466. *Synthetical Experiments in the Chelidonine–Sanguinarine Group of the Alkaloids. Part III.*

By A. S. Bailey, Sir Robert Robinson, and R. S. Staunton.

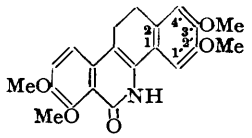
7 : 8 : 2′ : 3′-Tetramethoxy-3 : 4-dihydro-1 : 2-benzphenanthridone of which the synthesis was described in Part II (*J.*, 1950, 1375) has been converted into the related tetramethoxybenzphenanthridine. The methosulphate of the latter base is changed on reduction into a tetramethoxy-*N*-methyldihydrobenzphenanthridine which has been obtained by Späth and Kuffner (*Ber.*, 1931, **64**, 3034) from either sanguinarine or chelerythrine. The synthesis of the reference compound confirms the correctness of the structures of these two alkaloids deduced from degradative evidence.

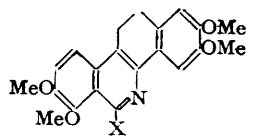
The work of Part I in an isomeric series has been carried further and the tetramethoxy-*N*-methylbenzphenanthridinium salt which is an analogue of sanguinarine has been prepared.

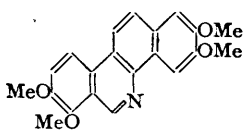
7 : 8 : 2′ : 3′-Tetramethoxy-3 : 4-dihydro-1 : 2-benzphenanthridone * (I) is changed by phosphoryl chloride into 9-chloro-7 : 8 : 2′ : 3′-tetramethoxy-3 : 4-dihydro-1 : 2-benzphenanthridine (II; X = Cl) which easily affords a 9-anilino-derivative (II; X = NHPh). The chloro-compound is reduced by hydrogen in the presence of palladised strontium carbonate to 7 : 8 : 2′ : 3′-tetramethoxy-3 : 4-dihydrobenzphenanthridine (II; X = H), which is dehydrogenated by means of palladised charcoal in boiling *p*-cymene solution with formation

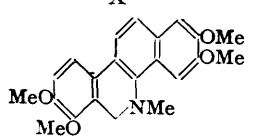
* A misprint occurs in the numbering of this formula in *J.*, 1950, 1377, where it is allotted number (VIII).

of 7 : 8 : 2′ : 3′-tetramethoxybenzphenanthridine (III). It is also possible to transform (II; X = Cl) into (III) in one operation under similar conditions.

(I.) 

 (II.)

(III.) 

 (IV.)

The methosulphate of (III) could be reduced by means of zinc and aqueous hydrochloric acid to 7 : 8 : 2′ : 3′-tetramethoxy-10-methyl-9 : 10-dihydro-1 : 2-benzphenanthridine (IV), which was identical with a specimen prepared by S. N. Sarkar from dihydrosanguinarine (replacement of two methylenedioxy- by four methoxy-groups) using the method of Spāth and Kuffner (*Ber.*, 1931, **64**, 3034). We are grateful to Dr. Sarkar for the provision of this valuable specimen. The identity was established by mixed melting points. Further, we are deeply indebted to Mrs. D. M. Hodgkin and Miss P. M. Cowan (Department of Crystallography, Oxford University) for their examination of the crystals of the two specimens : they were reported to be identical.

FIG. 1.

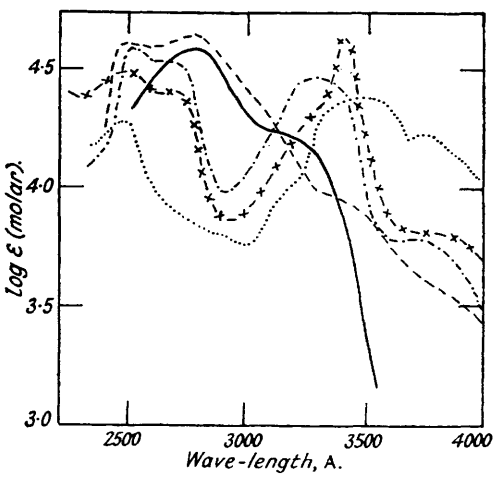


FIG. 2.

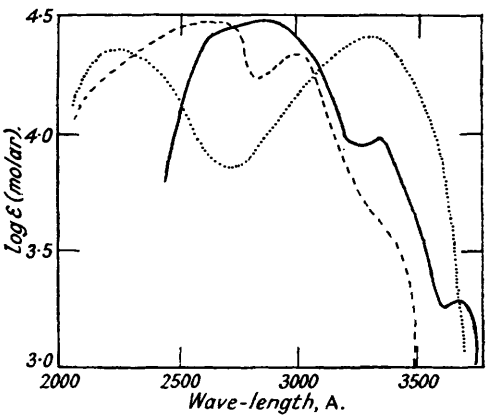


FIG. 1. . . . . 7 : 8 : 2′ : 3′-*Tetramethoxy*-3 : 4-*dihydro*-1 : 2-*benzphenanthridone* (*in* $CHCl_3$).
– – – – – – – – 7 : 8 : 2′ : 3′-*Tetramethoxy*-1 : 2-*benzphenanthridine* (*in* $CHCl_3$).
——— 7 : 8 : 2′ : 3′-*Tetramethoxy*-10-*methyl*-9 : 10-*dihydro*-1 : 2-*benzphenanthridine* (*in* EtOH).
× — × — × 9-*Chloro*-7 : 8 : 2′ : 3′-*tetramethoxy*-3 : 4-*dihydro*-1 : 2-*benzphenanthridine* (*in* EtOH).
— · — · — · — 7 : 8 : 2′ : 3′-*Tetramethoxy*-3 : 4-*dihydro*-1 : 2-*benzphenanthridine* (*in* EtOH).

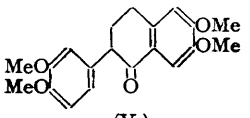
FIG. 2. ——— 6 : 7 : 2′ : 3′-*Tetramethoxy*-1 : 2-*benzphenanthridine* (*in* $CHCl_3$).
– – – – – – – – 6 : 7-*Dimethoxy*-2-(3 : 4-*dimethoxyphenyl*)*naphthalene* (*in* EtOH).
- - - - - - - - - - 6 : 7-*Dimethoxy*-2-(3 : 4-*dimethoxyphenyl*)-3 : 4-*dihydronaphthalene* (*in* EtOH).

Since Sarkar (*Nature*, 1948, **162**, 265) found that sanguinarine chloride was toxic to rats it was of interest to examine the methochloride of (III) which is of sanguinarine type. This was kindly undertaken by Dr. L. A. Stocken (Biochemistry Department, Oxford University) who reports that the substance is not toxic to rats at the concentrations used in the case of sanguinarine.

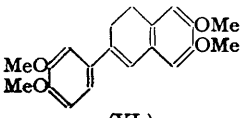
The synthesis of (V) was described in Part I (Richardson, Robinson, and Seijo, *J.*, 1937, 835) and this tetralone was converted into 6 : 7 : 2′ : 3′-tetramethoxy-3 : 4 : 11 : 12-tetrahydro-1 : 2-benzphenanthridine (tetrahydro-derivative of VII). The latter has now been

dehydrogenated to (VII); the metho-salts of this base are so sparingly soluble that their pharmacological properties could not be observed.

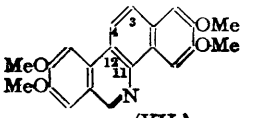
In applying the Leuchart reaction to (V) (main product, >CO ⟶ >CH·NH·CHO), a by-product, namely 6 : 7-dimethoxy-2-(3 : 4-dimethoxyphenyl)-3 : 4-dihydronaphthalene (VI), was obtained. Two hydrogen atoms could be added to, or removed from, this substance with formation of the related tetralin or naphthalene derivative, respectively.



(V.)



(VI.)



(VII.)

The ultra-violet absorption of some of the new compounds is shown in Figs. 1 and 2. We are indebted to Dr. F. B. Strauss for these determinations. Comparison with the previously observed absorption of dihydrosanguinarine shows that the substitution of two methoxy-groups for a methylenedioxy-group has a considerable effect in this series. The ultra-violet absorption spectrum of (VI) is similar to that of *trans*-stilbene, and its dehydrogenation product (– – – – in Fig. 2) resembles the curve for 2-phenylnaphthalene in this respect (Fieser and Hershberg, *J. Amer. Chem. Soc.*, 1938, **60**, 944; Bills and Noller, *ibid.*, 1948, **70**, 957; cf. Braude, *Ann. Reports*, 1945, **42**, 105).

Experimental.

9-Chloro-7 : 8 : 2′ : 3′-tetramethoxy-3 : 4-dihydro-1 : 2-benphenanthridine (II; X = Cl).—A mixture of 7 : 8 : 2′ : 3′-tetramethoxy-3 : 4-dihydro-1 : 2-benzphenanthridone (6 g.) and phosphoryl chloride (30 c.c.) was refluxed (oil-bath at 140°) for 1 hour. Addition of the deep-red solution to ice, followed by treatment with ammonia gave a grey solid which was collected, washed well with water, dried, and extracted with boiling benzene (3 × 30 c.c.). The extracts were concentrated to approx. 30 c.c. and cooled, giving 5·6 g. of crude crystals. The *9-chloro*-compound crystallised from benzene in cream-coloured plates, m. p. 176—178°, which became slightly yellow when kept (Found: C, 65·2, 65·3; H, 4·9, 5·2; Cl, 9·9, 8·7. $C_{21}H_{20}O_4NCl$ requires C, 65·3; H, 5·2; Cl, 9·2%). It was insoluble in dilute mineral acids but dissolved in 6N-hydrochloric acid to a dark red solution from which an unstable hydrochloride separated. This lost hydrogen chloride at 70° giving the free base and the analysis was unsatisfactory.

9-Anilino-7 : 8 : 2′ : 3′-tetramethoxy-3 : 4-dihydro-1 : 2-benzphenanthridine.—A solution of 9-chloro-7 : 8 : 2′ : 3′-tetramethoxy-3 : 4-dihydro-1 : 2-benzphenanthridine (0·1 g.) in aniline (0·2 c.c.) was heated on a steam-bath. After 5 minutes needles started to separate from the mixture, and after 10 minutes the mixture was solid. Methanol (2 c.c.) was added, and the solid (m. p. 141—143°) collected, and crystallised from ethanol. The *9-anilino*-compound separated from ethanol as clusters of rods, m. p. 143—144° (Found: C, 73·1; H, 5·8; N, 6·2. $C_{27}H_{26}O_4N_2$ requires C, 73·3; H, 5·9; N, 6·3%). Solutions of the substance in organic solvents were colourless and exhibited an intense blue fluorescence; the yellow solutions in dilute mineral acids were non-fluorescent.

7 : 8 : 2′ : 3′-Tetramethoxy-3 : 4-dihydro-1 : 2-benzphenanthridine (II; X = H).—A mixture of 9-chloro-7 : 8 : 2′ : 3′-tetramethoxy-3 : 4-dihydro-1 : 2-benzphenanthridine (0·5 g.), potassium hydroxide (0·2 g.), 2-methoxyethanol (30 c.c.), and palladised strontium carbonate (0·5 g.) was shaken under hydrogen for 2 hours. The filtered solution was concentrated to a small volume and water added. The solid which separated (m. p. 161—162°; quantitative yield) was collected, washed with water, and crystallised from ethanol. *7 : 8 : 2′ : 3′-Tetramethoxy-3 : 4-dihydro-1 : 2-benzphenanthridine* formed colourless rods, m. p. 162—163° (Found: C, 71·5; H, 6·0; N, 4·1. $C_{21}H_{21}O_4N$ requires C, 71·9; H, 6·0; N, 4·0%). Solutions of the base in dilute mineral acids were yellow.

7 : 8 : 2′ : 3′-Tetramethoxy-1 : 2-benzphenanthridine (III).—(*a*) A solution of 9-chloro-7 : 8 : 2′ : 3′-tetramethoxy-3 : 4-dihydro-1 : 2-benzphenanthridine (5 g.) in *p*-cymene (45 c.c.) was refluxed for 6 hours with palladised charcoal (0·6 g. of 30%) in a stream of hydrogen; evolution of hydrogen chloride had then almost ceased. The filtered solution slowly deposited a solid which, when collected and washed with light petroleum (b. p. 40—60°), had m. p. 210—214° (3·8 g.). This product was completely soluble in 2N-hydrochloric acid to a pale yellow solution and hence contained no trace of unchanged starting material. Crystallisation from pyridine–ethanol (4 : 1) gave a cream-coloured solid. A solution of the latter in chloroform–benzene (1 : 2 by vol.) was passed through an alumina column and the blue-violet fluorescent band (ultra-violet lamp) was eluted with the same mixture. Evaporation of the eluate and crystallisation of the residue from pyridine–ethanol gave *7 : 8 : 2′ : 3′-tetramethoxy-1 : 2-benzphenanthridine* as colourless, lanceolate plates, m. p. 218—219° (decomp.) (Found: C, 71·8, 72·1; H, 5·4, 5·3; N, 3·9. $C_{21}H_{19}O_4N$ requires C, 72·3; H, 5·5; N, 4·0%). Solutions of the compound showed a weak blue-violet fluorescence in daylight; they were intensely fluorescent in ultra-violet light.

(*b*) A solution of 7 : 8 : 2′ : 3′-tetramethoxy-3 : 4-dihydro-1 : 2-benzphenanthridine (0·4 g.) in *p*-cymene (5 c.c.) was refluxed for 2 hours with palladised charcoal (0·1 g. of 30%), under hydrogen. The crude product, m. p. 205—210°, crystallised from pyridine–ethanol (4 : 1) in lanceolate plates (0·2 g.), m. p. and mixed m. p. with a specimen prepared as under (*a*) 217—219° (decomp.) (Found: C, 72·3; H, 5·6%).

The *hydrochloride* crystallised from ethanol–water (4 : 1) as clusters of tiny, golden-yellow needles, m. p. 265—267° (decomp.), freely soluble in water (Found: C, 59·5; H, 5·9. $C_{21}H_{19}O_4N,HCl,2H_2O$ requires C, 59·7; H, 5·7%).

Methosulphate. After a solution of 7 : 8 : 2′ : 3′-tetramethoxy-1 : 2-benzphenanthridine (2 g.) had been boiled in purified xylene (80 c.c.) for a minute, methyl sulphate (5 c.c.) was added and the mixture refluxed for 40 minutes; a further 2 c.c. of methyl sulphate were added after 15 minutes. The orange-yellow solid which rapidly separated from the solution was collected next day and washed with light petroleum (b. p. 40—60°). The product (2·1 g.), m. p. 255—258° (decomp.), was easily soluble in water. Crystallisation from ethanol–water (8 : 1) gave the *methosulphate* as clusters of orange-yellow needles, m. p. 255—257° (decomp.) (Found: C, 56·5, 56·3; H, 5·5, 5·6; N, 2·3; S, 6·3. $C_{23}H_{25}O_8NS,H_2O$ requires C, 56·0; H, 5·5; N, 2·8; S, 6·5%).

Treatment of a solution of the salt in 50% aqueous ethanol with ammonium chloride solution gave long, silky needles of the corresponding *chloride*, m. p. 207—210° (decomp.) (Found: C, 60·3; H, 6·2; Cl, 7·6. $C_{22}H_{22}O_4NCl,2H_2O$ requires C, 60·6; H, 6·0; Cl, 8·2%).

Addition of potassium cyanide to an aqueous solution of 7 : 8 : 2′ : 3′-tetramethoxy-1 : 2-benzphenanthridine methosulphate containing a few drops of dilute hydrochloric acid gave a white precipitate of 9-*cyano*-7 : 8 : 2′ : 3′-*tetramethoxy*-10-*methyl*-9 : 10-*dihydro*-1 : 2-*benzphenanthridine*, which crystallised from ethyl acetate in colourless rhombs, m. p. 178—180° (decomp.) (Found: C, 70·6; H, 5·6; N, 6·8. $C_{23}H_{22}O_4N_2$ requires C, 70·8; H, 5·6; N, 7·2%).

7 : 8 : 2′ : 3′-*Tetramethoxy*-10-*methyl*-9 : 10-*dihydro*-1 : 2-*benzphenanthridine* (IV).—A mixture of 7 : 8 : 2′ : 3′-tetramethoxy-1 : 2-benzphenanthridine methosulphate (1 g.), water (150 c.c.), concentrated hydrochloric acid (10 c.c.), and granulated zinc (20 g.) was refluxed, concentrated hydrochloric acid (10 c.c.) being added at hourly intervals. After 3 hours the solution had a very pale yellow colour, and a cream-coloured solid began to separate. The liquid was decanted and kept in the refrigerator overnight, and the solid was then collected, washed with water, and shaken with chloroform and 5N-ammonia. The chloroform extract was washed with water and dried ($MgSO_4$), the solvent removed, and the semi-solid residue digested with methanol (10 c.c.). Crystallisation of the resulting solid from chloroform–methanol gave a grey solid, m. p. 180—183° (0·31 g.). Sublimation at 170°/10^{-4} mm. gave a product, m. p. 182—184°. A benzene solution of the latter was chromatographed on alumina, forming a blue-fluorescent band (ultra-violet lamp). This was eluted with benzene, the eluate evaporated, and the residue crystallised from ethanol. 7 : 8 : 2′ : 3′-*Tetramethoxy*-10-*methyl*-9 : 10-*dihydro*-1 : 2-*benzphenanthridine* formed colourless prisms, m. p. 183·5—185° (slight decomp.) (Found: C, 72·6, 72·7, 72·4; H, 6·5, 6·1, 6·4; N, 3·9. Calc. for $C_{23}H_{23}O_4N$: C, 72·3; H, 6·3; N, 3·8%). The m. p. was not depressed by a specimen of the substance supplied by Dr. S. N. Sarkar; the ultra-violet absorption spectra of both specimens were identical.

Mrs. D. M. Hodgkin and Miss P. M. Cowan report that both specimens crystallise in the form of strongly birefringent plates, elongated along *b*. The crystals are biaxial positive with slow extinction parallel to the longest edge *b*. Powder and " single " crystal photographs show that the two specimens are identical, the unit cell is monoclinic, and the space group $P_{2_1/a}$. Cell dimensions are: $a = 21{\cdot}36$; $b = 13{\cdot}39$; $c = 13{\cdot}73$ A.; $\beta = 108°$.

The substance is insoluble in dilute minerals acid. Suspensions in aqueous acids become yellow on the addition of a drop of ferric chloride solution, owing to oxidation to the quaternary salt.

β-(3 : 4-*Dimethoxybenzoyl*)-α-(3 : 4-*dimethoxyphenylpropionitrile*.—The following method is more convenient than that of Richardson, Robinson, and Seijo (*loc. cit.*). Potassium cyanide (22 g.) in water (40 c.c.) was added during 3 minutes to a stirred solution of veratrylideneacetoveratrone (50 g.) in 2-methoxyethanol (150 c.c.) containing glacial acetic acid (9 c.c.) at 100°. Heating was continued for a further 10 minutes (after 8 minutes a white solid began to separate). Water (75 c.c.) was then added and the mixture allowed to cool. The solid which separated was collected, washed well with water, and dried (46 g.); it had m. p. 141—143°. A specimen, crystallised from acetone, had m. p. and mixed m. p. 143—144°.

This nitrile was converted into 1-keto-6 : 7-dimethoxy-2-(3 : 4-dimethoxyphenyl)-1 : 2 : 3 : 4-tetrahydronaphthalene (V) as described in Part I (*loc. cit.*). The 2 : 4-*dinitrophenylhydrazone* formed crimson prisms (from dioxan), m. p. 228—229° (decomp.) (Found: C, 59·5; H, 5·0; N, 10·6. $C_{26}H_{26}O_8N_4$ requires C, 59·6; H, 5·2; N, 10·7%).

1-*Formamido*-6 : 7-*dimethoxy*-2-(3 : 4-*dimethoxyphenyl*)-1 : 2 : 3 : 4-*tetrahydronaphthalene* (cf. " Organic Reactions," Vol. V, p. 301).—A solution of the above tetralone (8 g.) in formamide (20 c.c.) containing formic acid (1 c.c.) and ammonium sulphate (1 g.) was refluxed for 3 hours (oil-bath; 180°), formic acid (1 c.c.) being added every hour. The cold mixture was diluted with water and then extracted with chloroform. The chloroform extract was washed with water and dried (Na_2SO_4), the solvent removed, and the residual oil triturated with methanol (8 c.c.). Next day the solid which had separated was collected and dried. This solid was digested with acetone (10 c.c.), and the acetone-insoluble fraction crystallised from dioxan–ethanol (9 : 1) (5·2 g. of m. p. 200—202°) (Found: C, 67·7; H, 6·7; N, 3·9. Calc. for $C_{21}H_{25}O_5N$: C, 67·8; H, 6·7; N, 3·9%). Richardson, Robinon, and Seijo (*loc. cit.*) give m. p. 202—203°.

The acetone extract was evaporated and the residue (m. p. 126—128°) crystallised from ethanol afforded hexagonal plates (*ca.* 1 g.) of 6 : 7-*dimethoxy*-2-(3 : 4-*dimethoxyphenyl*)-3 : 4-*dihydronaphthalene* (VI), m. p. 129—130° [Found: C, 73·5; H, 6·9; *M* (cryoscopic in camphor), 321. $C_{20}H_{22}O_4$ requires C, 73·6; H, 6·8%; *M*, 326]. The substance decolorised alkaline permanganate solution.

Increasing the time of heating in the Leuchart reaction to 7 hours gave a 40% yield of the dihydronaphthalene.

6 : 7-*Dimethoxy*-2-(3 : 4-*dimethoxyphenyl*)-1 : 2 : 3 : 4-*tetrahydronaphthalene*.—A solution of 6 : 7-dimethoxy-2-(3 : 4-dimethoxyphenyl)-3 : 4-dihydronaphthalene (1·5 g.) in dioxan (10 c.c.) was hydrogenated at the room temperature over platinum oxide (50 mg.) as catalyst. After 1 mole of hydrogen had been absorbed the catalyst was removed, the solvent evaporated *in vacuo* on the steam-bath, and the residual oil triturated with light petroleum (b. p. 40—60°), giving a white solid, m. p. 104—110°. Two crystallisations from methanol gave 6 : 7-*dimethoxy*-2-(3 : 4-*dimethoxyphenyl*)-1 : 2 : 3 : 4-*tetrahydronaphthalene* as colourless rhombs, m. p. 117—118° (Found : C, 73·0; H, 7·3. $C_{20}H_{24}O_4$ requires C, 73·2; H, 7·3%).

6 : 7-*Dimethoxy*-2-(3 : 4-*dimethoxyphenyl*)*naphthalene*.—A mixture of 6 : 7-dimethoxy-2-(3 : 4-dimethoxyphenyl)-3 : 4-dihydronaphthalene (0·5 g.) and palladised charcoal (0·1 g. of 30%) was heated at 240° (metal-bath) for 30 minutes. Hydrogen was rapidly evolved and the melt solidified on cooling. The solid was taken up in chloroform, the solvent removed, and ethanol added to the resulting syrup, which then solidified. Crystallisation from ethanol–dioxan (9 : 1) and then from benzene afforded 6 : 7-*dimethoxy*-2-(3 : 4-*dimethoxyphenyl*)*naphthalene* (270 mg.) as very thin, irregular plates, m. p. 179—180° (Found : C, 74·3; H, 6·3. $C_{20}H_{20}O_4$ requires C, 74·1; H, 6·2%).

Equimolecular quantities of the naphthalene derivative and trinitrobenzene in hot ethanol gave an orange-coloured solution. Nevertheless, colourless plates of tetramethoxyphenylnaphthalene separated on cooling.

6 : 7 : 2′ : 3′-*Tetramethoxy*-1 : 2-*benzphenanthridine* (VII).—1-Formamido-6 : 7-dimethoxy-2-(3 : 4-dimethoxyphenyl)-1 : 2 : 3 : 4-tetrahydronaphthalene was converted into 6 : 7 : 2′ : 3′-tetramethoxy-3 : 4 : 11 : 12-tetrahydro-1 : 2-benzphenanthridine as described by Richardson, Robinson, and Seijo (*loc. cit.*). The substance formed colourless prisms from pyridine–ethanol, m. p. 230—231° (Found : N, 4·1. Calc. for $C_{21}H_{23}O_4N$: N, 4·0%).

(*a*) An attempt to dehydrogenate tetramethoxytetrahydrobenzphenanthridine in boiling *p*-cymene was unsuccessful because the product was almost insoluble therein and crystallised on the catalyst from which it was obtained in small quantity by chloroform extraction.

(*b*) The tetrahydro-compound (300 mg.) was heated at 240° (metal-bath) with palladised charcoal (100 mg. of 30%). It melted and resolidified almost immediately. After 40 minutes the temperature of the bath was raised to 310°, whereupon the solid again melted; after 10 minutes at this temperature the solid was sublimed at 260/0·1 mm. and the sublimate crystallised from pyridine, giving a product (130 mg.), m. p. 299—301°.

(*c*) The tetrahydro-compound (1 g.) was heated at 250° for 30 minutes with palladised charcoal (0·2 g. of 30%). The cold solid was powdered and extracted with chloroform (3 × 30 c.c.), the solvent removed, and the residue crystallised from pyridine (30 c.c.), giving 6 : 7 : 2′ : 3′-*tetramethoxy*-1 : 2-*benzphenanthridine* (0·62 g.) as colourless, diamond-shaped plates, m. p. and mixed m. p. with the specimen prepared as under (*b*) 302—304° (decomp.) (Found : C, 72·4, 72·3; H, 5·4, 5·5; N, 4·2. $C_{21}H_{19}O_4N$ requires C, 72·3; H, 5·5; N, 4·0%). The base is insoluble in the common organic solvents except pyridine and nitrobenzene. The hydrochloride and sulphate are yellow solids which are extremely sparingly soluble in water, the liquid remaining colourless even on boiling.

Methosulphate. A solution of 6 : 7 : 2′ : 3′-tetramethoxy-1 : 2-benzphenanthridine (0·5 g.) in xylene (5 c.c.) and nitrobenzene (10 c.c.) was boiled for a short time and methyl sulphate (1 c.c.) then added to the boiling solution. A yellow precipitate rapidly formed and after 5 minutes the solution was cooled and ether (10 c.c.) added. The solid was collected and washed with ether (quantitative yield). Crystallisation from ethanol–water (1 : 1) gave 6 : 7 : 2′ : 3′-*tetramethoxy*-1 : 2-*benzphenanthridine methosulphate* as fine, pale yellow needles, m. p. 305—308° (decomp.) (Found : C, 56·1; H, 5·4; N, 3·1. $C_{23}H_{25}O_8NS,H_2O$ requires C, 56·0; H, 5·5; N, 2·8%). The *methochloride* formed lemon-yellow needles (from water), m. p. 293—295° (decomp.) (Found : C, 63·0; H, 5·8. $C_{22}H_{24}O_4NCl,H_2O$ requires C, 63·2; H, 5·7%).

Addition of potassium cyanide to an aqueous solution of the methosulphate gave an amorphous white precipitate of the pseudo*cyanide*. This was extracted with chloroform, the solution washed with water and dried ($MgSO_4$), and the solvent removed. The resulting syrup solidified on the addition of methanol, and crystallisation of the crude product, m. p. 225°, from 2-methoxyethanol gave colourless prisms, m. p. 227—229° (decomp.) (Found : C, 70·5; H, 5·6; N, 7·1. $C_{23}H_{24}O_4N_2$ requires C, 70·8; H, 5·6; N, 7·2%).

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