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THE STRUCTURE OF METATHEBAINONE

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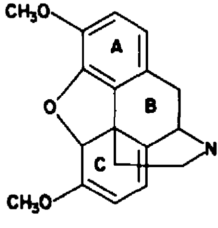
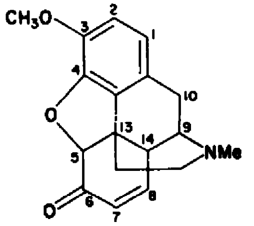
Abstract—The generally accepted structure (IX) for metathebainone has now been confirmed by an unambiguous synthesis of the nitrogen-free degradation product (XIII).

Metathebainone is formed[1,2] by the catalytic reduction of thebaine (I) in cold conc. hydrochloric acid solution, or by the reduction of thebaine or codeinone (II) with stannous chloride in hot conc. hydrochloric acid. The product was originally allotted structure III until it was realized[4] that a migration of the side-chain must have occurred during its formation. This view was later confirmed when the true Δ^7-thebainone (thebainone-A) III was isolated.[5] The conditions of the stannous chloride reduction can be modified so that either metathebainone or Δ^7-thebainone predominates. References in the literature to "thebainone" prior to 1927 refer to metathebainone. The term "thebainone" was defined[6] as applying to ketones of the morphine group which possess a phenolic hydroxyl group at C_4, and a carbonyl group and one double bond in ring C. They are more strictly regarded as arising from $\Delta^{6,8(14)}$-dehydrothebainol methyl ether (β-dihydrothebaine) IV and $\Delta^{5,8(14)}$-dehydrothebainol methyl ether (dihydrothebaine-ϕ) V, rather than from thebaine (I) which is an enol ether of codeinone (II). In addition to Δ^7-thebainone (III), three other "thebainones" are known;[6] these are the C_{14} epimer of III, $\Delta^{8,(14)}$-thebainone VI (thebainone-B) and thebainone-C, whose structure is now[7] known to be VII.



I



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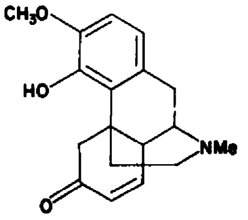

III

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[1] K. W. Bentley, *The Chemistry of the Morphine Alkaloids* Chap. 16. Clarendon Press, Oxford (1954) and Ref. therein cited.

[2] H. L. Holmes, in R. H. F. Manske and H. L. Holmes, *The Alkaloids* Vol. II; pp 1 and 162. Academic Press, New York (1952).

[3] G. Stork, in R. H. F. Manske and H. L. Holmes, *The Alkaloids* Vol. VI; p. 219. Academic Press, New York (1960).

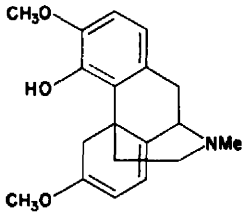
[4] C. Schöpf and F. Borkowsky, *Liebigs Ann.* **458**, 148 (1927).

[5] C. Schöpf and H. Hirsch, *Liebigs Ann.* **489**, 224 (1931).

[6] K. W. Bentley, *The Chemistry of the Morphine Alkaloids* Chap. 15. Clarendon Press, Oxford (1954).

[7] K. W. Bentley and H. M. E. Cardwell, *J. Chem. Soc.* 3245 (1955).

[8] M. Tiffeneau, *Bull Soc. Chim. Fr.* **17**, 109 (1951).



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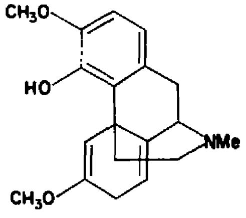

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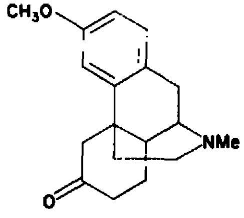

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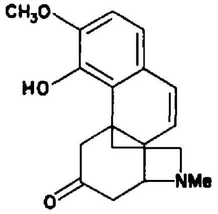

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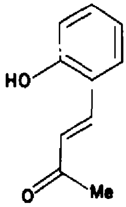
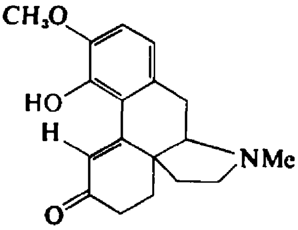
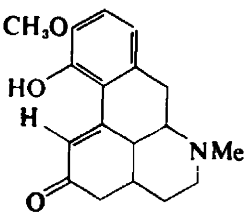


VIII

Metathebainone, $C_{18}H_{21}NO_3$, is an optically active, phenolic tertiary base; it contains one methoxyl group and an α,β-unsaturated carbonyl system (IR band at 1689 cm^{-1}) and readily reacts with two molecules of hydroxylamine. The UV spectrum of metathebainone is very similar to that of *o*-hydroxybenzylidene acetone (VIII), and the NMR spectrum (taken in $CDCl_3$ as solvent and tetramethylsilane as internal reference) exhibits a sharp singlet at 6·51 ppm, indicative of only one olefinic proton. In metathebainone methyl ether this hydrogen appears as a sharp singlet at 6·39 ppm. In order to accommodate an α,β-unsaturated ketone grouping conjugated to the aromatic ring, the nitrogen-containing ring must have migrated from C_{13} during the formation of metathebainone. The most plausible structures are IX and X. Metathebainone is reported[8] to be stable to acetolysis, but the conditions described are milder than those normally employed for such degradations in the morphine group of alkaloids. Metathebainone methyl ether methine is easily obtained on Hofmann degradation of the base and this, on heating with acetic anhydride is converted into 3,4-dimethoxyphenanthrene. This product would not be expected from structure X, whereas loss of the C_6 oxygen function from structure IX is also unusual. The properties and reactions of metathebainone are in agreement with structure IX, and some of



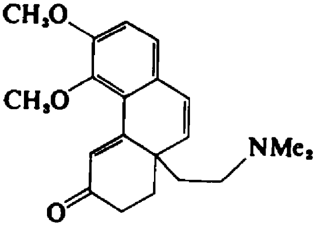
IX



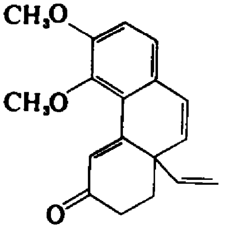
X

the rearrangement reactions of thebaine can be satisfactorily explained[8,9] mechanistically if this structure is correct. Nevertheless positive proof of the structure of metathebainone has, until now, been lacking.

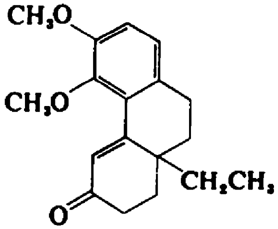
On the basis of structure IX for metathebainone, the methyl ether methine would be XI, and the UV and NMR spectra are compatible with the introduction of unsaturation between C_9 and C_{10}, so that one end of the nitrogen bridge is still attached at C_9 in metathebainone. The methine (XI) had previously[10] been further degraded by the N-oxide method, to 6,7,8,14-tetrahydro-3,4-dimethoxy-6-oxo-14-vinylphenanthrene (XII), and this, upon catalytic hydrogenation absorbs two moles of gas to yield XIII. The structure XIII has now been proved in an unambiguous synthesis, and this constitutes a proof of structure IX for metathebainone itself.



XI

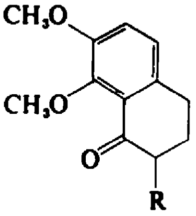


XII

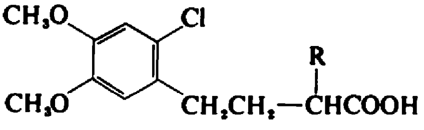


XIII

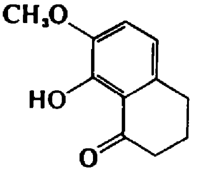
The most obvious route to XIII would involve a Michael reaction[11] between 2-ethyl-7,8-dimethoxytetralone-1 (XIV, R = Et) and methyl vinyl ketone (or the Mannich base, 4-diethylaminobutanone-2), followed by ring-closure of the intermediate 1,5-diketone. This ring-extension reaction has been used very successfully in steroid syntheses.[12] 7,8-Dimethoxytetralone-1 (XIV, R = H) had been prepared previously[13] by ring-closure of the butyric acid (XV, R = H) followed by reductive[14] removal of the protecting chlorine atom. Many attempts were made to alkylate XIV (R = H) to the required 2-ethyl tetralone without success. The β-keto-ester (XIV,



XIV



XV



XVI

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[9] G. Stork, in R. H. F. Manske and H. L. Holmes, *The Alkaloids* Vol. II; p. 189. Academic Press, New York (1952); K. W. Bentley, *The Chemistry of the Morphine Alkaloids*. Clarendon Press, Oxford (1954).

[10] K. W. Bentley, J. C. Ball and J. P. Ringe, *J. Chem. Soc.* 1963 (1956).

[11] E. D. Bergmann, *Organic Reactions* 10, 179 (1959).

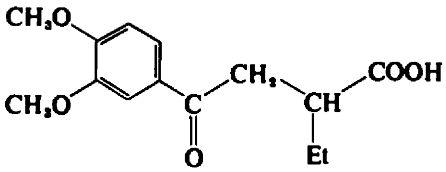
[12] J. W. Cornforth, *Progress in Organic Chemistry* Vol. 3; p. 1. Butterworths, London (1955); I. V. Torgov, *The Chemistry of Natural Products* Vol. 2; p. 525. Butterworths, London (1963).

[13] R. Ghosh and R. Robinson, *J. Chem. Soc.* 506 (1944).

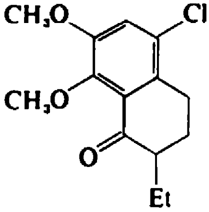
[14] D. B. Bruce and R. H. Thomson, *J. Chem. Soc.* 1089 (1955).

R = $COOCH_3$) was prepared, in poor yield, via the glyoxalate (XIV, R = $COCOOCH_3$) according to the method of Bachman *et al.*,[15] but all attempts to alkylate it failed, the starting material being recovered in each case. Similar attempts to alkylate the hydroxymethylene derivative (XIV, R = CHO) also failed. The tetralone (XIV, R = H) would not form an enamine with pyrrolidine when Stork's conditions were used[16,17], and attempts at direct alkylation of XIV, (R = H), using powdered potassium in xylene[18] resulted in demethylation to XVI.

An alternative approach to the preparation of XIV, (R = Et) would be a ring-closure of XV, (R = Et). In a previous attempt[19] to prepare the related butyric acid without the nuclear chlorine, 3,4-dimethoxyphenylethyl chloride was reacted with ethyl diethyl malonate, but a base-catalysed elimination of hydrogen chloride, followed by polymerization of the resulting styrene, occurred instead of condensation. We have now found that the β-aroylpropionic acid (XVII) can be obtained, in poor yield, by the condensation of ω-bromoacetoveratrone with ethyl diethyl malonate in the presence of sodium hydride in dimethylformamide, followed by hydrolysis and decarboxylation. The acid (XVII) was reduced by Clemmenson's method, chlorinated to XV, (R = Et), and ring-closed to XVIII. In an alternative route to XVIII, ethyl succinic anhydride was condensed with veratrole under conditions which are reported[20] to favour the formation of XVII rather than the isomeric β-ethyl-β-aroyl-propionic acid. The mixture of acids obtained could not be easily separated, and it was reduced, chlorinated and ring-closed to a mixture of XVIII and the isomeric 3-ethyltetralone-1. This mixture of ketones was cleanly separated on a column of alumina to give the required tetralone (XVIII) as a yellow oil, and the 3-ethyltetralone-1 as a pale yellow solid. The yellow oil, and its derived semicarbazone were shown to be identical with the corresponding compounds derived from acetoveratrone. The chlorine atom was reductively removed from XVIII, and the required tetralone (XIV, R = Et) was condensed with methyl vinyl ketone in the presence of potassium *t*-butoxide in ether. The product (XIII) was isolated by chromatography of the reaction mixture over silica gel. The m.p. of the semicarbazone was undepressed upon admixture with the semicarbazone derived from the degradation product of metathebainone, and it was also



XVII



XVIII

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[15] W. E. Backmann, W. Cole and A. L. Wilds, *J. Amer. Chem. Soc.* **62**, 824 (1940).

[16] G. Stork, A. Brizzolara, H. Landesmann, J. Szmuszkovicz and R. Terrell, *J. Amer. Chem. Soc.* **85**, 207 (1963).

[17] G. Stork and S. R. Dowd, *J. Amer. Chem. Soc.* **85**, 2178 (1963).

[18] C. A. Grob and W. Jundt, *Helv. Chim. Acta* **31**, 1691 (1948).

[19] K. W. Bentley and S. F. Dyke, *J. Chem. Soc.* 3151 (1961).

[20] W. Cocker, A. K. Fateen and C. Lipmann, *J. Chem. Soc.* 927 (1951); W. Cocker, B. E. Cross, A. K. Fateen, C. Lipmann and D. R. A. Whyte, *Chem. & Ind.* 651 (1949).

shown that the IR spectra, in bromoform solution, of the semicarbazones and 2,4-dinitrophenylhydrazones of the synthetic and natural ketones were identical.

EXPERIMENTAL

6,7,8,9,10,14-*Hexahydro*-3,4-*dimethoxy*-6-*oxo*-14-*ethylphenanthrene* XIII. A solution of XII[10] (0·25 g) in MeOH (25 ml) was hydrogenated at room temp and atm. press. in the presence of 5% Pd–$SrCO_3$ (0·5 g). The theoretical uptake of H_2 for 2 moles was complete in 25 min. The filtrate from the catalyst was evaporated to leave XIII as a pale yellow oil. The *semicarbazone* was obtained as yellow needles from MeOH, m.p. 219–220°. (Found: C, 66·7; H, 7·4; N, 12·1. $C_{19}H_{25}N_3O_3$ requires: C, 66·4; H, 7·4; N, 12·2%.) λ_{max} (EtOH) at 215 and 308 mμ ε_{max} 17,000 and 30,200. The 2,4-*dinitrophenylhydrazone* crystallized from EtOH as red feathery needles, m.p. 182–183°. (Found: C, 61·5; H, 5·7; N, 11·9. $C_{24}H_{26}N_4O_6$ requires: C, 61·7; H, 5·6; N, 12·0%.) λ_{max} (EtOH) 220, 265(s), 305 and 400 mμ. ε_{max} 24,000, 11,500, 14,000 and 31,600.

Attempted alkylation of 7,8-*dimethoxytetralone*-1 *in the presence of potassium in xylene*. A solution of 1·0 g XIV (R = H)[13,14] in xylene (10 ml) was added to a stirred suspension of powdered K (0·21 g) in xylene (15 ml) and the mixture was heated under reflux in a stream of N_2 for 40 min. After cooling somewhat, EtI (1·0 ml) was added, and heating was continued for 30 min. The next day the mixture was acidified with dil. H_2SO_4, then extracted with ether. Removal of organic solvents left a brown oil which was distilled. The fraction b.p. 148–154°/6·10^{-4} mm was collected and crystallized from petrol (40–60) to give 7-*methoxy*-8-*hydroxytetralone*-1 (XVI) as square plates, (0·09 g), m.p. 75–77·5°. (Found: C, 68·5; H, 6·05. $C_{11}H_{12}O_3$ requires: C, 68·7; H, 6·3%.) ν_{max} (Nujol) 1635 cm^{-1}.

7,8-*Dimethoxy*-2-*glyoxalotetralone*-1 (XIV, R = COCOOMe). After a solution of Na (1·64 g) in MeOH (20 ml) had been evaporated to dryness at 100° under vacuum, dimethyl oxalate (8·4 g) and then benzene (100 ml) were added. The mixture was stirred and boiled under N_2, and when almost all the solid had dissolved, 7,8-dimethoxy-tetralone-1 (7·3 g) in benzene (40 ml) was added. The mixture was left stirring, in an atm. of N_2, overnight. Water was added and the layers separated. Acidification of the aqueous layer gave a yellow precipitate (3·25 g). Crystallization from petrol (60–80) gave 7,8-*dimethoxy*-2-*glyoxalotetralone*-1 as yellow blades, m.p. 94–95°. (Found: C, 65·2; H, 5·7. $C_{15}H_{16}O_5$ requires: C, 65·0; H, 5·8%.) ν_{max} (Nujol) 1735, 1690, 1680, 1640, 1600 cm^{-1}. 7,8-Dimethoxy-tetralone-1 (5·2 g) was recovered from the benzene solution.

7,8-*Dimethoxy*-2-*carbomethoxytetralone*-1 (XIV, R = $COOCH_3$). The above glyoxalate (2·72 g) was placed in a boiling tube and melted. Powdered glass (1·4 g) was then added and the mixture stirred and heated at 150° until effervescence ceased (about 45 min). The cooled residue was extracted with benzene, the benzene solution was treated with charcoal and evaporated. The dark residual oil was distilled and the fraction b.p. 127–145/2·5 mm was collected. Crystallization from petrol (40–60) gave white flakes of 7,8-*dimethoxy*-2-*carbomethoxy*-*tetralone*-1 m.p. 52–54°. (Found: C, 64·3; H, 5·95. $C_{14}H_{16}O_5$ requires C, 64·2; H, 6·05%.) ν_{max} (Nujol) 1740, 1685 and 1065 cm^{-1}. All attempts to ethylate this β-ketoester failed.

Ethyl diethyl acetoveratrylmalonate. Diethyl ethyl malonate (1·88 g) in dimethylformamide (20 ml) was stirred and warmed gently with NaH (0·5 g of a 50% dispersion in oil). The brown solution was then cooled and ω-bromo-acetoveratrone[21] (2·6 g) in dry benzene (20 ml) was added dropwise. After boiling 5 hr, the mixture was cooled, poured into water and extracted with benzene. Evaporation of the benzene left a sticky solid (1·9 g) which was crystallized from petrol (60–80) to give ethyl diethyl acetoveratrylmalonate as white flakes, m.p. 74–75°. (Found: C, 62·35; H, 6·9. $C_{19}H_{27}O_7$ requires: C, 62·1; H, 7·3%.) ν_{max} (Nujol) 1750, 1720, 1670, 1595 and 1085 cm^{-1}.

Powdered Na in benzene was also successfully used as condensing agent.

α-*Ethyl*-β-(3,4-*dimethoxybenzoyl*)*propionic acid* (XVII). The above malonic ester (1·6 g) was boiled 3 hr with a solution of KOH (2·0 g) in water (2·0 ml) and EtOH (25 ml), then cooled and poured into water. Acidification, followed by ether extraction gave, ultimately a light brown oil whose IR spectrum indicated the presence of carbonyl and carboxyl groups. This crude substituted malonic acid was heated at 160–170° until evolution of CO_2 ceased (about 30 min). The cooled, brown mass was triturated with ether–petrol to give a buff solid (0·54 g), and this, on crystallization from aqueous EtOH yielded α-*ethyl*-β-(3,4-*dimethoxybenzoyl*) *propionic acid* m.p. 100–101° as white flakes. (Found: C, 63·1; H, 6·8. $C_{14}H_{18}O_5$ requires: C, 63·1; H, 6·8%.) ν_{max} (Nujol) 1690, 1670, 1590 and 1255 cm^{-1}.

α-*Ethyl*-γ-(3,4-*dimethoxyphenyl*)*butyric acid*. The above propionic acid (0·55 g) was boiled 5 hr

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[21] C. Mannich and G. Hahn, *Ber. Dtsch. Chem. Ges.* **44**, 1549 (1911).

with amalgamated Zn (1·2 g), water (2·5 ml) and conc. HCl (2·0 ml), then cooled and poured into water. Extraction with $CHCl_3$ and working up in the usual way gave a yellow oil which was distilled under vacuum. The fraction b.p. 204–212° (bath)/0·3 mm was collected (0·59 g) as *α-ethyl-γ-(3,4-dimethoxyphenyl)butyric acid*. (Found: C, 66·75; H, 8·05. $C_{14}H_{20}O_4$ requires C, 66·7; H, 7·9%.) ν_{max} (liquid film) 1700, 1590 and 1260 cm^{-1}.

5-Chloro-7,8-dimethoxy-2-ethyltetralone-1 (XVIII). A solution of the above butyric acid (0·59 g) in glacial acetic acid (5 ml) was stirred and cooled in a cold water bath while a solution of Cl_2 (0·2 g) in acetic acid (10 ml) was added dropwise. The mixture was stirred 2 hr, briefly boiled, cooled and poured into water. The product was extracted with ether and the ethereal solution washed with water, dried and evaporated to leave a brown oil (0·55 g) which was dissolved in benzene (10 ml). This solution was warmed to 50° and PCl_5 (0·7 g) was added in portions. The mixture was kept at 50–55° for 2 hr, then cooled to 0° and $SnCl_4$ (0·6 ml) added. The mixture was left in the refrigerator for 2 days, then poured over ice (20 g) and conc. HCl (10 ml). Extraction with $CHCl_3$, then work up in the usual way gave a brown oil which was distilled under red. press. The fraction (0·23 g) b.p. 185–191°/1·0 mm was collected as *5-Chloro-7,8-dimethoxy-2-ethyltetralone*-1. (Found: C, 62·9; H, 6·05; Cl, 13·5. $C_{14}H_{16}O_3Cl$ requires: C, 62·8; H, 5·9; Cl, 13·2%.) ν_{max} (liquid film) 1690, 1585, 1180, 970 and 930 cm^{-1}. The *semicarbazone* was obtained as white needles from EtOH, m.p. 205–207°. (Found: C, 55·8; H, 5·8; Cl, 10·65; N, 13·3. $C_{15}H_{19}N_3O_3Cl$ requires: C, 55·5; H, 5·9; Cl, 10·9; N, 12·9%.)

Friedel-Crafts acylation of veratrole. Ethyl succinic anhydride (21·35 g) and veratrole (25·3 g) were added to a solution of anhydrous $AlCl_3$ (44 g) in nitrobenzene (200 ml), cooled to 0°. After 65 hr, the mixture was warmed to room temp and left for 5 hr. The complex was decomposed with ice and conc. HCl aq, the nitrobenzene was removed by steam distillation, and the residue extracted with ether. The ether solution was in turn extracted with dil. NaOH aq, and this aqueous phase was acidified and extracted with $CHCl_3$. Evaporation of the $CHCl_3$ left a brown gum (19·77 g). This crude reaction mixture was boiled for 5 hr with amalgamated Zn (50 g), conc. HCl aq (60 ml) and water (40 ml). Work-up gave a brown acidic oil (17·64 g). Distillation at 2 mm gave some ethyl succinic anhydride b.p. 160° and a mixture of β-ethyl-γ-(3,4-dimethoxyphenyl)butyric acid and α-ethyl-γ-(3,4-dimethoxyphenyl) butyric acid was collected in the range 162–206°. This mixture of butyric acids was chlorinated and ring-closed as previously described to give a mixture of the 2-ethyl and 3-ethyltetralone-1. This mixture (10·52 g) was chromatographed over alumina (400 g); elution with 2% $CHCl_3$ in petrol (40–60) gave a brown oil (0·72 g) which was non-ketonic. Elution with 5% $CHCl_3$ in benzene gave 5-chloro-7,8-dimethoxy-2-ethyltetralone-1 as a pale yellow oil (4·35 g). This was shown to be identical with an authentic specimen prepared above. Elution with 6% $CHCl_3$ in petrol (40–60) gave a pale yellow oil (3·12 g), which solidified on standing. Crystallization from petrol (60–80) gave white flakes, m.p. 68–69° of *5-chloro-7,8-dimethoxy-3-ethyltetralone*-1. (Found: C, 62·6; H, 6·4; Cl, 13·5. $C_{14}H_{16}O_3Cl$ requires: C, 62·8; H, 6·0; Cl, 13·2%.) ν_{max} (liquid film) 1685, 1580, 980 and 950 cm^{-1}. The *semicarbazone* was obtained as white needles from EtOH, m.p. 201·5–202·5°. (Found: C, 55·6; H, 6·0; N, 12·95; Cl, 10·8. $C_{15}H_{19}N_3O_3Cl$ requires: C, 55·5; H, 5·85; N, 12·9; Cl, 10·9%.)

β-Ethyl-β-(3,4-dimethoxybenzoyl)propionic acid. Anhydrous aluminium chloride (15 g), nitrobenzene (40 ml), ethyl succinic anhydride (6·4 g) and veratrole (7·5 g) were stirred together at 0° for 1 hr, then left in the refrigerator for 65 hr before decomposing the complex as above. The product obtained by alkali extraction was a yellow oil which gave a white solid (0·7 g) when triturated with a mixture of petrol and ether containing a little acetone. Crystallization from aqueous EtOH gave white flakes, m.p. 138·5–139·5 of what later proved to be *β-ethyl-β-(3,4-dimethoxybenzoyl)propionic acid*. (Found: C, 63·6; H, 6·85. $C_{14}H_{18}O_5$ requires: C, 63·1; H, 6·8%.) ν_{max} (Nujol) 1730, 1635, 1580 and 1275 cm^{-1}.

β-Ethyl-γ-(3,4-dimethoxyphenyl)butyric acid. The above propionic acid (1·5 g) was reduced with amalgamated Zn and HCl aq as described previously. *β-Ethyl-γ-(3,4-dimethoxyphenyl)butyric acid* was obtained as a pale yellow oil (1·1 g) b.p. 190–200/2 mm. (Found: C, 66·8; H, 8·1. $C_{14}H_{20}O_4$ requires: C, 66·7; H, 7·9%.) ν_{max} (liquid film) 1710, 1595 and 1265 cm^{-1}.

5-Chloro-7,8-dimethoxy-3-ethyltetralone-1. This was prepared by chlorination and ring-closure of the above butyric acid as previously described. The product was shown to be identical with that isolated from the alumina column as described above.

7,8-*Dimethoxy-2-ethyltetralone*-1 (XIV, R = Et). 5-Chloro-7,8-dimethoxy-2-ethyltetralone-1 (4·35 g) in EtOH (10 ml) and 10% ethanolic KOH (23 ml) was shaken with H_2 and 10% Pd–$CaCO_3$ (2·0 g) at room temp and atm. press. The uptake of H_2 ceased after 1 mole and the catalyst was removed. The filtrate was evaporated and the residue taken up in ether, washed with $NaHCO_3$ aq, dried and evaporated. The residual red oil was distilled and 7,8-*dimethoxy-2-ethyltetralone*-1 was collected at 195–200°/0·9 mm. (Found: C, 71·8; H, 7·65; $C_{14}H_{17}O_3$ requires: C, 72·1; H, 7·3%.) ν_{max} (liquid film) 1690, 1600 cm^{-1}. The *semicarbazone* crystallized from EtOH as white needles, m.p. 198–199°. (Found: C, 60·7; H, 7·1; N, 15·0; $C_{15}H_{20}N_3O_3$ requires: C, 61·0; H, 7·1; N, 14·65%.)

6,7,8,9,10,14-*Hexahydro*-3,4-*dimethoxy*-6-*oxo*-14-*ethylphenanthrene* (XIII). Potassium t-butoxide (from K (0·32 g) and t-butanol (7 ml)) was suspended in ether and stirred, in an atm. of N_2, whilst a solution of 7,8-dimethoxy-2-ethyltetralone-1 (1·74 g) in ether (8 ml) was added, drop-wise. The mixture was stirred at room temp for 3 hr, then methyl vinyl ketone (0·6 g) in ether (10 ml) was added during 30 min. The reaction mixture was stirred overnight, heated under reflux for 8 hr, then allowed to stand overnight at room temp. The mixture was poured into dil. HCl aq (70 ml), extracted with CH_2Cl_2 (3 × 40 ml) and the organic layer was washed with water, dried and evaporated. The residual brown oil was dissolved in the minimum volume of $CHCl_3$ and chromatographed over silica gel (40 g). Elution with 10% $CHCl_3$ in petrol (60–80) gave unchanged tetralone-1 (1·2 g), then a mixture of this tetralone-1 and product (0·15 g) and finally pure product (0·2 g). The semicarbazone crystallized from MeOH as pale yellow prisms, m.p. 217–219°, undepressed upon admixture with the semicarbazone of the compound derived from metathebainone. (Found: C, 66·1; H, 7·4; N, 12·1. $C_{19}H_{25}N_3O_3$ requires: C, 66·5; H, 7·3; H, 12·2%.)

The IR spectra, in bromoform solution, and UV spectra of this material, its semicarbazone and its 2,4-dinitrophenylhydrazone were identical with the corresponding substances derived from metathebainone.