

Synthesis and Reactions of 4,6-Dimethoxyindole, an Unusual Indole System

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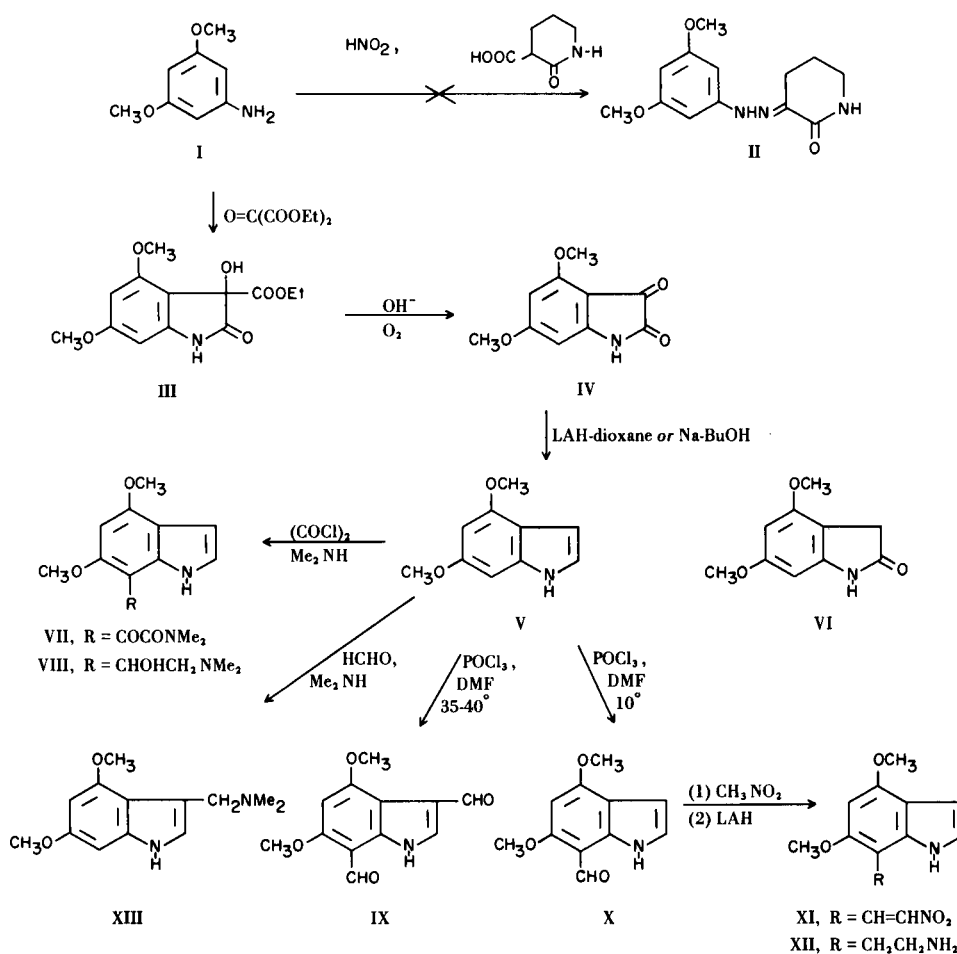
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A synthesis of 4,6-dimethoxyindole is described. Formylation or oxalation reactions gave substitution at position 7 rather than the usual 3-substitution characteristic of other indoles. A synthesis of *N,N*-dimethyl-4,6-dimethoxytryptamine is presented along with NMR data for 3 and 7-substituted compounds in this series.

In connection with some behavioral studies (1a) being conducted on a variety of substituted tryptamines we had occasion to prepare *N,N*-dimethyl-4,6-dimethoxytryptamine (XIX). Snyder and Merrill (2) had predicted that this compound would possess interesting pharmacological properties, particularly as a hallucinogenic agent. The

4,6-dimethoxyindole system was previously unknown, but did not appear to present any unusual synthetic problems. However, because of the anomalous behavior of this system toward electrophilic substitution, conventional reactions common to the indole area could not be used for the synthesis of the tryptamine (XIX).

SCHEME 1



Our original approach (Scheme I) was to prepare 4,6-dimethoxytryptamine *via* the Japp-Klingemann reaction of diazotized 3,5-dimethoxyaniline (I) with 3-carboxy-2-piperidone. This method has found wide application for the synthesis of a variety of tryptamines (3a-e); however, we were unable to obtain any of the expected 3,5-dimethoxyphenylhydrazone of 2,3-dioxopiperidine (II). A bright red solid was isolated which was apparently some type of phenylazo coupling product of 3,5-dimethoxyaniline. Since 3,4,5-trimethoxyaniline has been successfully employed in this reaction (3e), the lack of substitution at the *para* position in I must permit diazonium coupling in the activated aromatic ring.

3,5-Dimethoxyaniline (I) was condensed with diethyl mesoxalate in acetic acid (4) and the resulting hydroxy ester (III) was air-oxidized in 5% sodium hydroxide to afford 4,6-dimethoxyisatin (IV). Several methods for the reduction of IV to 4,6-dimethoxyindole (V) were explored, but the only satisfactory one (43% yield) was lithium aluminum hydride (LAH) in refluxing dioxane. Sodium and *n*-butanol reduction afforded a 16% yield of V, accompanied by a small amount of 4,6-dimethoxyoxindole (VI). Conventional reaction of V with oxalyl chloride and dimethylamine gave an *N,N*-dimethylglyoxamide (VII). However, reduction of the glyoxamide with LAH in tetrahydrofuran surprisingly yielded only a hydroxylamine (VIII). Prolonged treatment of the hydroxylamine with diborane in tetrahydrofuran or LAH in boiling dioxane failed to effect further reduction. Biswas and Jackson (5) have shown that diborane will reduce even 1-methyl-3-indolylcarbinols, which are known to be resistant to LAH. Since *N,N*-dimethyl-4-methoxy-3-indolglyoxamide was completely reduced by LAH in tetrahydrofuran (6), interference by the 4-methoxy group was not a factor.

The NMR spectra of the glyoxamide (VII) and hydroxylamine (VIII) indicated that oxalylation had not occurred at C-3, but in the benzenoid ring. The NMR spectrum of 4,6-dimethoxyindole (V) showed well defined signals at τ -0.78 (NH), 2.99 (triplet, C-2H), 3.52 (doublet, C-7H), 3.70 (triplet, C-3H), 3.87 (doublet, C-5H). The glyoxamide showed a shifted NH (-1.26), the C-2H remained as a triplet at 2.90, the C-5H became a singlet with the C-3H triplet superimposed at 3.58, and the C-7 proton disappeared. Reduction to the aminocarbonol returned the NH to τ -0.26 and the C-5H to 3.72. If substitution had taken place at position 3, no triplets should be observed and the 5 and 7 protons should continue to appear as doublets (*meta* coupling between 5 and 7). Molecular orbital calculations (2) show the 7-position to be favored over the 5-position for electrophilic substitution, which indicated that we had obtained the 7-substituted compounds (VII and VIII).

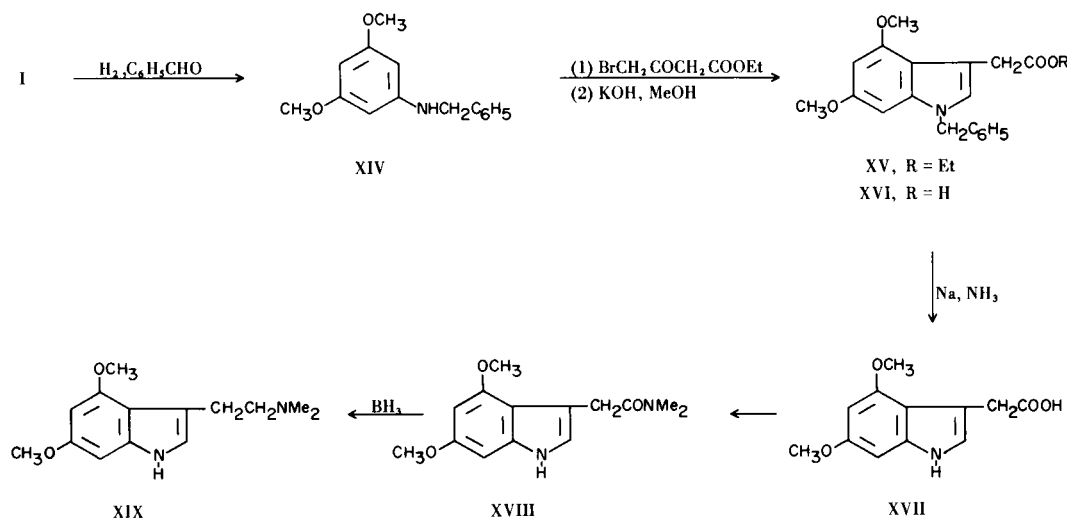
Treatment of V with the phosphoryl chloride-dimethyl formamide reagent at 35-40° (7) afforded the 3,7-dialdehyde (IX). The infrared spectrum showed two carbonyl bands at 5.95 and 6.08 μ . Reaction with nitromethane gave a mononitrovinyl derivative and removed the 5.95 μ band. The NMR spectrum of IX showed τ -2.00 (NH), the C-2 proton now as a doublet and shifted to 2.26, while the C-5 proton appeared as a sharp singlet at 3.44. When the reaction was conducted at 10° and with inverse addition, a monoaldehyde was obtained. The NMR was very similar in the NH and aromatic region to the glyoxamide (VII) indicating this to be the 7-aldehyde (X). The carbonyl group appeared at 6.10 μ in the infrared, also similar to the glyoxamide. The nitrovinyl derivative (XI) was prepared from X and reduced with LAH to give the 7-aminoethyl compound (XII).

Further evidence for C-7 substitution rather than C-5 is afforded by comparison of NMR spectra for 4,5,6-trimethoxyindole and its 3-formyl derivative, both prepared by the method of Carlsson, *et al.* (8). In the simple indole the 7-proton is found at τ 3.28, shifted downfield to 3.15 in the aldehyde. We have assigned the C-5 proton as the high upfield proton at 3.87 in V, which is shifted downfield to 3.60 in the aldehyde (X) and to 3.58 in the glyoxamide (VII). The C-7 proton, seen at τ 3.52 in V, should have been shifted even further downfield if acyl substitution had removed the C-5 proton. It is interesting that 4,5,6-trimethoxyindole undergoes formylation only at C-3.

4,6-Dimethoxygramine (XIII) was obtained in a 23% yield by reaction of V with formaldehyde and dimethylamine. The low yield is probably due to competing amino alkylation in the benzenoid ring. The NMR was as expected for the 3-substituted indole showing three doublets centered at τ 3.17, 3.61 and 3.94 for the C-2, C-7, and C-5 protons, respectively.

We were able to synthesize the tryptamine (XIX) by the general method of Julia (9) (Scheme II). 3,5-Dimethoxyaniline (I) was treated with benzaldehyde in a hydrogen atmosphere and the resulting *N*-benzyl derivative (XIV) was condensed with ethyl 4-bromoacetoacetate (10) in ethanol (24 hours at reflux). The resulting 1-benzyl-4,7-dimethoxy-3-carbethoxymethylindole (XV) was saponified to the carboxylic acid (XVI), which was in turn readily debenzylated by sodium-liquid ammonia reduction. The NMR spectrum of the resulting 4,6-dimethoxy-3-indoleacetic acid (XVII) was in agreement with that of the gramine (XIII). The acid (XVII) was converted to the *N,N*-dimethylamide (XVIII) by the mixed anhydride method followed by reduction with diborane to the *N,N*-dimethyltryptamine (XIX). The compound was isolated as a bispicrate. One mole of picric acid is apparently involved in salt formation and the other as a

SCHEME II



molecular complex. We have observed similar bispicate formation with 5-hydroxy- α -methyltryptamine and 5-methoxy-6-hydroxy- α -methyltryptamine (11).

The method of Tacconi (12) involving the condensation of an isatin with acetaldoxime at position-3 was totally unsuccessful. 4,6-Dimethoxyisatin (IV) failed to react even under forcing conditions and probably reflects the hindrance caused by a C-4 substituent.

Only preliminary investigation of the biological properties of XIX has been conducted. The compound has about one-third the hallucinogenic potency of *N,N*-dimethyltryptamine as measured by the method of Uyeno, *et al.* (1b).

EXPERIMENTAL

NMR Spectra were measured at 100 mc using tetramethylsilane as an internal standard in deuteriodimethylsulfoxide.

4,6-Dimethoxy-3-hydroxy-3-carbethoxyoxindole (III).

Following the general procedure of Benington, *et al.* (4) a mixture of 12.4 g. of 3,5-dimethoxyaniline, 14 ml. of diethyl mesoxalate and 50 ml. of acetic acid was heated on the steam bath for 10 minutes, then allowed to stand for 2 hours. The white precipitate was washed with petroleum ether and dried to afford 20 g. (88%), m.p. 188.5-190.5°. An analytical sample, m.p. 191.5-194°, was obtained by recrystallization from acetic acid.

Anal. Calcd. for $\text{C}_{13}\text{H}_{15}\text{NO}_6$: C, 55.5; H, 5.38; N, 4.98. Found: C, 55.4; H, 5.33; N, 4.90.

4,6-Dimethoxyisatin (IV).

A solution of 19.4 g. of the hydroxy ester (II) in 200 ml. of 5% sodium hydroxide was aerated at 95-100° for 24 hours. The solution was acidified (pH 4) with formic acid and allowed to stand for 15 hours. The orange precipitate was collected, washed with water and dried to give 10.9 g. (76%). Recrystal-

lization from 2-methoxyethanol afforded an analytical sample, m.p. 300°.

Anal. Calcd. for $\text{C}_{10}\text{H}_9\text{NO}_4$: C, 58.0; H, 4.38; N, 6.76. Found: C, 57.8; H, 4.52; N, 6.92.

4,6-Dimethoxyindole (V).

Method A.

To an ice cold, stirred suspension of 4.62 g. of lithium aluminum hydride in 200 ml. of dioxane was slowly added 5.0 g. of 4,6-dimethoxyisatin. The mixture was cautiously heated to boiling over a 5-hour period, then maintained at reflux for 15 hours. The mixture was cooled and treated with absolute ethanol and water followed by removal of the solvent *in vacuo*. The residue was thrice extracted with chloroform and the combined extracts were dried over magnesium sulfate and evaporated *in vacuo* to leave a purple solid residue. Chromatography on silica gel with elution by chloroform gave 1.82 g. (43%) of white crystals. An analytical sample, m.p. 119-120.5°, was obtained by recrystallization from a benzene-cyclohexane mixture; NMR τ -0.78 (NH), 2.99 (triplet, C-2H), 3.70 (triplet, C-3H), 3.52 (doublet, C-7H), 3.87 (doublet, C-5H), 6.22 and 6.29 (CH_3O). 4,5,6-Trimethoxyindole (8) showed τ -0.83 (NH), 2.86 (triplet C-2H), 3.28 (C-7H), 3.57 (triplet C-3H).

Anal. Calcd. for $\text{C}_{10}\text{H}_{11}\text{NO}_2$: C, 67.8; H, 6.26; N, 7.91. Found: C, 67.9; H, 6.22; N, 7.93.

Method B.

To a boiling solution of 5.0 g. of 4,6-dimethoxyisatin in 250 ml. of *n*-butanol was rapidly added 5.0 g. of sodium. After 30 minutes the sodium had disappeared and the solution was cooled and treated with 250 ml. of ice water. The layers were separated and the aqueous portion was extracted with ether. The combined organic extracts were dried and evaporated *in vacuo* to leave a dark gum. Treatment with ether caused the separation of 41 mg. of crystalline material which was removed by filtration. The filtrate was chromatographed as above to yield 0.69 g. (16%) of white crystals, m.p. 116-120°. The material was identical to that prepared by Method A.

The ether insoluble material, m.p. 201-203°, is believed to be 4,6-dimethoxyindole (VI); IR λ max (Nujol), 3.18 (NH), 5.9 μ (C=O).

Anal. Calcd. for C₁₀H₁₁NO₃: C, 62.2; H, 5.74; N, 7.25. Found: C, 61.9; H, 5.78; N, 7.10.

4,6-Dimethoxy-7-indolyl-N,N-dimethylglyoxamide (VII).

To an ice cold mixture of 3.0 g. (17 mmoles) of 4,6-dimethoxyindole and 75 ml. of ether was added dropwise, 3.6 ml. (42.4 mmoles) of oxalyl chloride. The mixture was stirred at 0-5° for 30 minutes followed by the dropwise addition of 18 ml. of anhydrous dimethylamine in 30 ml. of ether. Stirring was continued for 4.5 hours at room temperature; then the solid was collected and washed with ether and water to afford 3.74 g. (80%) of yellow crystals. Recrystallization from 2-propanol gave an analytical sample, m.p. 196.5-199°; NMR τ -1.26 (NH), 2.90 (triplet, C-2H), 3.58 (2H multiplet, C-3 and C-5 H's), 6.02 and 6.16 (each 3H, OCH₃), 7.10 and 7.20 (each 3H, NCH₃).

Anal. Calcd. for C₁₄H₁₆N₂O₄: C, 60.9; H, 5.84; N, 10.1. Found: C, 61.2; H, 5.90; N, 10.0.

4,6-Dimethoxy-7-(2'-dimethylamino-1'-hydroxy)ethylindole (VIII).

A mixture of 0.65 g. of lithium aluminum hydride, 0.95 g. of the glyoxamide (VII) and 40 ml. of tetrahydrofuran was stirred at reflux for 15 hours. The mixture was chilled and carefully treated with ethanol, followed by water. The solvent was removed *in vacuo* and the residue was extracted with chloroform. The chloroform was dried over magnesium sulfate and evaporated to leave 0.12 g. of white solid, whose infrared spectrum was devoid of carbonyl. Recrystallization from benzene gave white crystals, m.p. 141-143°; NMR τ -0.26 (NH), 3.01 (triplet, C-2H), 3.72 (2H multiplet, C-3 and C-5 H's), 4.76 (quartet, C-H of carbinol), 6.18 and 6.24 (each 3H, OCH₃), 7.80 (6H, NCH₃). Elemental analysis was not quite acceptable for the free base, so it was characterized as the picrate, red crystals, m.p. 185-190° (dec.).

Anal. Calcd. for C₂₀H₂₃N₅O₁₀: C, 48.7; H, 4.70; N, 14.2. Found: C, 48.8; H, 4.70; N, 14.4.

4,6-Dimethoxy-3,7-diformylindole (IX).

To 0.50 ml. of dimethylformamide was slowly added 0.14 ml. (1.52 mmoles) of phosphoryl chloride at 15°. A solution of 0.20 g. (1.13 mmoles) of 4,6-dimethoxyindole in 0.20 ml. of dimethylformamide was then added slowly, using a cold water bath for cooling. The solution was warmed at 35-40° for 45 minutes and poured into 5 ml. of ice water. The aqueous mixture was made strongly alkaline with 10% sodium hydroxide and warmed 5 minutes on the steam bath. The solid was collected, washed with water and dried to leave 0.21 g. of IX. Recrystallization from methanol afforded 0.12 g. of white crystals, m.p. 242-248°: IR λ max (Nujol), 3.18 (NH), 5.95, 6.08 μ (CH=O); NMR τ -2.00 (NH), -0.18 and -0.25 (CHO), 2.26 (doublet, C-2H), 3.44 (C-5H), 5.96 and 6.03 (each 3H, OCH₃). 4,5,6-Trimethoxy-3-formylindole (8) showed τ -2.00 (NH), 2.01 (C-2H), 3.15 (C-7H).

Anal. Calcd. for C₁₂H₁₁NO₄: C, 61.8; H, 4.75; N, 6.01. Found: C, 61.7; H, 4.83; N, 6.41.

A nitromethane solution of IX containing a catalytic amount of ammonium acetate was refluxed 10 minutes and cooled. The red precipitate was collected and recrystallized from glacial acetic acid to give a mononitrovinyl derivative, m.p. 248-251°; IR λ max (Nujol), 3.07 (NH), 6.07 (CH=O), 7.90 μ (NO₂).

Anal. Calcd. for C₁₃H₁₂N₂O₅: C, 56.5; H, 4.38; N, 10.2. Found: C, 56.6; H, 4.38; N, 10.2.

4,6-Dimethoxy-7-formylindole (X).

To an ice cold solution of 0.20 g. (1.13 mmoles) of 4,6-dimethoxyindole in 0.20 ml. of dimethylformamide was added dropwise, an ice cold solution of the formylating reagent prepared from 0.35 ml. of dimethylformamide and 0.105 ml. (1.13 mmole) of phosphoryl chloride. The solution was kept at 10-15° for 1 hour, poured into 5 ml. of ice water and worked up in the same manner as for the dialdehyde (IX) to yield 0.13 g. (56%) of white crystals after trituration with ethanol. Recrystallization from ethanol afforded white crystals, m.p. 201-202°; IR λ max (Nujol), 3.00 (NH), 6.10 μ (CH=O); NMR τ -1.20 (NH), -0.26 (CHO), 2.95 (triplet, C-2H), 3.60 (multiplet, 2H, C-3 and C-5 H's), 6.02 and 6.08 (each 3H, OCH₃).

Anal. Calcd. for C₁₁H₁₁NO₃: C, 64.4; H, 5.40; N, 6.83. Found: C, 64.6; H, 5.62; N, 7.02.

4,6-Dimethoxy-7- β -nitrovinylindole (XI).

A mixture of 0.94 g. of X, 0.31 g. of ammonium acetate and 15 ml. of nitromethane was refluxed 6 hours and evaporated to dryness *in vacuo*. The residue was stirred with water, filtered and the solid was dried to leave 1.02 g. (89%) of red crystals. A portion was recrystallized from methanol to give an analytical sample, m.p. 233°.

Anal. Calcd. for C₁₂H₁₂N₂O₄: C, 58.1; H, 4.87; N, 11.3. Found: C, 57.8; H, 5.00; N, 11.3.

4,6-Dimethoxy-7- β -aminoethylindole Picrate (XII).

A mixture of 1.02 g. of the nitro compound (XI), 0.47 g. of lithium aluminum hydride and 80 ml. of tetrahydrofuran was stirred at reflux for 15 hours. Excess reagent was destroyed with ethanol and water and the solvent was removed *in vacuo*. The residue was twice extracted with chloroform and the chloroform extracts were dried and evaporated to leave 0.61 g. of a dark gum. The gum was dissolved in ether, filtered and the filtrate was treated with dry hydrogen chloride. The gummy hydrochloride salt so obtained was treated with 0.44 g. of picric acid in water to afford 0.30 g. of crystalline picrate. Recrystallization from aqueous ethanol gave an analytical sample, m.p. 214-218°.

Anal. Calcd. for C₁₈H₁₉N₅O₉: C, 48.1; H, 4.26; N, 15.6. Found: C, 48.4; H, 4.53; N, 15.7.

4,6-Dimethoxy-3-dimethylaminomethylindole (4,6-Dimethoxygramine, XIII).

A mixture of 0.93 ml. (5.1 mmoles) of 25% aqueous dimethylamine, 0.29 ml. (5.1 mmoles) of glacial acetic acid, 0.42 ml. (5.1 mmoles) of 37% formaldehyde and 0.90 g. (5.1 mmoles) of 4,6-dimethoxyindole was stirred at 50° for 3.5 hours. The brown mixture was diluted with water and a small amount of insoluble material was removed by filtration. The filtrate was alkalinized with 10% sodium hydroxide and the precipitate was extracted into ethyl acetate. The extract was dried over magnesium sulfate and evaporated *in vacuo* to leave a dark syrup which was triturated with benzene to afford 0.27 g. (23%) of tan crystals, m.p. 118-129°. Further recrystallization from benzene yielded an analytical sample of off-white crystals, m.p. 128-132°; NMR τ -0.62 (NH), 3.17 (doublet, C-2H), 3.61 (doublet, C-7H), 3.94 (doublet, C-5H), 6.26 and 6.31 (each 3H, OCH₃), 6.43 (2H, CH₂), 7.88 (6H, NCH₃).

Anal. Calcd. for C₁₃H₁₈N₂O₂: C, 66.6; H, 7.74; N, 12.0. Found: C, 66.6; H, 7.65; N, 11.9.

1-Benzyl-4,6-dimethoxy-3-carbomethoxymethylindole (XV).

A mixture of 20.0 g. (0.13 mole) of 3,5-dimethoxyaniline (I), 14.6 ml. (0.15 mole) of freshly distilled benzaldehyde, 1.0 g.

of platinum oxide and 300 ml. of ethanol was stirred under one atmosphere of hydrogen for 3 hours; the calculated amount of gas was consumed. The catalyst was removed and the solvent was evaporated *in vacuo* to leave 31.8 g. (100%) of XIV as a syrup; the infrared spectrum showed a single NH at 3.0 μ and the absence of carbonyl absorption.

The above *N*-benzyl compound (31.8 g., 0.13 mole), 13.7 g. (0.065 mole) of ethyl 4-bromoacetoacetate (10) and 300 ml. of absolute ethanol was stirred at reflux for 24 hours. The solvent was evaporated *in vacuo* and the residue was stirred with 1 liter of ether for 15 hours. The mixture was filtered and the filtrate was evaporated to leave 19.1 g. (83%) of XV as an amber syrup; IR λ max 5.75 (ester C=O), 13.8, 14.3 μ (phenyl), no NH at 3.0 μ . Chromatography on silica gel did not change the spectral properties, so the material was used directly for the next step.

1-Benzyl-4,6-dimethoxy-3-indoleacetic Acid (XVI).

A mixture of 18.4 g. of the crude ester (XV), 120 ml. of 10% potassium hydroxide and 120 ml. of methanol was refluxed for 2 hours. Methanol was removed *in vacuo* and the aqueous residue was further diluted with water and washed with ether. The alkaline solution was acidified to pH 1-2 with 6*N* hydrochloric acid and the precipitate was extracted with dichloromethane. The extract was dried over magnesium sulfate and evaporated *in vacuo* to give a dark syrup. Crystallization from a benzene-cyclohexane mixture afforded 5.2 g. (31%) of tan crystals. A small portion was recrystallized from benzene to give an analytical sample, m.p. 147-150°.

Anal. Calcd. for $C_{19}H_{19}NO_4$: C, 70.1; H, 5.89; N, 4.31. Found: C, 70.4; H, 5.80; N, 4.33.

4,6-Dimethoxy-3-indoleacetic Acid (XVII).

To a mixture of 3.8 g. of sodium and 130 ml. of liquid ammonia at -75° was added dropwise 5.38 g. of the *N*-benzyl acid (XVI) in 50 ml. of tetrahydrofuran. Stirring was continued at -75° for 2 hours and the ammonia was allowed to evaporate overnight. The residue was chilled and treated with absolute ethanol, followed by saturated ammonium chloride. The mixture was further diluted with water and acidified with 6*N* hydrochloric acid. The product was extracted into ethyl acetate, which was dried and evaporated to leave 1.83 g. (47%) of light green crystals. Recrystallization from acetone gave material melting at 173-175°. IR λ max (Nujol) 2.98 (NH), 5.80 μ (COOH), no benzyl at 13.8 or 14.3 μ ; NMR τ -0.58 (NH), -1.84 (COOH), 3.13 (doublet, C-2H), 3.57 (doublet, C-7H), 3.92 (doublet, C-5H), 6.26 and 6.28 (each 3H, OCH₃), 6.33 (2H, CH₂).

Anal. Calcd. for $C_{12}H_{13}NO_4$: C, 61.3; H, 5.57; N, 5.96. Found: C, 61.3; H, 5.68; N, 5.83.

N,N-Dimethyl-4,6-dimethoxy-3-indoleacetamide (XVIII).

To a solution of 0.72 g. of the acid (XVII) in 15 ml. of tetrahydrofuran was added 0.43 ml. of triethylamine. The mixture was stirred for 30 minutes, cooled to 0-5° and 0.40 ml. of isobutyl chloroformate was added dropwise. The mixture was stirred for 2 hours at 0-5° and 1.8 ml. of anhydrous dimethylamine was added. After 15 hours the solvent was removed and the residue was treated with ether and water, most of the material being insoluble in ether. The mixture was filtered and the cake dried to leave 0.38 g. of crystals. The ether layer in the filtrate was evaporated to leave a gum which afforded another 50 mg. of

crystals upon trituration with benzene to give a total of 0.43 g. (51%). Recrystallization from benzene gave an analytical sample, m.p. 107-109°.

Anal. Calcd. for $C_{14}H_{18}N_2O_3$: C, 64.1; H, 6.92; N, 10.7. Found: C, 64.3; H, 6.88; N, 10.5.

N,N-Dimethyl-4,6-dimethoxytryptamine Bispicrate (XIX).

To a solution of 0.38 g. of dimethylamide (XVIII) in 15 ml. of tetrahydrofuran was added 2.9 ml. of 1*M* borane in tetrahydrofuran. The mixture was refluxed 1 hour, chilled and treated with 5 ml. of 2*N* hydrochloric acid. The solvent was removed *in vacuo* and the residue was diluted with water and washed with chloroform. The aqueous portion was alkalinized to pH 10-11 and extracted with chloroform. Evaporation of the chloroform gave a yellow syrup, which was extracted with hot cyclohexane. Evaporation of the cyclohexane yielded 61 mg. of clear syrup, which was dissolved in a small amount of alcohol and treated with 1% picric acid in water until precipitation was complete. After 15 hours the crystalline bispicrate was collected (95 mg.) and twice recrystallized from methanol to give yellow crystals, m.p. 155-160°.

Anal. Calcd. for $C_{14}H_{20}N_2O_2 \cdot 2 C_6H_3N_3O_7$: C, 44.2; H, 3.71; N, 15.9. Found: C, 44.3; H, 4.01; N, 15.8.

Acknowledgment.

The NMR measurements were performed by Mrs. L. Stietzel, with assistance in interpretation by Dr. R. M. Silverstein. Biological measurements were performed by Dr. E. T. Uyeno.

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Received June 11, 1969

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