 g.), ethyl acetosuccinate (43 g.) (G. M. Robinson, *loc. cit.*), and dry ether (47 c.c.)]. After the mixture had been kept for two days at room temperature, the clear solution was decanted, washed successively with water and aqueous sodium carbonate solution, and then dried (Na_2SO_4). Evaporation of the solvent gave an oil [containing compound (X)] which was stirred for 2 days with a solution of potassium hydroxide (31·5 g.) in water (2000 c.c.). The resulting solution was acidified (concentrated hydrochloric acid) and the solid product filtered off. (A further quantity of product was obtained by ether-extraction of the filtrate.) Treatment of an ethanolic solution of this material with aqueous semicarbazide acetate, in the usual way, yielded a product which, after recrystallisation from ethanol, gave the *semicarbazone* of 2-(3 : 5-dimethoxybenzoyl)-propionic acid (5 g.) in slender needles, m. p. 156—158° (Found: C, 53·0; H, 5·8. $C_{13}H_{17}O_5N_3$ requires C, 52·9; H, 5·8%). [3 : 5-Dimethoxybenzoic acid (17 g.) was recovered from the mother-liquors.] This semicarbazone was heated under reflux for ½ hr. with 2N-hydrochloric acid, and the product was extracted with benzene. Evaporation of the solvent and crystallisation of the residue from benzene–light petroleum (b. p. 40—60°) gave β-(3 : 5-*dimethoxybenzoyl*)-*propionic acid* (2·6 g., 6% calc. on acyl chloride), m. p. 104—106° (Found: C, 60·2; H, 5·8. $C_{12}H_{14}O_5$ requires C, 60·5; H, 5·9%).

(ii) *Route C*. A solution of 3 : 5-dimethoxybenzoyl chloride (13·3 g.) in dry benzene (100 c.c.; " AnalaR ") was added, dropwise, with stirring, to a solution of benzyl sodioethane-1 : 1 : 2-tricarboxylate (16·9 g.) (Bowman, *loc. cit.*, p. 329) in benzene. The mixture was heated under reflux for ½ hr. and then poured into ice-water containing a small amount of dilute sulphuric acid. The organic layer was separated and the aqueous solution was extracted with benzene. The combined benzene solutions were dried (Na_2SO_4) and the solvent removed, first at 30—40°/*ca.* 15 mm., and secondly at 100°/0·5 mm,. to give a yellow-brown, viscous oil (XII). A solution of this material in ethanol (50 c.c.) and ethyl acetate (50 c.c.) was hydrogenated at atmospheric pressure using first palladium–charcoal (10%; 0·5 g.) followed by palladium–strontium carbonate (10%; 0·6 g.) as catalysts. A total of 3·66 l. of hydrogen was absorbed (maximum rate 1 l./hr.). The catalysts were removed and the solution was boiled under reflux for ½ hr., brisk evolution of carbon dioxide occurring. The solvents were evaporated and the residue was heated under reflux with 2N-sodium hydroxide for ½ hr. The resulting solution was cooled and acidified with 20N-sulphuric acid. The product, isolated by ether-extraction, was crystallised from very dilute acetic acid, to give β-(3 : 5-dimethoxybenzoyl)propionic acid (10 g., 63% from acyl chloride) in colourless plates, m. p. 90—96°. Recrystallisation from the same solvent gave material of m. p. 104—106° (semicarbazone, m. p. 156—158°).

γ-(3 : 5-*Dimethoxyphenyl)butyric Acid* (IX).—(i) *Route A*. A solution of 2-(3 : 5-dimethoxyphenyl)ethyl bromide (16 g.) in benzene (50 c.c.) was added slowly, and with stirring, to a benzene suspension of ethyl sodiomalonate [prepared from ethyl malonate (11 g.), " powdered " sodium (1·86 g.), and benzene (*ca.* 50 c.c.)]. After the mixture had been heated under reflux, with stirring, for 8 hr., the benzene was evaporated and the residue was mixed with water. The product, isolated by ether-extraction, was distilled. Collection of the distillate of b. p. <156°/0·1 mm. gave crude ethyl 2-(3 : 5-dimethoxyphenyl)ethylmalonate (VIII) (7·4 g., 35%). This ester was hydrolysed under reflux with 2N-sodium hydroxide for 2 hr. The solution was cooled and acidified and the 2-(3 : 5-dimethoxyphenyl)ethylmalonic acid (*ca.* 6 g.) was isolated by ether-extraction. This acid was decarboxylated at 180° for 1 hr., and the product was crystallised from *n*-hexane, or light petroleum (b. p. 40—60°), to give γ-(3 : 5-*dimethoxyphenyl*)-*butyric acid* (3·4 g., 23% from the bromide) in prisms, m. p. 56—58°. Recrystallisation from light petroleum (b. p. 40—60°) gave a specimen, m. p. 58—60° (Found: C, 64·0; H, 6·9. $C_{12}H_{16}O_4$ requires C, 64·3; H, 7·2%).

(ii) *Route B or C*. β-(3 : 5-Dimethoxybenzoyl)propionic acid (XI) was reduced by the Huang-Minlon procedure as described above for the β-2 : 4-isomer. The reduced material, when isolated in the usual way and crystallised from light petroleum (b. p. 40—60°), gave a product (yield 32%) which was identical with that described in method (i).

6 : 8-*Dimethoxytetral*-1-*one*.—(i) A mixture of the butyric acid (3 g.) and sulphuric acid (75%, 8 c.c.) was heated for 1 hr. on the steam-bath and then poured on ice. The ethereal solution of the product, having been washed first with dilute aqueous ammonia and then with water, was dried (Na_2SO_4) and the solvent was evaporated. (None of the original acid was recoverable from the alkaline washings.) The residue (*ca.* 1 g.) was extracted with successive quantities of boiling light petroleum (b. p. 60—80°). When the extracts were cooled, 6 : 8-*dimethoxytetral*-1-*one* (0·82 g., 30%) separated in pale-yellow, slender prisms, m. p. 62—64° (Found : C, 70·2; H, 6·4. $C_{12}H_{14}O_3$ requires C, 69·9; H, 6·8%). The 2 : 4-*dinitrophenylhydrazone* crystallised from chloroform–methanol in needles, m. p. 214—216° (decomp.) (Found : C, 55·6; H, 4·9; N, 14·4. $C_{18}H_{18}O_6N_4$ requires C, 56·0; H, 4·7; N, 14·5%).

(ii) Ring-closure of the butyric acid by use of " polyphosphoric acid " at 145° (for method see above) gave a 24% yield of the tetralone.

(iii) Phosphorus pentachloride (3·8 g.) was added to a solution of the butyric acid (4 g.) in benzene (20 c.c.) at 0—10° and the solution was then warmed to 50° for a few minutes. A solution of stannic chloride (3·3 c.c.) in benzene (5·3 c.c.) was added, dropwise and with shaking, to the benzene solution of the acyl chloride, the temperature being kept below −5°. The mixture was then allowed to reach room temperature and, after having been warmed at 50° for 1 hr., was stirred into a mixture of ice and hydrochloric acid. The product was collected in ether, and the ethereal solution was washed successively with 2N-hydrochloric acid, saturated sodium hydrogen carbonate solution, potassium hydroxide solution (5%), and water. Evaporation of the solvent from the dried (Na_2SO_4) ethereal solution produced a residue which distilled at 170—190° (bath)/0·1 mm. to give the tetralone (0·26 g., 7%), m . p. 63—66°.

2 : 4-*Bis*-p-*dimethylaminophenylimino*-1 : 2 : 3 : 4-*tetrahydro*-6 : 8-*dimethoxy*-1-*oxonaphthalene*.—This substance was prepared in a similar manner to that which was used for its isomer (see above) except that a second crop of crude material was obtained by evaporation of the mother-liquor. The combined crops (1·8 g. from 1·08 g. of the tetralone, 77%) were washed with a little ethanol and dried. This *dianil* crystallised from benzene–light petroleum (b. p. 40—60°) in clusters of almost black needles, m. p. 206—208° (decomp.) (Found : C, 70·8; H, 6·1. $C_{28}H_{30}O_3N_4$ requires C, 71·5; H, 6·4%).

3 : 5 : 7-*Trimethoxy*-1 : 4-*naphthaquinone*.—The foregoing dianil (1·8 g.) was hydrolysed under reflux with 30% sulphuric acid (40 c.c.) and, by a method similar to that used for isolating the compound (III; R = Me, R′ = H), there was obtained crude 3-hydroxy-5 : 7-dimethoxy-1 : 4-naphthaquinone. This material (*ca.* 0·15 g.) was methylated with methanolic hydrogen chloride, and the product collected in benzene. Chromatography on a column of acid-washed alumina gave a broad, yellow band which was readily eluted with benzene containing 10% v/v of ether. Evaporation of the solvents from the eluate and crystallisation of the residue from benzene–light petroleum (b. p. 40—60°) gave 3 : 5 : 7-*trimethoxy*-1 : 4-*naphthaquinone* (60 mg.) in yellow, slender prisms, m. p. 197—199° (altered to *ca.* 165° on admixture with its isomer) [Found : C, 62·8; H, 5·1; OMe, 37·6. $C_{10}H_3O_2(OMe)_3$ requires C, 62·9; H, 4·9; OMe, 37·5%]. Ultraviolet light absorption : $\lambda_{max.}$, 213, 267, 293, 402 mμ (log ε 4·54, 4·18, 4·23, 3·56 respectively).

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