proceeded and ammonia was evolved. After cooling, water (700 ml.) was added, the mixture acidified with concentrated hydrochloric acid, and the product extracted with ether. The ether extract was washed with water, dried over sodium sulfate, and evaporated, and the residue was dissolved in hot aqueous alcohol and filtered hot [Norit]. The product was collected from the cooled filtrate and washed with a little 50% ethanol when 11 g. of light brown crystalline material, m.p. 165–167°, was obtained. Recrystallization from 50% ethanol afforded Compound L as white prisms, m.p. 166–167°; $[\alpha]_D^{21}$ −18.2° ($CHCl_3$, c 0.99).

Anal. Calcd. for $C_{26}H_{32}O_7$: C, 68.4; H, 7.1. Found: C, 68.6; H, 7.2.

The *methyl ester*, prepared by esterification of the acid with diazomethane in ether, was recrystallized from methanol when it was obtained as white rods, m.p. 161–162°.

Anal. Calcd. for $C_{27}H_{34}O_7$: C, 68.9; H, 7.3. Found: C, 68.9; H, 7.2.

Reaction of methyl ester of Compound L with phenylmagnesium bromide. Compound L methyl ester (11 g., 0.023 mol.) in benzene (120 ml.) was added over a period of 15 min. to a stirred mixture of phenylmagnesium bromide [prepared from magnesium (9 g.) and bromobenzene (42 ml.) in the usual way] and ether (100 ml.). The mixture was refluxed for 3 hr. with stirring, and then poured onto crushed ice (400 g.) and concentrated hydrochloric acid (65 ml.). The aqueous layer was extracted with benzene (2 × 100 ml.) and the combined benzene-ether solution washed with 2*N* hydrochloric acid, water, 5% sodium hydroxide, and finally water. Most of the solvent was then removed and the residue steam distilled for 6 hr. to remove biphenyl. The residual liquid was extracted with ether when 13 g. of product was obtained. Recrystallization of this from ethanol gave Compound M as white prisms, m.p. 174–175°; $[\alpha]_D^{20}$ −14.6° ($CHCl_3$, c 0.82).

Anal. Calcd. for $C_{38}H_{42}O_6$: C, 76.8; H, 7.1. Found: C, 76.8; H, 6.8.

Dehydration of Compound M with acetic anhydride and formic acid. A solution of Compound M (1 g.) in acetic anhydride (8 ml.) and 100% formic acid (5 ml.) was refluxed for 2 hr., during which the initial deep blue color quickly turned to red. Water was added to the mixture and the precipitated light brown, amorphous material recrystallized from ethanol when Compound N was obtained as white needles, m.p. 164°; $[\alpha]_D^{20}$ +92° ($CHCl_3$, c 0.31); λ_{max} 2275, 2550, 2675, 2900, 3000, 3100, 3200 Å; ϵ_{max} 52,480, 25,700, 18,200, 19,050, 18,000, 19,000, 18,000.

Anal. Calcd. for $C_{38}H_{38}O_4$: C, 81.7; H, 6.9. Found: C, 81.6; H, 6.7.

The alcoholic liquors (from recrystallization of Compound N) were evaporated and the residue dissolved in a 1:1 mixture of benzene and light petroleum (b.p. 50–60°) and the solution passed down an alumina column. A blue fluorescent band (ultraviolet light) was eluted, the eluate evaporated, and the residue recrystallized three times from ethanol when Compound O was obtained as white needles, m.p. 153–154° which was depressed to 125° on mixing with a sample of Compound N; $[\alpha]_D^{20}$ −83° ($CHCl_3$, c 0.85); λ_{max} 2150, 2775 Å; ϵ_{max} 22,910, 7586.

Anal. Calcd. for $C_{38}H_{40}O_5$: C, 79.1; H, 7.0. Found: C, 79.4, 79.5; H, 6.7, 7.3.

ABERDEEN, SCOTLAND

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, THE UNIVERSITY, ABERDEEN]

Structure of Isothebaine

K. W. BENTLEY AND S. F. DYKE

Received September 21, 1956

4,6-Dimethoxy-5-ethoxyaporphine has been synthesized by a combination of the Bischler-Napieralski *iso*-quinoline and the Pschorr phenanthrene syntheses, and found to be identical with *iso*thebaine ethyl ether.

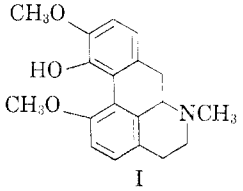
During the period of active growth of *Papaver orientale* the plant contains appreciable quantities of thebaine, but after the ripening and withering of the aerial plant very little, if any, of this alkaloid can be extracted. At the same time, however, the roots are found to contain a phenolic, optically active alkaloid, isothebaine, isomeric with thebaine.[1,2] It was originally postulated that thebaine is converted into isothebaine in the plant. Klee[3] examined the base thoroughly and found that Hofmann degradation of the methyl ether proceeded *via* a mixture of an optically inactive methine, and an optically active isomethine, to a trimethoxyvinylphenanthrene, which on oxidation, followed by decarboxylation, afforded a trimethoxyphenanthrene, isolated as the picrate. This was believed by Klee to be identical with the picrate of 3,4,5-trimethoxyphenanthrene obtained by Vongerichten and Dittmer[4] from morphenol (II) and subsequently synthesised by Pschorr and Koch.[5] On this basis Klee allotted structure I to isothebaine, the phenolic —OH being placed at C_4, without proof, to account for the apparent difficulty of methylation of the base (nascent diazomethane in *iso*amyl ether).

More recently Schlittler and Müller[6] have repeated these degradations and obtained the trimethoxyphenanthrene as a crystalline solid, which was found to be identical with the product of decarboxylation of synthetic 3,4,5-trimethoxyphenanthrene-9-carboxylic acid. Kiselev and Konovalova, who isolated[7] *iso*thebaine from *Papaver*

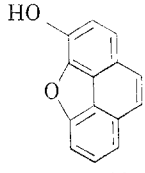
(1) J. Gadamer and W. Klee, *Arch. Pharm.*, **249**, 39 (1911).
(2) J. Gadamer, *Arch. Pharm.*, **261**, 625 (1913).
(3) W. Klee, *Arch. Pharm.*, **252**, 211 (1914).
(4) E. Vongerichten and O. Dittmer, *Ber.*, **39**, 1718 (1906).
(5) R. Pschorr and W. Koch, *Ann.*, **391**, 40 (1912).
(6) E. Schlittler and J. Müller, *Helv. Chim. Acta*, **31**, 1119 (1948).
(7) V. V. Kiselev and R. A. Konovalova, *J. Gen. Chem. (USSR)*, **18**, 142 (1948).

bracteatum, claim[8] that this degradation product is *not* identical with 3,4,5-trimethoxyphenanthrene picrate, since the mixed melting point was depressed, and they accordingly challenged the correctness of structure I. In view of the agreement reached between the independent workers, Schlittler and Müller and Klee, the contention of Kiselev and Konovalova regarding the identity of the degradation product may be discounted.

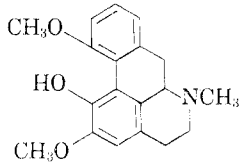
Several attempts to synthesize the aporphine of structure I, OH = OMe, have met with no success.[6,9,10]



I



II



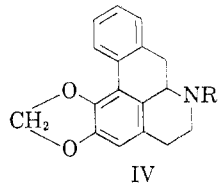
III

What appears to have escaped notice until we commented on it recently[11] is that all the facts about *iso*thebaine can be explained in terms of a 4,5,6-orientation of oxygen substituents—*i.e.* III, or some simple variant of this, as follows:

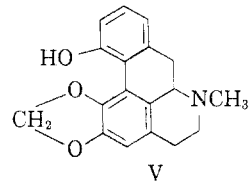
(a) A 3,4,5-trimethoxyphenanthrene would be expected on degradation of the methyl ether by Klee's method.

(b) The biosynthesis of III would require no abnormal ring closure even if the alkaloid arises directly from a tri-oxy precursor, whereas from such a precursor I would require *iso*quinoline ring closure *meta* to a hydroxyl group—a process that has not been accomplished in the laboratory.[9]

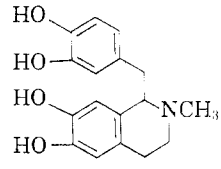
(c) All known naturally occurring aporphines and benzylisoquinolines whose structures have been deduced, contain oxygen functions at C_6 and C_7 of the isoquinoline system; even the dioxy aporphines, roemerine[12,13] (IV, R = Me) and anonaine[12] (IV, R = H), have their oxygen substituents in these positions. In particular, it is noted that the arrangement of oxygen substituents in I is without parallel in other naturally occurring aporphines.



IV



V



VI

(d) Several aporphine alkaloids are known with only one oxygen substituent in the "benzyl portion" of the molecule. Of these pukateine[14,15] (V) has exactly the orientation of substituents now postulated for isothebaine. Faltis[16] has suggested a reasonable mechanism whereby laureline and pukateine could arise from *nor*laudanosine (VI).

(e) It was suggested by Bently and Cardwell[17] that (−)-laudanidine (VII), which together with laudanine is found in *P. orientale*,[18−20] or a less methylated base, might be the precursor of thebaine. The variation in concentration of thebaine and isothebaine reported by Klee,[3] if correct, would be consistent[17] with the removal of (−)-laudanidine in the formation of thebaine, and the accumulation of (+)-laudanidine, which is used subsequently for the synthesis of isothebaine, which could occur by ring closure and loss of an oxygen function.

It is noted that I, or a variant with the groups methoxyl and hydroxyl interchanged could also arise from this precursor.

In order to test the essential correctness of III as the structure of isothebaine, the infrared and ultraviolet spectra of isothebaine methyl ether hydroiodide and (±)-4,5,6-trimethoxyaporphine hydroiodide[21] were examined and it was concluded[11] that isothebaine methyl ether is III, OH = OMe. The failure of isothebaine to couple with diazotized sulphanilic acid indicated the 5-hydroxy structure (III) for the alkaloid itself, rather than a 4-hydroxy structure, which would be the likely alternative.

The allocation of this structure to isothebaine has now been vindicated by the unambiguous synthesis of (±)-4,6-dimethoxy-5-ethoxyaporphine

(8) V. V. Kiselev and R. A. Konovalova, *J. Gen. Chem. (USSR)*, **19**, 148 (1949).
(9) R. K. Callow, J. M. Gulland, and R. D. Haworth, *J. Chem. Soc.*, 1444 (1929).
(10) J. Müller, *Helv. Chim. Acta*, **31**, 1111 (1948).
(11) K. W. Bentley and S. F. Dyke, *Experientia*, **12**, 205 (1956).
(12) S. Yunusov, R. A. Konovalova, and A. P. Orekhov, *J. Gen. Chem. (USSR)*, **9**, 1868 (1939).
(13) G. Barger and G. Weintauer, *Helv. Chim. Acta*, **22**, 1036 (1939).
(14) G. Barger and A. Girardet, *Helv. Chim. Acta*, **14**, 1481 (1931).
(15) G. Barger and E. Schlittler, *Helv. Chim. Acta*, **15**, 381 (1932).
(16) F. Faltis, G. Wagner, and E. Adler, *Ber.*, **77**, 686 (1944).
(17) K. W. Bentley and H. M. E. Cardwell, *J. Chem. Soc.*, 3252 (1955).
(18) O. Hesse, *Ann.*, **153**, 47 (1870).
(19) O. Hesse, *Ber.*, **4**, 693 (1871).
(20) O. Hesse, *Ann.*, **282**, 209 (1894).
(21) T. R. Govindachari and B. R. Pai, *J. Org. Chem.*, **18**, 1352 (1953).

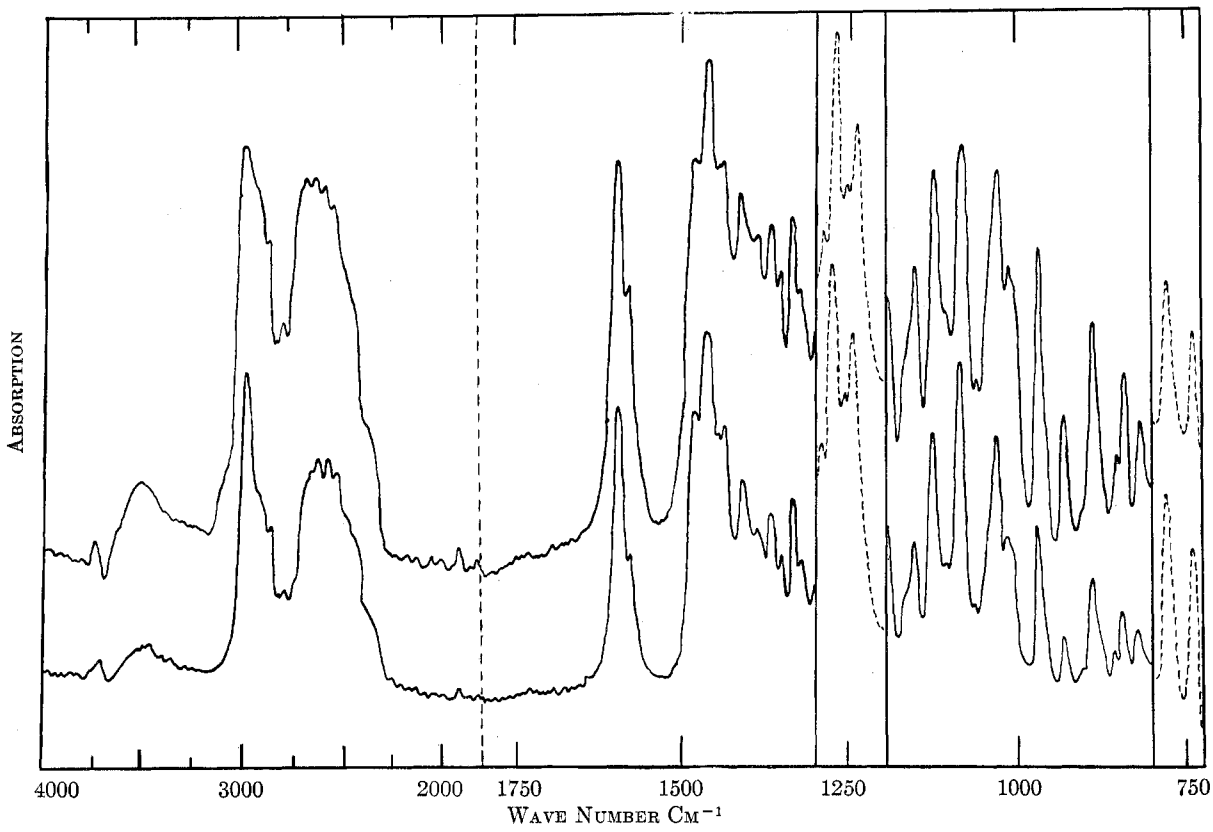
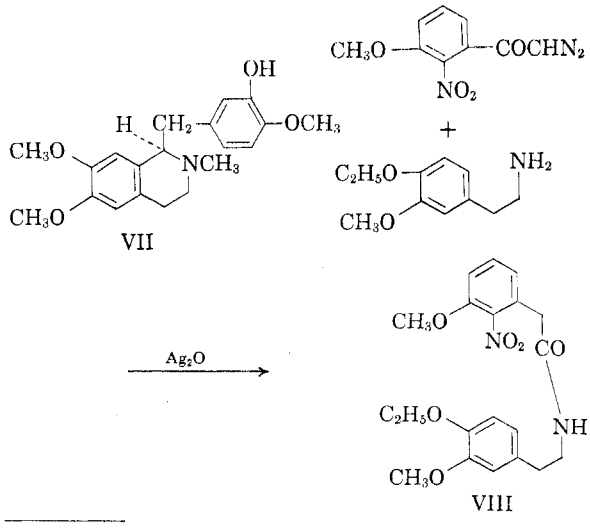


FIG. 1. INFRARED ABSORPTION SPECTRA OF ISOTHEBAINE ETHYL ETHER HYDROIODIDE (UPPER CURVE) AND 4,6-DIMETHOXY-5-ETHOXYAPORPHINE HYDROIODIDE (LOWER CURVE). Full line, chloroform solution. Broken line, bromoform solution.

III, OH = OEt by the standard route (*cf.* refs. 9,12,14) employing the Bischler-Napieralski *iso*-quinoline and Pschorr phenanthrene ring closures. The amide, VIII, required for the isoquinoline ring closure was prepared by a modification of the Arndt-Eistert reaction, first used by Eistert[22] in his synthesis of papaverine, and later by Hey and Lobo[23] in their aporphine syntheses. The yield of aporphine in the final step was extremely low, even lower than obtained by Govindachari and Pai[21] in the synthesis of the trimethoxy-compound; probably the larger ethoxy group makes ring closure more difficult.

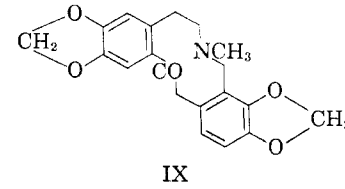


Insufficient synthetic aporphine precluded its resolution, but the infrared spectra of the synthetic hydroiodide and isothebaine ethyl ether hydroiodide, both in chloroform and bromoform solutions, are identical (Fig. 1). The differences in intensity between the two sets of curves are due to differences in concentration of solutions employed. The actual concentrations used were:

*Iso*thebaine ethyl ether hydroiodide
(a) in chloroform 12.0% w/v
(b) in bromoform 9.6% w/v and
4,6-dimethoxy-5-ethoxyaporphine hydroiodide
(a) in chloroform 9.7% w/v
(b) in bromoform 10.0% w/v

The ultraviolet spectra are also identical.

It has been shown[24] that the methylenedioxy



IX

(22) B. Eistert, *Z. Angew. Chem.*, **54**, 124 (1941).
(23) D. H. Hey and L. C. Lobo, *J. Chem. Soc.*, 2246 (1954).
(24) M. Scribney and S. Kirkwood, *Nature*, **171**, 931 (1953).

groups of protopine (IX) arise in the plant by oxidation of a methyl to a hydroxymethyl group, followed by ring closure with an adjacent hydroxyl group, rather than by a formylation followed by reduction and ring closure. If the methylenedioxy group of pukateine arises in a similar fashion then the relationship between this base and isothebaine is very close, since isothebaine could be a pukateine precursor further methylated at the least hindered of the two —OH groups.

EXPERIMENTAL

All melting points are uncorrected.

2-Nitro-3-methoxybenzoic acid.

(a). *2-Nitro-3-hydroxytoluene* was prepared, in 50 g. batches, essentially by the method of Gibson.[25] The product, a mixture of the 2- and 4-nitro-*m*-cresols, obtained as a yellow oil, was not further purified.

(b). *2-Nitro-3-methoxytoluene* was prepared in 83% yield by the general method of Haworth and Lapworth.[26]

(c). *2-Nitro-3-methoxybenzoic acid.* A suspension of 2-nitro-3-methoxytoluene (50 g.) in water (2.5 l.) was refluxed with potassium permanganate (98 g.) for 3.5 hr. Starting material (15 g.) was recovered from the precipitated manganese dioxide by ether extraction. The cold aqueous filtrate, after removal of the manganese dioxide, was acidified with concentrated hydrochloric acid, and after 30 min. the precipitated acid was collected and dried. This crude product was refluxed with chloroform (250 ml.) to remove 4-nitro-3-methoxybenzoic acid, and the solid was collected. This was crystallized from methanol, when 2-nitro-3-methoxybenzoic acid was obtained as tiny prisms. Yield 19.3 g., m.p. 252–253°.

Anal. Calcd. for $C_8H_7NO_5$: C, 48.7; H, 3.6; N, 7.1. Found: C, 48.9; H, 3.7; N, 7.3.

2-Nitro-3-methoxybenzoylchloride. Thionyl chloride (7.1 g., 1.1 moles) was added to a suspension of the above acid (10 g.) in dry benzene (100 ml.) and the mixture refluxed for 20 hr., when the acid gradually dissolved. The solvent and excess of thionyl chloride were removed *in vacuo*, the residue redissolved in dry benzene and the solution filtered from a small amount of insoluble material. This solution was employed for the preparation of the diazoketone without further purification. (Use of the purified acid chloride led to the same product in comparable yield.)

2-Nitro-3-methoxy-ω-diazoacetophenone. A solution of crude 2-nitro-3-methoxybenzoylchloride (from 5 g. of 2-nitro-3-methoxybenzoic acid) in dry benzene (100 ml.) was added slowly (15 min.) to a dry ethereal solution of diazomethane (from 12.5 g. N-nitrosomethylurea) at 0°. Nitrogen evolution was observed and *2-nitro-3-methoxy-ω-diazoacetophenone* was deposited as a pale yellow crystalline precipitate, rapidly turning violet in sunlight. Crystallization from benzene yielded fine yellow needles, m.p. 146–147° (dec.).

Anal. Calcd. for $C_9H_7N_3O_4$: C, 48.9; H, 3.2. Found: C, 48.8; H, 3.5.

3-Methoxy-4-ethoxy-ω-nitrostyrene. A solution of potassium hydroxide (8 g.) in methanol (100 ml.) was added dropwise to a stirred solution of ethyl vanillin (12 g.) and nitromethane (8 g.) in methanol (185 ml.), while the temperature was maintained below 10°. After 10 min. stirring, the cold yellow solution was poured in a thin stream into a well stirred solution of concentrated hydrochloric acid (60 ml.) in water (100 ml.), no attempt being made to control the temperature. After 30 min. the yellow precipitate was collected and dried, (10.6 g.); after one crystallization from benzene m.p. 148–149°.

β-[3-Methoxy-4-ethoxyphenyl]ethylamine. A hot solution of 3-methoxy-4-ethoxy-ω-nitrostyrene (20 g.) in benzene (300 ml.) was added to a slurry of lithium aluminum hydride (20 g.) in a mixture of ether (200 ml.) and benzene (100 ml.). The mixture was refluxed for 20 hr., and then excess of lithium aluminum hydride was decomposed with 2*N* sulfuric acid, sufficient excess of acid being added to dissolve all the solid matter. The organic layer was twice extracted with 2*N* sulfuric acid, and sodium potassium tartrate (200 g.) added to the combined acid solutions. The resulting solution was basified with 5*N* sodium hydroxide and repeatedly extracted with ether (3 l.). The residue obtained after removal of the ether was distilled and the fraction b.p. 156–157.5°/20 mm. collected, when the amine was obtained as a colorless, heavy liquid, which on long standing solidified to a white waxy solid. Yield 14.3 g.; it rapidly absorbed atmospheric carbon dioxide.

3′-Methoxy-2′-nitrophenylaceto-3-methoxy-4-ethoxyphenylethylamide. A solution of 2-nitro-3-methoxy-ω-diazoacetophenone (prepared from 5 g. 2-nitro-3-methoxybenzoic acid) in dry benzene (150 ml.) was treated with freshly prepared silver oxide (0.5 g.) and a solution of β-[3-methoxy-4-ethoxyphenyl]ethylamine (5 g.) in dry benzene (10 ml.). The mixture was maintained at 60–70° for 3 hr., during which time nitrogen was evolved. More silver oxide (0.5 g.) was then added and the mixture refluxed for 10 hr. After filtration through kieselguhr and norite, the orange solution was evaporated *in vacuo*. The dark brown solid residue was triturated with methanol, and the resulting crystalline material was recrystallized from methanol. *3′-Methoxy-2′-nitrophenylaceto-3-methoxy-4-ethoxyphenylethylamide* (4.1 g.) was obtained as feathery needles, m.p. 132–133°.

Anal. Calcd. for $C_{20}H_{24}N_2O_6$: C, 61.8; H, 6.2; N, 7.2. Found: C, 61.9; H, 6.2; N, 6.9.

1-[3-Methoxy-2-nitrobenzyl]-6-methoxy-7-ethoxy-3,4-dihydroisoquinoline. Phosphorus pentachloride (6.5 g.) was added portion-wise with ice-cooling, to a solution of the above amide (5 g.) in dry chloroform (75 ml.). After the initial vigorous reaction, the mixture was kept at room temperature for 48 hr., and shaken occasionally. The yellow crystalline precipitate which formed was collected (4 g.) and dissolved in hot water (400 ml.). The brown chloroform filtrate was evaporated *in vacuo* and the residue extracted with boiling water (400 ml.) when some brown resinous material remained undissolved. The combined aqueous solutions were basified with potassium carbonate and the resultant orange-yellow precipitate was collected and crystallized from methanol, when *1-[3-methoxy-2-nitrobenzyl]-6-methoxy-7-ethoxy-3,4-dihydroisoquinoline* was obtained as pale yellow prisms, m.p. 141–142°.

Anal. Calcd. for $C_{20}H_{22}N_2O_6$: C, 64.5; H, 6.0; N, 7.5. Found: C, 64.4; H, 5.9; N, 7.1.

The hydrochloride was obtained as white feathery needles from water, m.p. 219.5–220°.

Anal. Calcd. for $C_{20}H_{22}N_2O_5.HCl$: C, 59.0; H, 5.7; N, 6.9. Found: C, 58.8; H, 6.0; N, 7.0.

The methiodide, prepared by heating the base in benzene solution with excess of methyl iodide at 100–120° for 4–6 hr., was recrystallized from methanol and obtained as yellow needles, m.p. 220–221°.

Anal. Calcd. for $C_{21}H_{25}N_2O_5I.\frac{1}{2}MeOH$: C, 48.8; H, 5.2; N, 5.3. Found: C, 49.3; H, 5.2; N, 5.1.

(±)-4,6-Dimethoxy-5-ethoxyaporphine. Zinc dust (12 g.) was added during 30 min. to a suspension of the dihydroisoquinoline methiodide (3.2 g.) in hot hydrochloric acid (1:1 v/v), and the resulting colorless solution was heated on the water bath for a further 30 min., then filtered hot. The cooled solution was basified with dilute ammonia and exhaustively extracted with chloroform. Evaporation of the

(25) G. P. Gibson, *J. Chem. Soc.*, **123**, 1272 (1923).

(26) R. D. Haworth and A. Lapworth, *J. Chem. Soc.*, **123**, 2982 (1923).

chloroform afforded 2.1 g. of a resinous residue, which was dissolved in methanol (20 ml.) and 2*N* sulfuric acid (15 ml.). The brown solution was diazotized at 0° with the calculated amount of sodium nitrite (0.445 g.) in water (10 ml.), and the resultant red-brown solution maintained at 0° for 15 min. and then at room temperature for 30 min. Copper powder (2 g.) was then added, (nitrogen was evolved at this stage), the mixture was stirred for 1 hr., then kept at room temperature for 16 hr., and finally refluxed for 30 min. Concentrated hydrochloric acid (5 ml.) and zinc dust (3 g.) were added to the hot filtrate and the mixture refluxed for 50 min. The yellow solution was filtered hot, cooled, basified with dilute ammonia, and exhaustively extracted with ether. The dark brown material obtained from the extract was dissolved in a 7:1 mixture of benzene and petroleum ether (50–60°) and chromatographed on alumina. The column was eluted with 7:1 benzene:petroleum ether (50–60°). Upon removal of the solvent a yellow viscous oil (0.1 g.), which could not be induced to crystallize remained. This was dissolved in dilute hydrochloric acid and a saturated solution of potassium iodide was added. The yellow gummy precipitate was triturated with methanol when *4:6-dimethoxy-5-ethoxyaporphine hydroiodide* crystallized. Recrystallization from ethanol yielded prisms, m.p. 232–233° (charred).

Anal. Calcd. for $C_{21}H_{25}O_3N$:HI.H_2O: C, 51.9; H, 5.8; I, 26.2. Found: C, 51.6, 51.4; H, 5.6, 5.7; I, 26.0, 25.8.

Even after intensive drying (4 hr. at 120° *in vacuo*) the infrared spectrum, in chloroform solution still showed a diffuse band at 3600–3250 $cm.^{-1}$

Is*othebaine ethyl ether hydroiodide*. A small specimen of isothebaine, in absolute ethanol, was treated with an ethereal solution of diazoethane. The nonphenolic base was purified by chromatographing upon alumina, and elution of the column with 60:40 benzene:petroleum ether (50–60°). Two distinct fluorescent bands were observed, the first yielding only a trace of material. The second larger band gave a pale yellow viscous oil upon evaporation of the solvent. This was dissolved in dilute hydrochloric acid and treated with a saturated solution of potassium iodide. The precipitated *iso*thebaine ethyl ether hydroiodide was crystallized from ethanol, and obtained as prisms, m.p. 236–237° (charred).

ABERDEEN, SCOTLAND

[CONTRIBUTION FROM THE DIVISION OF ONCOLOGY, CHICAGO MEDICAL SCHOOL]

Synthesis of C^{14} Labeled Anthracene, 9-Methylanthracene and 1,2-Benzanthracene[1]

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Received October 23, 1956

The synthesis of anthracene, 9-methylanthracene, and 1,2-benzanthracene labeled with C^{14} in the 9,10 positions is described.

The noncarcinogenic hydrocarbons, anthracene and 9-methylanthracene, and the weakly carcinogenic hydrocarbon, 1,2-benzanthracene, were labeled with C^{14} in the 9,10- positions in order to compare their metabolism with that of the potent carcinogen, 9,10-dimethyl-1,2-benzanthracene,[3,4] a hydrocarbon already labeled[5] with C^{14}. The four members of this structurally related series of compounds were conveniently prepared from the same labeled intermediate, *viz.*, phthalic anhydride -7-C^{14}.[5] Thus, syntheses utilizing C^{14} labeled phthalic anhydride constitute a general and practical method for the preparation of C^{14} labeled polycyclic hydrocarbons.

The anhydride, I, was condensed with benzene using ethylene chloride as the solvent according to Baddeley's general procedure for the Friedel-Crafts reaction.[6] The most satisfactory cyclization of the resultant ketoacid utilized fuming sulfuric acid rather than concentrated sulfuric acid. Fieser[7] made the same observations for the ring closure of *p*-toluyl-*o*-benzoic acid. Anthraquinone, II, was reduced to anthrone, III, with tin, hydrochloric and acetic acids according to Meyer.[8] The simultaneous addition of stannous chloride (which Badger and Cook substituted for tin in the reduction of 1,2-benzanthraquinone[9]) hastened the solution of anthraquinone. It was necessary to control carefully the amount of acidic reagents and the period of heating in order to avoid resinous products.

The addition of methylmagnesium iodide to anthrone and subsequent *in situ* dehydration to 9-methylanthracene, IV, had been reported without details.[10,11] This sequence was developed to give purified 9-methylanthracene in 63% yield.[12] While the ultraviolet absorption spectrum of this material was identical with that reported,[13] the m.p. was

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