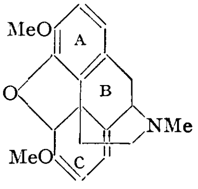
170. *The Structure of Phenyldihydrothebaine.*

By K. W. Bentley and Sir Robert Robinson.

The structure (II) of phenyldihydrothebaine, deduced from existing data on theoretical grounds, has been confirmed by oxidation of the base to benzaldehyde, benzoic acid, and 4-methoxyphthalic acid, and by exhaustive methylation of its methyl ether to a nitrogen-free substance that yields 5 : 6 : 5′-trimethoxydiphenic acid and the corresponding dialdehyde on oxidation with permanganate, and the same aldehyde on ozonolysis. Thebaine has been shown to react with anhydrous magnesium iodide, the product on reduction with lithium aluminium hydride being converted into a sensitive phenolic base.

The reaction between thebaine and phenylmagnesium bromide was first investigated by Freund (*Ber.*, 1905, **38**, 3234; D.R.-P., 181 510/1907; Frdl., **8**, 1171) who obtained in this way a phenolic base $C_{25}H_{27}O_3N$ which he called phenyldihydrothebaine. Subsequent investigations (Freund, *loc. cit.*; Freund and Holtoff, *Ber.*, 1916, **49**, 1287; Small, Sargent, and Bralley, *J. Org. Chem.*, 1947, **12**, 847) on this and on the corresponding methyldihydrothebaine (Small and Fry, *J. Org. Chem.*, 1939, **3**, 509) revealed that these compounds show remarkable chemical properties, inexplicable on the basis of any structure derived from the Gulland–Robinson formula for thebaine (I) unless a deep-seated rearrangement is assumed to occur during the entry of the phenyl group, an explanation rejected by Small, Sargent, and Bralley (*loc. cit.*) and by Small and Fry (*loc. cit.*).



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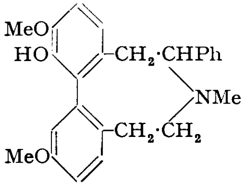

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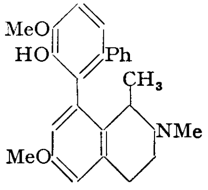

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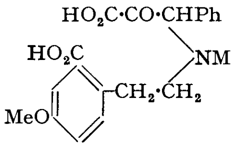
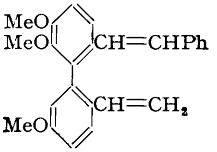


(IV)

A structure that appeared to embrace all the known facts was advanced by Robinson (*Proc. Roy. Soc.*, 1947, *B*, **135**, 14; *Nature*, 1947, **160**, 815), the evidence for which may be summarised as follows. The peculiar properties of phenyldihydrothebaine (resistance to hydrogenation; stability towards acids; retention of the vinyl group during exhaustive methylation) clearly indicate that in this substance the near-aromatic ring of thebaine has become fully aromatic. On this assumption it can be shown that the nitrogen-free product obtained by exhaustive methylation of phenyldihydrothebaine cannot owe its optical activity to the presence of an asymmetric carbon atom, and must therefore owe it to some other cause of molecular dissymmetry, most plausibly to restricted rotation about a carbon–carbon bond, probably in a diphenyl system. On the basis of these arguments, and a reasonably probable course for the Grignard reaction, the structure (II) was suggested for phenyldihydrothebaine. The objection of Small, Sargent, and Bralley (*loc. cit.*), that the ultra-violet absorption spectra of phenyl- and methyl-dihydrothebaine do not indicate the presence of a second aromatic ring in conjugation with the first in these compounds, is invalidated by the work of Picket, Walter, and France (*J. Amer. Chem. Soc.*, 1936, **58**, 2296) and O'Shaugnessy and Rodebush (*ibid.*, 1940, **62**, 2906) who showed that non-coplanar diphenyls do not exhibit typical diphenyl absorption in the ultra-violet, but only absorption characteristic of isolated aromatic nuclei. The structure (III) for phenyldihydrothebaine, considered for a short time, was rejected as it contains an unrestricted diphenyl system. The stages in the development of the argument are given in more extended form in an Anniversary Address to the Royal Society (*loc. cit.*) and an excellent account is included in Fieser and Fieser's "Natural Products Related to Phenanthrene," A.C.S. Monograph No. 70, pp. 19—22.

Confirmation of the structure (II) for phenyldihydrothebaine has been sought and obtained by permanganate oxidation of the base, which affords benzaldehyde (showing that the phenyl group is present as PhCH–), benzoic acid, and 4-methoxyphthalic acid (showing that ring C of thebaine has become aromatic in phenyldihydrothebaine, and bears no additional substituent), the latter being identified with an authentic specimen by mixed melting points of the acid, anhydride, and *N*-methylimide. In addition an amino-acid, inadequately characterised, was obtained; analytical data for the copper derivative of this acid agree closely with the values required for the copper salt of (IV). Exhaustive methylation of phenyldihydrothebaine methyl ether yielded an optically active substance (+)-3 : 4-dimethoxy-2-(5-methoxy-2-vinylphenyl)stilbene (V) (prepared by Freund,



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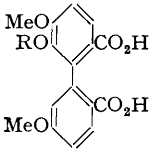

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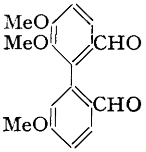

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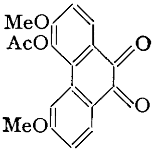
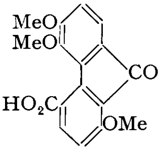


(VIII)

loc. cit., 1905, but wrongly analysed and stated to be optically inactive), which was racemised by heat. The heat treatment also caused some polymerisation (of the styrene system ?) to occur, a very sparingly soluble substance, of molecular weight >5000, being obtained. Oxidation of (V) with potassium permanganate in acetone afforded 5 : 6 : 5′-trimethoxydiphenic acid (VI; R = Me) and the corresponding dialdehyde (VII). The latter (which could be oxidised to the former) was also obtained, together with benzaldehyde, by the ozonolysis of (V).

5 : 6 : 5′-Trimethoxydiphenic acid was synthesised in stages from 4-acetoxy-3 : 6-dimethoxyphenanthrenequinone (acetylthebaolquinone; Freund and Göbel, *Ber.*, 1897, **30**, 1389) (VIII). This was oxidised by hydrogen peroxide in hot glacial acetic acid to 6-acetoxy-5 : 5′-dimethoxydiphenic acid (VI; R = Ac), which on hydrolysis yielded 6-hydroxy-5 : 5′-dimethoxydiphenic acid (VI; R = H); and thence on methylation 5 : 6 : 5′-trimethoxydiphenic acid (VI; R = Me). This acid and 1 : 5 : 6-trimethoxyfluorenone-4-carboxylic acid (IX), obtained by heating (VI; R = Me) with concentrated sulphuric acid at 50°, were identified by mixed melting points with the corresponding derivatives from the oxidation of (V). Attempts to convert (VI; R = Ac) into a fluorenonecarboxylic acid by treatment with sulphuric acid resulted in hydrolysis and decarboxylation, the product being 8 : 3′-dimethoxy-3 : 4-benzocoumarin (X), also obtained in the same way from (VI; R = H).



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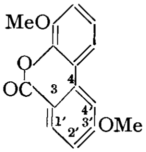
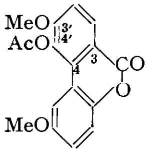


(X)



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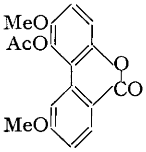
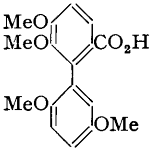


(XII)

The hydrogen peroxide oxidation of acetylthebaolquinone yielded, in addition to (VI; R = Ac), a lactone shown to be 4′-acetoxy-6 : 3′-dimethoxy-3 : 4-benzocoumarin (XI) and not the isomeride (XII), by hydrolysis to 4′-hydroxy-6 : 3′-dimethoxy-3 : 4-benzocoumarin and hydrolysis and methylation of the latter to 5 : 6 : 2′ : 5′-tetramethoxydiphenyl-2-carboxylic acid (XIII). The acid chloride of this on cyclisation with stannic chloride afforded 1 : 4 : 5 : 6-tetramethoxyfluorenone (XIV) together with a small amount of a by-product, also obtained as the only isolable product from the cyclisation with aluminium chloride and believed to be 1 : 6-dihydroxy-4 : 5-dimethoxyfluorenone (XV) formed by demethylation of the *o*- and *p*-methoxy-groups in (XIV).

Ample verification of the structure (II) for phenyldihydrothebaine is afforded by these degradations and in most cases the constitutions of the derivatives follow readily from (II). Those in which the vinyl group produced during exhaustive methylation has undergone cyclisation with the phenolic hydroxyl require special mention. As the aromatic nuclei in these must be virtually coplanar the restricted rotation isomerism would be expected to vanish, and indeed in the phenyldihydrothebaine series all the nitrogen-free cyclised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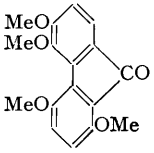
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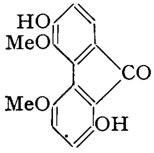
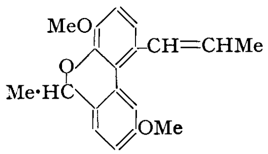

(XV)

products (containing no asymmetric carbon atom) are inactive. However, in the methyldihydrothebaine series a small optical activity (*ca.* 9°) has been observed for (XVI) (Small and Fry, *loc. cit.*)

As the optically active forms of (XVI) were obtained by degradation of (XVII), and this in turn was prepared by cyclisation of (XVIII), the explanation of the phenomenon is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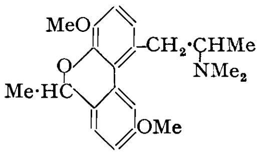
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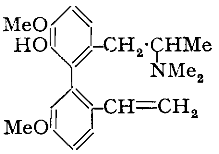
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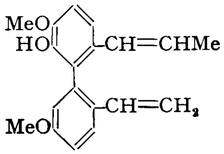
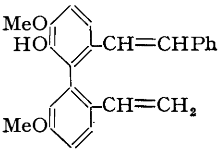

(XIX)

doubtless that the presence of an asymmetric carbon atom in the latter caused production of unequal amounts of the two diastereoisomers of (XVII) when the new asymmetric carbon atom was brought into being as a result of the cyclisation The effect of a slight excess of one diastereoisomer when degradation was pursued to the nitrogen-free product (XVI) would be to cause the latter to have a slight optical activity.

It is of interest that the two unsaturated groups in the uncyclised nitrogen-free product (XIX) of degradation of the methyldihydrothebaines are probably too small to cause restriction of complete rotation of the two phenyl nuclei, and indeed no convincing evidence has been produced to show that (XIX) has been obtained in an optically active form. The activity of the liquid product of degradation of δ-methyldihydrothebaine methine methyl ether is probably due to regeneration of some of the methine base (known to be active) from the quaternary salt. The "ethylphenylhexahydrothebaol" prepared by reduction of (XX) (Small, Sargent, and Bralley, *loc. cit.*) is clearly a tetrahydro-compound, and the "phenyl-6-methoxythebenane" prepared by the reduction of (XXI) (Small, Sargent, and Bralley) is clearly an octahydro-derivative arising from saturation of the double bond and external phenyl group, the analytical data agreeing better with these formulæ than with those allotted to them by Small, Sargent, and Bralley.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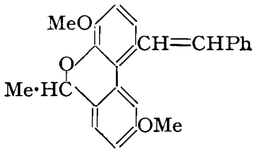
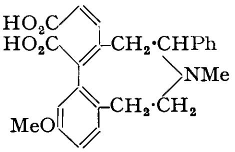
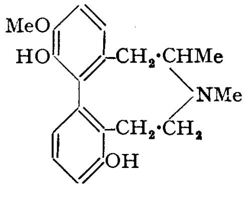

(XXI)


(XXII)

The first stage of the Hofmann degradation of phenyldihydrothebaine affords a methine and an *iso*methine, the former being a stilbene and the latter a styrene. The formation of the isomerides is dependent on the direction of elimination in the methohydroxide of (II). Now the *iso*methine is obtained in the larger relative amount and this means that $\gg$—$CH_2{\cdot}CH_2{\cdot}NR_3^+$ ⟶ $\gg$—$CH{:}CH_2$ is preferred to $\gg$—$CH_2{\cdot}CHPh{\cdot}NR_3^+$ ⟶ $\gg$—$CH{:}CHPh$. Fieser and Fieser (*op. cit.*) comment on this and see no explanation for the predominant elimination towards the group not under the influence of the introduced phenyl group. However, it is a proton in the β-position to NR_4^+ which is removed to initiate the elimination and this is not directly activated by the newly introduced phenyl group. Apart from this circumstance the two sides of the basic nitrogen atom are not symmetrically situated in that one leads to a catechol nucleus and the other to a phenol nucleus. We are hardly able at this stage to prognosticate the activation effects in this complex system.

Phenyldihydrothebaine on treatment with hydrogen peroxide and hydrochloric acid yields a dichloro-compound which has been degraded to a nitrogen-free product. Freund and Holtoff (*loc. cit.*) regarded this as formed by addition of chlorine to a double bond, but the analytical data for all the derivatives are equally compatible with formulæ containing two less hydrogen atoms, and it is clear that the two chlorine atoms have entered either the guaiacol or the anisole nucleus, or both nuclei. The reaction with bromine doubtless takes a similar course, yielding dibromophenyldihydrothebaine; this is reported by Freund and Holtoff to undergo electrolytic reduction with production of "phenyltetrahydrothebaine," which is very probably (+)-α-phenyldihydrothebaine, the melting points of the methiodides of these two compounds differing by only one degree. The small amount of (+)-δ-isomer, doubtless present in Freund and Holtoff's phenyldihydrothebaine, would be eliminated by the several crystallisations during this cycle of reactions. The reaction between phenyldihydrothebaine and hydrogen peroxide in boiling alkali yields a dibasic acid, $C_{24}H_{25}O_5N$ (Freund and Holtoff), for which structure (XXII) is now suggested.

With regard to the other anomalous products of the Grignard reaction, methyldihydro-ψ-codeinone (Small and Lutz, *J. Amer. Chem. Soc.*, 1935, **57**, 2651) is clearly (XXIII).



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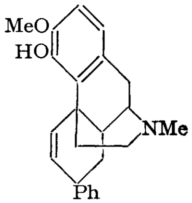
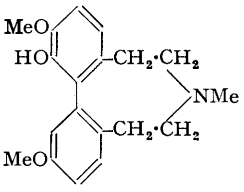


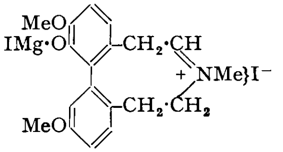
(XXIV)



(XXV)

The analytical data for phenyldihydrodeoxycodeine-C were interpreted by Small and Yuen (*ibid.*, 1936, **58**, 192) as agreeing with (XXIV) $C_{24}H_{27}O_2N$, but they are equally compatible with $C_{24}H_{29}O_2N$, which could be explained by assuming reduction of the double bond to have occurred during the reaction with the Grignard reagent, an unusual, but not altogether impossible, reaction. If this explanation is correct then the resistance of the base to hydrogenation is not surprising, and the absorption of four moles of hydrogen when the reaction is forced can be explained by assuming reductive scission of the nitrogen ring and saturation of the phenyl group. If methyldihydro-ψ-codeine methyl ether (Small, Turnbull, and Fitch, *J. Org. Chem.*, 1938, **3**, 204) has a structure analogous to (XXIII) it should contain two hydrogen atoms less than reported by its discoverers, and in this connection it is of interest to note that its production in *iso*propyl ether was reported to be accompanied by the production of a substance giving analytical figures for, and no melting-point depression with, tetrahydro-ψ-codeine methyl ether.

Attempts have been made to prepare the unsubstituted "dihydrothebaine" (XXV), but these have not so far met with success. On the assumption that the conversion of thebaine into phenyldihydrothebaine is initiated by the attack of the thebaine cyclic-ether oxygen atom by $MgBr^+$ the reaction between thebaine and anhydrous magnesium iodide was investigated. This was found to give a light brown solid that contained no thebaine, and that degenerated rapidly on exposure to moist air, but was shown to contain magnesium and iodine. The structure (XXVI) is possible for this substance, though no 4-methoxyphthalic acid was obtained by oxidising it with permanganate. (XXVI) differs little from the thebenine precursor (XXVII) suggested by Gulland and Robinson (*J.*, 1923, 980), and boiling this compound with dilute hydrochloric acid gave a substance having a fluorescence indistinguishable from that of thebenine in acid solution, but markedly different in alkali was obtained. Complete methylation of this acid-treatment product and chromatographic analysis of the resulting material afforded no identifiable substance, whilst thebenine (XXVIII) under the same conditions gave a good yield of the dimethyl ether quaternary methosulphate.



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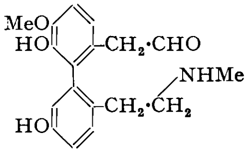

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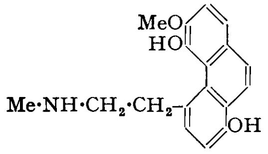
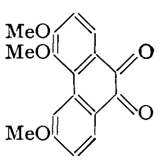


(XXVIII)

Reduction of the thebaine–magnesium iodide product with lithium aluminium hydride proceeds rapidly with evolution of gas (methane) and production of what appears to be a phenolic secondary amine that has so far defied all attempts to convert it into crystalline derivatives. If this substance is the *N*-demethylated derivative of (XXV) its non-crystalline nature could possibly be explained by assuming that it is a mixture of isomers, as examination of models shows that with no substituent on the nine-membered ring racemisation would be easy. The lithium aluminium hydride reduction of Schiff's base methiodides has been shown to give rise to secondary amines (Forbes, private communication). In spite of the unpromising nature of these results it is hoped to pursue this reaction further. The sodium–ammonia reduction of this substance yields an intractable phenolic base, whilst phenyldihydrothebaine was obtained by treating it with phenylmagnesium bromide. This last result encourages us in the belief that this substance (naturally the related bromide) is an intermediate in the production of phenyldihydrothebaine.



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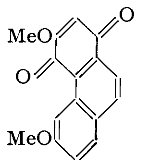

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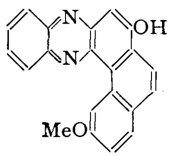
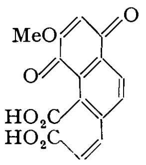


(XXXI)



(XXXII)

Oxidation of 3 : 4 : 6-trimethoxyphenanthrene by chromic acid in an attempt to prepare the 9 : 10-quinone (XXIX) led surprisingly to 3 : 6-dimethoxyphenanthra-1 : 4-quinone (XXX), identified by condensation with *o*-phenylenediamine to 3-hydroxy-7′-methoxynaphtho(1′ : 2′-1 : 2)phenazine (XXXI), which was alkali-soluble, by hydrogen peroxide oxidation to 8-carboxy-7-2′-carboxyvinyl-2-methoxy-1 : 4-naphthaquinone (XXXII), and by permanganate oxidation to benzene-1 : 2 : 3 : 4-tetracarboxylic acid. Structure (XXX) for the quinone was finally confirmed by its production by oxidation of 4-hydroxy-3 : 6-dimethoxyphenanthrene (thebaol) with chromic acid.

EXPERIMENTAL

(All m. p.s are uncorrected.)

Oxidation of Phenyldihydrothebaine.—A warm solution of potassium permanganate (75 g.) in water (1 l.) was added during 2 hours to a stirred solution of phenyldihydrothebaine perchlorate (15 g.) in 2N-sodium hydroxide (100 ml.). A considerable quantity of benzaldehyde was produced during the oxidation. When all the permanganate had been added the mixture was heated on the steam-bath for 2 hours, then filtered, and the residue washed three times with boiling water. The filtrate and washings were nearly neutralised with hydrochloric acid, concentrated to a small bulk, filtered, and acidified with hydrochloric acid. The precipitate (A) was collected and the filtrate (B) set aside (see below). The solid (A) was extracted three times with boiling water, and the hot extract boiled with animal charcoal, filtered, and allowed to cool. Benzoic acid, identified by mixed m. p. with an authentic specimen, was deposited from the solution. The residue from this extraction was warmed with sodium hydrogen carbonate solution, leaving an intractable tar. The carbonate solution was boiled with charcoal, cooled, and acidified with hydrochloric acid, and in this way a pale brown-grey solid (? IV) was obtained. This could not be crystallised but was converted into the *copper* derivative by addition of a solution of copper acetate in methanol to a solution of the acid in methanol. The copper derivative was extremely sparingly soluble in all solvents, and decomposed without melting above 250° (Found : C, 51·2; H, 4·51; Cu, 12·8. $C_{20}H_{19}O_6NCu,2H_2O$ requires C, 51·2; H, 4·9; Cu, 13·5. Found, after drying at 100°/0·1 mm. : C, 53·4; H, 4·4; Cu, 12·6. $C_{20}H_{19}O_6NCu,H_2O$ requires C, 53·2; H, 4·6; Cu, 14·1%).

All attempts to purify the acid or prepare other derivatives failed.

The filtrate (B) was saturated with ammonium sulphate and extracted eighteen times with ether, and the combined extracts were dried (Na_2SO_4) and evaporated. The syrupy residue partly crystallised when kept overnight in the refrigerator. It was triturated with chloroform, and the solid collected (2·1 g.). This substance afforded a fluorescein in the usual way, and on recrystallisation from boiling water was obtained as pale yellow needles, m. p. *ca.* 170° (rapid heating) undepressed on admixture with an authentic specimen of 4-methoxyphthalic acid (Found : C, 55·1; H, 4·0. Calc. for $C_9H_8O_5$: C, 55·1; H, 4·1%). The anhydride separated from benzene–light petroleum as bunches of pale yellow needles, m. p. 94° undepressed by addition of an authentic specimen (Found : C, 61·0; H, 3·2. Calc. for $C_9H_6O_4$: C, 60·7; H, 3·4%). The methylimide, prepared by evaporating a solution of the acid in aqueous methylamine and distilling the residue, crystallised from alcohol, as bunches of long, slender, very pale yellow needles, m. p. 156°, undepressed by admixture with an authentic specimen (Found : C, 62·8; H, 4·6; N, 6·8. Calc. for $C_{10}H_9O_3N$: C, 62·8; H, 4·7; N, 7·3%).

(+)-*α-Phenyldihydrothebaine Methyl Ether.*—Methyl sulphate (3·08 ml., 4·08 g.) in methyl alcohol (8 ml.) was slowly added to a solution of (+)-α-phenyldihydrothebaine hydrochloride (7 g.) in 10% aqueous sodium hydroxide (100 ml.) with constant shaking. The solid that separated as the reaction proceeded was collected, and dissolved in warm dilute perchloric acid. (+)-*α-Phenyldihydrothebaine methyl ether perchlorate* crystallised on cooling, and was obtained as colourless plates, m. p. 205°, on recrystallisation from alcohol, $[\alpha]^{21}_{D}$ +9·26° (in water) (Found : C, 62·2; H, 6·1; Cl, 6·7. $C_{26}H_{19}O_3N,HClO_4$ requires C, 62·0; H, 6·0; Cl, 7·0%). The *methiodide*, obtained by boiling the free base in methanol with methyl iodide, formed large colourless prisms, m. p. 205° after recrystallisation from alcohol (Found : C, 59·5; H, 5·9; N, 2·8; I, 22·5. $C_{27}H_{32}O_3NI$ requires C, 59·4; H, 5·9; N, 2·6; I, 22·3%).

(+)-α-Phenyldihydrothebaine methine methyl ether was prepared as directed by Freund (*Ber.*, 1905, **38**, 3252).

(+)-3 : *4-Dimethoxy-2-(5-methoxy-2-vinylphenyl)stilbene* (V).—A solution of sodium (12·5 g.) in methanol (250 ml.) was added to one of (+)-α-phenyldihydrothebaine methine methyl ether methiodide (from 21 g. of the base) in methanol (100 ml.), and the mixture refluxed for 2 hours, then poured into water, and the resulting suspension saturated with ammonium chloride and extracted with ether (3 × 250 ml.). The combined extracts were shaken with 2N-hydrochloric acid (3 × 25 ml.), washed well with water, and dried (Na_2SO_4), and the ether was removed. The crystalline residue (15 g.) was recrystallised from alcohol; it was obtained as very large, colourless prisms, m. p. 115°, $[\alpha]^{18}_{D}$ +59° (*c*, 2 in acetone) (Found : C, 80·3; H, 6·3; OMe 24·1. $C_{25}H_{24}O_3$ requires C, 80·6; H, 6·4; OMe, 24·9%). On being heated at 130° for 10 minutes it was converted into the *racemate*, obtained as colourless prisms, m. p. 124°, $[\alpha]^{17}_{D}$ 0·0° (in acetone), after recrystallisation from alcohol (Found : C, 80·1; H, 6·4%). In addition, a very sparingly soluble amorphous *polymer*, which had no definite m. p., was obtained after this heat treatment [Found : C, 80·4; H, 6·9%; *M* (in camphor), >5000].

(+)-2-(2-*Ethyl*-5-*methoxyphenyl*)-3 : 4-*dimethoxydibenzyl.*—(+)-3 : 4-Dimethoxy-2-(5-methoxy-2-vinylphenyl)stilbene (2 g.) was shaken under hydrogen at 3 atm. in ethyl acetate (50 ml.) in presence of the Raney nickel catalyst. The filtered solution was evaporated and the residual *dibenzyl*, which could not be crystallised, had b. p. 220°/0·1 mm., $[\alpha]^{18}_{D}$ +3·5° (in alcohol) (Found : C, 79·5; H, 7·8. $C_{25}H_{28}O_3$ requires C, 79·8; H, 7·5%). Partial racemisation probably occurred during the distillation; there was no evidence of the production of a hexahydro-derivative under these conditions.

Oxidation of (+)-3 : *4-Dimethoxy-2-(5-methoxy-2-vinylphenyl)stilbene.*—Potassium permanganate (4·25 g.) in warm acetone (350 ml.) was added during 1·5 hours to a warm stirred solution of (+)-3 : 4-dimethoxy-2-(5-methoxy-2-vinylphenyl)stilbene (1·7 g.) in acetone (25 ml.). The mixture was kept for 15 minutes, the acetone removed by distillation, the residue warmed with dilute sodium carbonate solution and filtered, and the residue washed well with sodium carbonate solution and ether. The combined filtrates were extracted twice with 30-ml. portions of ether, the combined ethereal extracts and residue washings were dried (Na_2SO_4), and the ether was removed by distillation, leaving a viscous oil. This gave the *bis*-2 : *4-dinitrophenylhydrazone* of 2 : 2′-diformyl-5 : 6 : 5′-trimethoxydiphenyl on being warmed with 2 : 4-dinitrophenylhydrazine in alcoholic sulphuric acid. The derivative (of VII) was obtained as orange-red, rhombic plates, m. p. 277° after recrystallisation from dioxan (Found : C, 53·0; H, 3·6; N, 16·3. $C_{29}H_{24}O_{11}N_8$ requires C, 52·7; H, 3·6; N, 16·9%).

The sodium carbonate solution, after extraction with ether, was concentrated to a small bulk, cooled in ice-water, and acidified with ice-cold hydrochloric acid. The solid mass that separated was resinous at the room temperature, but crystallised on trituration with aqueous methanol. In this manner 5 : 6 : 5′-*trimethoxydiphenic acid* (VI; R = Me) was obtained, and recrystallised as minute, colourless, slender prisms, m. p. 215°, from aqueous methanol, $[\alpha]_D^{19}$ 0° (Found : C, 61·5; H, 5·2. $C_{17}H_{16}O_7$ requires C, 61·4; H, 4·8%).

5 : 6 : 5′-Trimethoxydiphenic acid, heated with concentrated sulphuric acid at 50° for 30 minutes, was converted into 1 : 5 : 6-*trimethoxyfluorenone*-4-*carboxylic acid* (IX), which was obtained as a yellow solid when the mixture was poured into water; fine yellow needles, m. p. 256°, were obtained on recrystallisation from 50% acetic acid (Found: C, 64·7; H, 4·2. $C_{17}H_{14}O_6$ requires C, 65·0; H, 4·5%). The fluorenone was readily soluble in aqueous sodium carbonate; its 2 : 4-*dinitrophenylhydrazone* was obtained as a dark red amorphous powder, m. p. 286°, on attempted recrystallisation from dioxan–light petroleum (Found : N, 11·3. $C_{23}H_{18}O_9N_4$ requires N, 11·3%).

Conversion of Acetylthebaol into 5 : 6 : 5′-*Trimethoxydiphenic Acid.*—4-Acetoxy-3 : 6-dimethoxyphenanthraquinone (acetylthebaolquinone) was prepared by the oxidation of acetylthebaol with chromic acid (Freund and Göbel, *loc. cit.*). It was found advisable to carry out the oxidation in cold acetic acid rather than in hot. The product was obtained as long, bright yellow needles, m. p. 205° after crystallisation from acetic acid (Found : C, 65·9; H, 4·5. Calc. for $C_{18}H_{14}O_6$: C, 66·2; H, 4·3%). The related *phenazine* derivative was prepared by condensation of the quinone with *o*-phenylenediamine in acetic acid, and crystallised from nitrobenzene as minute, yellow prisms, m. p. 265° (Found : C, 72·0; H, 4·7; N, 7·1. $C_{24}H_{18}O_4N_2$ requires C, 72·4; H, 4·5; N, 7·0%).

4-Acetoxy-3 : 6-dimethoxyphenanthraquinone (10 g.) was dissolved in hot acetic acid (120 ml.), mixed with 30% hydrogen peroxide (16 ml.), and kept for 2 hours at 70—80°. Further hydrogen peroxide (16 ml.) was then added and the mixture heated for 5 hours at 100°. Next day the liquid was heated on the steam-bath, and water slowly added to incipient precipitation; on cooling, a quantity of crystalline material separated. This was collected and found to consist mainly of by-products (see below). The filtrate was further diluted until the total volume was approx. 1700 ml., and set aside overnight in the refrigerator, whereupon 6-*acetoxy*-5 : 5′-*dimethoxydiphenic acid* (VI; R = Ac) (5 g.) separated. This was collected, washed, and dissolved in dilute sodium hydrogen carbonate solution, and the solution was filtered and acidified with hydrochloric acid, the acid separating as a mass of fine needles. It crystallised from aqueous alcohol in long, slender, colourless needles, m. p. 229° (Found : C, 58·6; H, 4·5. $C_{18}H_{16}O_8,0·5H_2O$ requires C, 58·5; H, 4·6%).

When a solution of the acid in concentrated sulphuric acid was heated at 50° for 30 minutes and diluted with water, a light brown solid separated. This proved to be 8 : 3′-*dimethoxy*-3 : 4-*benzocoumarin* (X), and was obtained as long, slender, almost colourless needles, m. p. 148—149°, by recrystallisation from alcohol (Found : C, 70·0; H, 4·7. $C_{15}H_{12}O_4$ requires C, 70·3; H, 4·7%). This substance showed no ketonic properties, and dissolved in sodium hydroxide solution only on prolonged boiling.

6-Acetoxy-5 : 5′-dimethoxydiphenic acid (1·5 g.) was heated on the steam-bath with 20% aqueous sodium hydroxide (15 ml.) for 2 hours, and the solution cooled in ice and acidified with ice-cold hydrochloric acid. The solid that separated was collected, washed with water, and recrystallised from 50% aqueous alcohol, whereupon 6-*hydroxy*-5 : 5′-*dimethoxydiphenic acid* (VI; R = H) was obtained as colourless prisms, m. p. 172° with effervescence (lactone formation ?), resolidification, and remelting at 235° (Found, in material dried at 100°/15 mm. : C, 60·0; H, 3·9. $C_{16}H_{14}O_7$ requires C, 60·3; H, 4·4. Found, in material dried at 190°/0·01 mm. : C, 64·3; H, 4·0. $C_{16}H_{12}O_6$ requires C, 64·0; H, 4·0%). The acid was readily soluble in sodium hydrogen carbonate solution and in alcohol; its alcoholic solution gave no colour on addition of ferric chloride.

When heated with concentrated sulphuric acid at 50° for 30 minutes this acid was converted into 8 : 3′-dimethoxy-3 : 4-benzocoumarin, m. p. 148—149°, identical with the substance obtained in the same way from the 6-acetoxy-acid.

6-Hydroxy-5 : 5′-dimethoxydiphenic acid (1 g.) was dissolved in 20% aqueous sodium hydroxide (20 ml.), and methyl sulphate (1·78 ml., 2·25 g.) slowly added with constant shaking. The mixture was then heated on the steam-bath for an hour, cooled in ice, and acidified with ice-cold hydrochloric acid. 5 : 6 : 6′-Trimethoxydiphenic acid (VI; R = Me) separated as a semi-solid mass, and was obtained as colourless prisms, m. p. 213—214°, by crystallisation from aqueous alcohol. Recrystallised, it had m. p. 215°, undepressed by admixture with the acid obtained by oxidation of (+)-3 : 4-dimethoxy-2-(5-methoxy-2-vinylphenyl)stilbene. The acid, when heated for 30 minutes at 50° with concentrated sulphuric acid, was converted into 1 : 5 : 6-trimethoxyfluorenone-4-carboxylic acid, m. p. 256° undepressed on mixing with the specimen obtained from the degradation product.

The By-product of the Oxidation of 4-*Acetoxy*-3 : 6-*dimethoxyphenanthraquinone*.—The solid first separating from the products of oxidation of acetylthebaolquinone (see above) was shaken with dilute sodium carbonate solution, and the insoluble matter collected. Acidification of the filtrate yielded a small amount of 6-acetoxy-5 : 5′-dimethoxydiphenic acid. The residue was only slowly soluble in boiling sodium hydroxide solution, and was reprecipitated unchanged on acidification. It was obtained as bunches of very long, very pale brown needles, m. p. 192°, on recrystallisation from alcohol, and is regarded as 4′-*acetoxy*-6 : 3′-*dimethoxy*-3 : 4-*benzocoumarin* (XI) (Found : C, 64·8; H, 4·3. $C_{17}H_{14}O_6$ requires C, 64·9; H, 4·5%). A solution of this substance (7 g.) in alcohol (140 ml.) was refluxed for 4 hours with 20% alcoholic potassium hydroxide (31 ml.), with the addition of just sufficient 30% hydrogen peroxide to convert the dark brown solution to a pale straw colour. The mixture was cooled and acidified with ice-cold hydrochloric acid. The precipitated solid was collected and crystallised from alcohol, 4′-*hydroxy*-6 : 3′-*dimethoxy*-3 : 4-*benzocoumarin* being obtained as pale pink prisms, m. p. 172° (Found : C, 65·7; H, 4·4. $C_{15}H_{12}O_5$ requires C, 66·1; H, 4·4%). The substance is soluble in aqueous sodium hydroxide, but insoluble in sodium carbonate. Its alcoholic solution gives an intense blue colour with ferric chloride. The result of the hydrolysis was the same when no hydrogen peroxide was added, though in this case the product was much darker.

4′-Hydroxy-6 : 3′-dimethoxy-3 : 4-benzocoumarin (5 g.) was boiled with 10% aqueous potassium hydroxide (103 ml.), and methyl sulphate (16·9 ml., 22·3 g.) added during 2 hours with mechanical stirring. Potassium hydroxide (5 g.) was added and the solution boiled for ½ hour more, cooled, and acidified with hydrochloric acid, whereupon a gummy precipitate separated. This was obtained crystalline on trituration with aqueous alcohol, and the solid collected (4·1 g.). 5 : 6 : 2′ : 5′-*Tetramethoxydiphenyl*-2-*carboxylic acid* (XIII) was obtained as slender colourless needles, m. p. 162·5°, on recrystallisation from alcohol (Found : C, 63·8; H, 5·5. $C_{17}H_{18}O_6$ requires C, 64·1; H, 5·6%). The red solution in concentrated sulphuric acid, after being heated at 50° for 30 minutes, gave no precipitate on dilution with water.

Cyclisation of 5 : 6 : 2′ : 5′-*Tetramethoxydiphenyl*-2-*carboxylic Acid*.—(*a*) The acid was recovered mainly unchanged after 2 hours' heating on the steam-bath with syrupy phosphoric acid and phosphoric oxide.

(*b*) 5 : 6 : 2′ : 5′-Tetramethoxydiphenyl-2-carboxylic acid (1 g.) was converted into the acid chloride by boiling it with thionyl chloride (2 ml.) for 30 minutes. After removal of the excess of thionyl chloride, the acid chloride was dissolved in carbon disulphide, and the mixture heated under reflux with aluminium chloride (0·85 g.) until evolution of hydrogen chloride ceased. The carbon disulphide was removed by distillation and the residue decomposed by ice-water and hydrochloric acid, giving a gummy orange mass. This dissolved in hot alcohol, to give an intensely coloured solution, from which on cooling a quantity of light brown solid separated. This was collected and 1 : 6-*dihydroxy*-4 : 5-*dimethoxyfluorenone* (XV) (or an isomer) was obtained as colourless needles, m. p. 147° (Found : C, 66·4; H, 4·6. $C_{15}H_{12}O_5$ requires C, 66·1; H, 4·4%). The substance was readily soluble in aqueous sodium hydroxide, insoluble in aqueous sodium carbonate. Its alcoholic solution gave an intense green colour with ferric chloride. No definite substance could be obtained from the mother liquors of the crystallisation of this compound, though not all the material in these was soluble in alkali.

(*c*) Phosphorus pentachloride (0·83 g.) was added to a suspension of the tetramethoxydiphenylcarboxylic acid (1·2 g.) in dry benzene (10 ml.), and the mixture warmed on the steam-bath until conversion into the acid chloride was complete. It was then cooled in ice-water until crystallisation of the benzene began, and anhydrous stannic chloride (1·95 g.) in benzene (5 ml.) added. A dark violet solid separated. The mixture was kept at the room temperature for 6 hours; ice-water, hydrochloric acid, and ether were added, a bright orange solid then separating. The organic solvents were removed and the solid was collected (1·1 g.), washed well with water and crystallised from alcohol. A crop of stout yellow prisms was first obtained, followed by a much smaller crop of pale yellow needles. The prisms were recrystallised from alcohol, 1 : 4 : 5 : 6-*tetramethoxyfluorenone* (XIV) being obtained as bright yellow prisms, m. p. 183° (Found : C, 68·0; H, 5·4. $C_{17}H_{16}O_5$ requires C, 68·0; H, 5·3%). This substance was insoluble in alkali, and its alcoholic solution gave no colour with ferric chloride. Its dilute solutions exhibited an intense yellow fluorescence. The 2 : 4-*dinitrophenylhydrazone* was obtained as bunches of bright red needles, m. p. 290°, on recrystallisation from nitrobenzene (Found : C, 57·7; H, 4·0; N, 11·6. $C_{23}H_{20}O_8N_4$ requires C, 57·5; H, 4·2; N, 11·7%).

The needles obtained during the first crystallisation of the ketone were separated from the prisms, first by hand-picking, and then by repeated crystallisation from alcohol, being then obtained as almost colourless needles, m. p. 146°, undepressed on admixture with the product of the aluminium chloride cyclisation (*b* above) (Found : C, 66·1; H, 4·9%). The 2 : 4-*dinitrophenylhydrazone* from this compound had m. p. 285° after crystallisation from glacial acetic acid (Found : N, 12·3. $C_{21}H_{16}O_8N_4$ requires N, 12·4%).

Ozonolysis of (+)-3 : 4-*Dimethoxy*-2-(5-*methoxy*-2-*vinylphenyl*)*stilbene*.—Ozonised oxygen was passed through a solution of (+)-3 : 4-dimethoxy-2-(5-methoxy-2-vinylphenyl)stilbene (5·3 g.) in dry chloroform (30 ml.) cooled in ice-water, until a test portion no longer decolorised a carbon tetrachloride solution of bromine. The chloroform was removed by distillation, and the ozonide reduced by the addition of glacial acetic acid (20 ml.), ether (30 ml.), water (0·2 ml.), and zinc dust (5 g.). When the initial vigorous reaction had subsided the mixture was refluxed until a test portion no longer gave a colour with starch–potassium iodide paper; it was then filtered from solid matter and the residue washed well with ether. The filtrate and ethereal washings were collected, the ethereal layer was separated, and the aqueous layer extracted twice with ether. The combined ethereal extracts were washed, dried, and evaporated, leaving a brown oil smelling strongly of benzaldehyde. This was extracted three times with boiling light petroleum (b. p. 80—100°). The residue could not be crystallised but gave the bis-2 :4-dinitrophenylhydrazone of 2 : 2′-diformyl-5 : 6 : 5′-trimethoxydiphenyl on treatment with dinitrophenylhydrazine in alcoholic sulphuric acid. The derivative was obtained as orange-red plates, m. p. 277°, undepressed by admixture with a specimen of the 2 : 4-dinitrophenylhydrazone obtained from the product of potassium permanganate oxidation of this nitrogen-free substance. The parent *aldehyde* was obtained as a viscous light brown oil (2 g.), b. p. 215—219° (bath-temp.)/0·3 mm. (Found : C, 67·5; H, 5·6. $C_{17}H_{16}O_5$ requires C, 68·0; H, 5·3%).

The light petroleum extract, on cooling, deposited some of this aldehyde, and on decantation and evaporation of the solution, a small amount of benzaldehyde was obtained and identified by its odour and by preparation of its 2 : 4-dinitrophenylhydrazone, m. p. 236°.

On one occasion only, the residue from the light petroleum extract yielded a small amount of colourless prisms, m. p. 147°, from benzene (charcoal), becoming yellow on exposure to air (Found : C, 67·4; H, 5·3. $C_{17}H_{16}O_5$ requires C, 68·0; H, 5·3). This substance was devoid of ketonic properties; it dissolved in boiling aqueous sodium hydroxide, and was precipitated on acidification. It may possibly be the *lactone* of 5 : 6 : 5′-trimethoxy-2′(? 2)-hydroxymethyl-diphenyl-2(? 2′)-carboxylic acid produced by Cannizzaro reaction of the aldehyde.

Oxidation of 2 : 2′-*Diformyl*-5 : 6 : 5′-*trimethoxydiphenyl*.—Potassium permanganate (1·2 g.) in warm water (30 ml.) was slowly added to a stirred suspension of the dialdehyde (1·6 g.) in water (50 ml.) at 70° with passage of carbon dioxide. The mixture was heated at 70° for 30 minutes after the appearance of a permanent violet colour, and filtered from solid matter, which was washed with water, and the colour of the filtrate discharged by sulphur dioxide, whereupon 5 : 6 : 5′-trimethoxydiphenic acid was precipitated as a gummy solid. This was obtained, after three crystallisations from aqueous alcohol, as colourless prisms, m. p. 215°, undepressed by admixture with an authentic specimen.

2 : 2′-Diformyl-5 : 6 : 5′-trimethoxydiphenyl was converted into a black tar when heated at 100° with 25% aqueous sodium hydroxide; it was recovered unchanged after treatment with cold alkali, and also after being heated on the steam-bath for 24 hours with malonic acid and pyridine.

Reaction between Thebaine and Anhydrous Magnesium Iodide.—A solution of anhydrous magnesium iodide (5 g.) in dry benzene (40 ml.) and dry ether (10 ml.) was added during an hour to a boiling, vigorously stirred solution of thebaine (5 g.) in benzene (100 ml.). A black-green precipitate formed at once, this colour quickly changing to green, and to light brown after 4 hours' boiling. No further change in colour was noted though the mixture was boiled for 36 hours. The brown solid was collected, washed well with hot benzene and ether, and kept in a vacuum-desiccator. It rapidly degenerated to a black-brown substance when kept in moist air, and slowly to a greenish-grey substance on prolonged storage *in vacuo*. On treatment with water a substance was obtained that was soluble in alkali and gave an intense red colour with diazobenzenesulphonic acid, but this could not be crystallised, nor could any crystalline derivative be prepared.

On 3 minutes' boiling with 15% hydrochloric acid the thebaine–magnesium iodide product was converted into a gum, obtained on cooling the solution. This was found to have a fluorescence in acid media indistinguishable from that of thebenine, but the fluorescence of the two in alkali was markedly different. The gum was fully methylated by methyl sulphate and alkali, the product dissolved in benzene–chloroform, and the solution passed down a column of alumina. No band could be distinguished. Thebenine, when methylated and chromatographed in the same way, gave a bright green fluorescent band, that on elution proved to contain *NN*-dimethylthebenine *OO*-dimethyl ether methosulphate, obtained as minute colourless prisms, m. p. 280°, on recrystallisation from alcohol (Found: C, 59·4; H, 6·7; N, 3·0. Calc. for $C_{22}H_{28}O_3N,CH_3SO_4$: C, 59·3; H, 6·7; N, 3·0%).

The thebaine–magnesium iodide reaction product (8 g.) was oxidised in the same way as phenyldihydrothebaine, but no identifiable acid could be isolated, nor any that gave a fluorescein derivative on fusion with resorcinol and a trace of concentrated sulphuric acid.

Reaction between the Thebaine–Magnesium Iodide Product and Phenylmagnesium Bromide.—The thebaine–magnesium iodide reaction product (2 g.) was shaken with excess of phenylmagnesium bromide in dry benzene (40 ml.) for 24 hours at room temperature, the solution poured into excess of saturated aqueous ammonium chloride, and the benzene layer removed. The aqueous portion was extracted with benzene, and the basic substances were removed from the benzene layer with hydrochloric acid. The acid extract was made alkaline with ammonia and the base extracted with ether. On evaporation of the ethereal extract a viscous oil was obtained, and this gave phenyldihydrothebaine perchlorate (0·7 g.) on treatment with aqueous perchloric acid. On recrystallisation from alcohol this had m. p. 245°, undepressed by admixture with (+)-α-phenyldihydrothebaine perchlorate. No search was made for the (+)-δ-phenyldihydrothebaine on this scale.

Reduction of the Thebaine–Magnesium Iodide Product.—(*a*) The reaction product (5 g.) was suspended in liquid ammonia (100 ml.) with stirring, and sodium (0·49 g.) added in thin slices, the blue colour, at first rapidly discharged, finally persisting. The excess of sodium was removed by the addition of a few drops of alcohol, and the solution cautiously poured into water (100 ml.). The precipitate so obtained largely dissolved on the addition of 5 ml. of 10% aqueous sodium hydroxide. The solution was filtered from solid matter, and concentrated hydrochloric acid added drop by drop until precipitation of a near-white solid ceased, the solution remaining strongly alkaline throughout. The precipitate was extracted with chloroform in the presence of sodium dithionite (hydrosulphite), and the extract dried and evaporated to leave a brown gum. This dissolved readily in dilute acids and in alkali, the latter solutions giving an intense red colour with diazobenzenesulphonic acid. The only sparingly soluble derivative obtained from this substance was a *mercuri-iodide* [Found: I, 38·4. $(C_{19}H_{24}O_3N)_2,HgI_4$ requires I, 38·7%. This agreement is possibly fortuitous].

(*b*) Thebaine (10 g.) was treated with anhydrous magnesium iodide (9 g.) in benzene–ether, and the solution boiled under reflux with vigorous stirring throughout the addition of the magnesium iodide and for a further 4 hours. The benzene was largely removed, and dry ether (150 ml.) added, followed slowly by a solution of lithium aluminium hydride (1·5 g.) in ether (220 ml.). A vigorous reaction ensued, gas being evolved and the light brown solid becoming rapidly white. The mixture was stirred and refluxed for a further 1·5 hours, then cooled. A portion of the suspension was shaken with dilute acetic acid, the aqueous layer separated and treated with aqueous sodium perchlorate in the presence of sodium dithionite, whereupon a pale yellow oily perchlorate separated. The aqueous solution was decanted from the gum, which was washed well with water. All attempts to crystallise this perchlorate or to convert it into a crystalline salt failed. Of eighteen different salts of the base investigated, only the perchlorate, salicylate, picrate, and picrolonate were found to be sparingly soluble in water, and all were gums. All the salts were readily soluble in alcohol. The perchlorate, dissolved in hot water, was treated with ammonia in the presence of sodium dithionite; the oily base was precipitated, and proved to be surprisingly sparingly soluble in the usual extracting solvents; it possibly consists of a phenol-betaine. Addition of sodium nitrite solution to a well-cooled acetic acid extract of the original mixture, containing hydrochloric acid, gave an immediate copious orange-red precipitate, from which it is concluded that the base is a secondary amine. Though these results are discouraging it is hoped to investigate this interesting reaction further.

Oxidation of 3 : 4 : 6-*Trimethoxyphenanthrene.*—A solution of chromic acid (12·5 g.) in water (3 ml.) and acetic acid (18 ml.), cooled to −5°, was very cautiously added to a solution of 3 : 4 : 6-trimethoxyphenanthrene (12 g.) in acetic acid (30 ml.) immersed in ice–salt, with constant shaking, during about 1·5 hours. The rate of addition was controlled so that the temperature did not rise above 30°, otherwise the yield was considerably diminished. After addition of all the chromic acid the mixture was kept in ice for 30 minutes, and then allowed to attain the room temperature. The solid was collected, and washed with glacial acetic acid. 3 : 6-*Dimethoxyphenanthra*-1 : 4-*quinone* (XXX) was thus obtained as long, orange felted needles, m. p. 220° (4·5 g.); it had m. p. 223° after recrystallisation from glacial acetic acid (Found : C, 71·5, 71·4; H, 4·4, 4·3; OMe, 16·0. $C_{16}H_{12}O_4$ requires C, 71·6; H, 4·5; OMe, 23·1%). It was sparingly soluble in alcohol and readily soluble in acetone. Its solution in concentrated sulphuric acid was deep blue.

A solution of this quinone (0·25 g.) in glacial acetic acid (10 ml.), along with *o*-phenylenediamine (0·25 g.), was heated for 1 hour on the steam-bath. 3-*Hydroxy*-7′-*methoxynaphtho*-(1′ : 2′-1 : 2)*phenazine* (XXXI) separated as orange felted needles, m. p. 295—297°, sparingly soluble in all solvents (Found : C, 77·0; H, 4·5; N, 8·4; OMe, 8·4. $C_{21}H_{14}O_2N_2$ requires C, 77·3; H, 4·3; H, 8·6; OMe, 9·5. $C_{22}H_{16}O_2N_2$ requires C, 77·6; H, 4·7; H, 8·2; 2OMe, 18·7%). This dissolved readily in warm aqueous alkali, indicating its phenolic nature.

Oxidation of 3 : 6-*Dimethoxyphenanthra*-1 : 4-*quinone.*—Hydrogen peroxide (4 ml.; 30%) was added to a hot solution of 3 : 6-dimethoxyphenanthra-1 : 4-quinone (4 g.) in glacial acetic acid (75 ml.), and the mixture heated on the steam-bath for 19 hours, with the addition of 30% hydrogen peroxide (3 ml.) every 3 hours. The colour first darkened considerably, and then lightened to a pale yellow. The mixture was concentrated to a small bulk, a quantity of solid matter separating from the viscous oily residue. The mixture was triturated with water, the solid collected, washed well with water, and dissolved in aqueous sodium carbonate, and the solution boiled (charcoal), filtered, and acidified. A bright yellow solid separated (0·5 g.). On recrystallisation from aqueous alcohol, 8-*carboxy*-7-2′-*carboxyvinyl*-2-*methoxy*-1 : 4-*naphthaquinone* (XXXII) was obtained as minute, bright yellow prisms, m. p. 273—275° (decomp.) (Found : C, 58·2; H, 3·3. $C_{15}H_{10}O_7,0·5H_2O$ requires C, 57·9; H, 3·5. Found, in material dried at 180°/0·1 mm. : C, 59·4; H, 3·3. $C_{15}H_{10}O_7$ requires C, 59·6; H, 3·3%). The acid was readily soluble in sodium carbonate solution, and this solution readily decolorised potassium permanganate solution.

The major portion of the oxidation product, however, was soluble in water, and was never obtained in a form suitable for analysis. It was oxidised further as follows. The filtrate from the isolation of the solid acid above was made alkaline with sodium hydroxide, and aqueous potassium permanganate added until a permanent violet colour was obtained, whereafter the solution was heated on the steam-bath until all the manganese had been precipitated. The mixture was then filtered, the residue was washed several times with water, and the filtrate and washings were saturated with ammonium sulphate and extracted twenty times with ether. The combined extracts were evaporated, giving a semi-solid mass. This became crystalline on trituration with ethyl acetate, and the solid was collected at the pump. Colourless needles of benzene-1 : 2 : 3 : 4-tetracarboxylic acid were obtained by the slow evaporation of its solution in methyl acetate; these had m. p. 242—245° (Bamford and Simonsen, *J.*, 1910, **97**, 1904, give m. p. 238° for this acid) (Found : C, 47·7; H, 2·6. Calc. for $C_{10}H_6O_8$: C, 47·3; H, 2·4%). On fusion with resorcinol and a trace of sulphuric acid this acid gave a substance which exhibited an intense yellow-green fluorescence in alkaline solution. Methyl benzene-1 : 2 : 3 : 4-tetracarboxylate was prepared by the action of methyl iodide on the dry silver salt of the acid, and was obtained as colourless prismatic needles, m. p. 133°, after three recrystallisations from alcohol (Found : C, 54·1; H, 4·7. Calc. for $C_{14}H_{14}O_8$: C, 54·1; H, 4·7%). The crystals became violet on exposure to light. Bamford and Simonsen (*loc. cit.*) give m. p. 133° for this tetramethyl ester.

Oxidation of 4-*Hydroxy*-3 : 6-*dimethoxyphenanthrene* (*Thebaol*).—Chromic acid (1·9 g.) in water (0·5 ml.) and acetic acid (12 ml.) was slowly added to a solution of thebaol (1·5 g.) (Freund and Göbel, *loc. cit.*) in acetic acid (20 ml.) at the room temperature, with constant shaking, during 10 minutes. The mixture was finally kept at 40° for 10 minutes and then in the refrigerator for 3 hours. The solid that separated was collected, washed with acetic acid, and crystallised from the same solvent, being so obtained as long, slender, orange-red needles (0·4 g.), m. p. 233° alone or mixed with a specimen of 3 : 6-dimethoxyphenanthra-1 : 4-quinone prepared by the oxidation of 3 : 4 : 6-trimethoxyphenanthrene.

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